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Optimization of a hybrid process combining Nanofiltration and Electrodialysis for the treatment of surface water in the Mekong Delta region

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Abstract

The coastal area of the Mekong Delta is facing a huge problem of water supply quality due to pesticide (intensive agriculture) and salinity (sea water intrusion) contamination. Their simultaneous presence makes this water complex and requires advanced water treatment processes in order to meet the Vietnamese Guideline for drinking water quality. The objective of this work is to develop an efficient surface water treatment based on electrodialysis and nanofiltration technologies. The approach consists in using electrodialysis in a first stage for salinity removal to improve, in the second stage, the performance of nanofiltration for the

removal of pesticides. The question that arises is to what extent should electrodialysis desalination be carried out in order to effectively remove the pesticide and salinity in the second stage (nanofiltration) at a reasonable cost? To answer this question, an experimental design methodology was employed to describe and optimize the entire hybrid system. Experiments carried out under the optimal conditions deduced from the modeling gave experimental results in good agreement with the predictions allowing to validate the optimization approach.

1 Introduction

Access to safe drinking water is one of the most important challenges facing the world today, especially in the rural area of Mekong Delta, Vietnam (Grady *et al.*, 2018). The Mekong Delta region is famous for its abundant surface water resource from an interlacing network of rivers and canals (Renaud and Kuenzer, 2012; Whitehead *et al.*, 2019). Water quality in the main river channels is generally good since pollutants and contaminants are often diluted due to the enormous volumes of water. However, the surface water sources to which rural people have direct access for daily use come from smaller tributaries and canals near their homes. They contain a significantly higher concentration of pollutants and contaminants (Ly and Giao, 2018; Minh *et al.*, 2019).

Pesticide pollution in the Mekong delta is due to the co-occurrence of recently used pesticides. Their residues were detected and frequently exceed the guideline concentrations in many rivers and canals. It has been reported (Carvalho *et al.*, 2008) that the concentration of diazinon, and fenotrothion were from 0.003 to 0.043 µg/L in canal water samples near rice field. A study conducted in the two provinces of Can Tho and Dong Thap (Pham *et al.*, 2013) has revealed the presence of commonly used pesticide residues at high concentration in the

irrigation canals. In particular, isoprothiolane was detected in 100 % of the samples with the maximum concentration of 11.24 µg/L, followed by fenobucarb in 90.8 % of the samples with concentration ranging from 0.02 to 1.43 µg/L. Other pesticides with a high frequency in the sample analyzed were pretilachlor (68.9 %), buprofezin (58.7 %), fipronil (48.5 %) and propiconazole (45.9 %). The presence of these pesticides in canal waters in An Giang Province has also been reported with over 80 % of the samples containing more than five pesticides simultaneously and 95 % of samples exceeding the EC guideline value for concentration of total pesticides in drinking water (0.5 µg/L) (Chau *et al*., 2015). Based on the data presented above, the three most frequently detected pesticides were fenobucarb (an insecticide), isoprothiolane (a fungicide) and pretilachlor (an herbicide). These molecules were chosen for this study as representative of the pesticides that can be found in the surface waters of the Mekong Delta.

Before being used, rural people treat surface water by a basic method such as removing sediments with aluminium sulphate, followed by boiling. These procedures make the water appearance "cleaner", but they pose a potential threat to human health. It has been proved that boiling can remove most pathogens in water, but can actually increase the concentration of pesticides present (Pham *et al*., 2013). In addition, some pesticides have also been detected at concentrations above the European Commission's guideline values for drinking water in some purchased bottled water, which is generally considered safer water, (Chau *et al*., 2015). Thus, more effective water treatment methods need to be implemented at the household level in Mekong Delta rural area.

Accordingly, the integration of two different membranes technologies, namely electrodialysis (ED) and nanofiltration (NF), has been proposed to treat surface water in the coastal area of the Mekong Delta (Nguyen *et al*., 2019). This original combination seems to be well suited for the treatment of complex water containing biological pollution, high salinity and a high

concentration of pesticides. On one hand, NF is probably the most polyvalent membrane separation technique, which is characterized by a very high efficiency for the removal of biological compound, organic and inorganic compounds removal at a reasonable operating cost. NF is a membrane pressure driven process where pollutants are retained by both steric and electrostatic repulsion (Donnan) effect. Many applications for the treatment of water containing organic pollutants can be found in literature, such as the removal of pesticides and other micropollutants (Miralles-Cuevas *et al*., 2014; Nghiem *et al*., 2004; Ormad *et al*., 2008; Park and Snyder, 2020; Vergili, 2013; Wang *et al*., 2021), and that of pesticides and salts or inorganic pollutants at the same time (Košutić *et al*., 2005; Nikbakht Fini *et al*., 2019; Qiu *et al*., 2009; Sarkar *et al*., 2007; Thanuttamavong *et al*., 2002; Van der Bruggen *et al*., 2001). Concerning more specifically the removal of pesticides by NF, the rejection efficiency strongly depends on the membrane characteristic (membrane cut-off, materials, hydrophilicity, electrical charge…), the nature of the pesticide molecule (size, hydration radius, electrical charge, steric configuration, hydrophilicity…) and also on the presence/concentration of other compounds such as salts and organic matter. In particular, it has been proven that salinity has a strong negative impact on organic micropollutant retention (Nguyen *et al*., 2019; Plakas and Karabelas, 2008; Ren *et al*., 2017; Zhang *et al*., 2006). This effect has been explained by pore swelling, decrease of solute hydrodynamic radius (Stokes radius), possibly due to partial dehydration, or a combination of the above (Ren *et al*., 2017; Teixeira *et al*., 2005; Zhang *et al*., 2006; Zhao *et al*., 2005). On the other hand, ED can easily remove salinity by extracting ions through ion exchange membranes placed in an electrical field. Compared to other desalination membrane technologies based on pressure or thermal action, ED targets ions instead of the solvent. Therefore, ED is more energy efficient for treating water with salinity below 6 g/L (Al-Karaghouli and Kazmerski, 2013; Patel *et al*., 2020) and much more flexible in terms of treatment. Indeed, the desalination rate can be

1   adapted by simply adjusting the electrical charge and the hydraulic retention time. However,

2   this technology cannot remove pesticides, as most of these substances are neutral and cannot

3   be transported through the membrane by electrical force.

