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Technical Note

Improvement of aqueous nitrate removal by using continuous electrocoagulation/electroflotation unit with vertical monopolar electrodes

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SUMMARY

The present study is to investigate removal of nitrate from water solutions by the Electro-Coagulation-Flotation (ECF) process in continuous operation under different conditions. Experimental results indicated that the maximum nitrate removal was achieved by aluminum–aluminum electrode arrangement as anode–cathode. The increase in current density from 0.4 to 3.2 mA cm⁻² increased nitrate removal efficiency from 55 to 96% under optimum conditions of time and pH during the ECF. Continuous operation of the ECF reactor led to an increase of nitrate removal from 37% at a detention time of 10 min–96% at a detention time of 30 min. Mean energy consumption and current efficiency were found to be about 2.66 kWh g⁻¹ NO₃⁻ and 160%, respectively.

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1. Introduction

Pollution of water resources by nitrate occurs due to industrial wastewater containing nitrate, domestic wastewater, fertilizers in agricultural, discharges from animal operations, wastewater treatment facilities, septic systems and commercial activities [1–3]. It causes eutrophication problems of rivers, lakes and seas, destroys water quality and presents potential hazards on human health. The WHO guideline value for nitrate is 50 mg L⁻¹ [4]. It needs to be regulated in water basically because excess levels of nitrate effects on health by forming methemoglobinoma in children, hypertension, thyroid disability and carcinogenicity hazard of nitrosamine [5]. Current nitrate removal techniques include ion exchange, biological denitrification, chemical treatment, reverse osmosis, electro-dialysis, catalytic denitrification, hybrid systems based on fly-ash adsorption, membrane filtration, and electrocoagulation [6–9]. The use of chemical coagulation is limited due to its disadvantages, including generation of large quantities of sludge, the

hazardous waste categorization of metal hydroxides, and high costs associated with chemical treatments. Recently wastewater treatment using the electrochemical technologies to remove a large number of pollutants has gained prominence [10–12].

Electro-Coagulation-Flotation (ECF) process is characterized by easy operation, reduction of sludge production, and no need to handle chemicals. It has been applied efficiently to various water treatment processes [13]. ECF includes the generation of coagulants via the electro-dissolution of a sacrificial anode, which usually consists of iron or aluminum. The metal ion generation takes place at the anode; hydrogen gas is released from the cathode [14–16]. Also, hydrogen gas would help to float the flocculated particles out of the water. The aim of this paper is to investigate parameters affecting energy consumption in the removal of nitrate from the water by ECF in a continuous flow. The process was examined under different values of current density, pH and time, in order to determine optimum operating conditions. The electrode materials used in this study were iron and aluminum.

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2. Materials and methods

In this study a laboratory-scale reactor $24 \times 17 \times 18$ cm, made of Plexiglas sheets, was used. Reactor equipped with four blades made of aluminum or iron that installed in monopolar parallel. The electrode dimensions were $150 \times 160 \times 10$ mm. Plates were installed in parallel configuration with 1.5 cm interspace. A magnet was placed in the bottom of the tank for mixing (300 rpm). Settling chamber was made from Plexiglas in 24 cm (depth) \times 17 cm (width) \times 53 cm (length) and 21.5 L in volume for 30 min contact time. Electrocoagulation and settling reactor were attached to each other in series. In settling chamber 3 valves were implanted for providing the 30 min contact time in which their location was determined previously.

Solution passes slowly through the settling chamber and finally, the treated water comes out from valve. In each run 500 mL of synthetic solution of KNO_3 with initial NO_3^- concentration 100 mg L^{-1} was placed at the electrolytic cell. Then samples were tested using a UV Spectrophotometer (UV-1800 SHIMADZU) [17]. Electrode weights were recorded after each test. Four 12×15 cm metal plates (electrodes) from wrought iron ST-12 and 3003 aluminum with 1 mm diameter were used for this study. To remove the influence of mass transfer rate of pollutants to the electrodes (iron or aluminum salts produce electrode passivation and cause a 50% increase in treatment time and power requirements), high mixing was ensured by a magnetic stirrer. To maintain the same experimental conditions, electrodes were polished with grinding papers and then rinsed with soapy water and deionized water after each experiment. A transformer was used to supply DC current with adjustable amperage (0–60 V, 0–0.6 A). Since electrode surface and electrode interspaces are constant, by dissolving sodium chloride (increasing specific electrical conductivity of solution), voltage and electric current intensity were adjusted. Current level was adjusted for 0.4, 0.8, 1.6 and 3.2 mA cm^{-2} . A schematic of the electrochemical reactor is shown in Fig. 1. Experiments were done at 20°C .

