Environmental Engineering and Management Journal

June 2021, Vol.20, No. 6, 973-983
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

SIMULTANEOUS REMOVAL OF NITRATES AND NITRITES FROM WATER BY DONNAN DIALYSIS USING DOEHLERT DESIGN

Ikhlass Marzouk Trifi[1*], Beyram Trifi[2], Amira Djemal[1], Béchir Hamrouni[1]

[1]*Université de Tunis El Manar, Faculté des Sciences de Tunis, Laboratoire Dessalement et Traitement des Eaux (LDTE), Tunis, Tunisie*
[2]*Laboratoire Matériaux, Traitement et Analyse (LMTA), Institut National de Recherche et d'Analyse Physico-chimique (INRAP), Biotechpole Sidi Thabet, Tunisie*

Abstract

The simultaneous removal of nitrate and nitrite from water was investigated in this study using the Donnan dialysis. First, as a preliminary study, the removal of one component in the feed compartment was performed considering different parameters such as the concentration of counter-ion in the receiver compartment, concentration of nitrate and concentration of nitrite separately in the feed compartment. Then, the removal of nitrate and nitrite simultaneously in the feed compartment was conducted through three membranes, namely AFN, AMX and ACS. The membrane that displayed the most advantageous properties in the exchange is the one that provided the highest rate of counter-ion transport from the receiver to the feed; that has been afterwards used in the optimization according to the Response Surface Methodology.

Keywords: anion-exchange membrane, Doehlert, Donnan dialysis, nitrate, nitrite

Received: February, 2020; Revised final: September, 2020; Accepted: October, 2020; Published in final edited form: June, 2021

1. Introduction

The pollution of nitrogen (N) is due to the growth of population, industrialization and rapid urbanization. This pollution is often in the form of nitrate and nitrite and presents a water-quality problem (Aslan and Turkman, 2006). The eutrophication of water supplies and infectious diseases are the main environmental problems due to the presence of nitrate (Ward et al., 2010).

Nitrite is more dangerous than nitrate, because it is very toxic to human health. It can bind with hemoglobin to form methemoglobin in the body, decreasing the ability of red blood cells to carry oxygen. Moreover, it may convert into carcinogenic nitrosamine, which causes hypertension, leukemia, brain tumor, stomach, and bowel cancers (Tang et al., 2011). The World Health Organization (WHO) considers that 50 mg/L of nitrate concentration is the maximum in irrigation water and 0.5 mg/L of nitrite in drinking water in order to anticipate the harmful effects of high concentrations of nitrates and nitrites on human health (WHO, 1985).

Chemical processes such as chlorination and physico-chemical processes such as coagulation-flocculation were used to remove the nitrate and nitrite; unfortunately, they are not efficient to remove them both entirely. However, traditional biological treatments (Rossi et al., 2015) and other methods, such as bioadsorption (Taziki et al., 2015) photocatalytic denitrification (Ye et al., 2019), electrodialysis (Elmidaoui et al., 2001, 2002) and Donnan dialysis (Altintas et al., 2009; Ben Hamouda et al., 2017; Turki et al., 2015; Turki and Ben Amor, 2017), generally require a step of the oxidation of nitrite to nitrate for their removal.

The advantage of simultaneous removal of nitrate and nitrite is to overcome this oxidation step

*Author to whom all correspondence should be addressed: e-mail: ikhlasstrifi@gmail.com; Phone: +216 71871282; Fax: +216 71871282

and thereby reducing the use of chemicals products to oxidize the nitrite to nitrate.

The choice of using Donnan dialysis was essentially economical. This process is a continuous low-cost process, as it requires only few chemicals, pumping energy and it easy to handle. Donnan dialysis is a membrane process which consists in cross-ion exchange having the same electric charge through an ion exchange membrane between two solutions. The driving force in Donnan dialysis is the chemical potential gradient (Strathmann, 2004). Donnan dialysis is widely used to recover and eliminate various ions such as nitrates, fluorides, chromium and phosphates (Ben Hamouda et al., 2017; Dieye et al., 1998; DiNunzio and Jubara, 1983; Hichour et al., 1999, 2000; Sato, 2002; Marzouk et al., 2013, 2019; Seneviratne et al., 2000).

In order to investigate the simultaneous removal of nitrates and nitrites by Donnan dialysis, a statistical tool was applied. The Response Surface Methodology is an efficient statistical strategy to design experiments, to build models, to determine the optimum conditions and to evaluate the significance of factors, even the interaction between them (Weuster-Botz, 2000). Box–Behnken and central composite design are some models that can be used for optimisation but the Doehlert design has many other advantages (Nde et al., 2012). One of the advantages of Doehlert is the reduced number of experiments compared to the others design. Each variable does not have the same number of levels compared to the other variable which allows the choice to assign the large or the small number level to the variables. Preferably, the variable having the most important effect is placed in second factor in the matrix of Doehlert, because it had seven levels and allows us to obtain maximum information about the studied system.

The Doehlert design is considered more efficient than the central composite or Box–Behnken design because the number of coefficients of Doehlert design divided by the number of experiments is the lower than the other designs. The Doehlert designs describe a regular hexagonal form. So in the mapping space, the hexagons fill the space without overlap since they can occupy the space between the adjoining hexagons completely (Imandi et al., 2007). In addition, this matrix has the advantage that it is flexible, the possibility of increasing experimental domains or adding new factors to the design without necessarily repeating the experiments that have been already done (Nde et al., 2012). This method has been used by many authors (Dutra et al., 2006; Nde et al., 2015; Vanot et al., 2002) to determine the optimal conditions.

This paper focuses first on the removal of one component in the feed compartment which was performed with different parameters in order to determine the experimental field. Afterwards, the removal of two component (nitrate and nitrite) in the feed compartment was investigated by the Response Surface Methodology (RSM) using Doehlert design, in order to optimize the process and to understand the simultaneous transport of nitrites and nitrites.

2. Experimental

2.1. Anionic exchange membranes

Three anionic exchange membranes have been used: Neosepta® ***ACS***, Neosepta® ***AMX*** and Neosepta® ***AFN***. These membranes are homogenous and they have the same structural properties as to those of polystyrene/divinylbenzene. The ***AFN*** and ***ACS*** membrane were generously provided by Eurodia Industries S.A. and the ***AMX*** one was purchased. In Table 1 the characteristics and properties of anionic exchange membranes were presented.

