Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24984

172 (2019) 323–329
December

Desalination and fate of nutrient transport in domestic wastewater using electrodialysis membrane process

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Received 1 April 2019; Accepted 26 September 2019

ABSTRACT

The use of domestic wastewater (DWW) in irrigation offers numerous advantages because of its nutrient compositions. However, the direct use of DWW is risky to both human health and the environment. Hence to comply with circular economy principles, designing a strategy for treating and capturing nutrients from DWW is imperative. Electrodialysis (ED) is a promising technology to achieve this objective. This study investigated the effect of pH and potential difference (voltage) on the performance of the ED. The desalination and transport fate of some nutrients on real DWW is also monitored. The ED system attained an optimum desalination performance of 0.469 mS/cm in 20 min at voltage 15 V and pH 7. Under these conditions, the system achieved 90% nitrate and nitrite removal, while phosphate removal was at 67%. Under continuous flow conditions, the system managed to concentrate the target nutrients in a subsequent chamber. The removal of some organics was also attained.

Keywords: Ion-exchange; Electrodialysis; Desalination; Nutrients recovery; Membrane technology

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1. Introduction

The ever-increasing population has escalated the demand for food, energy, and water; the latter being the denominator. Water is a cardinal constituent for the functioning of any living organism; however, freshwater is diminishing at an alarming rate. Thus, there is a need to find ways to preserve, sustain and/or treat the available freshwater sources [1]. The best way to re-use wastewater is through irrigation—because it contains numerous nutrients. To use wastewater in irrigation, prior treatment is necessary [2]. Several technologies are used in wastewater treatment these include physical, chemical, biological, adsorption, and membrane technologies [3–6]. Membrane technology has gained a wide audience which includes reverse osmosis and electrodialysis [7].

Electrodialysis (ED) has been a long-existing technology used for desalination [8]. ED has a unique property of separating compounds to its constituent anion and cations using semi-permeable membranes [9]; attaining the desired results without compromising constituents of the end product. Furthermore, with the development of function tailored membranes, such as bipolar membranes it creates a new set of products [10]. ED has shown the potential which made it to be considered as a multifaceted technology with a wide range of applicability such as treatment of brackish water

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Presented at the 4th International Conference on Recycling and Reuse 2018 (R&R2018), 24–26 October 2018, Istanbul, Turkey

and production of salt [11]. However, a further treatment of wastewaters from sewage treatment plants using electrodialysis is still being researched.

Recent studies show that ED can be applied to domestic wastewater as a tertiary treatment to generate reusable water for industrial use, such as in cooling towers [12]. Goodman et al. [13] reports the use of electrodialysis reversal to remove salt and to provide a source of recycled water for agriculture. The comparison of sand filter/electrodialysis reversal and sand filter/ultrafiltration/reverse osmosis shows that ED is the most cost-effective process [14]. Nonetheless, few have applied ED on raw domestic wastewater. Therefore, in this study electrodialysis was used to treat domestic wastewaters. The desalination capacity of ED was monitored as well as the possibility of nutrient removal and recovery. The performance of the system under different conditions of pH and voltage was also investigated. The study primarily targeted nitrite, nitrate and phosphates as they are anionic nutrients that are permeable to anion exchange membranes. This enables the migration and the transport of the nutrients across the ED chambers when using a membrane-based electrodialysis process.

2. Materials and methods

2.1. Sample characterization

Domestic wastewater (DWW) was collected from Saray Advanced Biological Wastewater Treatment Plant, Istanbul Turkey. The DWW samples were collected in a 20-L jerry-can and stored at 4°C. The characteristic of the DWW is shown in Table 1.

2.2. Equipment and experimental procedure

2.2.1. Electrodialysis equipment

Experiments were carried out with a PCCell ED 64-004 cell, PCCell GmbH, Heusweiler, Germany. Four bolts at each corner side of the stack were used to hold membranes and spacers together. The bolts are equally tightened by applying a torque of 6.0 Nm. The stack configuration is composed of two cation exchange membranes and one anion exchange membrane separated by four spacers with a thickness of 0.5 mm. All membranes and spacers were supplied by PCA (PolymerChemie Altmeier GmbH, Heusweiler, Germany).