3. Results and discussion

The effects of various parameters (electrode materials, pH, current density and detention time) were investigated on the removal of nitrate by ECF. The results obtained from this study are presented

and discussed below. The conditions and runs relating to the ECF experiments are shown in Table 1.

3.1. Effect of electrode materials

Fig. 2 presents the effects of anode and cathode electrode materials and arrangement on the removal of nitrate by ECF process. As indicated in Fig. 2a, Al–Al as anode–cathode electrodes has a pronounced influence on ECF process. The nitrate removal percentages to anode–cathode electrode arrays of Fe–Fe, Fe–Al, Al–Fe, Al–Al, were obtained to be 87, 89, 92 and 96% respectively. It was found that Al–Al as anode–cathode electrodes has the highest efficiency on the removal of nitrate under the selected conditions. Rosie et al. used the Al–Al as anode–cathode electrodes in electrochemical process for leachate treatment. They observed a high removal efficiency by Al electrodes [18]. Shivayogimath and Watawati [19] also reached a similar result with present study.

3.2. Effect of pH

To determine the effect of pH on removal efficiency, pH changed from 3 to 11. The nitrate removal efficiency was achieved 96% in pH 7.0 and detention time of 30 min. It was no observed significant different in acidic and alkaline pHs; the removal efficiencies for pH values of 3 and 11 were close to 96%. This finding supports that variations of pH has no effect on the nitrate removal by ECF.

3.3. Effect of current density and detention time

Another important parameter influencing the performance and economy of the ECF is the density of current applied at the electrodes. It determines the coagulant dosage rate, bubble production rate, size and growth of the flocs. From Fig. 2b results, it is found that increasing applied current density between electrodes increases the anode weight loss resulting in increases in coagulant generation. This finding is in agreement with most other researchers [6,20–22]. The theoretical amount of loss in anode (Al) weight was calculated by Eq. (1). This calculation was based on the comparison of experimental weight loss of Al electrodes (m_{exp}) during ECF process with theoretical amount of Al dissolution (m_{theo}) according to the Faraday's law.

$$\Delta m_{\text{theo}} = \frac{MI t_{\text{EC}}}{nF} \quad (1)$$

where M is the molar mass of the aluminum, (g mol^{-1}), n the number of electron moles and F is the Faraday constant.

Fig. 2c shows variations of current density (0.4 – 3.2 mA cm^{-2}) versus detention time (5–30 min) under the conditions given in Table 1. As presented in Fig. 2c, the removal efficiency of nitrate was 59% for current density of 0.4 mA cm^{-2} at detention time 30 min. Further increase in current density to 3.2 mA cm^{-2} increased removal efficiency to 73% after 20 min of detention time. This is consistent with Faraday law (Eq. (2)), in which an increase in the current density and time, the anode dissolution rate increases that will increase Al^{3+} release from anode:

$$C_{\text{Al}} = \frac{M_w I t_{\text{EC}}}{ZFV} \quad (2)$$

where C_{Al} , Z , F , V , and M_w are the theoretical concentration of Al^{3+} (g m^{-3}), the chemical equivalence, Faraday's constant ($96,487 \text{ C mol}^{-1}$), volume of reactor (m^3), and molecular weight of aluminum (g mol^{-1}), respectively. And I is current (A) and t_{EC} the applied electrolysis time (s). Also with increasing in current density,