4   In a previous work (Nguyen *et al*., 2019), the feasibility of the hybrid process coupling ED

5   and NF for the treatment of surface water in the coastal area of Mekong Delta has been

6   evaluated. In this context, ED has been proposed as a pre-desalination step during the dry

7   season in order to improve the retention efficiency of pesticides in the subsequent NF stage

8   and also to enhance the overall salinity retention. It was found that a tight NF membrane such

9   as NF90 leads to produced water with a quality complying with the VN guideline for drinking

10 water. As previously mentioned, the specific energy consumption of ED varies greatly with

11 the quantity of salt to be extracted, whereas that of NF depends on the conversion rate. In

12 order to develop an energy-efficient system in the context of an implementation in the rural

13 area of the Mekong Delta, it is critical to optimize the energy consumption of both stages ED

14 and NF.

15 The present report aims at proposing clues for optimizing the overall performance of the ED -

16 NF integrated system in terms of pollutant removal and energy consumption for treatment of

17 matrices as complex as surface water in the Mekong Delta. The challenge in optimizing the

18 hybrid ED-NF process is that the performance of the first stage significantly affects the

19 efficiency of the second stage and then the cost of the overall process. For example, if the

20 salinity of the feed water was not sufficiently removed by ED, the pesticide removal capacity

21 by NF would be remarkably reduced due to the swelling effect of the membrane pores

22 (Nguyen *et al*., 2019). Otherwise, the energy consumption of ED would increase, if the TDS

23 concentration of the diluted compartment continued to decrease. Thus, each operation

24 parameter in the two stages is influenced by the others. In other words, the hybrid system is a

25 non-linear system, in which the outputs must involve not only the relationship with single

parameters, but also the interaction or combination between the parameters. The biggest problem in the application of non-linear methods to solve such systems arises from the often extreme sensitivity to noise (experimental measurement uncertainties) and the difficulty in choosing a good non-linear fitting function in the absence of a suitable physical model. Linear methods are more robust, less sensitive to noise, simpler to implement, and can lead to reasonable predictions for quantities by getting the trends right, although finer details may be lost by using a linear method for an inherently nonlinear system

Therefore, in order to determine the best compromise between removal efficiency and energy consumption, a multi-variable analysis based on response surface design was used to optimize the whole ED - NF system. Experimental design methodology (RSM) is a statistical tool than can be used to accurately assess the effect of the main parameters affecting each step as well as the interactions between the parameters of the entire hybrid process (Mäkelä, 2017). However, such a methodology may require a large number of experiments depending on the number of parameters involved. A specific approach was developed in order to minimize the number of experiments while maintaining a sufficient degree of information for accurate experimental modelling. Based on the developed models, an optimization was carried out taking into account the efficiency in terms of desalination rate and pesticide removal as well as the operating cost (energy consumption and membrane surface area). The optimal conditions determined by the modeling were then validated experimentally.

2   Materials and methods

2.1   *Chemicals*

All pesticides, organic solvents and inorganic salts used in this study were obtained from Sigma Aldrich at the analytical grade. Stock solutions of the pesticides isoprothiolane,

1   fenobucarb and pretilachlor were prepared in acetonitrile/water (50:50) at a concentration of

2   1000 mg/L and stored at 4 °C. Milli-Q water (at 18 MΩ.cm^{-1}) was used for the whole

3   experiment.

4   *2.2   Synthetic Mekong Delta surface water*

5   Ion composition of the synthetic Mekong Delta solution is shown in Table 1. These ion

6   concentrations correspond with their concentration at median values in the Mekong Delta

7   surface water in coastal areas during the dry season (Nguyen *et al*., 2020).

8

9

10   **Table 1**

11   Ion composition (mg/L) of the synthetic salt solution

Ion composition	Na$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	TDS
Concentration (mg/L)	1721	258	59	3197	459	5693

12

13   The pesticide concentrations in the synthetic solution were 300, 300 and 1000 ppb for

14   fenobucarb, isoprothiolane and pretilachlor, respectively. These concentrations were chosen

15   based on the instrument limit detection, so that pesticide residues in the permeate could be

16   determined with enough accuracy, even if removal values are greater than 95%. The pH of the

17   solution was 5.9 – 6.2.

18   *2.3   Membranes selection*

19   In the ED stage, the PC-SK and PC-SA membranes (PCA GmbH, Germany) were chosen as

20   cation and anion exchange membranes, respectively, while in the NF stage, NF90 (Dow-

21   Filmtech, DuPont Water Solutions, USA) was used. The latter membrane was selected to

achieve the best compromise in terms of salinity rejection, pesticide rejection and permeability (Nguyen *et al*., 2019).

2.4   Pesticide and ions analysis

Pesticide concentration was determined by direct injection liquid chromatography with tandem mass spectrometry method (DI-LC/MS/MS) by using Waters instruments (Wythenshawe, Manchester, UK). The analytical conditions and the detection limit were described in a previous study (Nguyen *et al*., 2019).

The ion concentration was determined by ion chromatography (ICS-900, Dionex) and the conductivity was measured by a conductivity meter (Cond 315i, WTW).

2.5   ED – NF integrated membrane experiments

The membrane set-up and the operating procedures were similar to those used in a previous report (Nguyen *et al*., 2019).

2.5.1   ED stage

The ED experiments were carried out on a PCCell ED 64-004 cell (PCA GmbH, Heusweiler, Germany) with 7 pieces of the PC-SA and 8 pieces of the PC-SK and a pair of electrodes made of Pt/Ir-coated titanium. The active membrane area was 64 cm^2. Flow paths of the diluate stream (referred to as ED permeate in this study) and concentrate stream were formed by plastic spacers between the membranes with width of 0.5 mm and their flow rate were maintained at 0.5 L/min. Initial concentrate stream was filled with 0.8 L synthetic solution. One liter of Na_2SO_4 0.2 mol/L solution was used as the electrode rinsing solution with flow rate maintained at 1.0 L/min.

1   ED operating conditions for ED, including applied voltage (V), which is controlled at a

2   constant value during each experiment, permeate volume (L) and processing time (min), were

3   setup for each experiment in the Box Behnken design.

4   *2.5.2   NF stage*

5   The NF stage was carried out in an NF pilot equipped with an Osmonics Sepa CF II cell

6   (Sterlitech Corp., Kent, WA). The NF90 membrane coupons of 140 cm^2 surface area were

7   rinsed and conditioned at 15 bar during 1 hour inside the NF pilot before being used. Then,

8   the tank of the NF pilot was filled with 5 L of feed solution and the experiment was

9   performed. The NF operating conditions such as applied pressure (bar), feed concentration

10 (mg/L) and NF processing time (min) were setup for each experiment in the Box Behnken

11 design. The feed solution temperature was kept constant at 25.0 ± 0.5 °C. The membrane

12 rejection *R* was calculated from the pesticide concentration in the feed solution and the

13 permeate according to equation 1:

14 $R = \left(1 - \dfrac{c_p}{c_f}\right) \times 100$ (1)

15 where C_p and C_f are the concentration of pesticides (mg/L) in the permeate and the feed

16 solution, respectively.

