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Integration of an Electrodialysis Process for Selective Nitrate Removal with Renewable Energy Sources

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Intensified agricultural activities with an excessive fertiliser utilisation result in high penetration rates for several chemical compounds through soil to the ground water reservoirs. One of the main components in fertilisers are nitrate ions, which at high concentrations have harmful effects on human health. There is a number of available technologies for nitrate removal, but the majority of them use chemical additives and generate waste that has to be treated before their release to the environment. One promising alternative is the electrodialysis (ED) process. To make the process more sustainable and allow the deployment of such systems to remote areas where limits on electric power consumption may be present, the ED system can be powered by photovoltaic (PV) solar panels. The challenge is to operate the system efficiently under the intermittence of the solar radiation and the variations in the water concentration of nitrates. In this work, a mathematical model describing the removal of nitrate ions, under a variety of meteorological conditions, and for a variable daily demand of drinking water has been developed. Solar radiation and nitrate feed are real data from an area with drinking water contamination problem. This simulation model predicts the removal rate of nitrate ions, the sizing of the solar panels and the capacity of the battery with respect to the battery's state of charge. Efficient energy management strategies are developed to ensure that the targeted pure water demand in terms of volume and concentration of nitrates is met and the use of non-renewable, externally provided electricity is minimised.

1. Introduction

As freshwater resources are drastically reduced by increasing pressures from climate change, population growth and rapid urbanisation, the use of unconventional water resources, is one of the most important solutions to confront water scarcity and increase the availability of water resources, especially in arid regions of the world. This need has resulted in the rapid development of desalination technologies, most notably the membrane filtration technologies. Among them, electrodialysis (ED) technology has shown particular precedence in recent years due to its competitive advantages, such as high clean water recovery, short treatment times, flexibility, and lower operating and maintenance costs (Strathmann, 2004). Another important advantage is the direct use of electricity to achieve ion separation, which favours its combination with renewable energy sources (RES), such as solar energy (Plakas et al., 2018). The hybrid $\mathrm{ED}-\mathrm{PV}$ system could be applicable to areas with excessive solar energy and electric power limitations. The challenge of implementing solar energy with ED is the intermittent production of electricity, in combination with the brine management. Another important challenge is the treatment of nitrate-contaminated (NO_3^-) brackish water in areas with agricultural activity. Groundwater in those areas is considered unsuitable for drinking due to high NO_3^- (> 50 mg/L) concentrations.

ED research over the last 10 y focused on the recovery of high value-added materials., such as lithium with desalination (Ji et al., 2017) as well as the removal of heavy metals (Gherasim et al., 2014). The use of ion exchange membranes for the recovery of nutrients has also found successful applications, such as municipal waste treatment (Vineyard et al., 2021), and the recovery of useful compounds from manure (Shi et al. 2021). However, there are only a few works regarding the selective removal of NO_3^- ions with ED, most of them treating

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wastewater instead of fresh water and lacking model-based investigations (Ye et al., 2019). Regarding the combined application of ED with renewable sources, all the publications reported systems where the RES (wind or solar energy) was directly connected to the ED unit, as indicated in the review of Mir et al. (2021). For instance, Cipolletta et al. (2021) studied a hybrid RES (wind and PV energy- ED) system for irrigation of banana cultivation. The lack of energy storage has very significant disadvantages as non-renewable sources should be used during power outages. There are also a few studies where energy storage is used, but only in a recent one has the overall system been optimized using systematic methods that take into account energy management (Bian et al., 2019). The previous work however is not implemented on nitrate removal. In the following presented work, an integrated system of ED and PV-battery was theoretically studied. For the application of the system to a case study for nitrate ions removal from a ground source, weather, feed and water demand data were collected, for the application of the $\mathrm{ED-PV}$ system. The electrodialysis unit size, the PV and the battery numbers were estimated with a dynamic model, so that the process could be controlled to meet energy and water demands.