Table 1
Wastewater characteristics

Parameter	Concentration	Unit
pH	7.60	–
Electrical conductivity (EC)	1.56	mS/cm
Chemical oxygen demand (COD)	405	mg/L
Ammonia (NH_3)	32.8	mg/L
Nitrite (NO_2^-)	0.301	mg/L
Nitrate (NO_3^-)	0.407	mg/L
Total nitrogen (TN)	49.3	mg/L
Phosphates (PO_4^{3-})	7.00	mg/L
Total phosphorus (TP)	14.0	mg/L
Sulphate (SO_4^{2-})	166	mg/L
Total dissolved solids (TDS)	312	mg/L

2.3. Experimental procedures

2.3.1. Preliminary treatment and the electrodialysis process

An ion-exchange column was used as a preliminary treatment method to reduce hardness to the accepted levels, 5 mg/L as $CaCO_3$. The ion exchange resins were activated with sodium chloride (NaCl). The samples were then filtered through 45 µm papers to remove suspended solids and other materials that were deemed to clog the membranes before feeding it to the electrodialysis.

After preliminary treatment DWW was fed to an ED cell consisting of three columns and an electrolyte compartment. In this study, the wastewater column is referred to as "dilute", while the second column is a "concentrate", the third column was not operated. The experimental setup is depicted in Fig. 1a. The pH and conductivity were monitored throughout the experiments on a Hach SC1000 device (Germany) and values were stored through an extensionally connected computer.

The wastewater was allowed to float in a tortuous configuration to allow maximum mixing and elimination of gas bubbles development within the stack. Fig. 2 illustrates the electrodialysis process applied. The standard electrolytes used in the concentrate and electrolyte compartment were 0.01 M sulphuric acid and 0.01 M sodium carbonate, respectively; they were circulated within the stack.

3. Results and discussion

3.1. Desalination and effect of pH

The effect of pH on the desalination capacity of electrodialysis (ED) on DWW was investigated at pH 3.0, 7.0 and 10.0. The system achieved an acceptable conductivity of 0.469 mS/cm within 49, 54 and 85 min at pH 10, 7 and 3.0, respectively. From Fig. 3 it is clear that the system is desalinating at a faster rate under alkaline condition. This is attributed to the presence of substantially more hydroxyl ions in the alkaline solutions. The massive immigration of hydroxyl ions alongside other smaller anions makes desalination faster as seen in the decreases in conductivity of the dilute chamber [15].

3.1.1. Conductivity fluctuations in the ED

Conductivity in ED chambers of a sample under the normal expected wastewater pH range can be observed in Fig. 4. The conductivity dropped in the dilute compartment, but then it slightly increased and then precede to decline afterward. These fluctuation phenomena are predominantly observed throughout the different experiments and more so with an increase in voltage.

3.1.2. Effect of voltage on desalination

The systems desalination performance under-voltage 5, 10, 15, 20 and 25 V was analyzed. From Fig. 5, 15 V performed better at achieving the target conductivity. As the voltage changed from 15 V, desalination was hindered. This

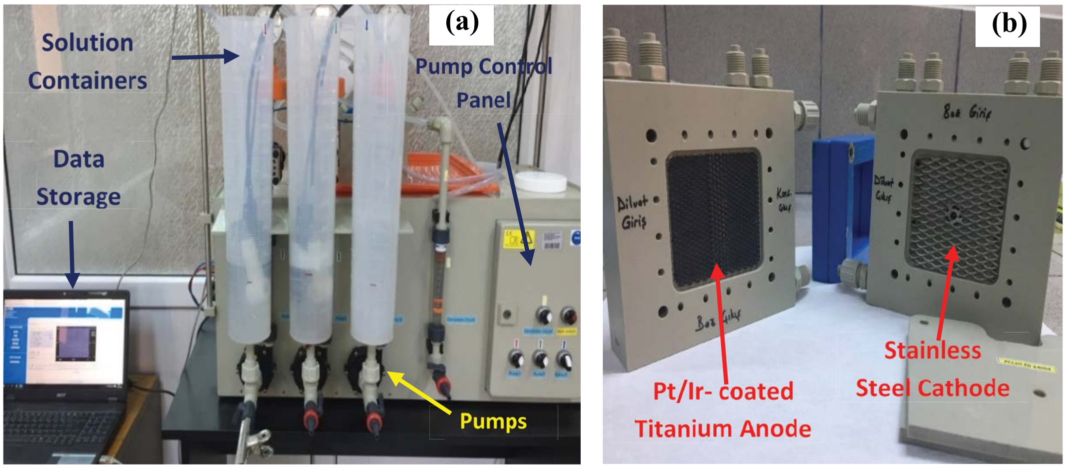

Fig. 1. Laboratory scale of ED system (a) ED pump unit, data storage, and solution containers and (b) ED cell unit: anode and cathode.