17 *2.6   Energy consumption calculation*

18 In this study, one of the important parameters for evaluating process efficiency is energy

19 consumption.

20 The specific energy consumption (*SEC*) often used to characterize the energy cost of the NF

21 process is the energy (from pump) needed to produce one cubic meter of permeate at the

22 desired water recovery. *SEC$_{NF}$* of the pump in kWh/m^3 is calculated by equation 2:

23 $SEC_{\mathrm{NF}} = \dfrac{\Delta P}{36\,\eta\,\gamma}$ (2)

1   where ΔP is the trans-membrane pressure (bar); η is the pump efficiency, assumed to be 0.8 in

2   this study; γ is the water recovery by the process and equals the ratio of the volume of the

3   permeate and the feed obtained after each experiment.

4   In the ED process, the electrical energy is consumed by the ED cell and the solution

5   circulation pumps. In this study, only the energy consumed by the ED cell was taken into

6   account, assuming that the consumption of pumps contributed negligibly to the overall energy

7   consumption under the operating conditions.

8   The specific energy consumption of the ED cell (SEC_{ED}, in kWh/m^3) for the transfer of ions is

9   the definite integral of the voltage and current with respect to time t, as follows:

10   $$SEC_{ED} = \int_{t_0}^{t} U\, I\, dt \qquad\qquad\qquad (3)$$

11   In fact, ED was carried out at constant voltage in this work. Based on the experimental data of

12   the total voltage and current recorded at time t, the specific energy consumption of the stack

13   can then be calculated using equation 4:

14   $$SEC_{ED} = U \int_{t_0}^{t} I\, dt \qquad\qquad\qquad (4)$$

15   *2.7   Optimization of the ED – NF coupled process with the Box–Behnken experimental*

16   *design*

17   It has been pointed out previously that the performances of these two processes are

18   interconnected. The extent to which the first stage removes salts, will inevitably influence the

19   efficiency of the second stage and the cost of the entire process. Therefore, a compromise

20   must be found between these two processes. At which desalination rate should ED be carried

21   out in order to provide a sufficient pesticide removal in NF step and sufficient overall

22   desalination rate to satisfy the VN guideline at a reasonable cost? To answer this question, a

23   specific Response Surface Methodology (RSM) was applied: the Box Behnken Design (BBD)

1   (Myers and Montgomery, 2002). Using this methodology, the process can be described (by

2   modeling) taking into account the interaction between the parameters. Moreover, a precise

3   optimization can be achieved using the developed mathematical model considering both the

4   efficiency and the cost of treatment. Box and Behnken have developed a family of efficient

5   three-level designs for fitting second-order response surface methodologies (Myers and

6   Montgomery, 2002). The methodology of design is interesting and quite creative. The class of

7   design is based on the construction of the balanced incomplete block designs. In the BBD,

8   each pair of factors is linked in a 2^2 factorial (scaling $\pm$ 1) while the other ones remain fixed at

9   the center of the experimental region investigated. Five experiments in the center of the

10   domain are also required in order to determine the experimental error (pure error) which could

11   be compared with the lack of fit, the error attributed to the inadequacy of the developed

12   models. The number of assays (N_a) required can be calculated using equation 5:

13   $$N_a = (2^2 \times n \times (n-1)/2) + 5 \tag{5}$$

14   where n is the number of variables. It has to be noted that the number of experiments is at the

15   "power" of the number of parameters.

16   In this study, only the main parameters affecting ED and NF were considered such as applied

17   voltage, product volume and treatment time for the ED stage and applied pressure, feed

18   concentration and operating time for the NF stage.

19   However, the ED and NF processes are linked since the NF feed solution corresponds to the

20   ED permeate. Then, a total of 5 parameters should be taken into account for the entire hybrid

21   process, which would lead to a large number of experiments ($N_a = 45$). Therefore, in order to

22   limit the number of experiments, these two processes were study (modeling) independently,

23   first the ED stage then the NF stage. The ED results were used to define the experimental

24   region of the NF process. Once the mathematical models for each process were validated,

1 another Box Behnken matrix was developed coupling the two processes. In that case, the

2 responses of this matrix were not experimentally recorded but rather extracted from the two

3 previously validated models. In addition to reduce the number of experiments, such strategy is

4 a step by step method allowing adjustment in case of unsuitable results (out of the scope of

5 this study).

6 The experimental region investigated for both ED and NF processes and the coded values are

7 shown in Table 2. The experimental data were analyzed using Design-Expert 8 software

8 including ANOVA in order to obtain the interactions between the process variables and to

9 evaluate the accuracy/correctness of the mathematical model. As mentioned above, three

10 input parameters, including voltage (X_1), permeate volume (X_2) and treatment time (X_3), were

11 taken into account in the case of ED for the modeling. Water recovery (Y_1), TDS

12 concentration of the diluted compartment (Y_2) and SEC_{ED} (Y_3) were recorded as responses. For

13 the NF stage, the input parameters were applied pressure (X_4), TDS concentration (X_5) and

14 treatment time (X_6). Similarly, water recovery (Y_4), permeate TDS concentration (Y_5) and

15 SEC_{NF} (Y_6) were recorded as responses with the addition of pesticide removal (Y_7).

16

17 **Table 2**

18 Box Behnken Matrix: Experimental range and levels of independent variables for ED and NF
19 processes expressed in coded (X_i) and real values (U_i)

| | Coded variables (X_i) | Factor (U_i) | Experimental field | | $U_{i,0}$ | ΔU_i |
			Minimum value (-1)	Maximum value (+1)		
ED	X_1	U_1 : Applied Voltage (V)	6	10	8	2
	X_2	U_2 : Permeate volume (L)	0.8	2.4	1.6	0.8

	X_3	U_3 : Treatment time (min)	20	40	30	10
	X_4	U_4 : Applied pressure (bar)	6.0	12.0	9	3.0
NF	X_5	U_5 : TDS (ppm)	600	4200	2400	1800
	X_6	U_6 : Treatment time (h)	3	6	4.5	1.5

1

2 *2.8 Calculation of the response for the BBD*

3 *2.8.1 Water recovery*

4 For the ED stage, the water recovery (Y_1) was calculated by the ratio between the ED

5 permeate volume (X_2, in L) and the total volume of the synthetic solution used in the permeate

6 (X_2) and concentrated tanks (V_c, in L) as shown in Equation 6.