2. Materials and methods

2.1 Electrodialysis energy consumption

Electrodialysis is an electrochemical process in which ions migrate through ion-selective membranes as a result of their attraction due to two electrically charged electrodes. To calculate the energy demand of electrodialysis ($\mathrm{E_{ED}, kW}$) the applied voltage ($\mathrm{V_{ED}}$), current density ($\mathrm{I_{ED}}$), and process time (t) are needed, as shown in Eq(1). The applied voltage and the process time were input variables to calculate the current density output parameters of the ED model.

$$E_{ED} = I_{ED} \cdot V_{ED} \cdot \mathrm{t} \tag{1}$$

2.2 Photovoltaic and battery model

A PV cell has the ability to convert photon energy into electrical energy in the form of direct current. Modeling for PV panels takes into account its electrical characteristics. The relationship between the voltage I and the voltage V of the equivalent circuit is given by calculating the currents $\mathrm{I_L}$, $\mathrm{I_D}$ and $\mathrm{I_{sh}}$, as shown below. Variables $\mathrm{I_L}$, $\mathrm{I_0}$, $\mathrm{R_s}$, α, are obtained by algebraic equations and are discussed in literature (Ulleberg, 1998). This equation demands from PV manufacture data the values of current and voltage at maximum power, the current at short circuit current conditions, the voltage at open voltage conditions, the values of temperature coefficient at short circuit and open voltage conditions, and the number of solar cells.

$$I_{PV} = I_L - I_D - I_{sh} = I_L - I_0 \cdot (e^{\frac{\mathrm{V}+I\cdot R_s}{\alpha}} - 1) - \frac{\mathrm{V} + R_s}{R_{sh}} \tag{2}$$

The output power from the PV array is given by:

$$P_{PV} = I_{PV} \cdot n_{conv} \cdot V_{PV} \tag{3}$$

where $\mathrm{n_{conv}}$ is the efficiency of a DC/DC converter (90-95 %). A lead-acid accumulator is an electrochemical device that converts electrical energy into chemical energy during the charging process and vice versa during the discharging process. The mathematical model calculates the charging and discharging current, voltage and the state of charge (SOC) of the accumulator. The SOC is the fraction of the current capacity of the accumulator at each time instant, divided by its nominal capacity (Manwell et al., 1993):

$$SOC_t = SOC_{t-1} \cdot (1 - \sigma) + I_{bat} \cdot n_{bat} \cdot \Delta t \tag{4}$$

where σ is the self-discharge rate (2.5 %), n_{bat} is the efficiency factor (95 %) and t is the time in h.

2.3 Power management strategy

A block diagram of the presented system is shown in Figure 1. The PV panels collect the solar irradiance and convert it to electrical energy, which is transferred to the battery accumulator, and then to the ED unit, where the current is used to process ground water. Depending on the battery's SOC the energy is managed differently. When the solar irradiance is sufficient, the current that is transferred to the battery charges the accumulator, and the battery's SOC is increased. On the other hand, when the irradiance is not enough, as the battery only provides load, it discharges, and its SOC decreases. In the 1st case of Figure 1, the battery's SOC ranges between minimum and maximum values, ($\mathrm{SOC_{min}} < \mathrm{SOC} < \mathrm{SOC_{max}}$) and the current load is transferred to the ED unit, where it is used to process groundwater. In the 2nd case, the battery's SOC is less than the minimum value (SOC

< SOC_{min}), and the current can't meet the ED unit demand and the ED unit is stopped. The battery is charged by the PV panels, until it's SOC exceeds SOC_{min} and the 1st case is implemented. In the 3rd case, when the solar irradiance is too high, and the battery is fully charged, there is excessive current produced that can be either sold to the grid, or serve other loads, such as hydrogen production (Ipsakis et al., 2009), although the latter is not investigated here. In this case, the system is oversized, and such energy surplus should be minimized.

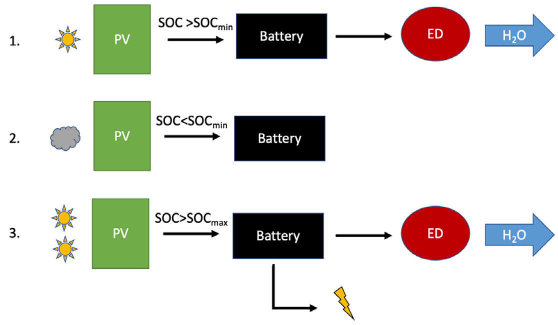


Figure 1: Block diagram of the proposed system

2.4 Proposed approach

In this work the goal is to investigate a scaled-up system for a real case in Thessaloniki, Greece. Firstly the ED size (membrane area A_m, number of cells N_{cell}) and operating characteristics (separation efficiency SP and voltage V) were evaluated based on the nitrate feed concentration, nitrate target concentration, and drinking water demand for about 20 houses of the nearby region (10 m^3/d).

