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Denitration of Coke Plant Wastewater Using A Bench-Scale Electrodialysis Unit Via Statistical Design

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Nitrate content in surface and underground water increased in some areas of the world caused by runoff from some industrial processes such as coking industry. Several degradation and separation techniques have been developed to eliminate nitrate efficiently from water. Electrodialysis (ED) represents a modern progressive electromembrane technology gaining an increasing attention in wastewater recovery. In this work, a bench-scale ED unit has been used to separate nitrate from synthetic solution and industrial wastewater collected from an Egyptian coke plant. Statistical design was applied to study the influence of different parameters (time, nitrate concentration and applied potential) those affecting the nitrate removal efficiency, and a mathematical model was generated. The results on synthetic solutions showed that all studied parameters are effective. The results have been collected at a 3-D cube that showed that at high levels of parameters (25 min, 15 V and 700 ppm) the nitrate removal efficiency was almost 100%, while a small nitrate removal efficiency of about 51% was obtained at the low levels (5 min, 5 V and 100 ppm). The wastewater sample was found to contain several inorganic and organic pollutants those could be separated together with nitrate. Only 2.5 hrs is sufficient to separate about 80% of nitrate at 15 V where longer time has no pronounce effect on nitrate separation. This is corresponding to about 15 ppm nitrate content in the output water, which is far less than the acceptable concentration of ≤ 44 ppm. After 5 hrs of ED operation, the removal efficiency of nitrate, sulphate, chloride, cyanide, ammonia phosphorus and phenol were 82, 99 , 96, 99, 98, 60 and 40%, respectively. These results revealed that electrodialysis can efficiently separate nitrate and most pollutants from coking wastewater for possible re-use. Spherical particles (5-20 µm) of mainly ammonium nitrate were obtained by evaporating the rejected water after ED operation.

Keywords: Nitrate, Coking Wastewater, Electrodialysis, Statistical Design

1. INTRODUCTION

Pollution of surface water, underground water and industrial wastewater by nitrate is a common problem in industrial and developing countries. The major causes of excess nitrate in water are agricultural runoff, poorly or untreated animal and human wastes and some industrial processes, especially coking, fertilizers, paper and munitions manufacturing. Removal of nitrate from drinking water has received increasing attention in recent years as the health effects of nitrate have come to the forefront. Contamination of drinking water with nitrate can endanger health especially for infants. Metabolically, nitrates may react with secondary and tertiary amines and amides, commonly derived from food, to form nitro amines which are known carcinogens. The World Health Organization's recommendation on the maximum admissible concentration (MAC) in drinking water is 10 mg NO_3 as N / L, which corresponds to 44 mg NO_3 / L [1-6].

Various methods have been tested for the denitration of water [2]. In principal, these can be divided into degradation processes including biological or catalytic nitrate reduction, and separation processes including electrodialysis (ED), distillation, ion exchange, donnan dialysis, reverse osmosis (RO) and electro deionization [7-14]. The use of micro-organisms for biological degradation of nitrate in drinking water poses the risks of the microbial or viral contamination. However, comparing with the known chemo-physical processes where the removed nitrate is returned unchanged to the environment, the biological processes have the advantage of the direct degradation of nitrate into molecular nitrogen. The disadvantage of the ion exchange process is the necessity of chemicals for regeneration. The bound nitrate ions are released back into the environment and may eventually re-enter the aquifer. The ED and RO processes are membrane based processes with proved reliability and efficiency in nitrate removal. Their advantages are the low chemical demand, and the reduction of water hardness as an added value. However, in RO the desalination is high and unselective. Only molecules about the size of water are retained and other substances are rejected into a waste stream [15]. The ED is a widely used electro-membrane process especially for desalination of brackish water and sodium chloride recovery from sea water [16]. The ED combines the advantages of selectivity and low chemical demand. The chemical demand is even less than that of the RO, and the water recovery is greater[8]. In the ED, the removal of ionic components from aqueous solution through ion exchange membranes is carried out under the driving force of an electrical field. The mandatory condition of ED process to be executed is an alternating order of cation and anion membranes and electric field applied across the entire assembly.

Coking wastewater is generated during high-temperature coal carbonization, coal gas purification and chemical products refining. A huge amount of this kind of wastewater is produced in coke plants. This wastewater contains a large number of biodegradable and refractory organic pollutants such as nitrate, ammonia, phenols, polycyclic aromatic hydrocarbons, pyridines, indoles and quinolines. Treatment by different methods can make some of the coke plant wastewater reusable in the coke quenching process, but a certain amount of wastewater is nevertheless discharged into the environment and ultimately ends up in the earth’s surface water bodies or agricultural ecosystems. It is known that the most common biological denitration of cokes wastewater can suffer from sudden failure due to the lack of inorganic carbon in aerobic reactor [17]. Small number of published works attempted to treat cocking wastewater for controlling their toxicity and almost no work was found on using ED technique for nitrate removal from this kind of wastewater that contain diverse organic and inorganic pollutants [18-19]. Therefore, it has become important to study the removal of nitrate pollutant from coking wastewater to ensure the safety around the coking areas. Statistical design is a developed approach which can be used for reaching optimum conditions by a minimum number of experimental runs to save time and cost of chemicals and other requirements.

The objective of this work is to study the removal of nitrate from wastewater of an Egyptian coking plant using the most promising and environmentally friendly ED technique. The first part deals with studying the function of different parameters affecting the nitrate removal from a synthetic solution using the experimental statistical design using Box-Behnken method. The second part reports the application of the obtained findings on removal of nitrate from cocking wastewater. The rejected water was concentrated to get ammonium nitrate byproduct.

