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# ELECTROCOAGULATION (EC) TECHNOLOGY FOR NITRATE REMOVAL

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## ABSTRACT:

High nitrate contamination in drinking water is a serious environmental pollutant, as it is generally a problem associated with anthropogenic activities. Sources of nitrate pollution include discharge of chemical fertilizers, human and animal wastes. Excessive application of agricultural fertilizers has been known to cause penetration of large quantities of nitrates into underground and surface waters. Nitrate is a stable and highly soluble ion with low potential for precipitation or adsorption. These properties make it difficult to remove using conventional water treatment method. Several methods have been proposed in the literature for the removal of nitrate. In this project, a laboratory batch electrocoagulation (EC) reactor was designed to investigate the effects of the different parameters, such as: electrolysis time, current value, and the pH of the solution on the nitrate removal efficiency. The influence of process parameters on denitrification was achieved using “synthetic” water. The results showed that at an operating current of 2.5A, the nitrate removal efficiency was 90% when initial nitrate concentration and electrolysis time respectively were kept at 45 mg/L –N and 90 min. The denitrification process is more efficient for pH ranging from 9 to 11. Further it is shown that a linear relationship exists between the electrolysis time for total nitrate removal and the initial nitrate concentration. It is concluded that the electrocoagulation technology for denitrification can be an effective process provided that the ammonia byproduct can be removed effectively.

**KEY WORDS:** Aluminium electrodes, Electrocoagulation (EC) process, and Nitrate removal

## 1. Introduction:

Nitrogen compounds are very important pollutants in domestic and industrial wastewaters when these wastewaters discharged into drinking water reservoirs and cause several environmental problems [1]. Among several N species, nitrate is the most stable and it is produced when nitrogen from ammonia or other sources combines with oxygenated water [2]. In water, nitrate has no taste or smell and can be identified by a chemical test. Nitrate is a serious environmental pollutant, as it is generally a problem associated with anthropogenic activities. Ordinary sources of nitrate pollution include discharge of chemical fertilizers, animal wastes, septic tanks, and municipal sewage treatment systems. Fertilizer is the largest supplier to nitrate pollution. Excessive application of agricultural fertilizers has been known to cause penetration of large quantities of nitrates into underground and surface waters [3].

The maximum acceptable concentration of nitrate in drinking water is 10 mg/L as N or 45 mg/L as nitrate [4]. High nitrate contamination in drinking water can cause methemoglobinemia, usually called “blue-baby syndrome”, which is especially unfavourable to babies less than six months old [5]. Some studies show that increased levels of nitrate concentration are being detected in the groundwater in some countries. A US Environmental Protection Agency report on nitrate level in groundwater showed that about 1.7 million people (including 270,000 infants) were exposed to water with nitrate concentrations in excess of the regulatory limits in drinking water (10 mg/L as N) [6]. Nolan et al. [7] also reported that 9% of domestic wells sampled by the U.S. Geological Survey’s National Water-Quality Assessment (NAWQA) had nitrate concentrations over the acceptable level of 10 mg/L as N.

There are different technologies to remove nitrates from drinking water such as: ion exchange [8], reverse osmosis [9-10], electrodialysis [11-13], catalytic denitrification [14-15], biological denitrification [16], and electrochemical denitrification [17-18]. Biological denitrification is the reduction of nitrate or nitrite to gaseous nitrogen oxides and molecular nitrogen by essentially anaerobic bacteria, as both  $N_2O_{(g)}$  and  $NO_{(g)}$  can be produced and consumed by denitrification [19]. Chemical denitrification is the reduction of  $NO_3^-$  and  $NO_2^-$  by chemical reductant, while nitrification is the biological oxidation of ammonium ( $NH_4^+$ ) to  $NO_2^-$  or  $NO_3^-$  under aerobic conditions [20].

Using chemical coagulants for precipitation is one of the most essential processes in conventional water and wastewater treatment. Generation of large volumes of sludge, the hazardous waste categorization of metal hydroxides, and high costs associated with chemical treatments have made chemical coagulation less acceptable compared to other processes [21]. The removal of nitrates from the natural waters represents a difficult problem due to the fact that they cannot be removed either by precipitation or by complexation [22]. Effective process for nitrate removal has been studied by using electrochemical reduction with metallic soluble anodes [23-24]. The reduction of

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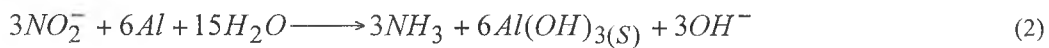
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nitrate to N<sub>2</sub> gas can also be possible in this process and nitrate removal has been accomplished with the precipitation of Fe(OH)<sub>3</sub> produced in water using soluble Fe anode [24]. Previous studies by the authors [25-26] have demonstrated that electrocoagulation (EC) using aluminium anodes are effective in defluoridation. The main aim of this paper is to present results of denitrification experiments using aluminium electrodes in an ECF reactor. Batch experiments were designed and conducted to investigate the effects of the different parameters, such as: electrolysis time, current value, and the pH of the solution on the nitrate removal efficiency.