Before the use of the anionic exchange membranes, a treatment was done according to French standard NF X 45-200 (1995). The treatment consists in preparation and conditioning of the membranes.

2.2. Donnan dialysis

Donnan dialysis is a continuous low-cost process, as it requires only a few chemicals, pumping energy and being easy to handle. The cell of Donnan dialysis was machined in a Plexiglas bar. It comprises four parts assembled together by means of threaded rods. The aligning of the different parts is ensured by shoulders. The end caps have a bore in which a star-shaped magnetic stirrer is housed. The bar is driven by a rotating magnetic field generated outside the cell.

The two central compartments are bored over their entire length by a hole, their centering is ensured by a shoulder; the membrane introduced into the bottom of the shoulder is sealed between these two elements. The receiver and feed tanks with a 1000 ml Erlenmeyer flask were used to supply the two cell compartments using a controlled peristaltic pump by a variable speed drive and fitted with two identical pump ensuring equal flow rates in the two compartments. Fluid circulation takes place in flexible pipes. During the dialysis operations, the nitrite and nitrate concentration, at the receiver compartment, were determined by the UV-spectrophotometry method (Rodier, 2009). The nitrate analysis was carried out according to a spectrophotometric method (with the sodium salicylate, nitrates give paranitrosalicylate sodium with a colored yellow which was followed by absorbance measurements at 415 nm using a UV–visible spectrophotometer). And the nitrite analysis was according to the diazotization of amino-4-benzenesulfonamide by nitrites in an acid medium and its coupling with N-(naphthyl-1) diamino-1,2-ethane dichloride gives a purple-colored complex which was followed by absorbance measurements at 543 nm using a UV–visible spectrophotometer. The removal rate of nitrate ($Y_1\%$) and nitrite ($Y_2\%$) was calculated by (Eqs. 1, 2):

$$Y_1\% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$Y_2\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of nitrate or nitrite (mg/L) and C_e is the equilibrium concentrations of nitrate and nitrite (mg/L).

The cell of Donnan dialysis is presented in a previous study (Marzouk et al., 2019).

2.3. Response Surface Methodology

2.3.1. Doehlert design

The Response Surface Methodology (RSM) using Doehlert design was the experimental design applied in this study. The objective is to optimize simultaneously the levels of these factors to attain the best system performance. With multiple responses, the optimum condition was established by superimposing the contours of the response surfaces in an overlay plot. The graphical optimization is presented in three-dimensional plots of different variables in the experimental field and the regions of optimal response would have a red colour. The calculated predictions must be close to the experimental values (Goupy and Greighton, 2006). The number of experiments for k factors is N = k^2 + k + 1. A total number of 15 experiments including three replicates at the centre field were considered (Hannachi et al., 2016; Hosni et al., 2019; 2020).

2.3.2. Experimental field

The studied factors are the initial concentration of nitrate, initial concentration of nitrite and concentration counter-ion in the receiver compartment. The rang of these factors were fixed according to the preliminary study (presented in section 3.1) with one component in the feed compartment. In Table 2, the experimental field of studied factors are presented.

2.3.3. Modeling of Donnan dialysis

The Doehlert design is a matrix that allows that possibility to estimate the coefficients of a second order function, which is able to predict, at any point in the experimental domain, the values of the answer (Ouejhani et al., 2008). The chosen model describes the predicted values of the responses Y using polynomial equation (Eqs. 3, 4). *bi* are estimation of the principal effect of the factor *i*; *bii* are the estimation of the second order effects; *bij* are the estimation of the interactions between factor *i* and factor *j* and *Xi* are the coded variable. The coefficients of the model were determined using NEMRODW Software.

$$Y_1\% = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \quad (3)$$

$$Y_2\% = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \quad (4)$$

2.3.2. Validation of models

In order to evaluate the models, two indicators were used: the percentage absolute error of deviation (*AED*) and the regression coefficient (R^2) between experimental and theoretical results. The *AED* was calculated from Eq. (5):

$$AED(\%) = 100 / N . \Sigma \left| \frac{Y_{exp} - Y_{theo}}{Y_{exp}} \right| \quad (5)$$

where Y_{exp} are the experimental responses and Y_{theo} are the theotrical responses. *N* is the number of points at which measurements were carried out.

The validation of the model is considered valid when $R^2 > 0.7$ and *AED* < 10% (Nde et al., 2012).

3. Results and discussion

3.1. Donnan dialysis with one component in the feed compartment

3.1.1. Effect of concentration of counter- ion

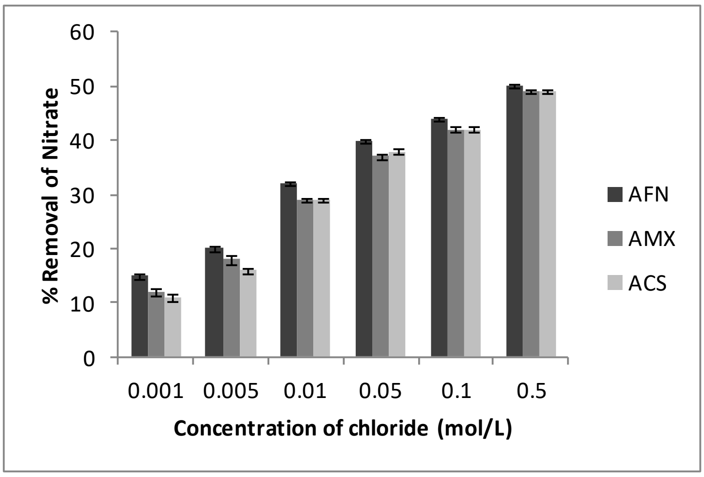
In this study we focused on the influence of counter-ion concentrations in the compartment receiver on the removal of nitrate and nitrites from the feed compartment separately. The counter-ion is one of the important parameters affecting the removal of nitrates and nitrites through the membrane. The chloride seems to be the most used counter-ion due to this high mobility.