2. EXPERIMENTAL

2.1. Water sample and reagents

A water sample was collected from inlet of the biological treatment station of Al-Nasr Company for Coke and Basic Chemicals Manufacturing, Helwan, Cairo, Egypt and kept in sealed plastic bottles. Composition, pH, hardness and alkalinity of the collected sample are presented in table 4. Reagent grade nitric acid, Sigma-Aldrich, 69%, was used for preparation of nitrate synthetic solution. Pure hydrochloric acid, ADWIC, 36 %, was used for cleaning of membrane stack of the ED unit. Pure sodium sulfate, ADWIC, 99%, was used for preparation of the electrolyte for rinsing the electrodes of the ED unit. Other chemicals used were of technical grade. Doubly distilled water is used throughout.

2.2. Electrodialysis system

An image of the used ED system (EUR 2C 7, EURODIA INDUSTRIE SA, France) is shown in Fig. 1. The separation mechanism by ED is graphically illustrated in Fig. 2. The specification of the ED unit is given in Table1. The unit is mainly comprised of membrane stack, three cylindrical tanks of dilute, electrolyte and concentrate solutions, three circulating pumps, DC power source, power control, three flowmeters and three valves. The membrane stack consisted of alternating series of 12 cation exchange membranes (type CMX; permeable only for cations) and 10 anion exchange membranes (type AMX; permeable only for anions) separated by gaskets and spacers where an electrical potential difference is applied between anode and cathode. The active area of each membrane is 2 dm^2. The anode is made of Pt coated titanium (Ti/Pt) and the cathode is made of stainless steel. The feed solution containing both positive and negative ions enters the membrane stack in a specific flow rate to which a voltage is applied, thus causing the migration of the ions toward their respective electrodes. The cation exchange membranes allow the transfer of cations but inhibit the transfer of anions. Conversely, anion exchange membranes allow the transfer of anions but inhibit the transfer of cations. The result is alternating compartments containing streams of dilute ion concentration (dilute) and streams rich in ion concentration (concentrate) exiting the stack [20]. The ionic rinse solution is circulated past the electrodes to maintain conductivity of the membrane stack while preventing potentially corrosive ions of the feed solution from contacting the electrodes. The circulation of solutions was assured by pumps.

2.3. Procedures

In the start up of the ED unit, the dilute compartment contained 2 L of a synthetic solution of the required nitrate concentration (prepared by dissolving ammonium nitrate in distilled water) or untreated industrial wastewater. The electrolyte compartment contained 2.5 L of 0.1 M Na_2SO_4 used as electrode rinse and the concentrate compartment contained 2 L of distilled water. The three solutions were circulated through the membrane chamber of the ED unit where a potential was applied between the anode and the cathode. Under the influence of direct current, the negatively charged nitrate ions in dilute migrate towards the anode, move through the anion exchange membrane and stopped by the cation exchange membrane in the concentrate compartment. During the test, water samples have been taken periodically from the dilute and concentrate streams at different time intervals and the nitrate ion concentrations were determined analytically.

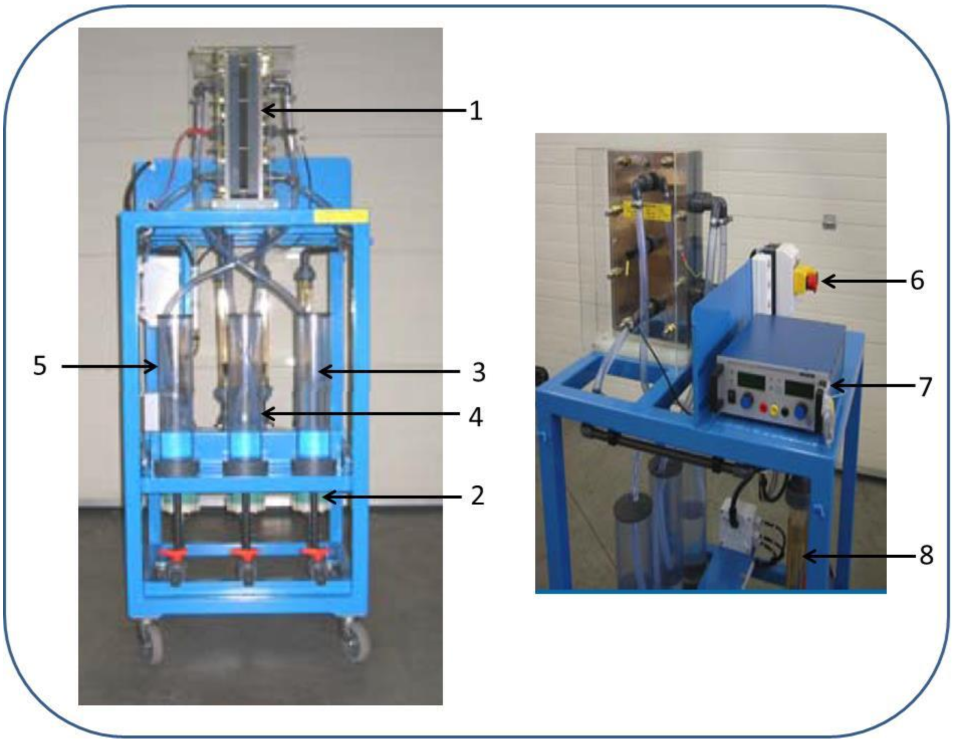

Figure 1. EUR 2C 7 electrodilysis unit. 1 membrane stack, 2 circulating pumps, 3 dilute, 4 electrolyte, 5 concentrate, 6 power source, 7 power control , 8 flowmeters.