7 $$Y_1 = \frac{X_2}{X_2 + Vc} \tag{6}$$

8 For the NF stage, the water recovery (Y_4) was calculated based on the feed volume (V_f, equal

9 to 5 L) and the permeate (V_p, in L) obtained after a batch experiment according to Equation 7:

10 $$Y_4 = \frac{V_p}{V_f} \tag{7}$$

11 The total water recovery of the coupled ED - NF process is then equal to:

12 $$Y_8 = Y_1 \times Y_4 \tag{8}$$

13 *2.8.2 Energy consumption calculation*

14 In the ED process, the energy consumption comes mainly from the electrical energy required

15 by the stack (Equation 4). The SEC$_{ED}$ (Y_3) is therefore inversely proportional to the volume of

16 permeate produced (X_2, in L):

17 $$Y_3 = \frac{U}{X_2} \int_0^{X_3} I \, dt \tag{9}$$

13

1 where the definite integral of current with respect to time from the beginning of experiment (t_0

2 $= 0$) to the treatment time as mentioned in Table 2 ($t = X_3$, in min).

3 In the NF process, the specific energy consumption (Y_6) was calculated according to Equation

4 2. Thus, the overall specific energy consumption of the integrated process (Y_{10}) is equal to the

5 sum of specific energy consumption of the two stages:

6 $Y_{10} = Y_6 + Y_3$ (10)

3   Results and discussion

A feasibility study of an innovative process for treating surface water in the Mekong Delta containing both high salinity and pesticides has been previously conducted (Nguyen *et al.*, 2019). Only one NF stage is not able to reject pesticides to the level necessary to meet the Vietnamese guideline for drinking water when the salinity is too high. For this reason, it has been proposed to couple NF with a pre-desalination stage by ED ensuring about 50% of salt removal. As a result, a permeate water complying with the Vietnamese guideline for drinking water was produced with a recovery in the range of 30-50% depending on the initial salinity. In addition, the specific energy consumption of the NF stage could be reduced due to the lower salinity of the input water. By contrast, the energy consumption of the ED stage is heavily dependent on the quantity of salt to be removed. Therefore, the crucial issue for the feasibility and perspective of ED-NF hybridization is the optimization of the obtained performance in terms of quality and recovery with respect to the consumed energy in each stage. In order to determine the best compromise, a response surface design was used.

3.1   Electrodialysis process modeling

In this section, ED process is described using a BBD design. The data, including natural levels, design, and responses values, are shown in Table S1.

The experimental design consisted of 12 experiments, where each pair of factors is linked in a 2^2 factorial (assays 1–12) plus five additional assays conducted at the center of the experimental region investigated (assays 13–17). Water recovery depends exclusively on the permeate volume and was varied from 50 to 75% (model not shown). Under these conditions, the experimental TDS concentration (Y_2) in the ED permeate ranged from 322 to 4287 ppm, corresponding to a desalination efficiency varying from 94.6% to 28.6%. On the other hand, the corresponding calculated SEC_{ED} (Y_3) ranged from about 3.87 to 0.60 kWh/m^3.

1   The regression models for Y_2 and Y_3 can be expressed (in terms of coded variables) by the

2   following second-order polynomial equations:

3

4     $Y_2 = 2552.6 - 656.7X_1 + 1166.6X_2 - 734.4X_3 - 163.9X_1X_3 + 387.4X_1^2 - 342.5X_2^2$ (11)

5     $Y_3 = 1.89 + 0.823X_1 - 0.774X_2 + 0.398X_3 - 0.316X_1X_2 + 0.145X_1X_3 - 0.133X_1^2 +$

6     $0.168X_2^2 - 0.027X_3^2$ (12)

7

8   The coefficients of the polynomial model (quadratic model) were calculated using the Design-

9   Expert® V11 program software. Their respective weights presented in Figure S1 (Appendix

10   A) show that X_2 (permeate volume) is the most prominent factors affecting ED desalination

11   (Y_2) followed by the treatment time (X_3) and the applied voltage (X_1). Concerning SEC_{ED} (Y_3),

12   the applied voltage (X_1) is the most relevant parameter, which is logical because it is a square

13   effect factor on this response (according to the Ohm's law, intensity is proportional to

14   voltage). Obviously, the processing time (X_3) is also a very important factor impacting the

15   energy consumption as well as the permeate volume (X_2). Considering the interactions

16   between the different parameters, voltage and treatment time interact significantly with each

17   other (X_1X_3) on the desalination efficiency, since the amount of salt transported from the

18   permeate compartment to the concentrate compartment is governed by the electrical charge

19   which is simply the product of current intensity (consequence of the voltage) and time. The

20   same interaction can be observed in the Y_3 modelling (energy consumption) because the

21   dissipated power is the product of the electrical charge and the voltage. There is also a strong

22   interaction between voltage and permeate volume, X_1X_2 on energy consumption. This can be

23   explained by the fact that during the ED process, the overall resistivity of the system increases

24   with the treatment time (due to the decrease in salinity of the permeate compartment) leading

1   to a decrease of the resulting intensity. The reduction in conductivity is related to both

2   treatment time and permeate volume. The smaller the permeate volume, the larger the drop in

3   intensity (lower overall electrical charge). This phenomenon is even more pronounced when

4   the desalination rate is high, that is when the treatment time is longer. In other words, at

5   constant voltage (potentiostatic mode), the lower the permeate TDS concentration, the lower

6   the applied electrical charge and the slower the desalination rate. Under such operating

7   conditions (constant voltage), the desalination rate is self-limited contrary to the case of the

8   galvanostatic operating mode.

9   The analysis of variance (ANOVA) of regression parameters of the predicted response surface

10   quadratic models for the two Y_2 and Y_3 outputs shows that both models have a high Fisher

11   coefficient value (F value) and a low probability value (Pr >F < 0.0001) indicating that they

12   are significant (Table 3). Correlation coefficient (R^2 = 0.9895 for Y_2 and R^2 = 0.9944 for Y_3)

13   indicate that only ~ 1 % of the total variation could not be explained by the empirical model.

14   It can be noted that according to Joglekar and May (J Joglekar and May, 1987), a good model

15   fit should have an R^2 value of at least 0.80.