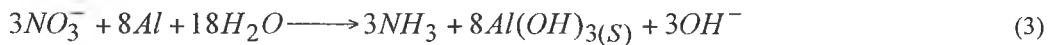
## 2. Fundamentals:

### 2.1 Theory of nitrate reduction

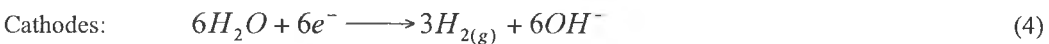
A review of the existing literature indicates that an effective technology for nitrate removal from groundwater is chemical denitrification with aluminium powder [27]. In the pH range 9-10.5, nitrate can be reduced to ammonia with aluminium powder. Ammonia can then be removed by air stripping or using other processes such as thermo-energy ammonia recovery process [28], or using sulphuric acid for recovering ammonia to ammonium sulphate [29]. It only works when the pH of the solution is sufficiently high (pH>8), because protective oxides have been observed to form on the surface of aluminium particles at low pH, thereby preventing them from reacting with the nitrate. Murphy [27] described that powdered aluminium reduces nitrate to ammonia and nitrite on the basis of the following mechanisms:



Overall,



Murphy [27] reported that the removal of the nitrate with aluminium (chemical reduction) may first happen by adsorption onto the particles. Electrocoagulation (EC) involves the application of an electric current to sacrificial electrodes inside a reactor tank. When aluminium electrodes are used, the aluminium dissolves at the anode and hydrogen gas is released at the cathode. The main mechanism of nitrate removal by EC process may be due to possible oxidation of aluminium at the anode that can reduce nitrate from solution. The electrolytic dissolution of Al anodes by oxidation in water produces aqueous Al<sup>3+</sup> species [30] and the electrode reactions are outlined below:



In the pre-anodic area, the nitrate ions are reduced to ammonia as follows:



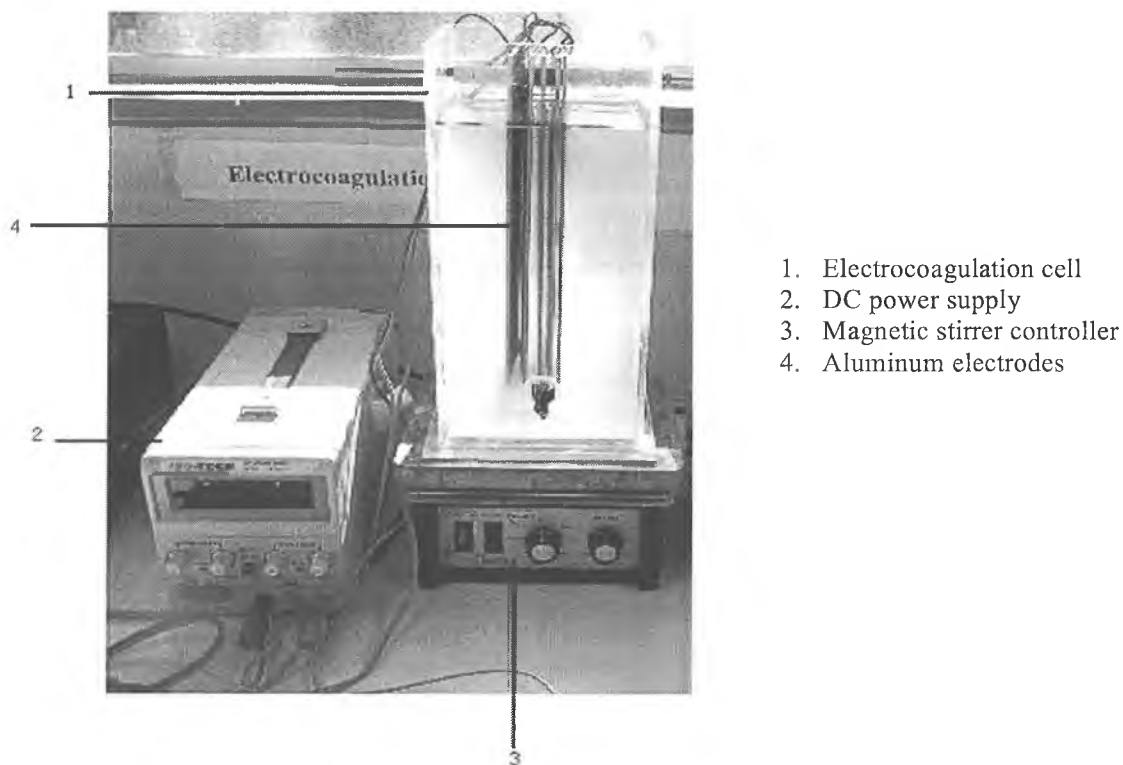
Aluminium can be consumed in water in water as shown in Eq. 7 to a solid Al(OH)<sub>3</sub> precipitate.