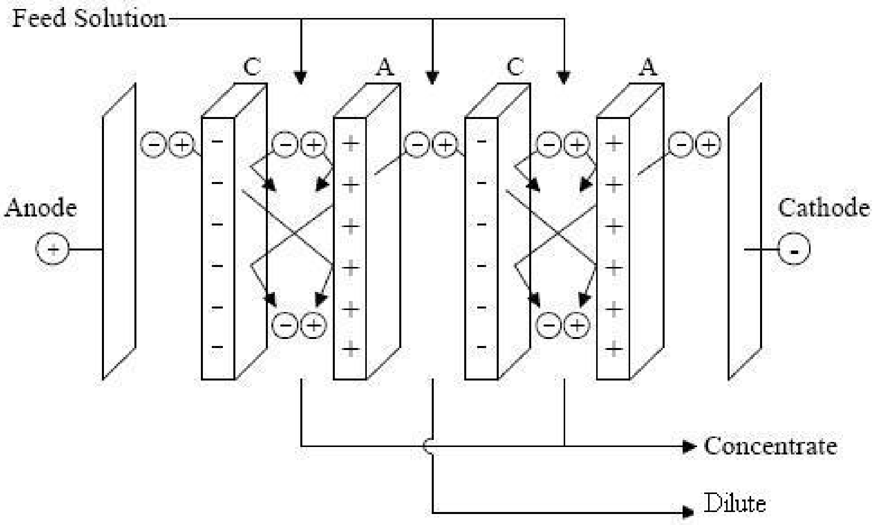

Figure 2. Graphical representation of ions separation by electrodialysis.

Table 1. Specification of main parts of the bench-scale ED unit

Item	Specification
Ion Exchange membrane	NEOSPTA-TOKUYAMA SODA
Cationic membrane:	CMX Sb12
Anionic membrane:	AMX Sb10
Effective area:	2 dm^2
Material of other parts	
Gasket:	EPDM
Spacer and distributor:	PE + PP
Electrodes	
Anode:	Ti/Pt
Cathode	Stainless Steel
Electrode chamber	P.V.C
Press plate	Steel, JIS SS -41
Operation control	
Dilute compartment	180 L/H
Concentrate compartment	180 L/H
Electrode chamber	
Anode	150 L/H
Cathode	150 L/H
Current	10 A Max.
Voltage	1 V/cell max.

To prevent scaling and fouling of the membrane by other ions in wastewater, it was cleaned by 0.35% HCl solution for 20 minutes after each run. The nitrate removal efficiency (%R) was expressed by the relation in equation 1 :

$$\%R = \frac{[NO_3^-]d - [NO_3^-]c}{[NO_3^-]d} \times 100 \qquad \textbf{(1)}$$

where $[NO_3^-]_d$ and $[NO_3^-]_c$ are initial nitrate concentration in the dilute compartment and in concentrate compartment after certain working time, respectively.

2.4. Chemical analysis

Nitrate was determined according to Allen's modification of the devarda' method [21], COD was determined using the potassium dichromate oxidation method; NH_3–N was determined using the Nessler's reagent spectrophotometry method; CN^- was determined using the isonicotinic acid-pyrazolone photometric method [12].Other chemical analyses were performed according to standard methods.

2.5. Crystallization of ammonium nitrate

In case of treatment of industrial wastewater by ED unit, a volume of produced ammonium nitrate solution in the concentrate compartment was collected, evaporated to dryness and the obtained crystals were dried, analyzed and investigated.

2.6. Characterization

Powdered samples (100 % -200 mesh) was analyzed using X-ray powder diffraction (XRD), Bruker AXS diffractometer (D8-ADVANCE) with Cu Kα radiation, operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ values between 0º and 80º and the scanning rate was 0.5º min^{-1}. Types of the phases in the samples were identified using the X-ray powder data file, published by the American Standard for Testing Material (ASTM). JEOL instrument (Japan) model JSM-5410 scanning electron microscope (SEM) was used for investigating the morphology of ammonium nitrate and the obtained products.

3. RESULTS AND DISCUSSION

3.1. Statistical experimental design

An experimental Box–Behnken design [22] was used to study the effect of some variables (working time, nitrate concentration and applied voltage) on removal of nitrate from synthetic solutions or industrial wastewater by the ED unit. The design-matrix of different runs, 15 experiments, as well as the levels of each factor are shown in Table 2. The used variables were: applied voltages in volts (5, 10, 15), nitrate concentrations in ppm (100, 400, 700) and working times in minutes (5, 15,25).

Table 2. Experimental Box Behnken Design with 3 levels and 3 variables

Run No.	Coded Factor Levels		
	Volt	Time	Concentration
1	-1	-1	0.0
2	-1	+1	0.0
3	+1	-1	0.0
4	+1	+1	0.0
5	-1	0.0	-1
6	-1	0.0	+1
7	+1	0.0	-1
8	+1	0.0	+1
9	0.0	-1	-1
10	0.0	-1	+1
11	0.0	+1	-1
12	0.0	+1	+1
13	0.0	0.0	0.0
14	0.0	0.0	0.0
15	0.0	0.0	0.0

Levels

Variables	-1.0	0.0	+1.0
Volt, V	5	10	15
Time, min	5	15	25
Concentration, ppm	100	400	700

Nitrate removal efficiency was the response used for evaluation and comparing experimental results. Box–Behnken experimental design for the variables is shown in Table 3. Plots of the response (removal efficiency of nitrate) surface contours and the best predictive models for estimate of the response variable were developed. The Box–Behnken design in Table 3 can fit the following model [23] following a second order polynomial function by which correlation between studied factors and response was generated.

$$E(y) = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} X_i X_j \qquad (2)$$

where y is the estimate of the response variable and Xi's are the values of independent variables [volt, time, and concentration] those are known for each experimental run. The parameters β_0, β_i and β_{ij} are the regression parameters.

Software package, Design-Expert 6.1, Stat-Ease, Inc., Minneapolis, USA, was used for regression analysis of experimental data and to plot response surface. Analysis of variance (ANOVA) was used to estimate the statistical parameters. The extent of fitting the experimental results to the polynomial model equation was expressed by the determination coefficient, R^2. F-test was used to estimate the significance of all terms in the polynomial equation within 95% confidence interval.