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Table 3

ANOVA for TDS concentration in ED permeate (Y_2) and SEC_{ED} (Y_3)

| Source	Analysis of Variance (ANOVA)				
	df	Sum of Square	Mean of Square	F value	Pr>F
ANOVA results of Y_2	$R^2 = 0.9895$; adjusted $R^2 = 0.9832$; predicted $R^2 = 0.9756$				
Model	6	1.983E+07	3.305E+06	157.44	< 0.0001
Residual	10	2.099E+05	20990.51		
Lack of Fit	6	69163.48	11527.25	0.3276	0.8923
Pure error	4	1.407E+05	35185.40		
ANOVA results of Y_3	$R^2 = 0.9944$; adjusted $R^2 = 0.9901$; predicted $R^2 = 0.9701$				
Model	8	12.14	1.52	187.66	< 0.0001
Residual	8	0.0647	0.0081		
Lack of Fit	4	0.0487	0.0122	3.04	0.1532
Pure error	4	0.0160	0.0040		

4

5

6 Figure 1 and Figure 2 show the 3D contour plot for Y_2 and Y_3 respectively with the

7 corresponding correlation between actual values versus predicted values. For both responses,

8 the experimental (actual) values fit very well with the predicted values, which demonstrates a

9 very good adequacy of the models. From the 3D contour plot of Y_2, it can be observed that the

10 effect of the treatment time is accentuated at high voltage and vice versa (X_1X_3 interaction).

11 Likewise, the strong interaction between the applied voltage and the permeate volume (X_1X_2)

12 can be easily observed in the 3D contour plot of Y_3 (Figure 2).

1 **Figure 1**

2 a) 3D plot of TDS permeate concentration (Y_2) as a function of ED treatment time (X_3) and

3 voltage (X_1). b) Correlation between predicted values vs actual values.
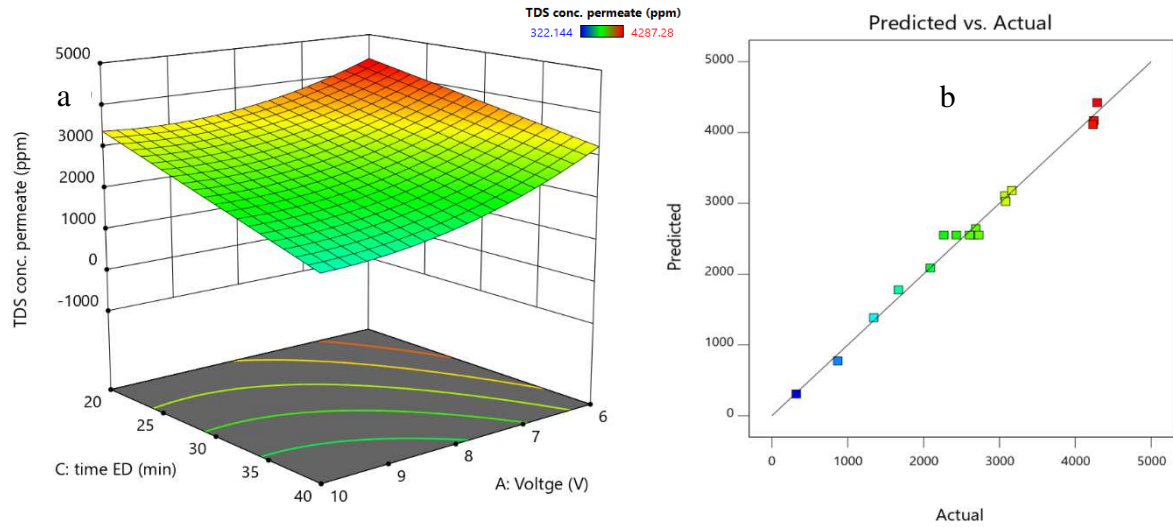
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5
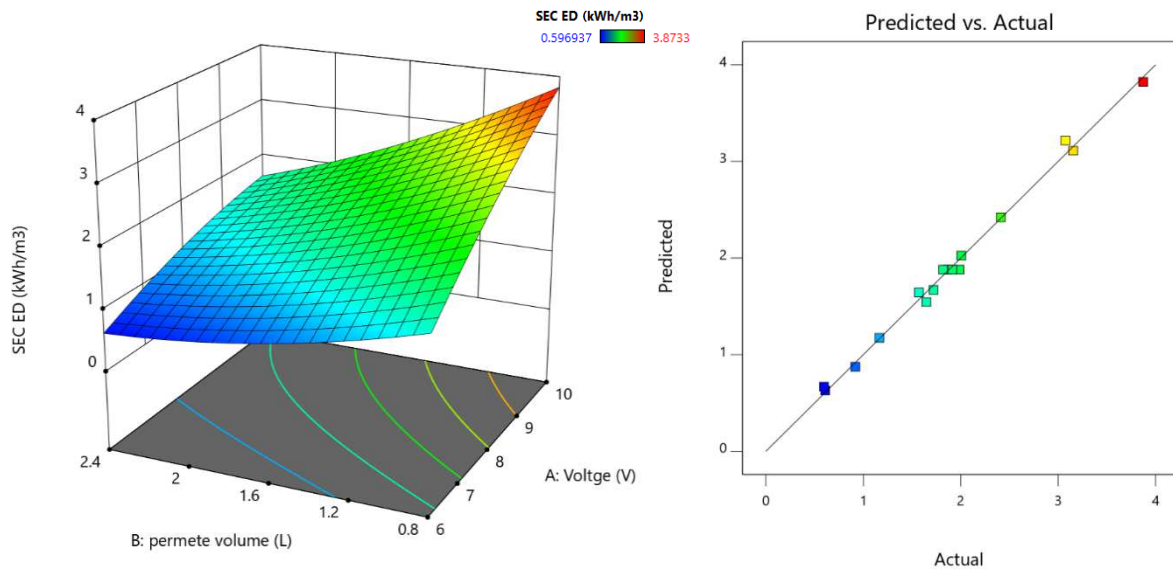
6 **Figure 2**

7 a) 3D plot of SEC$_{ED}$ (Y_3) as a function of ED permeate volume (X_3) and voltage (X_1). b)

8 Correlation between predicted values vs actual values.

9

10

11

1 *3.2 Nanofiltration process modeling*

2 The NF stage was described using the same BBD approach. The applied pressure (X_4), the

3 TDS concentration in the ED permeate (X_5) and the treatment time (X_6) were considered as

4 the main parameters of this study. Similarly, the water recovery (Y_4), the TDS concentration

5 in the NF permeate (Y_5) and the SEC_{NF} (Y_6) were recorded as responses with in addition the

6 pesticide removal (Y_7). The data, including natural levels, design, and responses values for the

7 NF process, are shown in Table S2. Based on the experimental input matrix, the water

8 recovery (Y_4) varies from 26.6 to 86.1% (mean at 63.5%), the TDS concentration (Y_5) which

9 is the result of the two processes (ED + NF) varies from 22.3 to 541.3 ppm (mean at 155.9

10 ppm), and SEC_{NF} (Y_6) from 0.304 to 0.912 kWh.m^{-3} (mean at 0.156 kWh.m^{-3}). Regarding the

11 pesticide removal (Y_7), it was calculated from the mean of the three pesticides (fenobucarb,

12 isoprothiolane and pretilachlor). Whatever the experimental condition, the concentration of

13 isoprothiolane is below the detection limit corresponding to a rejection of more than 99.5%.