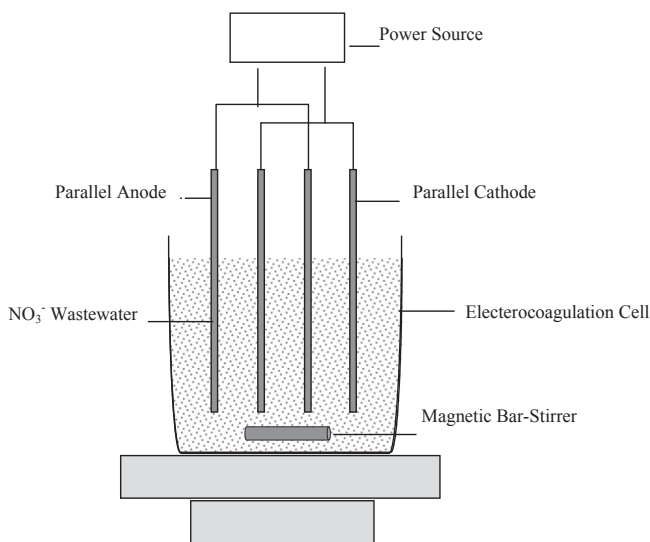


Fig. 1. A schematic diagram of the electrochemical reactor.

Table 1
The runs and operational conditions of ECF experiments.

| Run | Operation mode | Experiment | Operational conditions | | | |
|-----|----------------|--|--------------------------|------|--|----------------------|
| | | | Material (anode–cathode) | pH | Current density (mA cm ⁻²) | Detention time (min) |
| 1 | Continuous | Effect of electrodes material | Al, Fe | 7 | 3.2 | 30 |
| 2 | Continuous | Effect of pH | Al–Al | 3–11 | 3.2 | 30 |
| 3 | Continuous | Effect of current density and detention time | Al–Al | 7 | 0.4–3.2 | 5–60 |

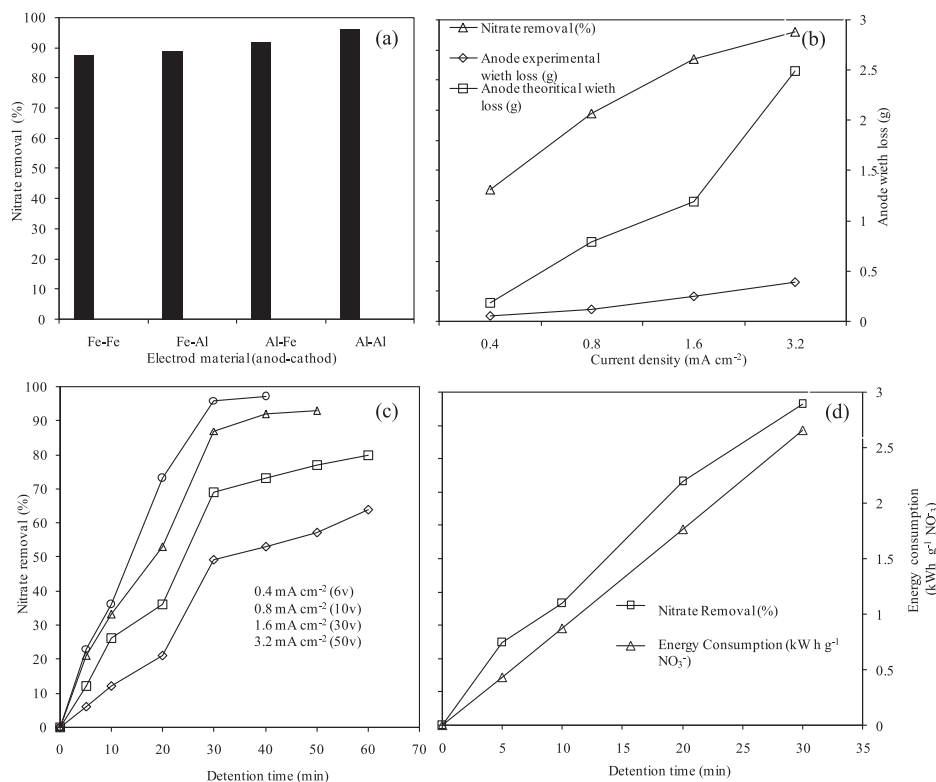
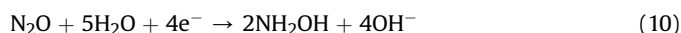
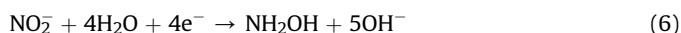
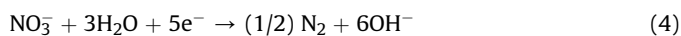


Fig. 2. The effect of anode–cathode electrode materials on the removal of nitrate (a); nitrate removal and anode (Al) weight loss as a function of current densities applied in the ECF (b); the effect of current density on the removal of nitrate (c); the effect of detention time on the energy consumption and the removal efficiency of NO₃⁻ (d).