$$\begin{aligned} &\min V, N_{cell}, A_m \\ &\max SP \qquad (5) \\ &s.t.\ V_{min} < V < V_{max},\ N_{cell}^{min} < N_{cell} < N_{cell}^{max},\ A_m^{min} < A_m < A_m^{max} \end{aligned}$$

In the second step, the calculated output current density from the designed ED was used to determine the PV (N_{PV}) and battery (N_{BAT}) numbers, in order to meet the ED load demand. The different options for PV and battery numbers, that would cover the energy demand without connection to the electrical grid, were evaluated to attain the maximum daily water production (W_{Prod}), and the minimum renewable energy loss (E_{loss}) of the system, with respect to the battery SOC (%), as follows:

$$\begin{aligned} &\min N_{PV}, N_{BAT}, E_{loss} \\ &\max W_{Prod} \qquad (6) \\ &s.t.\ SOC_{min} < SOC < SOC_{max},\ N_{PV}^{min} < N_{PV} < N_{PV}^{max},\ N_{BAT}^{min} < N_{BAT} < N_{BAT}^{max} \end{aligned}$$

Both problems were addressed through exhaustive numeration. The dynamic ED model, used as described in previous work (Voutetaki et al., 2020), was validated with experimental data from literature for the nitrate ions (Mohammadi et al., 2021). The current load demand for ED, and the solar radiation data of the case study's region, were used to design the PV-battery system. A PV-battery model was developed (Ipsakis et al., 2009), and the power management strategies were obtained from Giaouris et al. (2013). Electrodialysis is usually a batch process. Under current application a specific water volume is recirculated for enough time to meet the drinking water specifications. Then, the ED unit stops (load demand=0), and the ED batch is replaced with another batch. The challenge of this work was to design enough batches, for the battery's SOC not to decrease more than SOC_{min} and so that the drinking water produced from the batches would be maximized. The diluted water stream produced from ED is for consumption, and the concentrated water stream, is for irrigation.

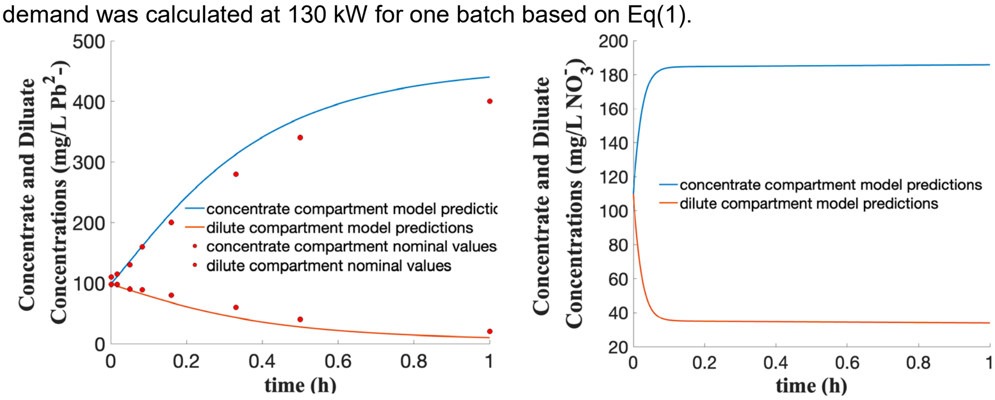
3. Implementation

The study was implemented in a region near Thessaloniki, with nitrate contamination of ground water. The initial nitrate concentration was 100 mg/L, and the target was for the water to meet drinking level, which means that nitrate has to be reduced to < 50 mg/L. The ED size and operating parameter estimation was for V= [20- 40 V], N_{cell}= [45- 65], A_m= [0.03- 0.06 m^2]. The PV and battery estimation were made with solar radiation data of the case study's region that were collected for 1 y. The number of batteries and PV panels were ranged within N_{BAT} = [2, 6] and N_{PV}= [9, 20], so that the load demand of the ED was satisfied. The battery capacity and PV panel model values were 866 Ah and 0.64 m^2, with 9.85 % efficiency for the PV and 95 % for the battery, making the overall system efficiency 9.3 %. The daily water production was estimated using a water tank with initial volume of 5 m^3, that fills with 2 m^3/batch, and empties at a constant hourly rate. The energy loss (surplus) is calculated from the multiplication of the time duration at which the SOC is above SOC_{max}, to the respective load that exceeds the battery's capacity. The SOC range is SOC =[50, 90 %] of the total battery capacity.