Table 1. Properties of three anion-exchange membranes

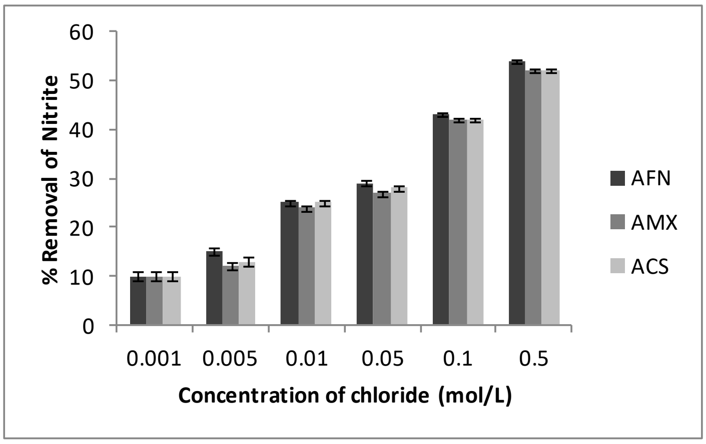
Membrane	*Neosepta® AFN*	*Neosepta® AMX*	*Neosepta® ACS*
Ion-exchange capacity (mmol/g)	3.00	1.30	1.85
Water content %	47.8	26.0	18.9
Thickness (mm)	0.12	0.13	0.15

Table 2. Experimental field for the removal of nitrate and nitrite

Factor	*Symbol*	*Coded variable*	*Rang and level*		
			Lower limit	*Centre field*	*Upper limit*
Initial concentration NO_2^- (mg/L)	[NO_2^-]	X_1	10	55	100
Initial concentration NO_3^- (mg/L)	[NO_3^-]	X_2	50	275	500
Concentration of Cl^- (mol/L)	[Cl^-]	X_3	0.1	0.3	0.5



(a)



(b)

Fig. 1. (a) The plot represent the variation of the removal of nitrates with different concentrations of Cl^- in the receiver compartment; (b) The plot represent the variation of the removal of nitrites with different concentrations of Cl^- in the receiver compartment

The variation of concentration of counter-ion Cl^- from 0.001 mol/L to 0.5 mol/L in the receiver compartment was investigated to study the impact of increasing the concentration of Cl^- onto the removal nitrates (100 mg/L) and nitrites (20 mg/L) separately from feed compartment to the receiver compartment. All three membranes ***AFN***, ***AMX*** and ***ACS*** have been tested and the dialysis operations lasted four hours. Variation of nitrate and nitrite concentrations at the outlet of receiver solution is presented in Fig. 1(a) and Fig. 1(b). According to Fig. 1, it was noticed that the increase in the concentration of Cl^- from 0.001 mol/L to 0.5 mol/L caused an increase in the percentage of nitrate and nitrite removal for the three membranes during four hours. When the Cl^- concentration was from 0.001 mol/L to 0.005 mol/L, the nitrate and nitrite concentration in receiver compartment were very low.

Then the increasing of Cl^- concentration from 0.01 mol/L to 0.5 mol/L, improved greatly the removal of nitrates and nitrites. This is explained by the fact that the concentration gradient of the counter-ions increases, hence the cross-ion transfer between Cl^- and nitrates and nitrites improves in order to maintain the electroneutrality. It has been observed that in Donnan dialysis with three membranes, the increase in the concentration of counter-ions in the receiver compartment is associated with the improvement in the removal of nitrates and nitrites in the feed compartment; this is reflected by improving the kinetics of the exchange. The obtained results are in accordance with Ben Hamouda (2017) and Turki (2015) works.

3.1.2. Effect of initial concentration of nitrate and nitrite in the feed compartment

In natural waters, the contents of nitrate and nitrite were at different levels depending to the geographic location. For this reason, the effect of the concentration of nitrate and nitrite were explored separately in the feed compartment. The conditions undertaken for this study are the variation of the initial concentration of nitrate from 10 mg/L to 500 mg/L and the variation of nitrite concentration from 5 mg/L to 100 mg/L. In the receiver compartment a solution of Cl^- with 0.1 mol/L concentration is considered. The results obtained are presented respectively in Figs. 2a and 2b. According to Fig. 2(a), it may be observed that with the increase of the initial concentration of the nitrate from 10 mg/L to 500 mg/L, the rate of removal increased significantly for the three membranes. At the lowest concentration of nitrate (10 mg/L), the removal was 28 ± 0.28% for ***AFN***, 24 ± 0.41% for ***AMX*** and 15 ± 0.66% for ***ACS***, but the increase of nitrates from 50 mg/L to 500 mg/L improve their removal from 38 ± 0.26 to 69 ± 0.23% with ***AFN***, from 30 ± 0.40 to 61 ± 0.29% with ***AMX*** and from 34 ± 0.41 to 50 ± 0.44% with ***ACS***. When the Donnan dialysis process was conducted with the ***AFN*** membrane, the efficiencies of nitrate exchange for chloride ions were the best.

According to the results obtained in Fig. 2(b), it can be noticed that the increase of the initial concentration of the nitrite from 5 mg/L to 100 mg/L, the rate of removal increased significantly for the three membranes. At the lowest concentration of nitrate in the feed (5 mg/L), the removal was 15 ± 0.53% for ***AFN***, 13 ± 0.76% for ***AMX*** and 14 ± 0.71% for ***ACS***. Increasing the concentration of nitrites from 10 mg/L to 100 mg/L, improved the removal efficiency from 17 ± 0.58% to 70 ± 0.22% with ***AFN***, from 15± 0.8% to 65 ± 0.27% with ***AMX*** and from 16 ± 0.87 to 66 ± 0.33% with ***ACS***.

It seems that the ***AFN*** membrane had the best removal of nitrites. It can be concluded that irrespective of the three membranes ***AFN***, ***AMX*** and ***ACS***, the removal of nitrates and nitrites was improved essentially due to the increase in the initial concentration of nitrates and nitrites. This can be explained by the rise of concentration gradient of nitrates and nitrites, which enhanced the chloride ion flux from the receiver compartment to the feed compartment, hence the cross ion transfer between Cl^- and nitrates and nitrites improves in order to maintain the electroneutrality (Wisniewski et al., 2005).