Al(OH)₃ flocs generation and bubble generation rate also increase with the bubble size decreasing.

3.4. The main mechanism of nitrate removal by ECF process

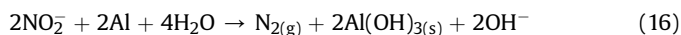
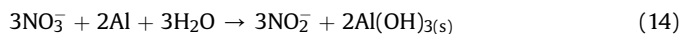
The main cathode electrochemical reactions involved in the reduction of nitrate are presented in the following [23]:



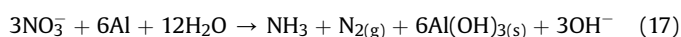
By applying electrical current to the electrodes, anode oxidation and cathode reduction reactions takes place in the electrolyte. Nitrate in the vicinity of the cathode is reduced and is mainly converted to products such as nitrite, ammonia and nitrogen. Also water adjacent to the cathode electrode is reduced and the tiny bubbles of hydrogen gas produced. Best case, is electrochemical reduction of nitrate to nitrogen gas. If electrolyte solution to be acidic, byproducts of nitrate reduction include: nitrites, ammonia, hydrazine and hydroxylamine. But if the electrolyte is alkaline or neutral, byproducts of the electrochemical reduction include: nitrates, nitrites and ammonia. Since hydroxide ion is produced in the cathode reaction, pH electrolyte rises quickly, and most products are nitrite and ammonia. When aluminum is used as the anode and cathode electrodes, Al³⁺ and hydrogen gas are produced due to oxidation at the anode and water reduction at cathode respectively, in accordance with the following reactions:



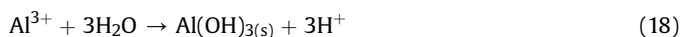
Aluminum reduced nitrate to nitrite, ammonia and nitrogen gas according to the following reactions:



Overall



Finally, due to the presence of hydroxide ions in solution, Al^{3+} will form aluminum hydroxide.



3.5. Electric energy consumption

The important economical parameters in ECF are electrical energy consumption (E) and the current efficiency (φ) which are the major operating cost of the electrochemical process. The plot of E versus detention time is shown in Fig. 2d. The minimum amount of energy consumption was 2.66 kWh g^{-1} NO_3^- at a current density of 3.2 mA cm^{-2} for a 30 min reaction time that was calculated using the following equation:

$$E = UIt_{\text{EC}} \quad (19)$$

where E is the electrical energy in Wh, and U = the cell voltage in volt (V). The φ is expressed by comparison of m exp with m theo during ECF process and is calculated by Eq. (20) [24–26].

$$\varphi = \frac{\Delta m_{\text{exp}}}{\Delta m_{\text{theo}}} 100 \quad (20)$$

The specific electrical energy consumption (SEEC) was calculated as a function of aluminum electrodes weight consumption during EC in kWh g^{-1} Al using Eq. (21):

$$\text{SEEC} = \frac{nFU}{(3.6)10^3 M\varphi} 100 \quad (21)$$

These calculations were carried out after optimizing the operational parameters in ECF process [25,26]. The calculated values were 2.66 (kWh g^{-1} NO_3^-), 160% and 0.98 (kWh g^{-1} Al) for E, φ and SEEC, respectively.

4. Conclusions

ECF process was tested for the removal of NO_3^- from water solutions. The effect of operational parameters such as pH, current density and detention time on NO_3^- removal efficiency was investigated and optimized. It was observed that the Al–Al electrode arrangement gives the highest performance for the removal of NO_3^- under the conditions studied. Continuous operation of the ECF process led to removal efficiency of 96% of nitrate at a detention time of 30 min, pH 7.0 and current density 3.2 mA cm^{-2} . Mean energy consumption, Φ and SEEC were figured at about 2.66 kWh g^{-1} NO_3^- , 160% and 0.98 kWh g^{-1} Al, respectively. Therefore, it can

be concluded that the ECF with the Al–Al electrode arrangement is an efficient, reliable and therefore promising technique for the treatment of NO_3^- in water solutions.

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