4. Results and discussion

4.1 Electrodialysis unit validation and size estimation

The ED unit validation for nitrates was made with experimental data from Mohammadi et al. (2021), and is shown in Figure 2a. Clearly, the developed model matches the experimental data sufficiently, as the deviation was estimated to range between 1- 10 %, with an average of 5 %. For the determination of the ED unit characteristics, as per the first step of the proposed approach, the unit processed 4 m^3/batch, so the concentrate and dilute volumes were 2 m^3 each. Several simulations were made for different ED unit parameters, and the optimum solution was selected for minimum energy consumption and maximum nitrate ions removal. The ED unit was estimated to have 68 cell pairs, and membrane sizes of 0.038 m^2. For treating 4 m^3 of ground water with initial concentration of 100 mg/L, the final concentration for nitrate was $[NO_3]^-$ =40 mg/L, that was achieved with 25 volts, 150 L/h of flow rate, and 1 h of treatment. The nitrate removal with ED is shown in Figure 2b. The ED load demand was calculated at 130 kW for one batch based on Eq(1).

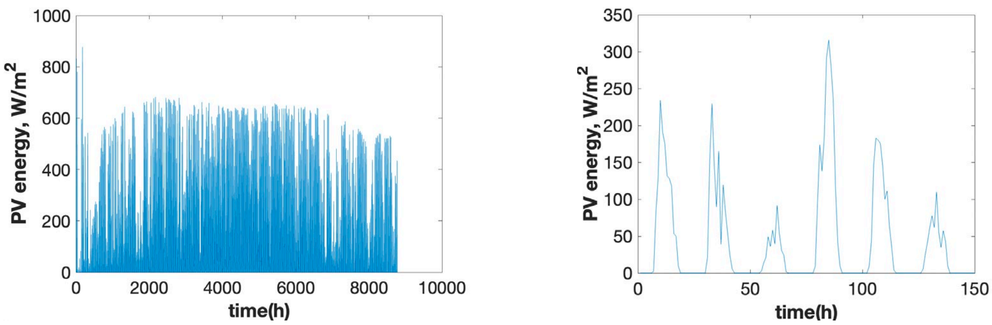


(a) (b)

Figure 2: a) model validation for nitrate b) nitrate removal results with ED

4.2 Photovoltaics and battery number estimation

The estimation was made for 6 consecutive cloudy days, (1,680-1,829 h of Figure 3a). In Figure 3b, the PV energy for the 6 cloudy days is presented. In Table 1, the minimum number of PV panels, produced water flowrate, and energy loss for the different battery system values are presented.



a) b)

Figure 3: a) Annual solar irradiance of Thessaloniki, b) solar irradiance of 6 cloudy days

Table 1: Different battery-PV systems evaluation

N_{BAT}	N_{PV}	W_{Prod}, m^3/d	E_{loss}, MWh/y
2	20	10.8	1,920
3	15	9.6	854.4
4	12	8.88	367.2
5	10	11.52	384
6	9	10.56	2.1

The 6-battery/10-PV panel system has high water production (10.56 m^3/d) and the minimum energy loss (2.1 MWh/y). The battery SOC % and hourly water production are shown in Figures 4a and 4b. In this 6- battery system every hour 0.44 m3 is drawn from the water tank. On the other hand, the 5-battery system, whose SOC and water production are presented in Figure 4c and 4d, has the highest fresh water production (11.52 m^3/d) and relatively low energy loss (384 MWh/y). In this 5-battery/10 PV system, a quantity of 0.48 m^3 is drawn hourly from the tank. Both cases represent viable systems that meet the drinking water target. Note that the energy loss values are high, because the system capacity is small and the area has intense solar irradiation. Apparently, the energy loss-battery cost trade-off is an important feature in this area that is not considered in this work.