3.2. Donnan dialysis with two components in the feed compartment

3.2.1. Membranes selection

For the selection of anion exchange membranes, the complexity of the correlation of their characteristics listed in catalogues with the actual performances in Donnan dialysis process, three membranes ***AFN***, ***AMX*** and ***ACS*** membranes were tested.

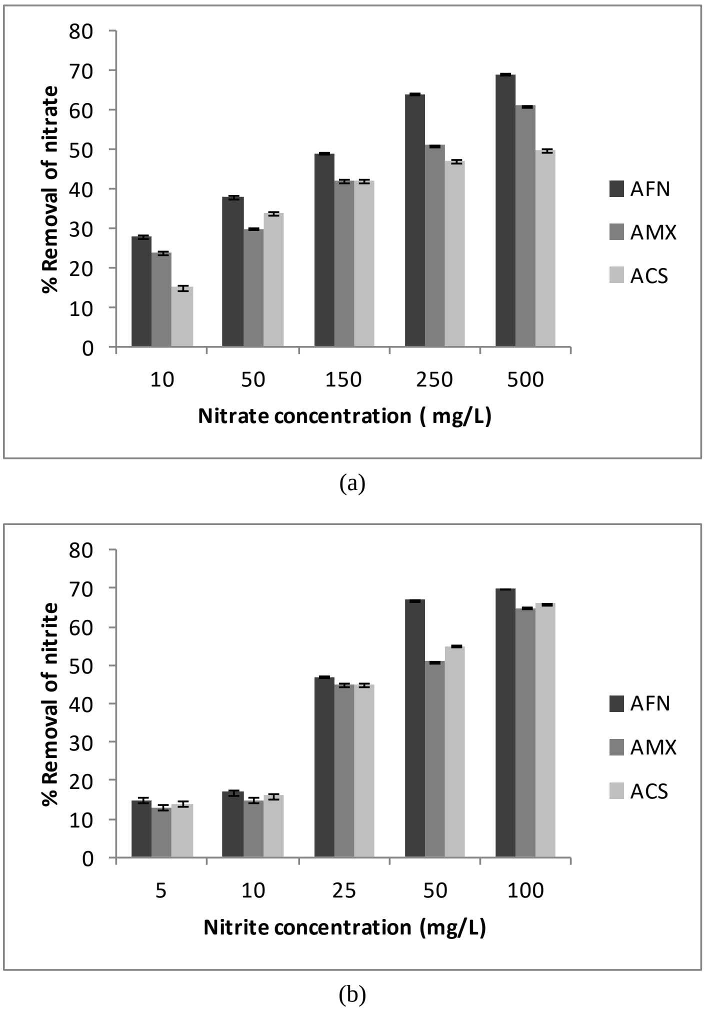


Fig. 2. (a) The plot represent the variation of the removal of nitrates with different concentrations of nitrate in the feed compartment; (b) The plot represent the variation of the removal of nitrites with different concentrations of nitrite in the feed compartment

Donnan dialysis was performed with a concentration of counter-ions of 0.5 mol/L, an initial concentration of nitrate 100 mg/L and 20 mg/L for nitrite. Fig. 3 shows the removal of nitrites and nitrates both in the same compartment simultaneous tested with three membranes (***AFN***, ***AMX*** and ***ACS***).

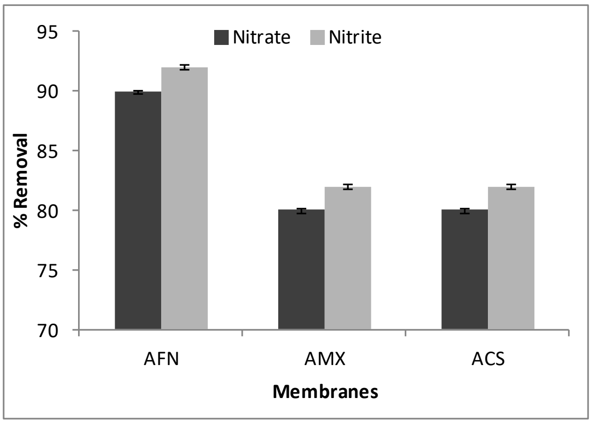


Fig. 3. Selecting of membrane types

Fig. 3 shows the removal of nitrites and nitrates in the same compartment simultaneously through three membranes (***AFN***, ***AMX*** and ***ACS***). The presence of nitrite and nitrite in the same compartment improves their elimination, this is explained by the fact that a higher proportion of nitrates and nitrites ions in the feed compartment increase the overall flow, so in return a higher proportion of the counter-ions is transported from the food to the receiver.

The ***AFN*** membrane shows the best performance compared to the ***AMX*** and ***ACS*** membranes. The membrane is the Neosepta ***AFN*** which has a macro-porous structure that contains a low amount of a cross-linked agent and a large concentration of inorganic groups. This membrane has relatively high ion-exchange capacity and the highest water content (Hichour, 2000).

3.2.2. Optimization by Response Surface Methodology

In this study, RSM via Doehlert design was employed with the membrane ***AFN*** for the optimization of the simultaneous removal of nitrates and nitrates. Doehlert experimental design was conducted with a total number of 15 experiments including three replicates at the centre field (Table 3). In fact, the replication reduces the variability in the experimental results, thereby increasing their significance and the confidence level; the repetition of measurements on the same centre field could result in essentially the same value for our response, thus inducing a significant lack of fit (Handbook, 2014).

Using the experimental results from Table 3, the second order polynomial equation was fitted to the appropriately data. The constants ***P*** values, $\boldsymbol{R^2}$ and ***AED*** were presented in Table 4. For both responses, $\boldsymbol{R^2}$ are greater than 0.7 and ***AED (%)*** was less than 10%. These confirm the validation of the models suggesting that the model is suitable to describe the removal of nitrate and nitrite.

In order to justify the adequacy of the models, the analysis of variance (ANOVA) was performed. In this regard, the results are presented in Table 5. The p-value is defined as the ratio of the mean square effect and the F-ratio is defined as the mean square error.

For determining the effects which are statistically significant effects, the P-value has been used. The P-value is very important as it is near to zero, this indicates that the data are significant. According to the table of Fischer, for 5% of error, 1 degree of freedom and 16 factorial tests, the Fischer value ($F_{0.05, 1, 1.16}$) is equal to 4.77. It seems that all the effects are significant because all their value are higher than 4.77. The Fischer value of the experimental model is much higher than the critical F value at a level of 5%. Therefore, the model is considered statistically significant. The graphic analysis of this isoresponse curves at the chosen experimental field delimited by a circle confirmed the results of the preliminary study (section 3.1).