3.2. Synthetic nitrate solutions

Synthetic solutions containing different concentrations of ammonium nitrate were fed to the dilute compartment of the ED unit and several runs were carried out at different applied voltages and conducting times. The obtained results of nitrate removal efficiency for each run are represented in Table 3. It can be seen from this table that all the studied factors are significant regarding the nitrate removal efficiency. The statistical design data showed that the standard deviation was 4.73. The good predictability of the models can be indicated by correlation coefficient R^2 was 0.9032.

The correlation between the nitrate removal efficiency and the process parameters (applied potential, working time and nitrate concentration) is shown in the following model that is generated from experimental data in table 3:

$$\text{Nitrate Removal Efficiency, (\%)} = 24.61 + 1.98A + 1.46B + 0.11C - 9.67E\text{-}005C^2 - 0.04AB - 5.17E\text{-}004BC \quad (3)$$

where A is the applied potential (Volt), B is the working dialysis time (min) and C is the nitrate concentration (ppm). The estimated values of nitrate removal efficiency using the above model are presented also in Table 3. These values declares the agreement of the generated model and the experimental results.

Table 3. Removal efficiency of nitrate according to the experimental statistical design conditions

Run No.	**Variables**			**Response**	
	Volt,V	**Time, min**	**Concentration, ppm**	**Removal Efficiency, %**	
				Experimental	**Estimated***
1	5	5	400	72.3	68.30
2	5	25	400	94.5	89.37
3	15	5	400	83.4	86.10
4	15	25	400	98.3	99.17
5	5	15	100	60.3	62.67
6	5	15	700	70.3	77.60
7	15	15	100	80.3	76.47
8	15	15	700	92.6	91.40
9	10	5	100	60.3	59.49
10	10	5	700	85.2	77.52
11	10	25	100	80.3	79.65
12	10	25	700	92.5	91.47
13	10	15	400	88.9	85.74
14	10	15	400	87.1	85.74
15	10	15	400	86.2	85.74

*By applying the mathematical model in eq. 3.

Figure 3 shows the interaction between the effect of time (min) and potential difference (V) on nitrate removal efficiency at different nitrate concentrations (Fig. 3.a : 100 ppm, Fig. 3.b : 400 ppm, and Fig. 3.c : 700 ppm) in the input water. These results showed that the removal efficiency of nitrate from the dilute compartment increased gradually by increasing its concentration due to increasing the electric conductivity. At 100 ppm nitrate, the removal efficiency increased from 55% to 84% with increasing working time from 5 to 25 min and potential from 5 to 15 V. However, at 400 ppm nitrate, the removal efficiency increased from 72% to 100% with increasing working time from 5 to 25 min and potential from 5 to 15 V. At nitrate concentration of 700 ppm, nearly similar results to the later were obtained under similar conditions of working time and applied potential. It can be thus concluded that starting with nitrate concentration of 400 ppm or higher preserve high process efficiency at these conditions.

