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Energy efficient electrocoagulation using a new flow column reactor to remove nitrate from drinking water – Experimental, statistical, and economic approach

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Abstract

In this investigation, a new bench-scale electrocoagulation reactor (FCER) has been applied for drinking water denitrification. FCER utilises the concepts of flow column to mix and aerate the water. The water being treated flows through the perforated aluminium disks electrodes, thereby efficiently mixing and aerating the water. As a result, FCER reduces the need for external stirring and aerating devices, which until now have been widely used in the electrocoagulation reactors. Therefore, FCER could be a promising cost-effective alternative to the traditional lab-scale EC reactors.

A comprehensive study has been commenced to investigate the performance of the new reactor. This includes the application of FCER to remove nitrate from drinking water. Estimation of the produced amount of H_2 gas and the yieldable energy from it, an estimation of its preliminary operating cost, and a SEM (scanning electron microscope) investigation of the influence of the EC process on the morphology of the surface of electrodes. Additionally, an empirical model was developed to reproduce the nitrate removal performance of the FCER.

The results obtained indicated that the FCER reduced the nitrate concentration from 100 to 15 mg/L (World Health Organization limitations for infants) after 55 min of electrolysing at initial pH of 7, GBE of 5 mm, CD of 2 mA/cm^2, and at operating cost of 0.455 US \$/m^3. Additionally, it was found that FCER emits H_2 gas enough to generate a power of 1.36 kW/m^3. Statistically, the relationship between the operating parameters and nitrate removal could be modelled with R^2 of 0.848. The obtained SEM images showed a large number dents on anode's surface due to the production of aluminium hydroxides.

Keywords: Nitrate removal; electrocoagulation; aluminium; perforated electrodes; SEM; hydrogen gas; modelling.

1. Introduction

Nitrate is identified as one of the environmentally problematic pollutants that result from industrial and agricultural activities, as its presence at high concentration in water causes serious health problem such as the blue-baby syndrome and gastric cancer (Ghafari *et al.*, 2008; Li *et al.*, 2010; Vasudevan *et al.*, 2010; Kamaraj *et al.*, 2016). In addition, its presence in industrial waste considerably increases the volume of treated waste and a negatively influence its cohesion (Li *et al.*, 2009). Moreover, water pollution with nitrate become a growing problem due to the wide usage of nitrogenous fertilizers, and recycling of domestic wastewater in rivers (Emamjomeh and Sivakumar, 2005; Pak, 2015).

Based on these facts and serious impacts that nitrate has on human health, the World Health Organisation (WHO) has limited nitrate concentration in drinking water to 50 mg/L (for adults) (Abdallah *et al.*, 2014; Kamaraj *et al.*, 2016), but for infants the WHO limitations are stricter (15 mg/L) (Li *et al.*, 2009).

Recently, to meet these limitations, many researchers have shown a great deal of interest in the electrocoagulation (EC) method as a promising alternative to remove nitrate from water due to many attractive advantages (Vasudevan and Oturan, 2014; Govindan *et al.*, 2015; Sharma and Chopra, 2015). For instance, it does not require chemical handling, it is easy to perform, removes high concentrations of nitrate at relatively low operating cost, and it enables the operator to control the pollutant reduction through both the material of the electrodes and the operating parameters (Ghosh *et al.*, 2008a; Aoudj *et al.*, 2013). Additionally, using this technology become possible in rural areas because the required power, to perform it, could be driven from a solar panel (Chaturvedi and Dave, 2012; Kuokkanen, 2016). Therefore, the EC technology has been applied, separately or integrated with other methods, to remove nitrate from water and wastewater. For instance, Emamjomeh and Sivakumar (2005) used an EC cell, supplied with five aluminium electrodes, to remove nitrate from drinking water. The results obtained showed that the maximum nitrate removal efficiency, 90%, was achieved within 90 minutes of electrolysing at a current value of 2.5 ampere. Another study was carried out by Malakootian *et al.* (2011), using four pairs of aluminium electrodes, to remove nitrate from the water of Kerman province, Iran. The obtained results from this study showed that this cell was efficient enough to reduce nitrate concentration from 100 to 10.3 mg/L (89.7%) within 60 minutes of treatment. The combination of electrocoagulation and electro-oxidation (EC-EO) methods was applied by Naje and Abbas (2013) to remove nitrate from textile effluent. The obtained results indicated that the EC-EO method reduced the nitrate concentration by 90% within 90 minutes at a current value of 0.6 ampere. Hossini and Rezaee (2014) combined an EC cell, which supplied with two aluminium anodes and two graphite cathodes, with an air stripping system to remediate nitrate from wastewater. The obtained results demonstrated that this combined system was efficient to remove as high as 97% of nitrate within 120 minutes of electrolysing at a current of 0.14 ampere.

In spite of the acknowledged advantages of the EC method to treat a wide spectrum of pollutants from waters and wastewaters, it still has a clear deficiency in terms of both, the lack of variety in reactor design, and the availability of models for its performance (Un *et al.*, 2013; Kuokkanen, 2016).
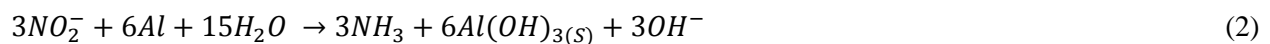
The current investigation therefore, has been carried out to fill a part of the gaps in the literature by using a new bench-scale electrocoagulation reactor (FCER), which utilises the concepts of flow column to mix and aerate the water, for drinking water denitrification. FCER reduces the use of external stirring and aerating devices which require extra power to work; these devices until now have been widely used in the EC reactors (especially laboratory scale ones). Therefore, FCER could be a cost-effective alternative to the traditional lab-scale EC reactors.