Table 3. Matrix of Doehlert and results

N°	X_1	X_2	X_3	$[NO_2^-]$	$[NO_3^-]$	$[Cl^-]$	Y_1 (%)	Y_2 (%)
1	1.0	0.000	0.000	100	275	0.300	86.3	98.2
2	-1.0	0.000	0.000	10	275	0.300	88.1	79.4
3	0.5	0.866	0.000	78	470	0.300	92.7	97.1
4	-0.5	-0.866	0.000	33	80	0.300	79.1	87.9
5	0.5	-0.866	0.000	78	340	0.300	76.3	97.2
6	-0.5	0.866	0.000	33	210	0.300	93.2	87.4
7	0.5	0.287	0.816	78	210	0.463	92.9	99.8
8	-0.5	-0.287	-0.816	33	405	0.137	69.9	82.3
9	0.5	-0.287	-0.816	78	340	0.137	65.7	89.7
10	0.0	0.577	-0.816	55	145	0.137	73.7	86.7
11	-0.5	0.287	0.816	33	340	0.463	92.7	90.9
12	0.0	-0.577	0.816	55	145	0.463	84.2	97.1
13	0.0	0.000	0.000	55	275	0.300	87.2	96.3
14	0.0	0.000	0.000	55	275	0.300	87.2	96.3
15	0.0	0.000	0.000	55	275	0.300	87.2	96.3

Table 4. Model constants, P values, R^2 and AED values for the nitrate and nitrite removal

	Y_1 (%)		Y_2 (%)	
	Coefficients	**P- values**	**Coefficients**	**P-values**
b_0	87.2	0.000	96.3	0.000
b_1	-1.36	0.000	9.11	0.000
b_2	8.70	0.000	-0.28	0.470
b_3	12.35	0.000	5.94	0.000
b_{11}	0.00	1.000	-7.50	0.000
b_{22}	-2.50	0.000	-2.70	0.000
b_{33}	-10.40	0.000	-5.27	0.000
b_{12}	1.33	0.148	0.23	0.781
b_{13}	2.22	0.061	0.84	0.412
b_{23}	1.03	0.274	-0.04	0.027
R^2	0.999		0.997	
AED (%)	0.262		0.311	

Table 5. Analysis of variance

Source model	*Degree of freedom*	*Sum of Square*	*Mean of Square*	*F-value*	F_{table} (α = 5%)	*P- value*
NO_3^-						
Regression	9	1149.0	1272.10	86.8865	4.77	0.000
Residual	5	7.3205	1.464			
Total	14	1152.2				
NO_2^-						
Regression	9	1806.89	61.93	223.9885	4.77	0.000
Residual	5	1.3825	0.2765			
Total	14	558.7693				

The three-dimensional (3D) response surface plots visualize the relationship between each variable and the studied response; they also indicate the interactions between two variables and the optimum values of the variables which indicate the maximum response (Box et al., 1978; Box and Draper, 1987). The three-dimensional representations of the same plots are given in Figs. 4 and 5.

Fig. 4(a) shows the combined influence of nitrates and nitrite concentration at constant chloride concentration of 0.3 mol/L. The removal of nitrate increases with nitrate concentration increases from 50 to 500 mg/L, but decreases with nitrite concentration increases from 30 mg/L to 100 mg/L. This is probably due to competition between nitrate and nitrite, because the nitrites are smaller than the nitrates. Fig. 4(b) presents the variation between concentration of chloride and the nitrite concentration and the nitrate concentration was fixed to 275 mg/L. It seems that at low concentration of chloride, the presence of nitrite in feed compartment decreases the removal of nitrate. But increasing of chloride concentration, the presence of nitrite didn't affect the removal of nitrate, this is due to the high gradient of concentration.

Fig. 4(c) shows the combination between concentration of chloride and the nitrate concentration at constant nitrite concentration 55 mg/L. At lower concentration of chloride, the removal of nitrate decreases, this is due to slow motion of cross-ion transfer between Cl^- and nitrates. The nitrate removal increases gradually as chloride concentration and nitrate concentration increases also, but at high concentration of chloride the removal of nitrate increases considerably. This was expected because the chloride concentration was the factor which had a positive effect on the removal of nitrate.

In fact, the removal of nitrate is influenced by the two factors but only the chloride concentration was the most important factor for the removal of nitrate. This means that the nitrate removal was improved with increasing the chloride concentration. Indeed the quantity of nitrate ions moving through the anion exchange membrane increases simultaneously with an increase of the driving force of Cl^- ions in order to maintain the electroneutrality. The concentration of nitrite was the factor which had a negative effect on the studied response. This means that increasing led to decrease of the removal due to the competition between the nitrates and the nitrites. Maximal yield is obtained for nitrites removal concentration ranging from 275 mg/L to 500 mg/L, for the nitrates concentration from 55 mg/L to 100 mg/L and chloride concentration between 0.3 mol/L and 0.5 mol/L.

Fig. 5(a) shows the combined influence of nitrates and nitrite concentration at constant chloride concentration 0.3 mol/L. The presence of nitrate on feed compartment affects the removal of nitrite only with lower concentration of nitrites. Fig. 5(b) indicates the variation between concentration of chloride and the nitrite concentration and the nitrate concentration was fixed to 275 mg/L. It seems that at lowest concentration of nitrite the increasing of chloride concentration had significant effect on the removal of nitrite. However, when the concentration of nitrite increases, the removal of nitrite improves.

Fig. 5(c) shows the combination between concentration of chloride and the nitrate concentration at constant nitrite concentration of 55 mg/L. At a lower concentration of chloride, the removal of nitrite decreases; this is due to the presence of nitrate in feed compartment. But at high concentration of chloride the removal increases considerably. This was expected because the chloride concentration was the factor which had a positive effect on the removal of nitrite.