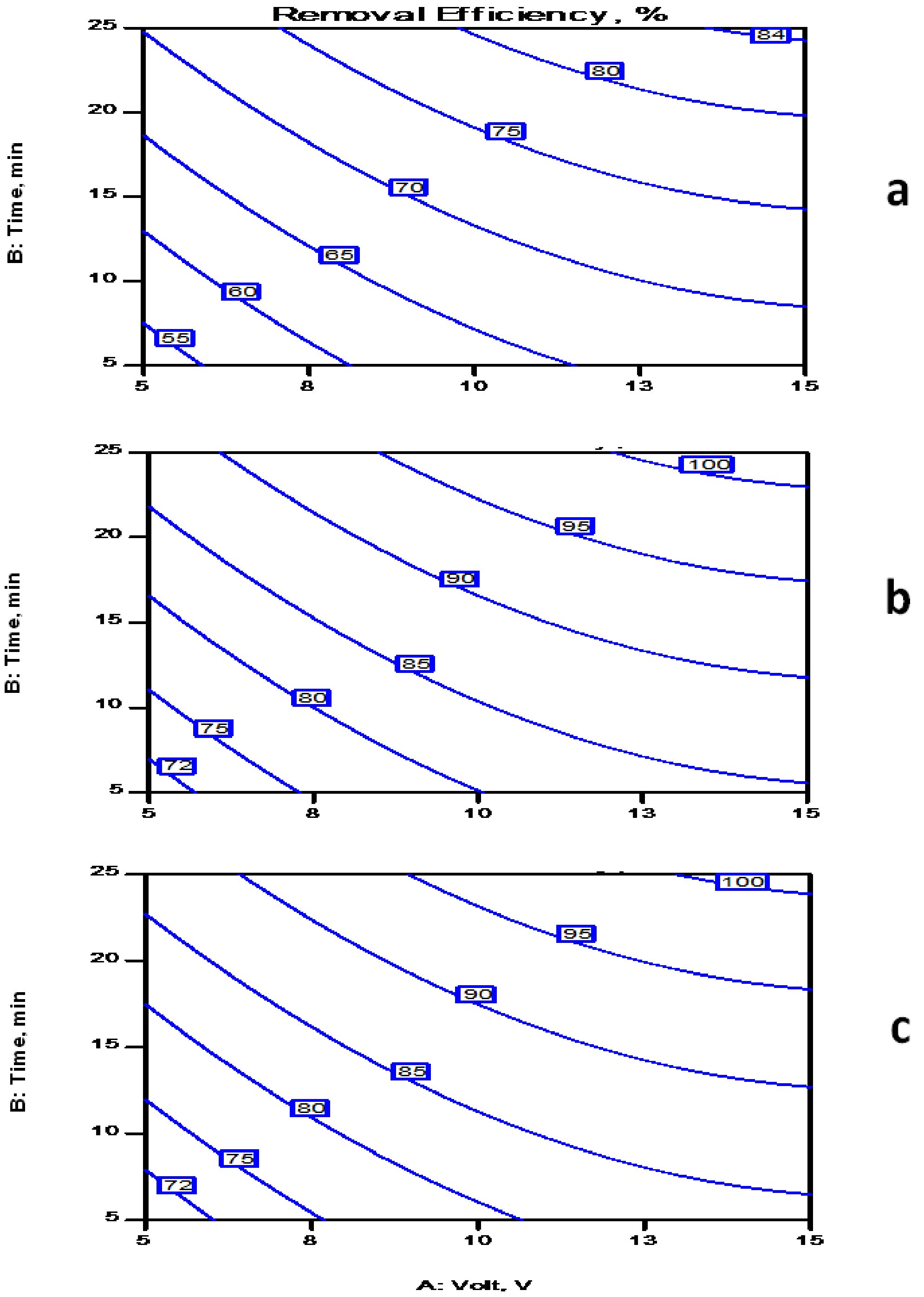

Figure 3. Effect of working time and applied volt on nitrate removal efficiency by ED unit at different nitrate concentrations (a: 100 ppm, b: 400 ppm, c: 700 ppm)

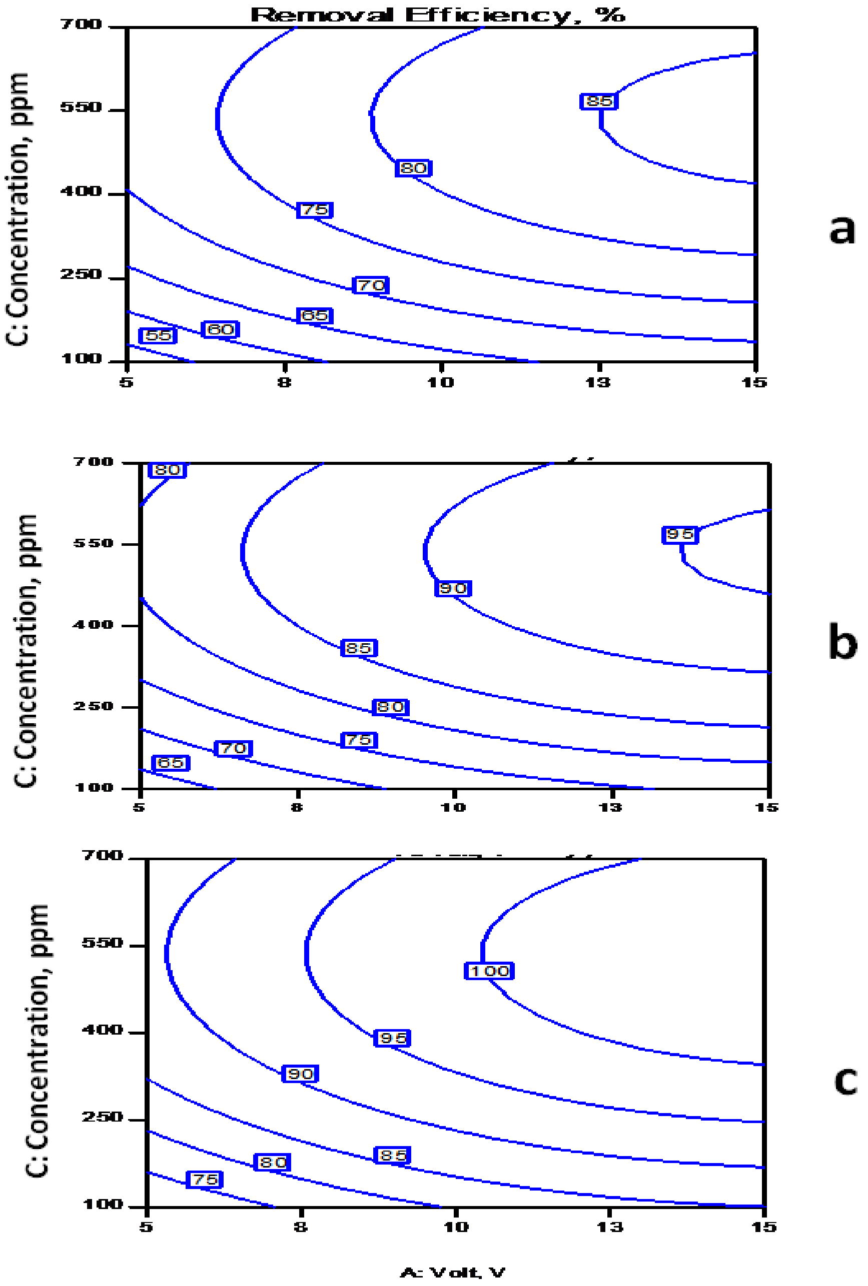

Figure 4. Effect of nitrate concentration and applied volt on removal efficiency by ED unit at different working times (a: 5 min, b: 15 min, c: 25 min)

It is common that, the degree of ion removal by the ED cell is mainly controlled by the applied potential which is considered the driving force for ion transport through the membrane. Figure 4 shows the effect of interactions of two factors; the applied potential and the nitrate concentration on the removal efficiency at different working times (5, 15 and 25 min). It can be generally observed that beyond working time of 5 min, the nitrate removal efficiency was increased rapidly with time at higher voltage and slowly at lower one. At working time of 5 min , the nitrate removal efficiency was increased from 55% to 85% with increasing the applied voltage from 5 to 15 V and increasing the nitrate concentration from 100 to 700 ppm, respectively. However, after working time of 15 and 25 min, the nitrate removal efficiency increased from 65% to 95% and from 75% to 100%, respectively, under similar conditions to the above.