2. Aims and objectives

The current study has been carried out to fill a part of the mentioned gaps in literature through; firstly, application of a new EC reactor (FCER), which utilises the concepts of flow column to mix and aerate water being treated, for denitrification of drinking water. The influence of key operating parameters, such as the initial pH (from 4 to 10), current density (CD) (1, 2, and 3 mA/cm^2), the gap between electrodes (GBE) (from 3 to 10 mm), electrolysing time (t) (from 0 to 70 min), and initial concentration of nitrate (C$_0$) (from 50 to 150 mg/L) on nitrate removal will be investigated. Secondly, development of an empirical model to reproduce the nitrate removal performance of the FCER within the studied values of the operating parameters. Thirdly, conducting a preliminary economic study to estimate the minimum operating cost for nitrate removal using FCER. Fourthly, estimate the emitted amount of hydrogen gas from this new reactor during the denitrification of drinking water. The yieldable energy from recycling this eco-friendly gas also will be estimated. Finally, the influence of the electrolysing process on the texture of the perforated anodes will be investigated using the SEM (scanning electron microscope) technology.

3. Theory of nitrate reduction

The literature demonstrates that one of the most effective technologies for the removal of nitrate from water is the chemical denitrification with aluminium (Murphy, 1991; Emamjomeh and Sivakumar, 2005; Pak, 2015). For instance, adding of powdered aluminium reduces nitrate to nitrite to ammonia and nitrite according to the following mechanisms (Murphy, 1991; Emamjomeh and Sivakumar, 2005):

$$3NO_3^- + 2Al + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_{3(s)} \tag{1}$$

$$3NO_2^- + 6Al + 15H_2O \rightarrow 3NH_3 + 6Al(OH)_{3(S)} + 3OH^- \tag{2}$$

In The EC method, when aluminium electrodes are used, the liberated aluminium ions from the anodes reduce the nitrate to nitrogen and ammonia as follows (Koparal and Ogutveren, 2002):

$$NO_3^- + H_2O + 2e \leftrightarrow NO_2^- + 2OH^- \tag{3}$$

$$NO_3^- + 3H_2O + 5e \leftrightarrow \frac{1}{2}N_2 + 6OH^- \tag{4}$$

$$NO_3^- + 6H_2O + 8e \leftrightarrow NH_3 + 9OH^- \tag{5}$$

$$NO_2^- + 2H_2O + 3e \leftrightarrow \frac{1}{2}N_2 + 4OH^- \tag{6}$$

$$NO_2^- + 5H_2O + 6e \leftrightarrow NH_2 + 7OH^- \tag{7}$$

This complex mechanism of nitrate reduction could be summarised in the following scheme (Govindan *et al.*, 2015):

Scheme 1. Reaction pathways for nitrate reduction by the EC method.

4. Materials and methods

3.1. Synthetic water samples

Synthetic nitrate stock solution, 200 mg/L, was prepared by dissolving potassium nitrate (KNO_3) in deionised water. 500 mL samples with lower nitrate concentrations, ranging from 50 to 150 mg/L, were diluted from the stock solution and electrolysed at different initial such as the initial pH, CD, GBE, t, and C_0. The initial pH value of the prepared samples was adjusted to the desired value, 4 to 10, using 1 M HCl or 1 M NaOH solutions. While water conductivity was adjusted to 0.32 mS/cm using the required amount of sodium chloride (NaCl).

All chemicals were supplied by Sigma-Aldrich and used as supplied.

3.2. Batch EC reactor

In the current investigation, a new flow column reactor (FCER) has been used for water denitrification, Figure 1. This reactor consists of a Perspex cylinder container, 25 cm in height and 10.5 cm in diameter, with a controllable working volume of 0.5 up to 1 L. This container is supplied with a flow column that

consists of 10 aluminium perorated discoid electrodes, 10.4 cm in diameter and 1 mm in thickness of 99.5% purity provided by LJUM laboratories. Aluminium has been used as electrodes material because of its cost effectiveness, ready availability, and it requires comparatively less oxidation potential (Ghosh *et al.*, 2008a). The perforated electrodes were vertically installed inside the container using three PVC (Polyvinyl chloride) supporting rods and fixation tubes. Each electrode, which has 48 holes of 5mm in diameter, was offset horizontally by an angle of 22.5 degrees from the one above it to ensure that the water will flow in a convoluted path, which achieves high mixing and aeration efficiency. As a result, the stirring and aerating devices that until now have been widely used in the electrocoagulation reactors are unnecessary.

The flow column was designed to be movable that enables the operator to exclude the accumulated air bubbles on electrodes surfaces, which negatively influence the electrical resistance and the energy consumption as consequence (Gao *et al.*, 2013).

This reactor was connected to a peristaltic pump (Watson-Marlow type, Model: 504U) to circulate the water and a rectifier (HQ Power; Model: PS 3010, 0-10 A, 0–30 V) to generate the required electrical current. Additionally, this bench scale unit was supplied with a 3 in 1 sensor (type: Hanna; Model: HI 98130) to monitor water temperature, conductivity, and pH during the electrolysing process.
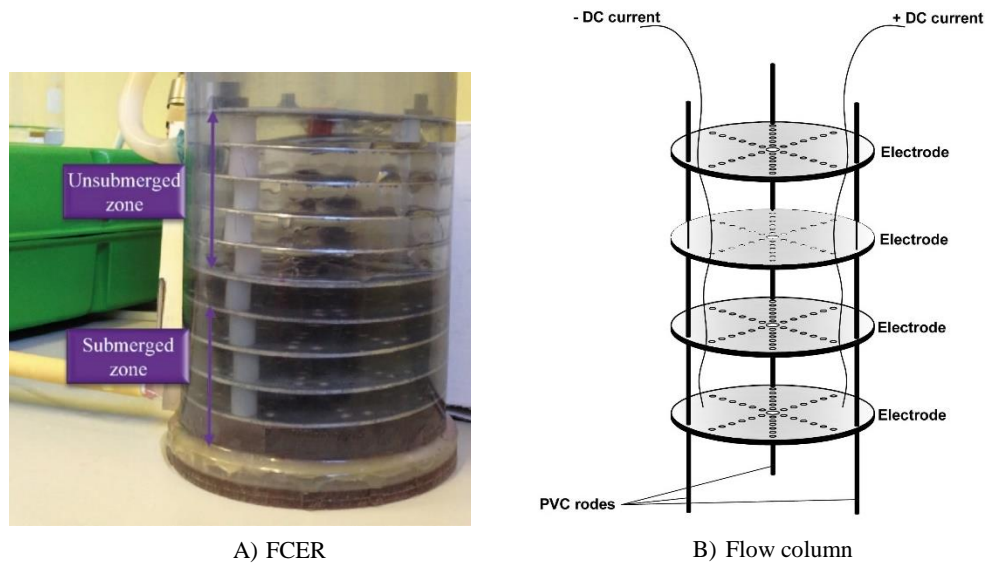

| A) FCER | B) Flow column |

Fig. 1. The new EC reactor (FCER)