The removal of nitrite is also influenced by the two factors which are the concentration of nitrites and the concentration of chloride. The concentration of nitrite has a positive effect which means that the increase of the nitrite concentration improves the removal by Donnan dialysis. The improvement is attributed to the rise in the concentration gradient of nitrates and nitrites, which enhanced the chloride ion flux from the receiver to the feed solution, hence the cross-ion transfer between Cl^- and nitrates and nitrites improves to maintain the electroneutrality.

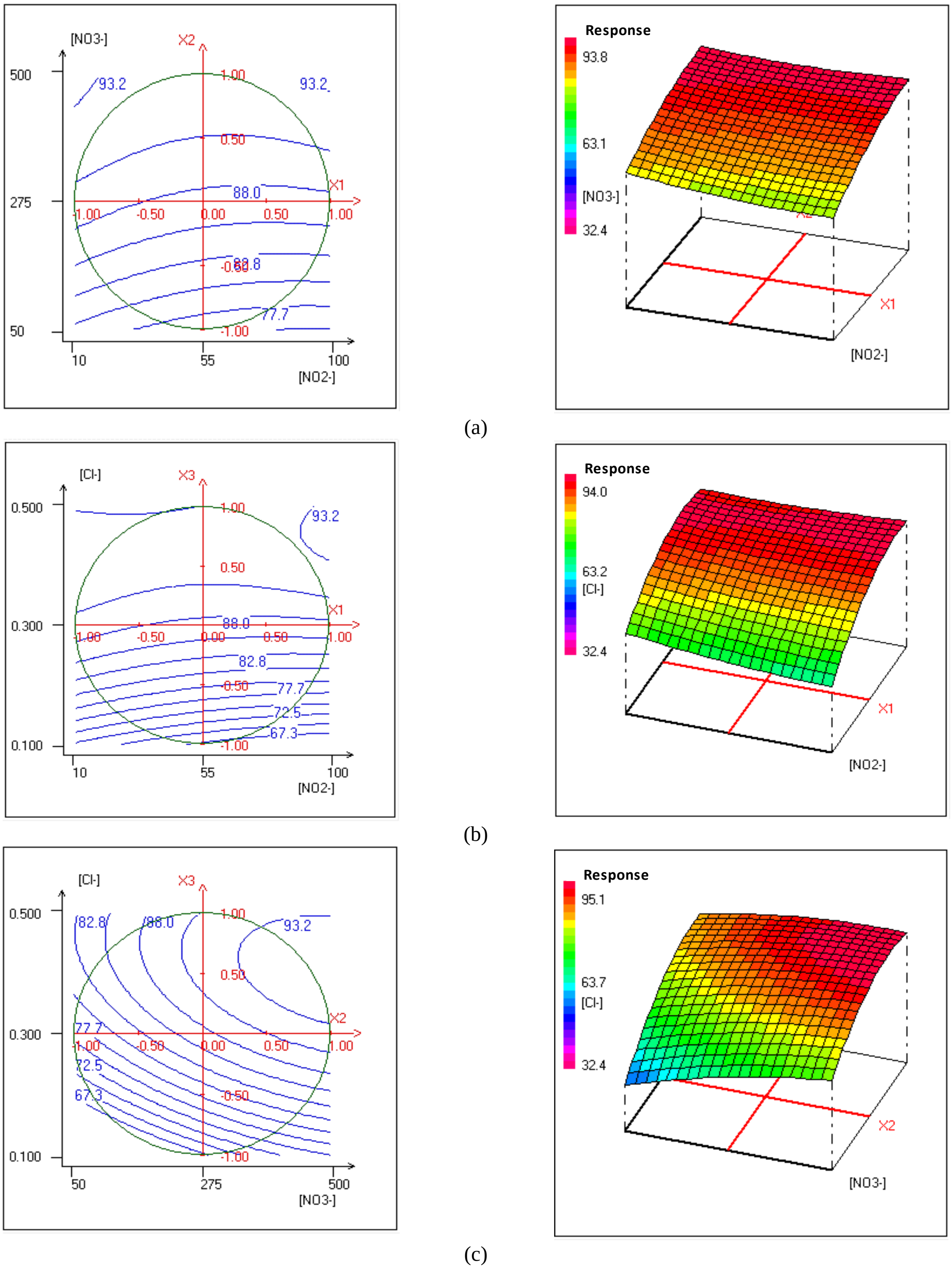


Fig. 4. Contour plots and the corresponding three-dimensional plots of: (a) nitrate concentration versus nitrite concentration; (b) chloride concentration versus nitrite concentration; (c) chloride concentration versus nitrate concentration