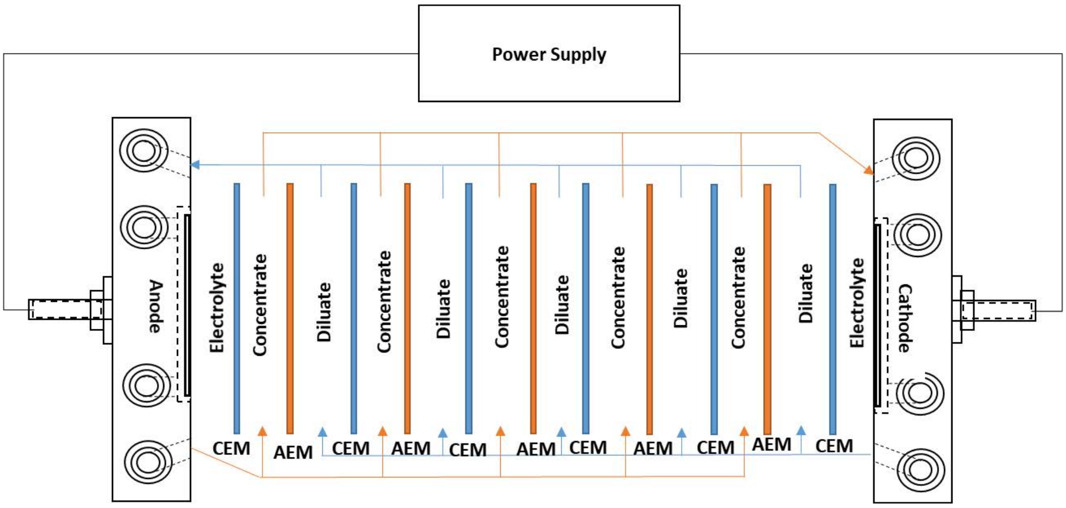

Fig. 2. Electrodialysis process.

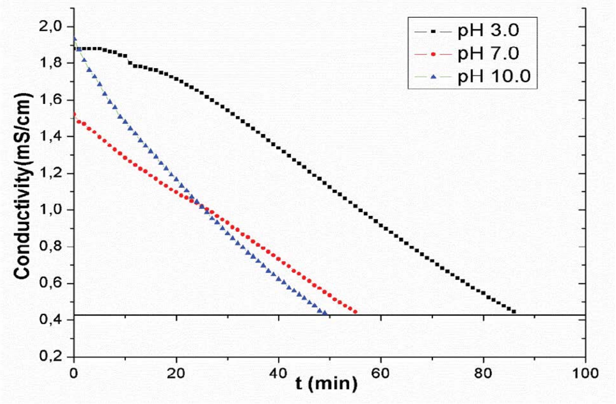

Fig. 3. pH effect on ED desalination capacity.

observation is a manifestation effect of concentration polarization phenomenon [16].

In the dilute compartment, the pH is relatively stable initially indicating that the system is operating under the stable condition and it can be argued that the rate of mass transfer is semi equal. However, as more and more ions start to be conducted at a faster rate in the stack than they are being transported from the solution, the formation of formation of a boundary layer that is depleted of ions occurs leading to water splitting and the formation of OH^- and H^+ as seen from the sharp decline of pH in the dilute and a sharp increase of pH in the concentrate chamber. This water-splitting affects the membranes. The H^+ ions that have been generated passes through the cation exchange membrane to the dilute compartment resulting in an increase in conductivity and decline in pH. While in the corresponding chamber OH^- ions are generated at the stack and are transported to the concentrate chamber; this increases the pH in the concentrate chamber. This observation can be justified by looking at the changes in pH for both compartments (concentrate and dilute) as shown in Fig. 6.