3.3. Experiments

Denitrification experiments were carried out at a room temperature ($\approx 20\ C^0$) with 500 mL of synthetic water samples. The nitrate solution was continuously circulated in the FCER using a peristaltic pump at a flow rate of 250 mL/min.

Several key operating parameters were investigated for their influence on nitrate removal from water, such as the initial pH (4 to 10), CD (1, 2, and 3 mA/cm^2), GBE (from 3 to 10 mm), t (from 0 to 70 min), and C_0 (from 50 to 150 mg/L).

At the end of the run, the power was switched off, and the electrodes were cleaned with HCl acid and deionised water.

3.4. Analytical Procedure

The change in the residual nitrate concentration, during the course of the experiments, was monitored by collecting five mL fractions from the FCER at 5 min intervals. The collected samples were filtered with a 0.45 µm Sigma-Aldrich filter before analysis (Abdallah *et al.*, 2014). The residual nitrate concentration, in the collected filtrate, was calculated by using NitraVer®5 nitrate reagent (supplied by Hach-Lange) and a preprogramed Hach-Lange spectrophotometer (Model: DR 2800).

The removal efficiency (Re %) was calculated using the following formula:

$$Re\% = \frac{C_0 - C_f}{C_f} \times 100\% \tag{1}$$

Where C_0 and C_f are the initial and residual concentrations of nitrate, in mg/L, respectively. While, the energy consumption (E) make as follows (Ghosh *et al.*, 2011):

$$E = \frac{I*V*t}{Vol.} \tag{2}$$

where E is the electrical energy consumption (kWh/m^3), I is the current (A), V is the potential (V), t is the time (H), and *Vol.* is the volume of solution (m^3). At the end of the run, the electrodes were cleaned with HCl acid and deionised water.

3.5. Statistical analysis

The model proposed in the current study has been developed using the Multiple regression (MR) technique. The latter has been used as a statistical tool because it has many attractive merits. For instance, it has the ability to investigate the complex relationships between one dependant variable (DV) and a set of independent variables (IVs) (Tabachnick and Fidell, 2001; Pallant, 2005). This technique based on a number of assumptions concerning the size of dataset, presence of outliers within the dataset, correlation between the studied variables, and the nature of the variables' relationship and the scores' distribution (Pallant, 2005).

3.5.1. Assumptions of the MR technique

I. Size of dataset

Though the MR technique possesses the ability to explore the complex relationships between sets of variables, it is not applicable for small datasets (Pallant, 2005). Therefore, the size of data sets must be checked before performing the MR technique. Tabachnick and Fidell (2001) suggested the following equation to calculate the minimum required number of data points to perform the MR technique:

$$N > 50 + 8IVs \tag{5}$$

Where N is the minimum required number of data points to perform the MR technique.

II. Multicollinearity

This phenomenon, which negatively influences the outcomes of the MR technique, takes place in a dataset when one or more IVs are linearly predicted from others (high correlation between IVs) (Tabachnick and Fidell, 2001). This phenomenon therefore, must be removed by removing one of the correlated IVs, or by generating a new IV from the correlated IVs (Pallant, 2005). The occurrence of multicollinearity can be detected by calculating the tolerance value (Eq. 6); high tolerance values (> 0.1) indicates the absences of multicollinearity (Tabachnick and Fidell, 2001; O'brien, 2007).

$$Tolerance = 1 - R^2 \tag{6}$$

Where R^2 is the coefficient of determination.

III. Outliers

Outlier could be define as a data point, or points, that lie an abnormal distance away from the other data points in a sample (Walfish, 2006). Such extreme data points must be removed, before performing the MR technique, as they skew calculations and make the outcomes of the statistical analysis invalid (Fitrianto and Midi, 2011; Field, 2008). The presence of outliers within a dataset can be detected by determining Mahalanobis distances, which should be less than the critical Mahalanobis distances (Tabachnick and Fidell, 2001). The latter is calculated depending on the number of the studied IVs, in the current study the critical Mahalanobis distances is 20.52 as the studied IVs were 5 (Pallant, 2005).

IV. Nature of the variables' relationship and the scores' distribution

The scatterplot provides the required information to check the data distribution, where it is expected, in the normal distribution, that not more than 1% of the standardised residual values of the data points outside the range 3.0 to -3.0 (Pallant, 2005).

3.5.2. Contribution of each IV to the developed model

The contribution of the studied IVs to the outcomes of the developed model varies from substantial to ignorable depending on its statistical significance (p) (Tabachnick and Fidell, 2001; Pallant, 2005). Any IV with a $p < 0.05$ substantially influences the outcomes of the suggested model, while IV with p-value ≥ 0.05 can be omitted due to its minor contribution to the suggested model (Pallant, 2005; Field, 2008). Additionally, the contribution of IVs to the outcomes of the developed model could be compared by calculating their Beta values; where the higher the Beta, the higher the contribution (Pallant, 2005).