## 3. Materials and Methods:

### 3.1 Batch ECF apparatus:

A laboratory batch electrocoagulation reactor was designed and constructed as shown in Figure 1. For the electrochemical cell, five aluminium (purity of Al 95–97%, Ullrich Aluminium Company Ltd, Sydney) plate anodes and cathodes (dimension 250×100×3 mm) were used as electrodes. The electrodes were connected using a monopolar configuration in the electrocoagulation reactor. The electrodes were dipped 200 mm into an aqueous solution (volume 3.6 L) in a Perspex reactor (dimension 300×132×120 mm). In the reactor, stirring was achieved using a magnetic bar placed between the bottom of the electrodes and the reactor. A draining tube was installed at the bottom of the box for cleaning.



**Figure 1. Batch monopolar electrocoagulation (EC) reactor**

Samples of treated water or wastewater were collected from a port located 50 mm above the bottom of the reactor. The gaps between the two neighbouring electrode plates were kept constant 5 mm for all experiments. The water temperature of all experiments were approximately at 25°C with an initial nitrate concentration of 45 mg/L as N. Current was varied over the range 1 – 2.5A, however, it was held constant for each run. The electrolysis time was altered between 5 to 90 min.

### 3.2 Experimental Procedure

The influence of the various parameters on the denitrification process was achieved using “synthetic” water (distilled water +  $\text{NaNO}_3$  salt +  $\text{NaHCO}_3$ ) in a batch reactor as shown in Figure 1. The nitrate solution (45 mg/L as N) was prepared by mixing sodium nitrate in deionized water samples. 1 M sodium hydroxide solution was added for pH adjustment. Nitrate concentration was determined using a UV spectrophotometer (Model UV-1700, SHIMADZU) at wavelength of 220 nm [31]. Acidification with 1N HCl was carried out to prevent interference from hydroxide or carbonate concentrations. Direct current from a DC power supply (0–30 V, 0–2.5 A, ISO-TECH, IPS-1820D) was passed through the solution via the five electrodes. Cell voltage and current were readily monitored using a digital power display. Ammonia concentration was determined using the ionometric standard method [31] with an ammonia selective electrode (Metrohm ion analysis, Ammonia ISE 6.0506.010). Total  $\text{Al}^{3+}$  ions concentration, pH, and conductivity were measured using Atomic Absorption Spectrophotometer (AAS), a calibrated pH meter and conductivity meter, respectively.

## 4. Results and Discussion:

Electrolysis time determined the rate of dissolution of  $\text{Al}^{3+}$  ions, as it strongly depends on the current intensity. Figure 2 shows the influence of electrocoagulation time on  $\text{NO}_3^-$  and  $\text{Al}^{3+}$  concentrations. The residual nitrate concentration decreases from 45 to 20 mg/L-N when electrolysis time is increased from 5 to 90 min at an operating current of 1 A. The aluminium concentrations are also found to increase from 9 to 176 mg/L. It can be concluded that when the current is kept at 1 A, the nitrate removal efficiency reached to 56% after 90 min electrolysis time.