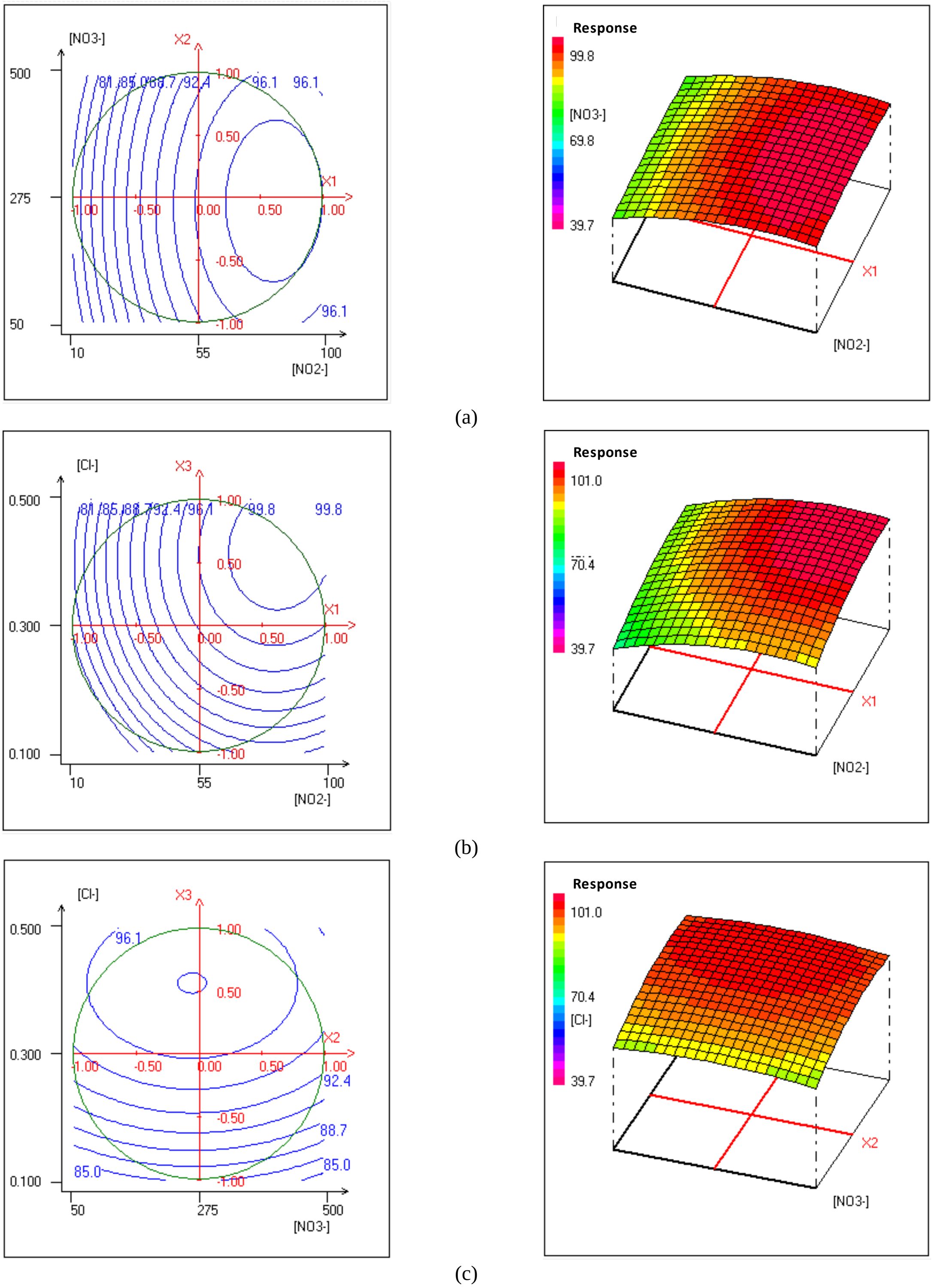


Fig. 5. Contour plots and the corresponding three-dimensional plots of: (a) nitrate concentration versus nitrite concentration; (b) chloride concentration versus nitrite concentration; (c) chloride concentration versus nitrate concentration

The concentration of chloride was clearly the factor which had a positive effect on the studied response. Maximal yield is obtained for nitrites concentration ranging from 275 mg/L to 500 mg/L, for the nitrate's concentration from 55 mg/L to 100 mg/L and chloride concentration between 0.3 mol/L and 0.5 mol/L.

In the software NEMRODW a function named desirability provided the optimum value. So, the optimum values for each factor are: 82 mg/L for the concentration of nitrite, 406 mg/L for the concentration of nitrate and 0.412 mol/L for the concentration of counter-ion. These conditions led to a maximum of the removal of nitrates (95.5%) and nitrites (100%). A three-time replicate of experiment was conducted in the optimum conditions, in order to verify the efficiency of predicting values. The coefficient of repeatability and of reproducibility was less than 1% and 5% respectively, so it can be concluded that the removal of nitrates and nitrites simultaneous by Donnan dialysis is reproducible. The statistical analysis of the experimental results indicated that the analysis has a normal distribution.

4. Conclusions

The use of RSM according to the Doehlert matrix in this study was performed in order to clearly illustrate the impact of each factor on optimal conditions and to obtain the optimum parameters for simultaneous removal of nitrate and nitrite by Donnan dialysis with a few numbers of experiments.

The RSM is very effective and facilitates reaching the optimum conditions, while taking into consideration interactions between experimental parameters. The experimental results and statistical analysis, allow obtaining the optimum conditions for the simultaneous removal of nitrates (95.5%) and nitrites (100%) through the AFN membrane, which were: 82 mg/L for the concentration of nitrite, 406 mg/L for the concentration of nitrate and 0.412 mol/L for the concentration of chloride.

Finally, RSM approach successfully determined the removal efficiency of the simultaneous removal of nitrites and nitrates by Donnan dialysis and optimization of process variables for the maximum removal.

References

Altintas O., Tor A., Cengeloglu Y., Ersoz M., (2009), Removal of nitrate from the aqueous phase by Donnan dialysis, *Desalination*, **239**, 276-282.

Aslan S., Turkman A., (2006), Nitrate and pesticides removal from contaminated water using biodenitrification reactor, *Process Biochemistry*, **41**, 882-886.

Ben Hamouda S., Touati K., Ben Amor M., (2017), Donnan dialysis as membrane process for nitrate removal from drinking water: Membrane structure effect, *Arabian Journal of Chemistry*, **10**, S287-S292.

Box G.E.P., Draper N.R., (1987), *Empirical Model Building and Responses Surfaces*, 1st Edition, John Wiley and Sons, New York.

Box G.E.P., Hunter W.G., Hunter J.S., (1978), *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, 1st Edition, John Wiley and Sons, New York.

Dieye A., Larchet C., Auclair B., Mar-Diop C., (1998), Elimination of fluorides by Donnan dialysis (in French), *European Polymer Journal*, **34**, 67-75.

DiNunzio J.E., Jubara M., (1983), Donnan dialysis preconcentration for ion chromatography, *Analytical Chemistry*, **55**, 1013-1016.

Dutra R.L., Maltez H.F., Carasek E., (2006), Development of an on-line preconcentration system for zinc determination in biological samples, *Talanta*, **69**, 488-493.

Elmidaoui A., Elhannouni F., Menkouchi Sahli M.A., Chay L., Elabbassi H., Hafsi M., Largeteau D., (2001), Pollution of nitrate in Moroccan ground water: removal by electrodialysis, *Desalination*, **136**, 325-332.

Elmidaoui A., Elhannouni F., Taky M., Chay L., Menkouchi Sahli M.A., Echihabi L., Hafsi M., (2002), Optimization of nitrate removal operation from ground water by electrodialysis, *Separation and Purification Technology*, **29**, 235-244.

Goupy J., Greighton L., (2006), *Introduction to Design of Experiments* (in French), 3rd Edition, Dunod, Paris.