3.5.3. Evaluating the model

The current step of the statistical analyses concerns the agreement between the outcomes of the suggested model and actual experimental results. This could be checked by calculating the coefficient of determination (R^2), Eq.8, for the suggested model (Pallant, 2005). R^2 varies on a 0-1 scale: An R^2 of 1 indicates perfect agreement between actual and predicted results; while R^2 of 0 indicates the disagreement between the outcomes of the suggested model and the actual data.

$$R^2 = SS_{reg}/SS_Y \tag{8}$$

Where SS_{reg} and SS_y are the sum of squares for regression and the total sum of squares respectively.

In this investigation, SPSS-22 package was used to conduct the required statistical analysis.

3.6. Hydrogen production and the yieldable energy from this gas

Hydrogen gas (H_2), which classified as eco-friendly high energy fuel ($122 \ kJ/g$), is emitted from EC units during the treatment process as a by-product (Nasution *et al.*, 2011; Hashim *et al.*, 2017; Lakshmi *et al.*, 2013). A broad body of literature demonstrate that this by-product gas could be recycled to produce electrical power, which in turn compensates a part of the required power to operate the EC system. For instance, Nasution *et al.* (2011) demonstrated that up to 54% of the electrical energy demand of the electrocoagulation process could be obtained from recycling the emitted H_2 gas.

The emitted amount of H_2 gas from an EC unit can be estimated using the following equation (Phalakornkule *et al.*, 2010):

$$Q_{H_2} = \frac{Cd . A . t . H}{F} \tag{9}$$

Where, Q_{H_2}, *Cd*, *A*, *t*, *H*, and *F* represent the generated H_2 gas (mole), applied CD in (A/m^2), effective surface area of electrodes (m^2), electrolysing time (sec), number of hydrogen molecules (1/2), and Faraday's

constant (96,500), respectively. While the yieldable energy from recycling the H₂ gas can be calculated as follows (Phalakornkule *et al.*, 2010):

$$E_{H_2} = m \left(0.244 \frac{MJ}{mole}\right) \tag{10}$$

Where E_{H_2} and m represent the yield energy (kJ), and the amount of H₂ gas (mole), respectively.

3.5. Microscopic characterisation of electrodes

Understanding how the EC process might influence the morphology of the electrodes is paramount for future development of any electrolysing system. Therefore, changes in the surfaces morphology of the aluminium electrodes have been investigated using scanning electron microscope (SEM) (Model: Quanta 200). This investigation was carried out by scanning 1cm² pieces of virgin and electrolysed electrodes.

5. Results and discussion

5.1. Influence of EC operating parameters on nitrate removal

5.1.1. Influence of initial pH

It has been well documented that the electrocoagulation (EC) process is highly influenced by the pH value of solution being treated, as the latter governs the ionic speciation, which in turn significantly influences the removal efficiency (Nanseu-Njiki *et al.*, 2009; Aoudj *et al.*, 2015; Zeboudji *et al.*, 2013).

In the present work therefore, the influence of the pH on the removal of nitrate by the EC method was investigated for initial pH ranging from 4 to 8. Initial pH values less than 4 were avoided as hydroxyl ions will not react with aluminium (Nanseu-Njiki *et al.*, 2009). Experimentally, 500 mL of nitrate solution was electrolysed, in each run, for 30 min at a constant CD of 2 mA/cm². The initial concentration of nitrate and GBE were also kept constant at 100 mg/L, and 5 mm, respectively.

It can be seen from Figure 2 that the residual nitrate concentration promptly decreased as the initial pH increased from 4 to 7, then it brought a slight decrease for the rest of studied values. This could be mainly attributed to the fact that the predominant species of aluminium, between pH 6 and 8, have high adsorption capacity such as $Al(OH)_3$, which in turn enhance nitrate removal efficiency. While in the alkaline environment (pH $\geq$ 9), $Al(OH)_4^-$, which has less adsorption capacity, is predominant (Emamjomeh and Sivakumar, 2009; Un *et al.*, 2013). Thus, it might be reasonable, in the current project, to use initial pH of 7 to carry out the rest of experiments.
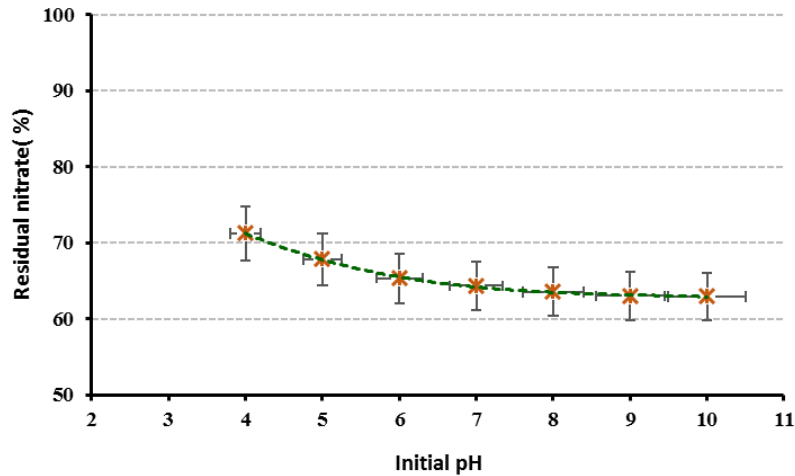
Fig. 2. Effects of initial pH on nitrate removal.

5.1.2. Influence of current density (CD)

A broad body of evidence in the literature demonstrated that the performance of the EC units is highly determined by the CD because the latter determines the anodic dissolution rate and hydrogen gas (H_2) generation (Daneshvar *et al.*, 2004; Emamjomeh and Sivakumar, 2005; Aoudj *et al.*, 2016). In the current study, to explore the influence of this key operating parameter on water denitrification, several sets of experiments were carried out at for 30 min at three different CDs (1, 2, and 3 mA/cm^2). The initial pH, nitrate concentration, and GBE were kept constant during the electrolysing process at 7, 100 mg/L, and 5 mm, respectively.