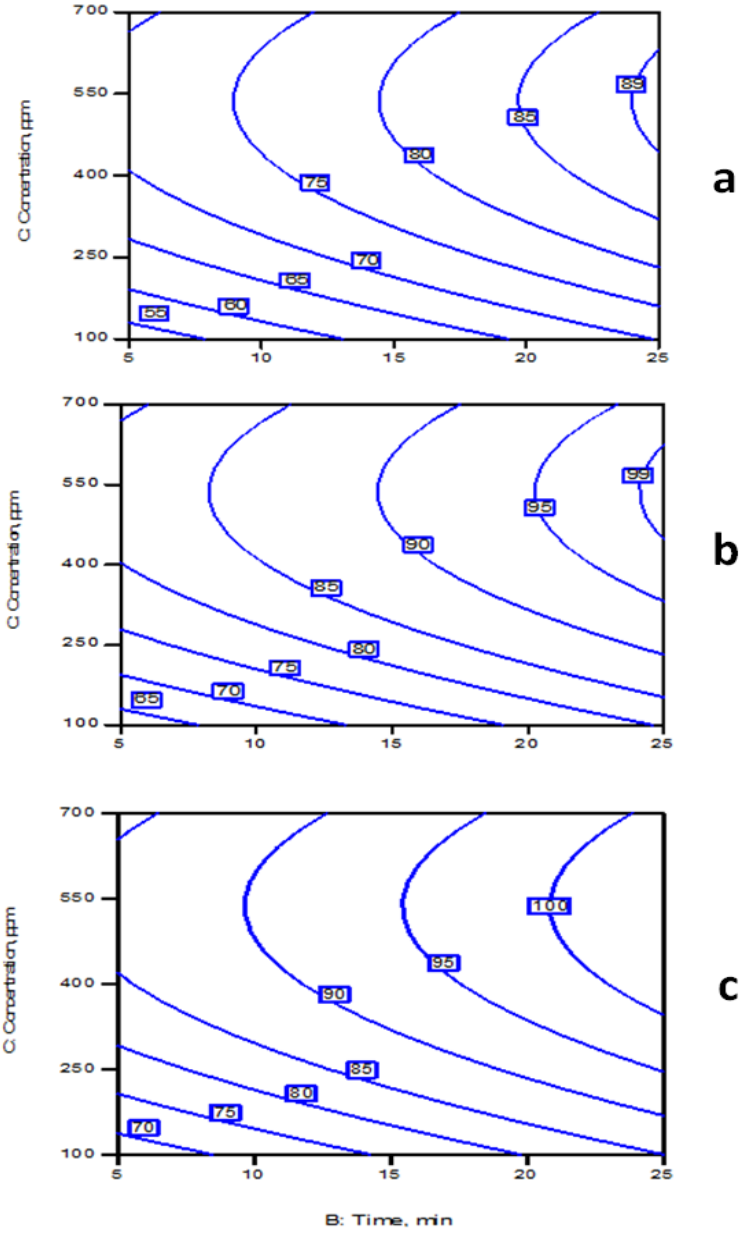

Figure 5. Effect of nitrate concentration and working time on removal efficiency by ED unit at different applied volts (a: 5V, b: 10V, c: 15V)

The working time of the ED unit is an important factor from the economical point of view, and the nitrate concentration in the input water may vary according to the operating and discharge conditions in the coke plant. Figure 5 shows the effect of two factors; the working time (5, 15 and 25 min) and the nitrate concentration (100, 400 and 700 ppm) on the nitrate removal efficiency at different applied voltages. The results showed that at 5V, the nitrate removal efficiency increased from

55% to 89% with increasing working time from 5 to 25 min and nitrate concentration from 100 to 700 ppm. At applied potential of 10V, the nitrate removal efficiency increased from 65% to 99% at similar conditions to the above. However increasing the applied potential to 15V, the removal efficiency increased from 70% to almost 100% under same conditions of time and nitrate concentration.

All the experimental data has been collected at the 3-D cube as shown in Figure 6. This cube show that the highest nitrate removal efficiency of 99.4% can be obtained at the highest levels of parameters. The smallest nitrate removal efficiency of about 51% was obtained at the lowest levels of parameters. Decreasing any of the main variables lead to the decrease of removal efficiency. These variables can be adjusted to obtain the desired nitrate concentration in the output water which should be close the acceptable level of 44 mg NO_3 / L [1-6].

3.3. Industrial Nitrate Wastewater

The composition of the collected sample of wastewater from the Egyptian coke plant is shown in Table 4. It can be seen that this water is polluted with several kinds of inorganic and organic components (e.g. nitrate, ammonia, cyanide and phenol). The total dissolved solids are as high as 1726 ppm. By figuring out the above study of synthetic nitrate solutions, the electrodialysis unit was operated for testing the de-nitration of this water sample at a moderate applicable potential of 15 V. It is understandable that other pollutants can be separated at the meantime together with nitrate, and this will be also examined. Samples have been collected during operation of the ED unit at different working times of 1.5, 2.5, 3.5, 4.5 and 5 hours. Because this water sample contained high amounts of salts, the working time was lengthened to 5 hours. Figure 7 shows the effect of working time of ED unit on nitrate removal efficiency from the wastewater sample at 15 V. It can be seen from this figure that the nitrate removal efficiency gradually increased with time until 2.5 hrs and then very slightly increased. The composition of the output water sample after treatment by the ED for 5 hrs is shown in Table 4. The results showed that, the removal efficiency of nitrate is about 82% and the nitrate concentration reached about 15 ppm as NO_3^-. This concentration is obviously much lower than the acceptable level.