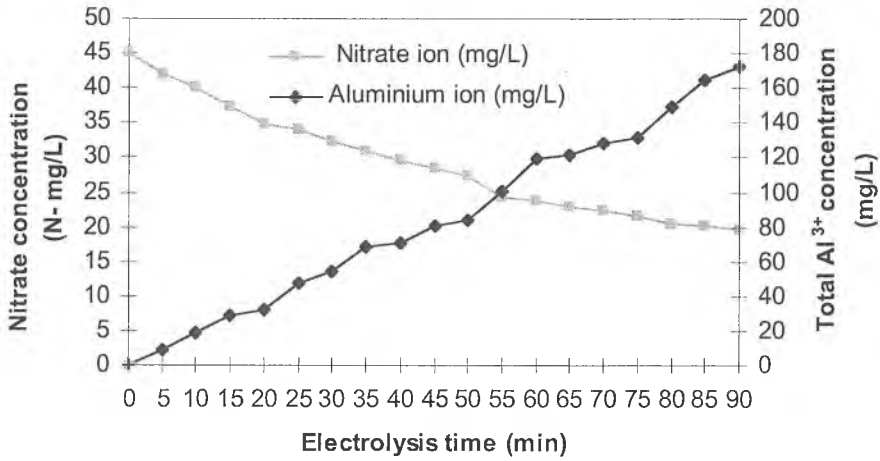


Figure 2. Effect of electrolysis time on the nitrate removal and production of aluminium ions in the EC process, ( $I=1A$ ,  $E_c= 400 \mu\text{mhos/cm}$ , and  $\text{pH} = 10.5$ )

In an electrochemical process, electrolysis time ( $t$ ) and current value ( $I$ ) are the most important parameters for controlling of the chemical reaction rate. At low current ( $1A$ ), removal time was longer due to slower coagulant addition or Aluminium oxidation. Conversely at high current ( $2.5A$ ), the removal time was shorter and it takes only 55 min to reduce the nitrate concentration to maximum acceptable level as illustrate in Figure 3.

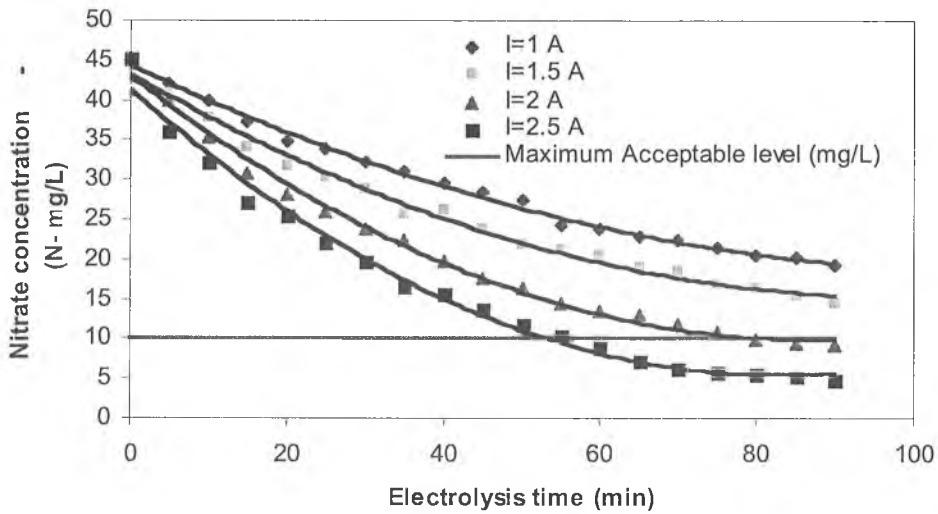


Figure 3. Variation of nitrate concentration with electrolysis time at different current inputs ( $E_c = 400 \mu\text{mhos/cm}$ , and  $\text{pH} = 10.5$ )

The current intensity determines the rate of dissolution of  $\text{Al}^{3+}$  concentration. The lower the current, the less aluminium is released from the anode and hence the nitrate reduction is low. The highest current ( $2.5A$ ) produced the quickest nitrate removal due to increase rate of dissolution of the aluminium. The rate of change of  $\text{NO}_3^-$  concentration can be expressed ( $dC/dt$ ) as a first order process, as follows:

$$\frac{dC}{dt} = -K_i C_i \quad (8)$$

Equation 8 can be arranged by simple integration to give:

$$C_t = C_o \cdot e^{-K_i t} \quad (9)$$

where  $C_t$ ,  $C_0$ , and  $K_i$  are the nitrate concentration at any time  $t$ , initial nitrate concentration, and kinetic constant, respectively. In Figure 4, plot of  $-\ln(C_t/C_0)$  with time is shown for various current intensities at a conductivity of 400  $\mu\text{mhos/cm}$ . The linear relation for each current rate confirms the fact that the kinetics of denitrification follows the exponential law with time.