14 Fenobucarb and pretilachlor follow the same trend with a retention ranging from 89 to 99.9%.

15 The regression models for Y_4, Y_5, Y_6 and Y_7 can then be expressed (in terms of coded

16 variables) by the following equations:

17

18 $$Y_4 = 68.78 + 15.01X_4 - 13.91X_5 + 10.21X_6 + 8.59X_4X_5 - 6.18X_4^2 - 5.16X_6^2 \qquad (13)$$

19 $$Y_5 = 221.88 - 15.94X_4 + 212.5X_5 + 18.49X_6 + 18.95X_5X_6 - 36.85X_4^2 + 39.35X_5^2 \quad (14)$$

20 $$Y_6 = 0.452 + 0.01X_4 + 0.144X_5 - 0.113X_6 - 0.106X_4X_5 + 0.047X_4X_6 - 0.081X_5X_6 +$$

21 $$0.045X_4^2 + 0.048X_5^2 + 0.057X_6^2 \qquad (15)$$

22 $$Y_7 = 98.03 - 0.221X_4 - 2.74X_5 - 0.126X_6 - 1.15X_5^2 \qquad (16)$$

23

1   The model was developed with Design Expert software V11 and adjusted by removing

2   insignificant terms. The respective weights of coefficients are shown in Figure S2 (Appendix

3   A). Table 4 shows the analysis of variance (ANOVA) of the regression parameters of the

4   predicted quadratic response surface models for the NF stage : water recovery (Y_4), TDS

5   permeate concentration (Y_5), SEC$_{NF}$ (Y_6) and pesticide removal (Y_7). All four model equations

6   are significant with negligible lack of fit. The regression coefficients R^2 are above 97%

7   (except for Y_7) with a quite closed value of adjusted R^2 and predicted R^2. The model equation

8   for Y_7 is not as accurate as the other models ($R^2 = 0.864$) but remains valid and significant (J

9   Joglekar and May, 1987). This observation can be easily explained. In fact, the small lack of

10 adjustment was attributed to the narrow range of the obtained experimental values

11 (approaching the analytical error) and also because only one parameter, the TDS

12 concentration, significantly impacts the pesticide rejection. Indeed, TDS concentration has a

13 very strong impact on pesticide removal and affects the responses (Y_7) with a contribution

14 over 99%, which is in agreement with the previous observation (Nguyen *et al.*, 2019).

15 Concerning water recovery (Y_4), the most influential factor is the pressure applied (X_4),

16 closely followed by the salinity of the NF feed solution (X_5,). These two parameters have

17 antagonist influence on the water flow rate because they are related to the effective driving

18 force and thus strongly affect the water recovery (for a given treatment time) (equation 7).

19 Hence, these two parameters are interrelated, which can be observed by the strong interaction

20 X_1X_2 in the Y_4 model.

21

22

1 **Table 4**

2 ANOVA for NF water recovery (Y_4), TDS permeate concentration (Y_5), energy consumption

3 (Y_6) and pesticide removal (Y_6).

Source	Analysis of Variance (ANOVA)				
	df	Sum of Square	Mean of Square	F value	Pr>F
ANOVA results of Y_4	**$R^2 = 0.9774$; adjusted $R^2 = 0.9638$; predicted $R^2 = 0.925$**				
Model	6	4769.21	794.87	71.95	< 0.0001
Residual	10	110.47	11.05		
Lack of Fit	6	79.28	13.21	1.69	0.3173
Pure error	4	31.19	7.80		
ANOVA results of Y_5	**$R^2 = 0.9744$; adjusted $R^2 = 0.9590$; predicted $R^2 = 0.9000$**				
Model	6	3.791E+05	63183.66	63.36	< 0.0001
Residual	10	9972.79	997.28		
Lack of Fit	6	5281.44	880.24	0.7505	0.6419
Pure error	4	4691.34	1172.84		
ANOVA results of Y_6	**$R^2 = 0.9914$; adjusted $R^2 = 0.9804$; predicted $R^2 = 0.9157$**				
Model	9	0.3857	0.0429	90.12	< 0.0001
Residual	7	0.0033	0.0005		
Lack of Fit	3	0.0019	0.0006	1.80	0.2867
Pure error	4	0.0014	0.0004		
ANOVA results of Y_7	**$R^2 = 0.864$; adjusted $R^2 = 0.8187$; predicted $R^2 = 0.7302$**				
Model	4	66.13	16.53	19.06	< 0.0001
Residual	12	10.41	0.8673		
Lack of Fit	8	6.64	0.8305	0.8826	0.5937
Pure error	4	3.76	0.9409		

4

1   In addition, because TDS retention varies only slightly with the NF operating conditions (X_4

2   and X_6), the TDS concentration in the permeate is therefore mainly related to the feed

3   concentration (X_5) (the higher the feed concentration the higher the permeate concentration

4   will be). Hence, this parameter has a huge impact on the response (Y_5), which has the

5   consequence of mitigating strongly, in the model, the effect of the two others parameters.

6   Pressure (X_4) has the effect of increasing both water flux (increase in driving force) and solute

7   flux (increase of concentration polarization and concentration factor). However, the dilution

8   effect due to an increased water flux is predominant leading to an increase in overall retention

9   with rising pressure (X_4 has a negative effect on Y_5). Similarly, treatment time (X_6) determines

10   the concentration factor (water recovery) but also leads to an increase of the salinity gradient

11   between the feed and the permeate side.