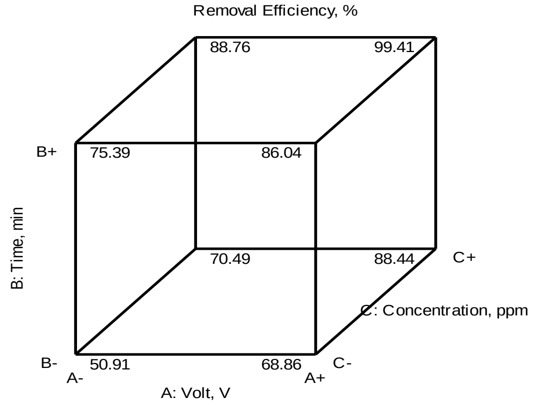

Figure 6. 3-D Plot for all the experimental data for synthetic solution of nitrate

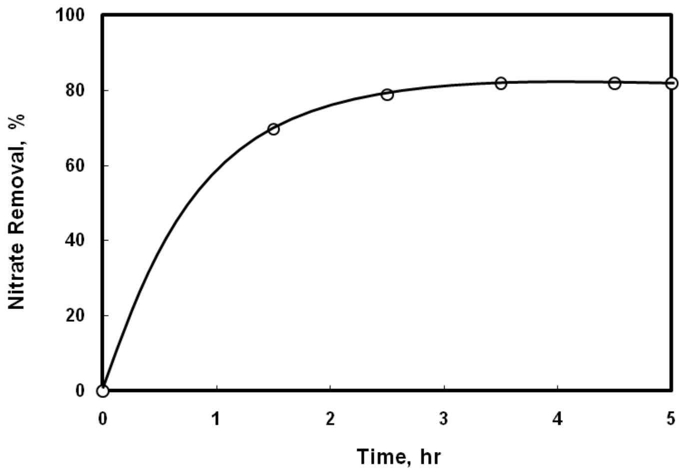

Figure 7. Removal efficiency of nitrate from cocking wastewater with increasing working time using ED unit at 15 V.

Table 4. Chemical analysis of treated and untreated industrial wastewater and the nitrate removal efficiency after 5 hours ED operation at 15 V.

Analyzed Parameter	Untreated water, ppm [Feed]	Treated water, ppm [product]	Removal efficiency %
Hardness	3.5	0.5	85.7
Alkalinity	7.6	0.6	92.1
Ammonia	251.6	4.08	98.4
pH	7.8	4	-
Phenol	4	2.4	40.0
Chloride	181	7.1	96.1
Nitrate	83.16	15.12	81.8
Sulphate	116.6	1.6	98.6
Cyanide	50.92	0.47	99.1
phosphorus	0.1	0.04	60.0
TDS	1726	0.0404	99.9
Oil	74	20	72.9
C.O.D	307.2	96	68.7
B.O.D	63.7	28.1	55.9

As shown in Table 4, the percentage removal efficiency of phenol, phosphorus, oil, alkalinity, chloride, ammonia, sulphate, cyanide and TDS are 40.0, 60.0, 72.9, 92.1, 96.1, 98.4, 98.6, 99.1 and 99.9, respectively. These high removal percentage of most pollutants and toxic materials from the coke wastewater sample make the ED more advantageous than other removal techniques.

3.4. Crystal Structure of separated solids

One important feature of the ED process is that it re-concentrates the depleted salt solutions. This solution can be further concentrated by the common methods to obtain a valuable product. A 100 ml from concentrate compartment, after operating the ED unit for 5 hrs at 15 V on synthetic solution and wastewater, was dried by evaporation. The XRD patterns of obtained solids are shown in Fig.8. It is obvious that the peaks have high intensities and sharp spectrum. All the diffraction peaks in crystals of synthetic solution are ascribed to the ammonium nitrate phase (JCPDS card # 83-0520). No other diffraction peaks or phases are detected in pattern. This indicates that the sample is pure ammonium nitrate. It is also showed in Fig. 8 that the crystals obtained from wastewater sample was composed of ammonium nitrate and small amounts of sodium nitrate (JCPDS card # 07-0271). SEM images of crystals from synthetic solution are shown in Fig 9. The photomicrographs were taken at different magnifications varying from 100 to 3500 x. The crystals showed a spherical shape and the mean diameter was 5-8 μm. The sample from wastewater after ED treatment (Fig. 10) showed the same shape with crystals agglomeration together due to presence of sodium nitrate and the mean diameter is 5-20 μm.