Handbook, (2014), *Handbook Design of Experiments in Protein Production and Purification Design of Experiments*, 1st Edition, GE Healthcare Life Sciences, Uppsala, Sweden.

Hannachi A., Hammami S., Raouafi N., Maghraoui-Meherzi H., (2016), Preparation of manganese sulfide (MnS) thin films by chemical bath deposition: Application of the experimental design methodology, *Journal of Alloys and Compounds*, **663**, 507-515.

Hichour M., Persin F., Molenat J., Sandeaux J., Gavach C., (1999), Fluoride removal from diluted solutions by donnan dialysis with anion exchange membranes, *Desalination*, **122**, 53-62.

Hichour M., Persin F., Sandeaux J., Gavach C., (2000), Fluoride removal from waters by Donnan dialysis, *Separation Purification Technology*, **18**, 1-11.

Hosni N., Bouaniza N., Selmi W., Assili K., Maghraoui-Meherzi H., (2019), Synthesis and physico-chemical investigations of $AgSbS_2$ thin films using Doehlert design and under DFT framework, *Journal of Alloys and Compounds*, **778**, 913-923.

Hosni N., Zehani K., Djebali K., Mazaleyrat F., Bessais L., Maghraoui-Meherzi H., (2020), Experimental design approach for the synthesis of 3D-$CoFe_2O_4$ nanoflowers thin films by low-cost process, *Materials Chemistry and Physics*, **255**, 123493.

Imandi S.B., Bandaru V.V., Somalanka S.R., Garapati H.R., (2007), Optimisation of medium constituents for the production of citric acid from by product glycerol using Doehlert experimental design, *Enzyme and Microbial Technology*, **40**, 1367-1372.

Marzouk I., Chaabane L., Dammak L., Hamrouni B., (2013), Application of Donnan dialysis coupled to adsorption onto activated alumina for chromium (VI) removal, *American Journal of Analytical Chemistry*, **4**, 420-425.

Marzouk Trifi I., Trifi B., Ben Ayed S., Hamrouni B., (2019), Removal of phosphate by Donnan Dialysis coupled to adsorption onto alginate calcium beads, *Water Science and Technology*, **80**, 117-125.

Nde B.D., Abi C.F., Tenin D., Kapseu C., Tchiegang C., (2012), Optimisation of the cooking process of sheanut kernels (*Vitellaria paradoxa* Gaertn.) using the Doehlert experimental design, *Food Bioprocess Technology*, **5**, 108-117.

Nde B.D., Boldor D., Astete C.E., (2015), Optimization of microwave assisted extraction parameters of neem (*Azadirachta indica* A. Juss) oil using the Doehlert's experimental design, *Industrial Crops and Products*, **65**, 233-240.

NF X 45-200, (1995), Ion Exchange Polymer Membranes (in French), AFNOR, French standard.

Ouejhani A., Hellal F., Dachraoui M., Lalleve G., Fauvarque J.F., (2008), Application of Doehlert matrix to the study of electrochemical oxidation of Cr(III) to Cr(VI) in order to recover chromium from wastewater tanning bath, *Journal of Hazardous Materials*, **157**, 423-431.

Rodier J., (2009), *Water Analysis* (in French), 9th Edition, Dunod, Paris.

Rossi F., Motta O., Matrella S., Proto A., Vigliotta G., (2015), Nitrate removal from wastewater through biological denitrification with OGA 24 in a batch reactor, *Water*, **7**, 51-62.

Sato K., (2002), Effects of the feed solution concentration on the separation degree in Donnan dialysis for binary systems of amino acids, *Journal of Membrane Science*, **196**, 211-220.

Seneviratne J., Holmstrom S.D., Cox J.A., (2000), Donnan dialysis preconcentration coupled with ion chromatography and electrocatalytic oxidation for the determination of cyanide, *Talanta*, **52**, 1025-1031.

Strathmann H., (2004), *Ion-Exchange Membrane Separation Processes*, 1st Edition, vol. IX, Elsevier, Amsterdam-Boston.

Tang Y., Jiang H., Bryan N.S., (2011), Nitrite and nitrate: cardiovascular risk–benefit and metabolic effect, *Current Opinion in Lipidology*, **22**, 11-15.

Taziki M., Ahmadzadeh H., Murry M.A., Lyon S.R., (2015), Nitrate and nitrite removal from wastewater using algae, *Current Biotechnology*, **4**, 426-440.

Turki T., Ben Amor M., (2017), Nitrate removal from natural water by coupling adsorption and Donnan dialysis, *Water Supply*, **17**, 771-779.

Turki T., Hamdi R., Tlili M., Ben Amor M., (2015), Donnan dialysis removal of nitrate from water: effects of process parameters, *American Journal of Analytical Chemistry*, **6**, 569-576.

Vanot G., Valérie D., Guilhem M., Phan-Tan-Luu R., Comeau L.C., (2002), Maximizing production of *Penicillium cyclopium* partial acylglycerol lipase, *Applied Microbial Biotechnology*, **60**, 417-419.

Ward M.H., Kilfoy B.A., Weyer P.J., Anderson K.E., Folsom A.R., Cerhan J.R., (2010), Nitrate intake and the risk of thyroid cancer and thyroid disease, *Epidemiology*, **21**, 389-395.

Weuster-Botz D., (2000), Experimental design for fermentation media development: statistical design or global random search?, *Journal of Bioscience and Bioengineering*, **90**, 473-483.

WHO, (1985), Health hazards from nitrate in drinking-water. Report on a WHO meeting: Copenhagen, 5-9 March 1984, Conference Report, WHO. Regional Office for Europe -Copenhagen, DK, EURO, On line at: https://www.ircwash.org/resources/health-hazards-nitrates-drinking-water-report-who-meeting-copenhagen-5-9-march-1984.

Wisniewski J., Rozanska A., Winnicki T., (2005), Removal of troublesome anions from water by means of Donnan dialysis, *Desalination*, **182**, 339-346.

Ye J., Liu S.Q., Liu W.X., Meng Z.D., Luo L., Chen F., Zhou J., (2019), Photocatalytic simultaneous removal of nitrite and ammonia via a zinc ferrite/activated carbon hybrid catalyst under UV–Visible irradiation, *ACS Omega*, **4**, 6411-6420.