12   The salinity gradient decreases salt retention, so X_6 has a positive effect on the response Y_5.

13   Finally, SEC_{NF} is mainly influenced by both salinity (X_5) and treatment time (X_6). Salinity

14   decreases the effective driving force (increase of osmotic pressure) leading to a water flux

15   decline (at the identical pressure) and thus positively impacts the SEC_{NF} value. In another

16   respect, it was pointed out previously that the longer the treatment time, the higher the water

17   recovery and consequently the lower the SEC_{NF}. Moreover, as pressure and initial salt

18   concentration determine the effective driving force, it is normal to observe a strong interaction

19   between these 2 parameters.

20

1 *3.3 Coupling the ED and NF process: optimization*

2 The objective of this section is to describe using modeling the entire hybrid system combining

3 ED and NF in order to optimize the process in term of efficiency (salt and pesticide removal)

4 and energy cost. Based on the models developed in the previous section for both ED and NF,

5 another experimental matrix was realized coupling the two stages. As mentioned above, the

6 experimental data of this matrix are deduced from the previously developed models for each

7 stage, considering for each experiment that the ED permeate is subsequently treated by NF.

8 The same parameters and ranges were taken into account except for the NF feed concentration

9 which is the results (outlet) of the ED stage. The ED-NF Box Behnken matrix including

10 experimental condition and results is provided in Appendix A (Table S3).

11 Additional responses were included, such as the overall water recovery (Y_8), TDS removal

12 (Y_9) and specific energy consumption (Y_{10}). Y_8 and Y_9 are the product of the water recovery

13 (Equation 8) and TDS removal of each stage respectively whereas the total specific energy

14 consumption (Y_{10}) is the sum of SEC_{ED} and SEC_{NF} (Equation 10). In addition, since sodium

15 and chloride are the majority ions (due to sea water intrusion), their concentrations could

16 exceed the Vietnamese regulations and should be considered as responses for the optimization

17 (Y_{11} and Y_{12} for chloride and sodium respectively).

18

19 $Y_8 = 45.06 + 3.33X_1 + 2.698X_2 + 3.733X_3 + 10.56X_5 + 6.938X_6 + 0.834X_1X_3 -$

20 $2.101X_1X_5 + 5.244X_2X_5 + 2.425X_2X_6 - 2.351X_3X_5 - 0.80X_3X_6 - 1.501X_5X_6 -$

21 $1.993X_1^2 - 2.138X_2^2 - 4.0.71X_5^2 - 3.412X_6^2$ (17)

22

1    $Y_9 = 95.762 + 1.484X_1 - 2.386X_2 + 1.568X_3 + 0.28X_5 - 0.359X_6 + 0.327X_1X_2 +$

2    $0.177X_1X_3 + 0.119X_1X_5 + 0.367X_2X_3 - 0.219X_2X_5 + 0.137X_3X_6 - 0.949X_1^2 +$

3    $0.433X_2^2 - 0.122X_3^2 + 0.647X_5^2 - 0.0077X_6^2$ (18)

4

5    $Y_{10} = 2.35 + 0.763X_1 - 0.683X_2 + 0.336X_3 + 0.0003X_5 - 0.12X_6 - 0.338X_1X_2 +$

6    $0.143X_1X_3 + 0.039X_1X_5 - 0.0295X_1X_6 - 0.0253X_2X_3 - 0.0688X_2X_5 + 0.0525X_2X_6 +$

7    $0.0435X_3X_5 + 0.033X_3X_6 + 0.0473X_5X_6 - 0.096X_1^2 + 0.156X_2^2 + 0.044X_5^2 + 0.055X_6^2$

8

9   (19)

10

11    $Y_{11} = 138.9 - 45.02X_1 + 78.76X_2 - 49.11X_3 - 10.99X_5 + 10.93X_6 + 2.075X_1X_2 -$

12    $11X_1X_3 - 3.25X_2X_3 + 25.75X_1^2 - 22.75X_2^2 + 1.12X_3^2$ (20)

13

14    $Y_{12} = 86.69 - 27.44X_1 + 48.42X_2 - 30.36X_3 - 8.21X_5 + 6.956X_6 - 6.825X_1X_3 -$

15    $1.925X_2X_3 + 15.99X_1^2 - 13.94X_2^2$ (21)

16

17 Because these models were developed based on the results predicted from the previous

18 validated models (for each process independently), they can be considered significant. The

19 respective values of coefficients in Equations 17-21 presented in Figure S3 (Appendix A)

20 show that the treatment time (X_6) and feed TDS (X_5) of the NF stage are predominant factors

21 for water recovery (Y_8) while the applied voltage (X_1), permeate volume (X_2) and treatment

22 time (X_3) of the ED stage are the predominant factors for total TDS removal (Y_8), and residual

23 chloride (Y_{11}) and sodium (Y_{12}) ions in the purified water. As expected, SEC_{ED} (Y_3) dominates

the hybrid ED/NF system SEC (Y_{10}). In addition, since the two processes are interrelated, interactions between the parameters of the two processes can also be observed especially in the case of Y_8 where cross coefficients between X_2 and X_3 of the ED stage and X_5 and X_6 have a significant influence. The optimization of the overall hybrid process was carried out by applying specific criteria in order to comply the Vietnamese regulations (QCVN 01-1:2018/BYT, 2018) regarding the concentration of pesticides, sodium and chloride while minimizing the operating cost (energy consumption and membrane surface area) and the investment cost (ED cells and NF membrane modules).

The criteria selected for the optimization of the entire hybrid system are the following:

(1) The TDS removal should be maximized (importance 3/5)

(2) The overall water recovery should be maximized (importance 3/5)

(3) The overall SEC should be minimized (importance 3/5)

(4) Chloride and sodium concentrations (Y_{11} and Y_{12}) have to be in the range of 50 to 250 ppm.

Moreover, in a more forward-looking perspective of system scaling up, it is necessary to take into account in addition to the energy consumption, the investment and operating costs related to the number of ED cells and the membrane surface area for each process (ED and NF). This dimensioning aspect is directly related to the hydraulic retention time (HRT) which is, in this case, dependent on the treatment time of each process. As a consequence, a fifth criterion was chosen corresponding to the system dimensioning:

(5) Minimization of the processing time for both ED and NF (importance 1/5).

It has to be noted that these criteria were selected in order to obtain a cost-effective hybrid process but it could be modified to adjust the configuration and the operating conditions more precisely according to the local constraints such as footprint, energy cost, membrane

1   availability…. Based on the five criteria defined above, the Design Expert V11 software

2   proposed the best solution (Table 5) in terms of desirability (best compromise to satisfy the

3   applied criteria) with a value close to 80%.