3.2. Fate of nutrients' transportation

Target nutrients in this study were nitrite, nitrate and phosphates. Alkaline conditions favored desalination; however,

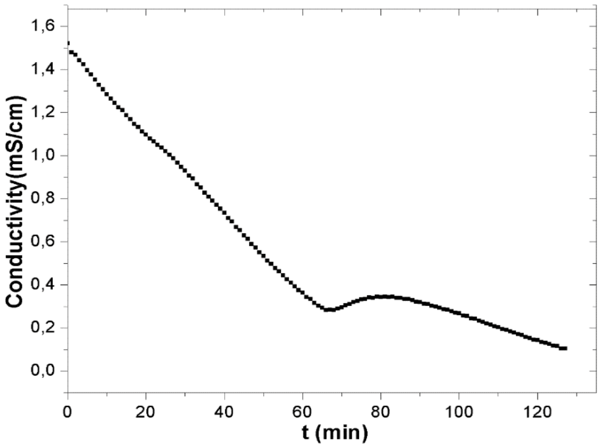

Fig. 4. Conductivity fluctuation in the dilute chamber.

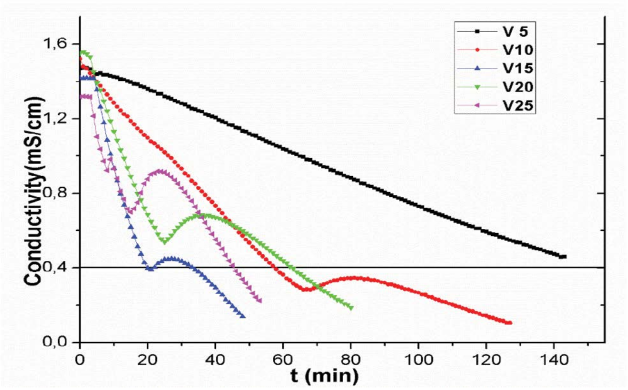

Fig. 5. Conductivity under different voltage in the dilute compartment.