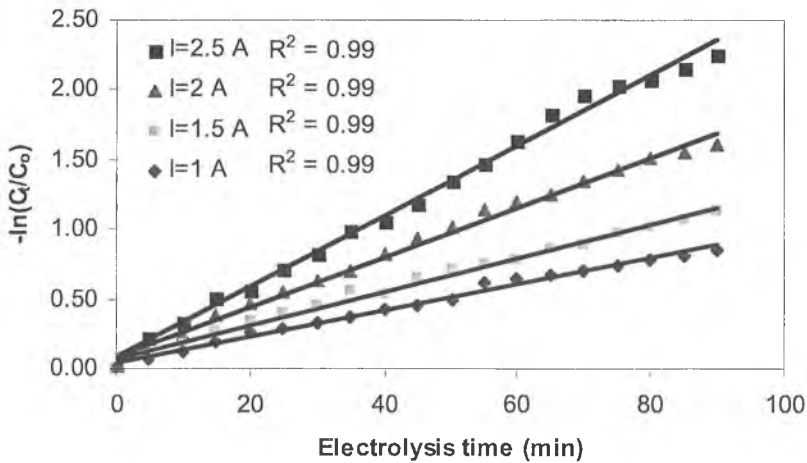


Figure 4. Determination of the kinetic constants of the denitrification process by EC at different applied current values ( $E_c = 400 \mu\text{mhos/cm}$ , Initial nitrate concentration = 45 mg/L-N, and pH = 10.5)

Figure 5 shows the influence of pH on the nitrate removal between the pH ranges of 8-12. The result illustrates the denitrification process is more efficient for a pH ranging from 9 to 11. The nitrate ion tends to dissolve the passivated surface of Al due to the increased alkalinity from the formation of nitrite.

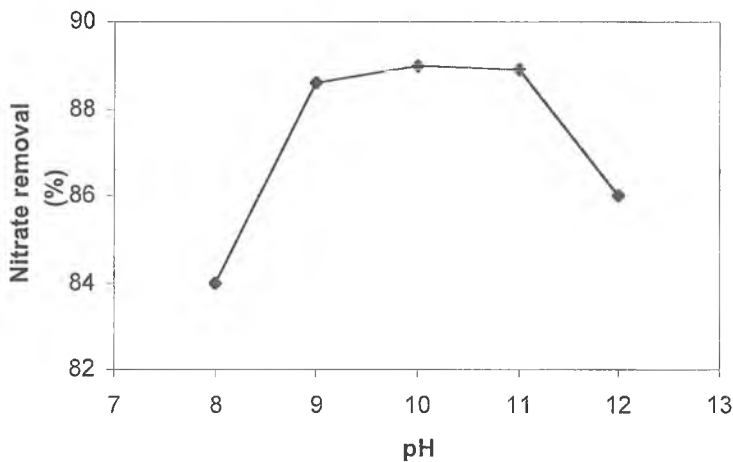


Figure 5. Influence of the constant pH on the denitrification process by EC ( $I = 2.5\text{A}$ ,  $E_c = 400 \mu\text{mhos/cm}$ , and Initial nitrate concentration = 45 mg/L-N)

Murphy [27] reported that the nitrate ions can be reduced to nitrite ions and then be converted to the ammonia and nitrogen gas at the pH range 9 -10.5. Figure 6 shows the influence of electrocoagulation time on reduction of  $\text{NO}_3^-$  concentration and production of  $\text{NH}_3$  concentration by ECF process. The ammonia concentration increased from 0.02 to 35 mg/L -N when nitrate concentration was decreased from 45 to 5 mg/L- N at a constant pH 10.5. It is clear that ammonia can be the principal reaction product in the solution. It is concluded that the electrocoagulation technology for denitrification can be an effective process provided that the ammonia byproduct can be removed effectively. For example, the ammonia recovery process (ARP), which is a low-cost process, can be used for converting ammonia into concentrated ammonium sulfate [28]. Nitrite concentration has been measured by IC method, when its concentration was very low (result not shown). It is because of quick changing to ammonia (Eq.

4). Re production of hydrogen and oxygen gases in the electrocoagulation system, it is strongly recommended that the system operation need to have well ventilation in over of installed electrodes. Thus, the  $N_2$  gas collection was impossible without covering of electrodes. Concerning to a safety process, the  $N_2$  gas was not measured in this research.