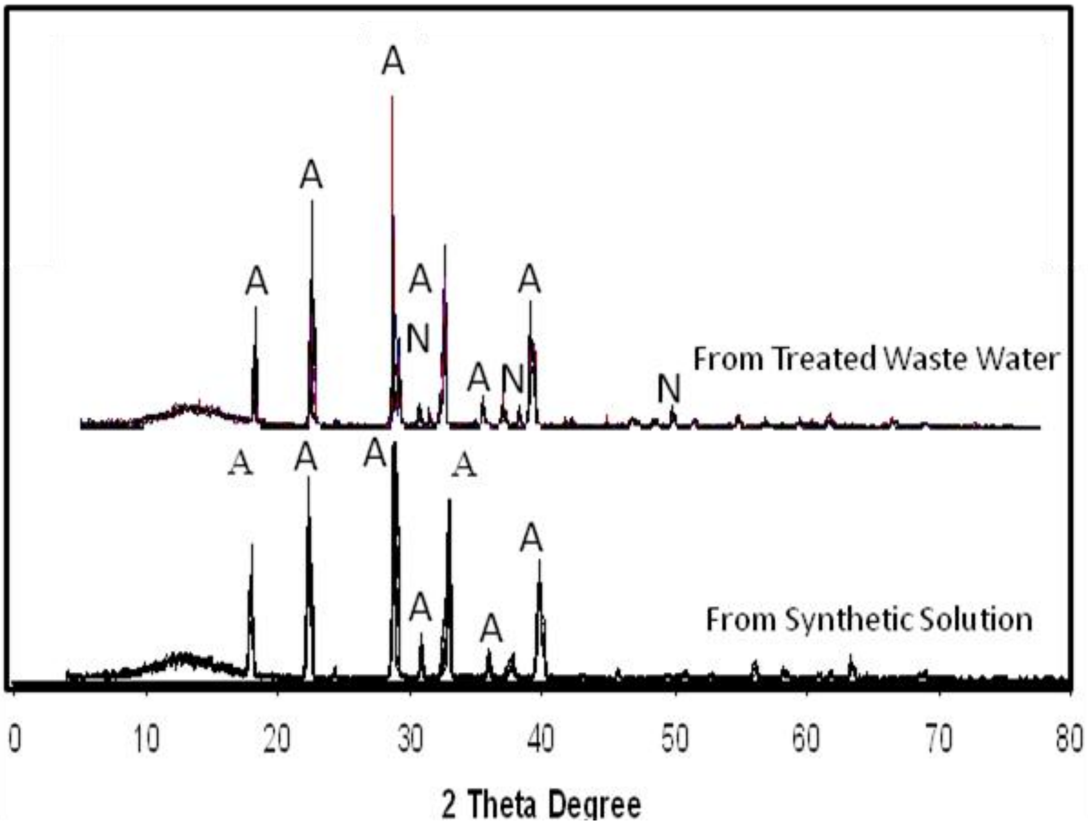

Figure 8. XRD patterns of removed solids from synthetic solution and wastewater by ED unit after 5 hrs at 15 V. A: ammonium nitrate, N: sodium nitrate.

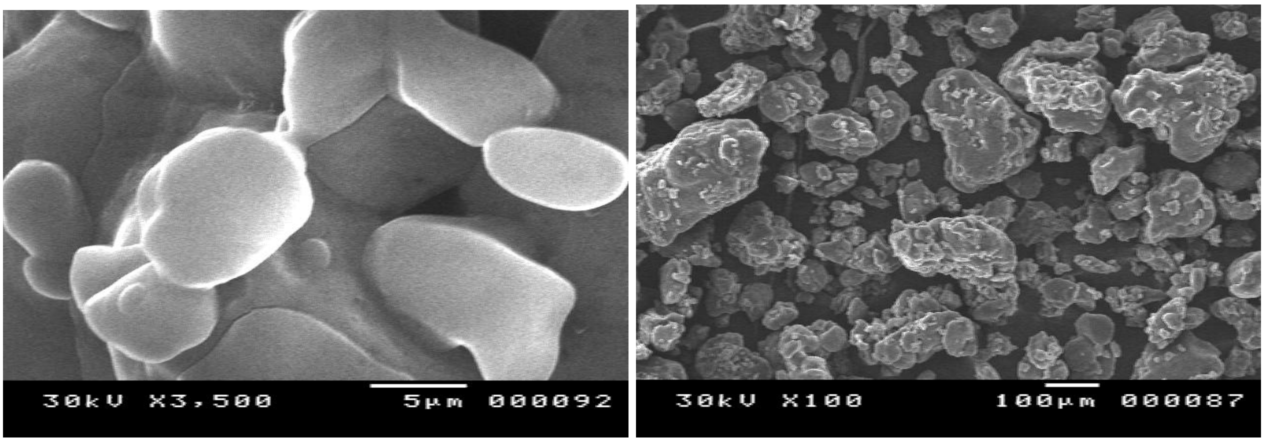

Figure 9. SEM images of solids from synthetic solution after treatment by ED for 5 hrs at 15 V.

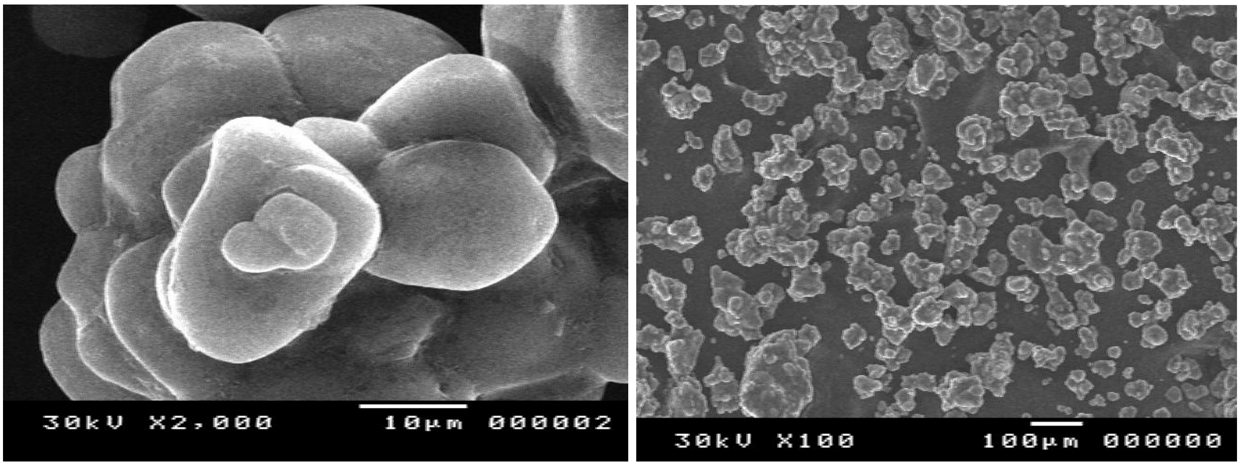

Figure 10. SEM images of solids from wastewater after treatment by ED for 5 hrs at 15 V.

4. CONCLUSION

Statistically designed experiments based on Box–Behnken procedure were used to study the effect of the three variables; time, nitrate concentration and volt on the removal efficiency of nitrate by electrodialysis from synthetic solution and industrial wastewater sample. The experimental results showed that with increasing time, volt and concentration to 25 min, 15 V, 700 ppm respectively the removal efficiency of nitrate increased to 99.4% and 81.8% for synthetic solution and industrial wastewater, respectively. Also industrial wastewater contains other contaminants which can be removed. So the electrodialysis operation not only removes nitrate but also the other ions and pollutants. The percentage of removal efficiencies of Phenol, Phosphorus, Oil, Alkalinity, Chloride, Ammonia, Sulphate, Cyanide and TDS are 40.0, 60.0, 72.9, 92.1, 96.1, 98.4, 98.6, 99.1 and 99.9, respectively. Spherical particles (5-20 µm) of almost pure ammonium nitrate were obtained by evaporating the rejected water after ED operation.

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