It can obviously be seen from Figure 3-(A) that the higher the CD was, the more rapid the nitrate removal was. For instance, it has been found that, after 30 min of electrolysing, the nitrate concentration was decreased by about 34% and 66.7% as the CD increased from 1 to 3 mA/cm^2, respectively. This increase in nitrate removal at high CDs could be attributed to the increase in anode dissolution rate, which in turn increases the removal efficiency (Ghosh *et al.*, 2008b; Nanseu-Njiki *et al.*, 2009; Kamaraj and Vasudevan, 2016).

Although the results obtained showed that increasing the CD enhanced the nitrate removal, it has been found that increasing this parameter negatively influenced the energy consumption of the EC unit. It can be seen from Figure 3-(B) that increasing the CD from 1 to 3 mA/cm^2 increased the energy consumption from 2.16 to 14.74 kW.h/m^3, respectively.

Therefore, in the current study, it might be reasonable to use a current density of 2 mA/cm^2 to carry out the rest of the experiments.
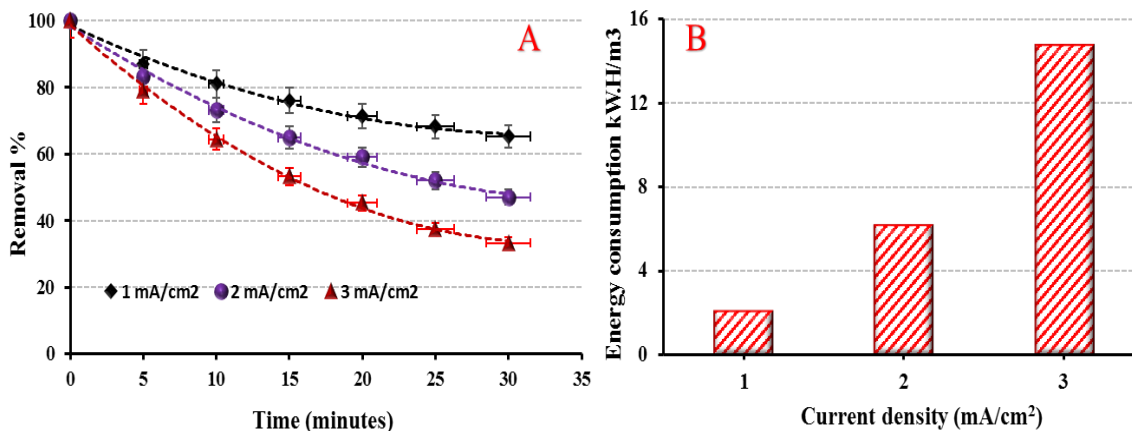
Fig. 3. (A) Nitrate removal as a function of CD, (B) variation of Energy consumption with CD.

5.1.3. Influence of gap between electrodes (GBE)

The effect of the GBE on nitrate removal from water at a constant CD (2 mA/cm^2) was investigated at 3, 5, and 10 mm. The initial pH and nitrate concentration were kept constant at 7, and 100 mg/L, respectively.

As shown in Figure 4-(A), the nitrate removal is reversely proportional to the GBE, where the residual nitrate concentration increased, after 30 min of electrolysing, from 42.8 to 53.2% as the GBE increased from 3 to 10 mm, respectively. In addition, Figure 4-(B) shows that increasing the GBE negatively influenced the energy consumption of the EC unit.

The GBE is an operating parameter that influences the performance of the EC unit due to increasing the electrical resistance for the current flow between the cathode and anode, which in turn increases the energy consumption (Attour *et al.*, 2014; Hakizimana *et al.*, 2016). Moreover, increasing the GBE promotes the growth of passive anodic layer, which negatively influences the removal efficiency of the EC method (Mameri *et al.*, 1998; Ghosh *et al.*, 2008a).

This could be explained by the fact that if the GBE increases then both the cell resistance and the growth of the passive anodic film will also increase. Therefore, the current will decrease, and the amount of floc formed will likewise decrease, hence the efficiency will change (Ghosh *et al.*, 2008a; Attour *et al.*, 2014; Hakizimana *et al.*, 2016).

In the current project, based on the obtained results, it might be reasonable to adopt a GBE of 5 mm to commence the rest experiments.
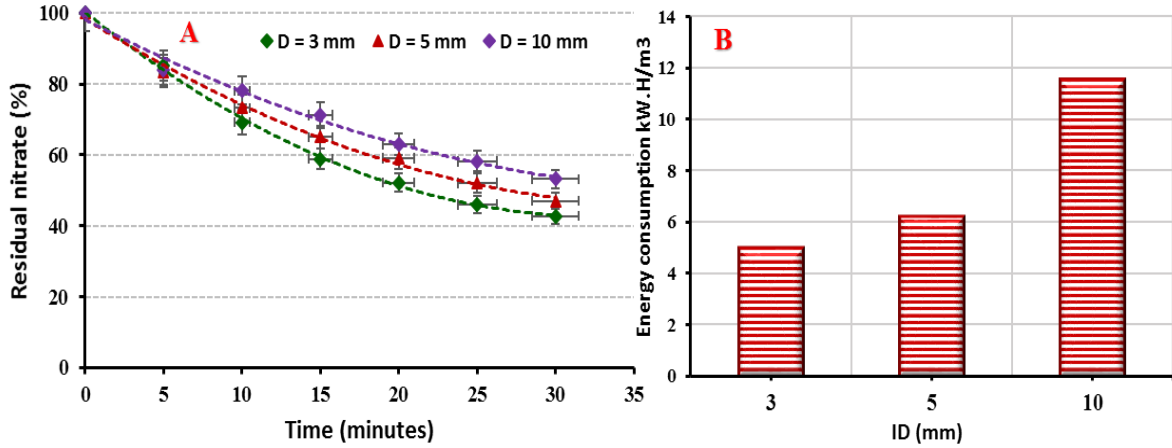
Fig. 4. (A) Nitrate removal as a function of GBE, (B) variation of Energy consumption with GBE.