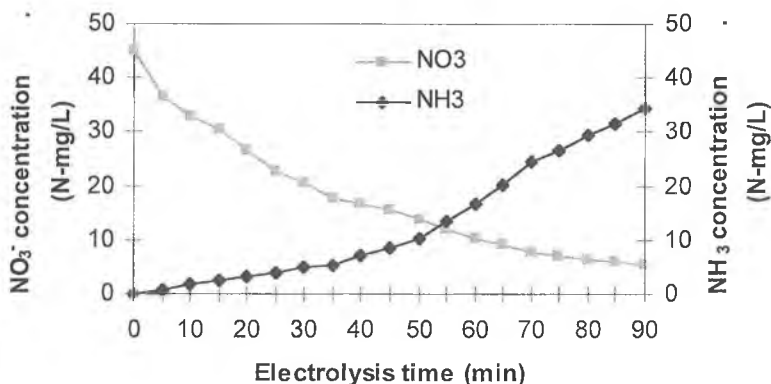


Figure 6. Variation of nitrate and ammonia concentration with electrolysis time ( $I=2.5A$ ,  $E_c=400 \mu\text{mhos/cm}$ , and  $\text{pH} = 10.5$ )

The composition of the sludge produced in the batch monopolar system was analyzed using X-ray diffraction (XRD) spectrum. As shown in Figure 7, The aluminum ions can be consumed in water and react as shown in Eq 7 to a solid  $\text{Al}(\text{OH})_3$  precipitate. The XRD traces of the dried settled sludge showed that the strongest peaks appeared at degree 18 and 20, which were identified to be aluminum hydroxide ( $\text{Al}(\text{OH})_{3(s)}$ ) with different mineral names of "Nordstrandite" and "Bayerite". Thus, the nitrate removal mechanism is due to a reduction-oxidation method and it cannot be caused by formation of some species between aluminum and nitrate ions in the solution. Using chemical equilibrium modeling software (MINEQL<sup>+</sup>) (results not shown), it was confirmed that there was no any species and components between aluminum and nitrate ions.

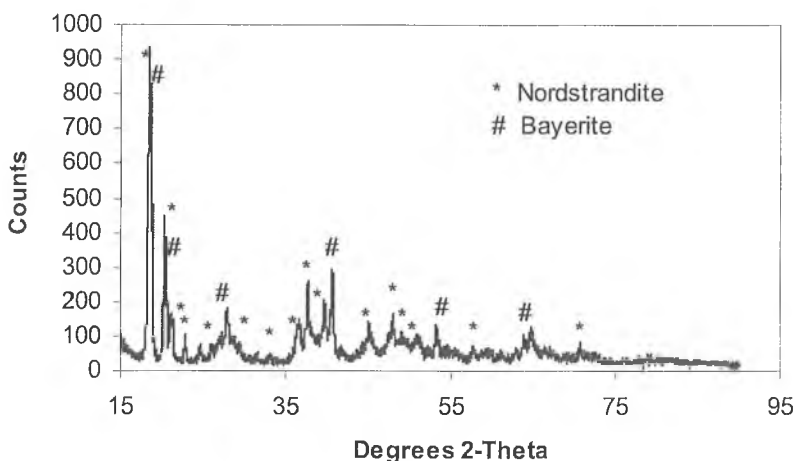


Figure 7. Composition of dried settled sludge analyzed by XRD spectrum ( $I=2.5A$ ,  $E_c=400 \mu\text{mhos/cm}$ ,  $\text{pH} = 10.5$ , and Initial nitrate concentration =  $45 \text{ mg/L-N}$ )

## 5. Conclusions

Batch experiments were designed to investigate the nitrate removal efficiency by EC process. Nitrate removal efficiency depends on electrolysis time and current values. At both low current and electrolysis time, the nitrate removal efficiency was lower. A minimum of 55 min electrolysis time is required to reduce nitrate concentration from  $45 \text{ mg/L-N}$  to maximum acceptable level at a current value of 2.5 A. At an operating current of 2.5A, the

nitrate removal efficiency can reach up to 90%. The experimental result showed that the rate of change of nitrate concentration can be expressed as a first order process. Maintaining high pH in the range 9 to 11 was favourable for this process. The results obtained indicate that the ammonia concentration increased when nitrate concentration was decreased in the solution. Although EC process can be used as a method for denitrification, it should be kept in mind that for the process to work satisfactorily, high pH is to be maintained and the ammonia generated may have to be removed.

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