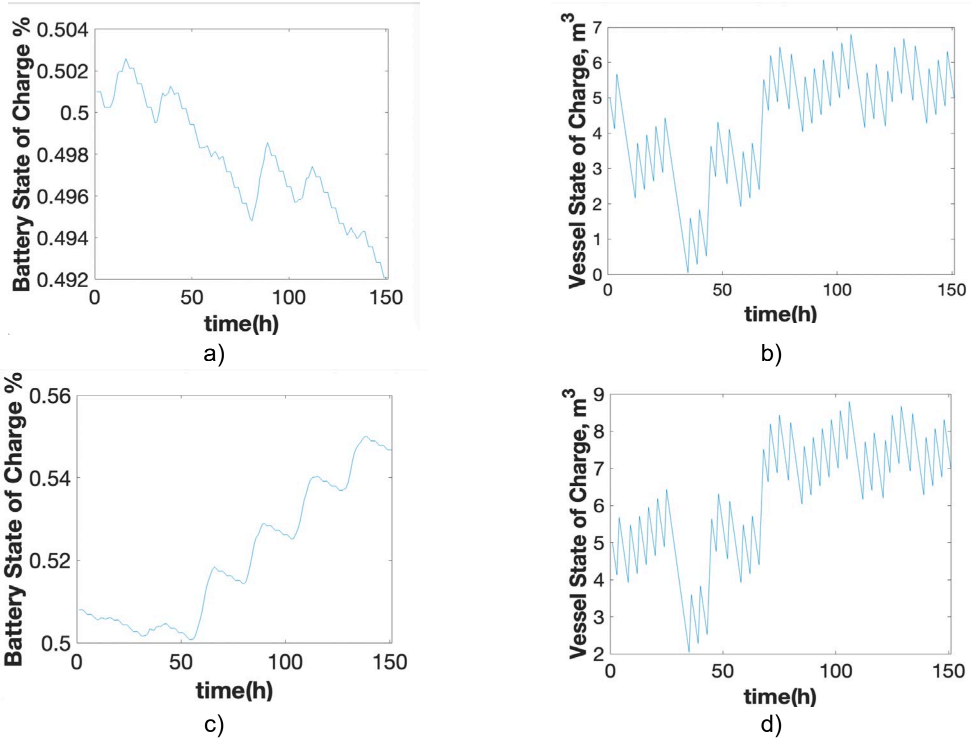


Figure 4: a) SOC and b) water production of a 6 battery/10 PV panel system, c) SOC and d) water production of a 5 battery/10 PV panel system

5. Conclusions

In this study, a hybrid $\mathrm{ED}-\mathrm{PV}$ system was theoretically studied to treat nitrate-contaminated water. The sizing of the ED unit and PV/battery systems were made with dynamic models properly adjusted to the case study's water characteristics, and water demand data using annual information of solar irradiation. The results showed that an ED unit of 68 cell pairs, 25 V, demands 130 kW/batch for treating 4 m^3 of water with 100 mg/L of nitrate. To produce enough energy, different systems of PV/Batteries were used, that were compared to each other on higher water production and lower energy surplus. The more suitable options were a 5 battery/10 PV system and a 6 battery/9 PV system. The first had the highest water production and the second the lowest energy surplus. For the selection of the most advantageous system, more factors have to be studied, such as equipment cost factors, and surplus energy management. The presented $\mathrm{ED}-\mathrm{PV}$ system is regarded to be a sustainable, environment friendly solution for treating nitrate contaminated waters and freshwater production, for areas with limited access to electrical grid.

Nomenclature

SOC – state of charge of accumulator, %
I_{PV} – operation current for the PV system, A
I_0 – diode reverse saturation current for the PV system, A
I_{sh} – shunt current for the PV system, A
I_L– light current for the PV system, A
R_{sh} – shunt resistance for the PV system, Ω
R_s – series resistance for the PV system, Ω
a – curve fitting parameter for the PV system, V
V– operation voltage for the PV system, V
I_{BAt}– charging/ discharging current, A
I_D – diode current for the PV system, A
t– time, h
E_{ED} – ED energy consumption, kW
I_{ED} – ED current density, A
V_{ED} – ED voltage, V
P_{PV}– PV power, W
V_{PV}– operation voltage of the PV system, V
N_{PV}– PV panels number
N_{BAT}– battery number
E_{Sur}– energy surplus, W
W_{prod}– water produced, m^3

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