5.1.4. Influence of treatment time

Faraday's Second Law (Eq. 11) indicates a direct proportion between the electrolysing time and the amount of the produced coagulants, which in turn enhances the pollutants removal efficiency.

$$X = \frac{(I)(t)(m)}{(Z)(F)} \tag{11}$$

where X is the released coagulants from the anode in grams, I the applied current in amperes, t electrolysing time (second), M is the molecular weight (26.98 g/mol), Z the number of electrons, and F is Faraday's constant (96487 C/mol).

In this part of the current project, the progress of nitrate removal with treatment time was investigated by electrolysing water samples containing 100 mg/L of nitrate for 70 min at initial pH of 7, GBE of 5mm, and CD of 2 mA/cm^2.

The obtained results, Figure 5, indicated that the longer electrolysing time was, the higher removal was. Where, it has been noticed that the residual nitrate concentration decreased from 38% to the vicinity of 4.5% as the electrolysing time increasing from 35 to 70 min, respectively. This could be explained by the fact that a constant amount of coagulation ions is liberated from the sacrificial anode for the same CD and electrolysing time. Consequently, increasing the electrolysing time increases the number of the produced aluminium ions (coagulants) in the solution (Aoudj *et al.*, 2010; Ganesan *et al.*, 2013; Lu *et al.*, 2015). Therefore, nitrate removal efficiency will also increase. Additionally, longer EC time gives longer contact time between pollutants and coagulants, which in turn enhances the removal efficiency (Lu *et al.*, 2015).
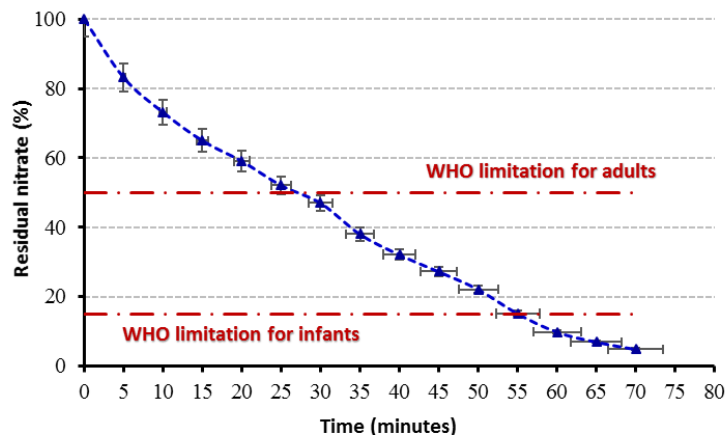
Fig. 5. Effects of electrolysis time on nitrate removal.

5.1.5. Influence of initial concentration

To explore the influence of initial nitrate concentration on the removal efficiency, 500 mL water samples with different nitrate concentrations (50, 100, and 150 mg/L) were electrolysed for 70 min at the optimum operating conditions (CD of 2 mA/cm^2, initial pH of 7, and GBE of 5mm).

The obtained results, Figure 6, showed that with an increase in the initial nitrate concentration, the required electrolysing time to attain the permissible nitrate concentration is also increased. For instance, at initial nitrate concentration of 100 mg/L, the FCER required 55 min to reduce the nitrate concentration to the allowable WHO limitations for infants. While at initial nitrate concertation of 150 mg/L, 70 min was not enough for FCER to meet these limitations.

One of the predominant pathways of pollutant removal by the EC method is the adsorption of pollutant molecules on the freshly produced metallic hydroxide flocs (Emamjomeh and Sivakumar, 2009; Dalvand *et al.*, 2011). According to Faraday's law (Eq. 11), a constant amount of coagulation ions is liberated from the sacrificial anode for the same CD and electrolysing time. Consequently, the same quantity of aluminium hydroxide flocs (coagulants) was produced in the solution. Therefore, the formed flocs, at high nitrate concentrations, were not sufficient to absorb all nitrate ions.

In conclusion, FCER is efficient to remove as high as 100 mg/L of nitrate from drinking water within 55 min of electrolysing at a CD of 2 mA/cm^2, and initial pH of 7.
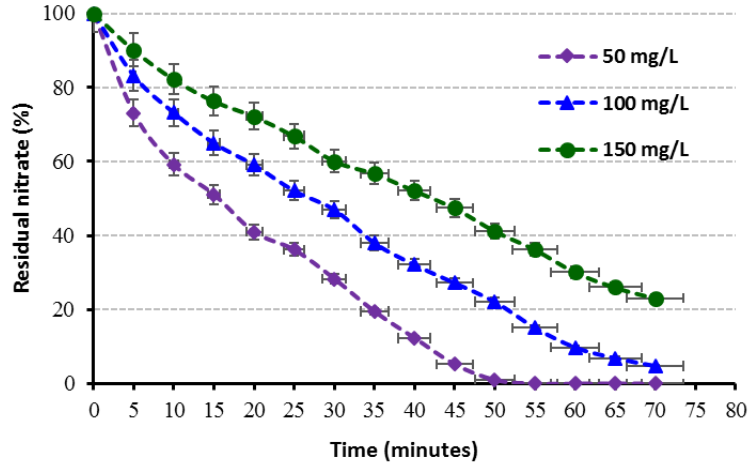
Fig. 6. Effects of initial nitrate concentration on removal efficiency.

3.2. Operating cost (OC)

The operating cost during the water treatment, in field work scale, includes cost of electricity, chemical reagents, sludge handling, maintenance, labour, and equipment (Ozyonar and Karagozoglu, 2011; Dalvand *et al.*, 2011). However, for the lab scale units, the most effective parameters in the determination of EC operating cost are the cost of the electrode material and the consumed amount of chemicals and energy (Bayramoglu *et al.*, 2004; Dalvand *et al.*, 2011). Therefore, in this preliminary cost study, the costs of electrode material, electricity, and chemical reagents were taken into account (Eq.12).

$$OC = \alpha \, C_{energy} + \gamma \, C_{material} + \beta \, C_{chemicals} \tag{12}$$

Where C_{energy} (kWh/m^3), $C_{material}$ (kg Al/m^3), and $C_{chemical}$ (kg /m^3) are the consumed energy electrode material, and chemicals respectively, α, γ, and β are the unit price of energy, aluminium, and chemicals according to the Iraqi markets 2016 (in the US $) respectively.