4   The experiments carried out under the optimal conditions deduced from the modeling gave

5   experimental results in good agreement with the predictions allowing to validate this

6   optimization approach. It can be seen that the desalination rate is higher than expected in the

7   ED stage, implying an overconsumption of energy, and that the conversion rate is lower in the

8   NF stage, probably due to the uncertainty of the pressure measurement related to the gauge

9   used (± 0.1 bar). In addition, the multivariable-linear analysis used for this non-linear system

10 can lead to small deviations between the predicted and experimental values, as mentioned

11 above.

12 Nevertheless, the observed deviations are acceptable with values of about 8% and 10% on

13 overall productivity (Y8) and specific energy consumption (Y10), respectively. Correlatively,

14 water was produced with a better quality due to higher rejection of salts and lower conversion

15 rate during the ED and the NF stages, respectively.

16

Table 5

Predicted and experimental responses obtained from the optimal conditions deduced from the modeling.

Optimal parameters	ED			NF		NF	
	X_1	X_2	X_3	X_4		X_5	
	9 V	2.4 L	27.1 min	11.1 bar		4.38 h	

Responses	ED			NF			
	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7
	(Y_{ED})	TDS $_{ED}$ permeate	SEC$_{ED}$	(Y_{NF})	TDS removal	SEC$_{NF}$	pesticide removal
	%	mg/L	kWh.m^{-3}	%	%	kWh.m^{-3}	%
Predicted	75	3382	1.36	72	90.4	0.53	96
Experimental	75	3233	1.56	66	91.9	0.57	> 99

Responses	ED –NF hybrid system				
	Y_8	Y_9	Y_{10}	Y_{11}	Y_{12}
	(Y_{tot})	(total TDS removal)	(total SEC)	[Cl$^-$]	[Na$^+$]
	%	%	kWh.m^{-3}	mg/L	mg/L
Predicted	54	94.5	1.89	186	114
Experimental	50	95.4	2.13	158	100
Desirability	78.5%				

The evolution of conductivity during the ED stage and of conductivity and permeate flux during the NF stage are presented in Appendix A (Figures S4 and S5). Table 6 summarizes the experimental ionic composition of the feed and permeates at each stage of the hybrid ED/NF system. Since monovalent ions constitute the majority ions in the feed, they dominate

1 the TDS rejection rate. The rejection of about 90% observed for monovalent ions by the NF90

2 membrane is in agreement with the values found in the literature (Kammoun *et al*., 2020). The

3 near quantitative rejection of sulfate ions in the NF stage counterbalances the low removal of

4 these ions in the ED stage, demonstrating the complementarity of the two processes.

5

6 **Table 6**

7 Experimental ionic composition of the feed and permeates at each stage of the hybrid process.

	Chloride	Sulfate	Sodium	Magnesium	Calcium	total TDS	TDS removal rate
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	%
Feed	3197	459	1721	258	59	5693	
ED permeate	1658	432	964	148	31	3233	
ED removal (%)	48	6	44	43	47	-	43.2
NF permeate	159	1.9	100	1.5	0.5	263	
NF rejection (%)	90	> 99	90	99	98	-	91,9
					Overall desalination rate		95.4

8

9 The experimental validation showed that the desalination rate reached about 95% for the

10 overall hybrid system. Operating conditions achieved a salinity of less than 3.5 g/L after the

11 ED stage, which is low enough for the subsequent NF treatment to meet Vietnamese

12 guidelines for sodium and chloride concentration and to remove about 99% of total pesticides.

1   During the dry season in 2020, the saline intrusion, with a salinity rate of 4 g/L can move up

2   to 50 – 130 km from the river mouth inside the delta (Loc *et al.*, 2021). More generally, it

3   forms a wide strip of land whose salinity is between 1 and 10 g/L from January to April

4   making the surface water undrinkable (Ly *et al.*, 2018; Whitehead *et al.*, 2019)]. In fact,

5   salinity varies with peaks during the months of February and March depending on the tide

6   amplitude and the river discharge (Tuan *et al.*, 2007). When the salinity is below about 3 g/L,

7   a single stage with a tight NF membrane (like NF90) (Kammoun *et al.*, 2020) is sufficient to

8   obtain drinking water that meets the Vietnamese standards in terms of both desalination and

9   pesticide removal. Beyond this value, ED/NF integration in a hybrid process becomes

10   necessary.

11   However, as can be seen in Table 5, the ED desalination stage contributes predominantly to

12   the energy consumption of the hybrid system in the case studied (TDS of about 5 g/L). This

13   contribution strongly depends on the amount of salt to be removed in order for the NF stage to

14   effectively remove pesticides: the greater this amount, the higher the energy consumption of

15   ED. This hybrid process will therefore become prohibitively expensive if salinity is very high

16   (in coastal areas for example) or if salinity peaks of high intensity occur and last for a long

17   time.

18

Conclusion

20   The complexity of Mekong Delta surface waters due to the simultaneous presence of high

21   levels of pesticides and salinity requires the use of advanced treatment techniques such as

22   membrane technologies to secure the water supply for the living population in the rural areas

23   of the Delta. In this work, a hybrid process was developed combining ED as a preliminary

24   treatment to reduce salinity and NF for the removal of pesticides and residual salinity. The

efficiency of pesticide removal by NF is highly dependent on the TDS concentration and thus on the performance of the preliminary ED stage. This study highlighted the following points:

- By using a specific surface response methodology, modeling of the entire hybrid system can be performed in terms of water quality (overall desalination and pesticide removal) and energy consumption.

- The experimental operating conditions resulting from the modeling confirmed the predicted performance of the coupled ED/NF system with water quality in compliance with Vietnamese regulations and a maximum deviation of about 8% and 10% on the conversion rate and energy consumption, respectively.

- It should be noted that the models developed using the experimental design methodology are only relevant to the experimental domain explored.

- Future works may consist of verifying the optimized conditions of the ED/NF process by applying it to real surface waters of the Mekong Delta. On the other hand, the integration of photovoltaic solar panels could make it possible to obtain an eco-friendly and autonomous system operating at low energy costs.

Such a treatment strategy could be a safe and reliable solution to provide drinking water during the dry season for remote population living in the Mekong Delta. This could also benefit many other agricultural and coastal area regions in the world where dry and rainy season become more and more pronounced due to climate change, resulting in severe drought and seawater intrusion.

Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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Graphical abstract

Optimization of a hybrid process combining Nanofiltration and Electrodialysis for the treatment of surface water in the Mekong Delta region

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