In this study, the unit prices were estimated according to the Iraqi market in August 2016. The consumed energy, at pH of 7, CD of 2 mA/cm^2, to reduce the nitrate concentration from 100 mg/L to less than 50 mg/L (WHO limitations for drinking water for adults) was 6.21 kW.h/m^3. While the consumed amount of electrode material was calculated using Faraday's Second Law (Eq. 11). According to the stated unit prices and the consumed materials and energy, the minimum cost for nitrate removal using the FCER is:

OC = 6.21 *2.5/100 + 1.53* 0.181 +0.02 = 0.155 + 0.28= 0.455 US $/m^3

Although this cost is comparable with those in literature, for instance, Emamjomeh and Sivakumar (2009) reported that the fluoride removal from drinking water costs from 0.36 to 0.61 AUD/m^3 (about 0.27 to 0.45 US $/m^3), FCER decreased the total treatment cost. Where FCER reduces the use of external stirring and aerating devices which require extra power to work; these devices until now have been widely used in the

EC reactors (especially laboratory scale ones). Therefore, FCER could be a cost-effective alternative to the traditional lab-scale EC reactors.

3.3. Statistical analysis

The results obtained from the experimental work demonstrate that the studied operating parameters influenced the nitrate removal performance of FCER. However, Figures 2-6 show that each operating parameter exerted a different degree of influence on nitrate removal.

Therefore, a statistical analysis was performed to estimate the simple and combined influence of the studied operating parameters on the nitrate removal performance of FCER. Additionally, the outcomes of the statistical analysis were used to develop a multiple regression model to reproduce nitrate removal from drinking water by FCER.

5.1.6. Testing the assumptions of the MR technique

The minimum required number of experimental data to develop a reliable MR model, according to Eq.5, is 90 points (because 5 IVs were investigated). This assumption has been met, as the actual measured data points were 102.

According to the results of Table 1, the presence of multicollinearity in the collected data is unexpected as the tolerance value for each IV is greater than 0.1. Additionally, no one of the determined Mahalanobis distances exceeded the critical value (20.52), which confirms the absence of outliers.

The last assumption, which relates to the nature of the variables' distribution, has been checked by calculating the standardised residuals. It can be seen from Table 1 that two data points have standardised residuals outside the permissible range (3.0 to -3.0), which indicates that this assumption has been violated. In such case, to check whether these points influence on the outcomes of the developed model as a whole, Tabachnick and Fidell (2001) recommended to determine the Cook's Distance (COO_1) of such points, any case with COO_1 greater than 1.0 represents a potential problem.

Therefore, the Cook's distances for these two values have been calculated. The results obtained, Table 1, confirm that these two cases do not exert a sensible influence on the outcomes of the developed model, as their COO_1 values were less than 1.0.

Table 1: Model coefficients

IVs	Tolerance	Max. detected Mahalanobis distance	Std. residual exceeds the acceptable range (3.0 to -3.0)		Max. COO_1	Sig.	Beta
			No. of cases	Value			
t	0.946					0.000	0.579
CD	0.942					0.000	0.297
Co	1.000	15.17	2	3.05	0.309	0.000	0.669
GBE	0.988			3.20		0.047	0.046
pH	1.000					0.252	

5.1.7. Contribution of each IV to the developed model

The influence of each single IV on the prediction of the DV was investigated by determining its relative Sig.

The results obtained, Table 1, indicate that all the studied IVs significantly influence the outcomes of the developed model except the initial pH. Where the Sig. of the initial pH was 0.252 (greater than 0.05), which means that the initial pH does not make a statistically significant unique contribution to the developed model. Therefore, the initial pH has been omitted from the current statistical study.

Basing on the results obtained from the statistical analysis of the collected data; the nitrate removal performance of FCER could be reproduced using the following formula:

$$Nitrate\ Re.\% = 100 - \frac{31.55 - 1.107\ t - 13.756\ CD + 0.753\ C_0 + 0.964\ ID}{0.01\ C_0} \tag{13}$$

Additionally, according to the calculated Beta values, Table 2, the initial concentration of nitrate has the strongest contribution to the outcomes of the suggested model, while the GBE has the lowest contribution. The contribution of the studied operating parameters to the suggested model followed the order of: $C_0 > t > CD > ID$.

Table 2: Beta values

IVs	t	CD	C_0	GBE
Beta value	0.579	0.297	0.669	0.046

5.1.8. Evaluating the suggested model

As mentioned before, checking how well the suggested model explains the variation in DV a is an essential step, and the best tool to check it is via the coefficient of determination (R^2). In the present study, the value of R^2 was 0.848; this means that the suggested model explains 84.8% of the variation in the nitrate removal performance of FCER.

Additionally, the developed model, Eq. 13, has been applied to a set of experimental data to investigate the agreement between the measured and predicted removal efficiencies. This set of data consists of 50 randomly selected experimental data points (at different operating conditions).

The results obtained, Figure 7, showed that the developed model possess an acceptable reproducibility for the nitrate removal performance of FCER. Where R^2 value for the correlation between the predicted and experimental efficiencies was 0.866.

In conclusion, the results obtained from the statistical analysis indicate that this model is suitable to reproduce the performance of FCER in terms of drinking water denitrification.
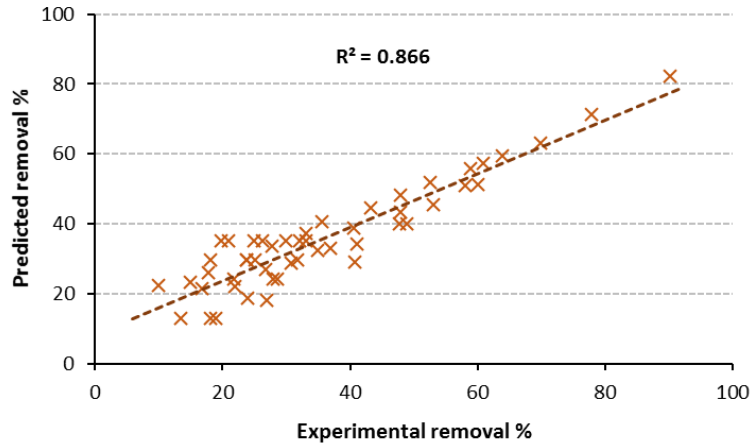

Fig. 7. Relationship between the predicted and experimental nitrate removal efficiencies.

3.4. Estimating the yieldable energy from recycling the harvested hydrogen gas

The emitted amount of H_2 gas from FCER, during drinking water denitrification process, has been estimated using Eq. 9. While the yieldable energy from recycling this gas was calculated using Eq.10.

The produced amount of H_2 gas, which has been calculated at operating conditions of 55 min of electrolysing, Cd of 2 mA/cm^2, and effective surface area of electrodes of 284 cm^2, was:

$$Q_{H_2} = \frac{20 * 0.0284 * 3300 * 0.5}{96500} = 0.01 \text{ mole}$$

17

This equivalent to 20 moles per each 1 m^3 of treated water, then the yieldable energy from this amount of H_2 gas is:

$$E_{H_2} = 20\ moles * 0.244\frac{MJ}{mole} = 4.88\ \text{MJ}$$

In terms of electricity production, recycling the produced amount of H_2 gas from the FCER during water denitrification is enough to generate 1.36 kW/m^3 (taking into accounts that each 3.6 MJ =1.0 kWh (Phalakornkule *et al.*, 2010)).

 According to these results, the produced amount of H_2 gas from filed scale treatment plants could be used to produce a considerable amount of electricity.

3.5. SEM characterisation of electrodes

The magnified SEM images for the virgin and electrolysed aluminium anodes are shown in Figure 8. It can obviously be seen from this figure that the surface of the virgin anode was uniform except few dents, which could have occurred due to the mechanical handling of metal sheets during electrode shaping process. While the surface of the electrolysed anode became non-uniform with a huge number of dents, which could be attributed to the dissolving of anode material at the active sites where the anode dissolution results in the generation of aluminium hydroxides (Ahlawat *et al.*, 2008; Vasudevan *et al.*, 2012).
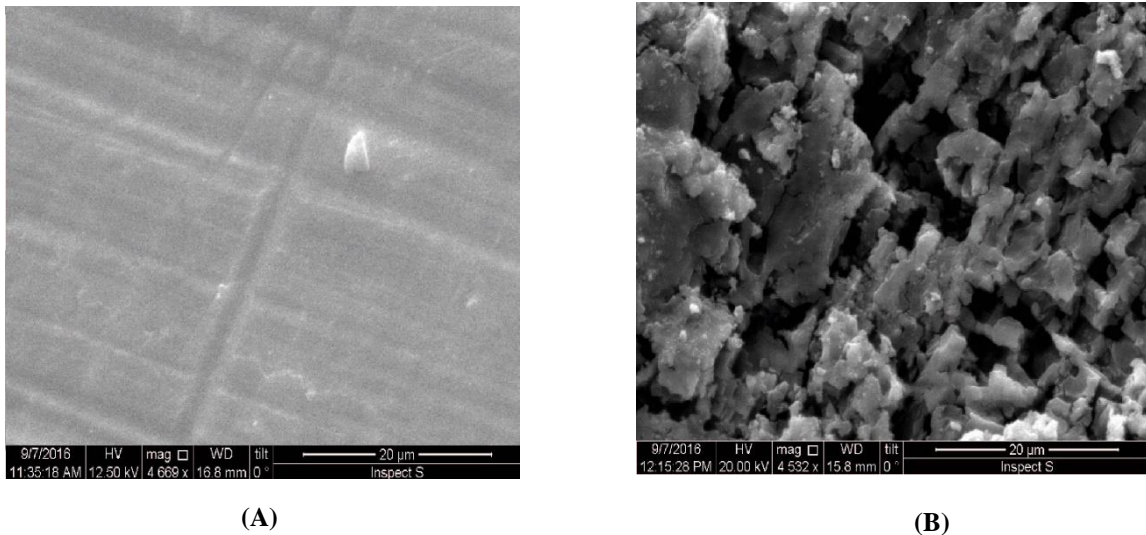

(A)   **(B)**

Fig. 8. SEM images of aluminium anode, (A) before EC process, and (B) After EC process.

4. Conclusion

The present study demonstrated a successful application of flow column in the design of EC reactors. The outcomes of the current project showed that a vertical flow column could be used to complete mixing and aerating of the solution being treated. As a result, the need for external stirring and aerating devices, which until now have been widely used in the traditional EC reactors, are unnecessary.

The new EC reactor, FCER, has been applied to remove nitrate from synthetic drinking water samples taking into accounts the influence of key operating parameters, such as the initial pH, CD, and GBE. The obtained results showed that the alkaline environment is preferred for nitrate removal, using the EC method, from drinking water. Additionally, it has been found that the liberated coagulants from the aluminium anode are proportional to a combination of both the applied current and the electrolysing time, which in turn influences denitrification process. Oppositely, denitrification of drinking water was found to be reversely proportional to both the initial concentration of nitrate and the inter-electrodes distance. In addition, the electrochemical reactions during the electrocoagulation of nitrate electrolyte generate a considerable amount of H_2 gas as a by-product. Harvesting of the latter by-product gas is a beneficial advantage of the EC method, as this gas is classified as an environmentally friendly fuel.

The obtained results from the statistical analysis indicated the relationship between nitrate removal and operating parameters could be modelled with R^2 of 0.848.

In conclusion, basing on the obtained results, FCER could be a cost-effective alternative to the traditional EC reactor, especially lab-scale ones, as it reduced the need for external stirring and aerating devices that required extra power to work.

Acknowledgement

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