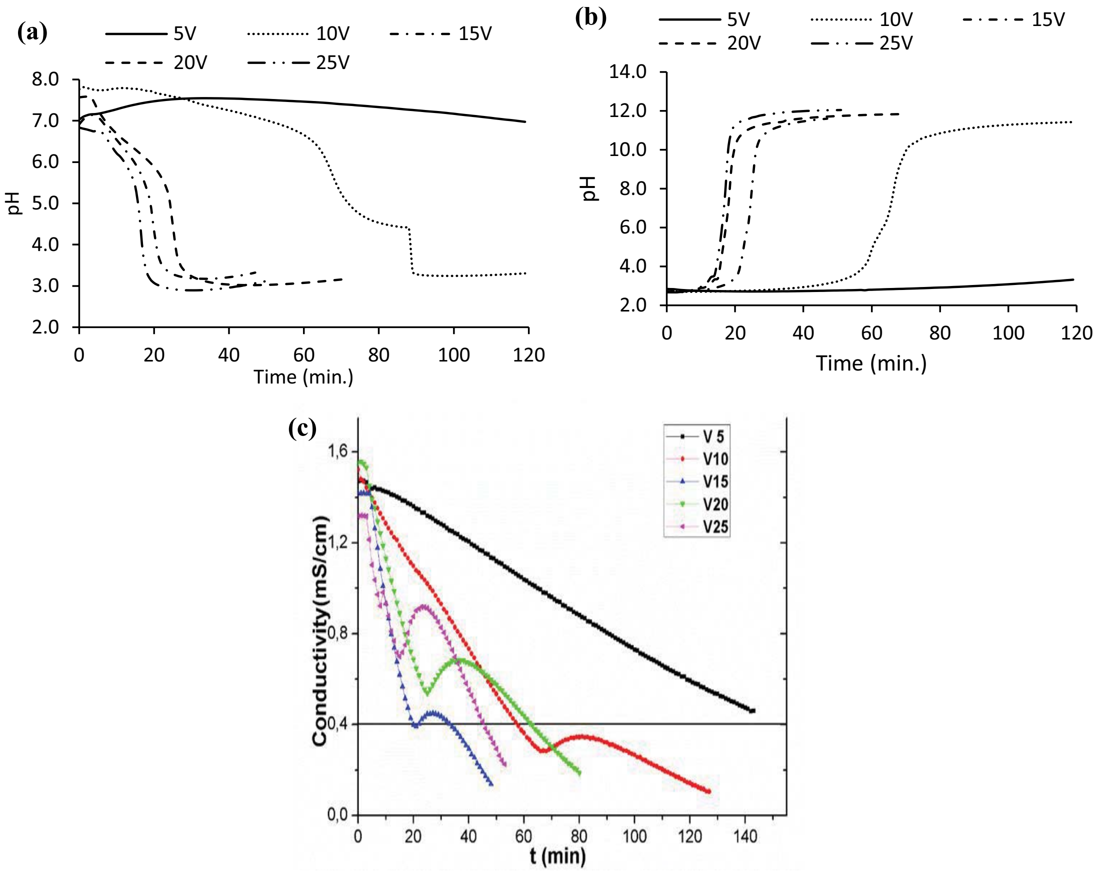

Fig. 6. Changes in pH values of the DWW in (a) dilute, (b) concentrate compartments, and (c) changes in conductivity values of dilute compartments under different potential differences.

as illustrated in Fig. 7 there is barely any noticeable difference in the nutrient removal capacity of the system under different ranges of pH. This observation is due to the massive hydroxyl ion migrations from the dilute chambers to the concentrate chamber, dropping the pH in this compartment. This creates equilibrium and the rate of nutrient movement is neither hindered nor improved.

3.2.1. Voltage effect on nutrient removal

It was presumed that increasing the voltage would yield better results for nutrient removal exponentially. However, as seen in Fig. 8 there a linear increase in treatment performance up to 15 V, and then after, a decrease in performance was noticed. 15 and 25 V showed better performance compared with other voltages—obtaining a recovery of 90% for nitrate and nitrites, while phosphate removal was 67.9%. 20 V showed the worst performance. The reason why voltage 20 V is performing less than voltage 15 V might be due to the resistance that is acting on the stack when the system is operating beyond the limiting current density.

3.2.2. Acting resistance on the stack

Two types of resistance have been reported to be acting on an ED stack, these are the membrane resistance and the diffusion boundary layer resistance [17]. The diffusion boundary layer resistance (resistance at the membrane-solution interface) is governed by concentration polarization. Moreover, previous works have shown that when the salt concentration of the solution is not high, the type of resistance that has the highest impact is resistance generated from the diffusion layer. The resistance of the membrane is negligible in comparison in this case. However, when the concentration of the salts is high, this is governed by the membrane resistance while the other has little effect [18].

The concentration polarization causes resistance in the diffusion layer to become large—affecting the mass transport of ions. This hindered the nutrients removal at 20 V. The increase in the performance at 25 V can be explained according to the current–voltage curve, Fig. 9 [16]. The first linear region is governed by Ohm's law for the electrolyte and membrane resistivity. The second region is characterized by a plateau resulting from the reduction of the number of ions in the layer adjacent to the membrane surface. In the third region, another linear increase in current is observed, this time above the limiting current. Operating at a voltage of 25 V, the ED starts to show improvements at achieving high removal of the target nutrients except for phosphate. Concentration polarization effects have a more impact on phosphates than any other nutrient within the scope of this study.

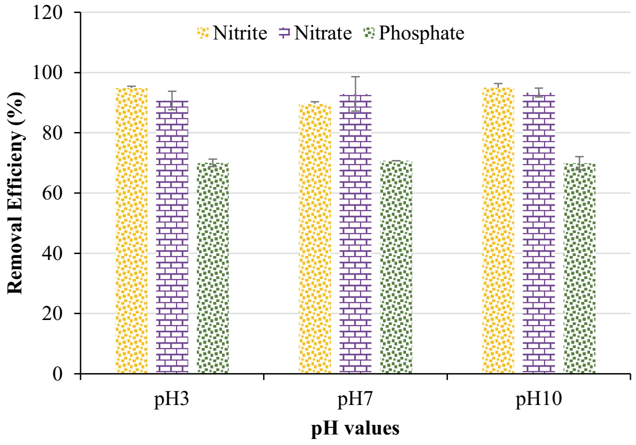

Fig. 7. Nutrient removal efficiencies in the dilute compartment under different pH.

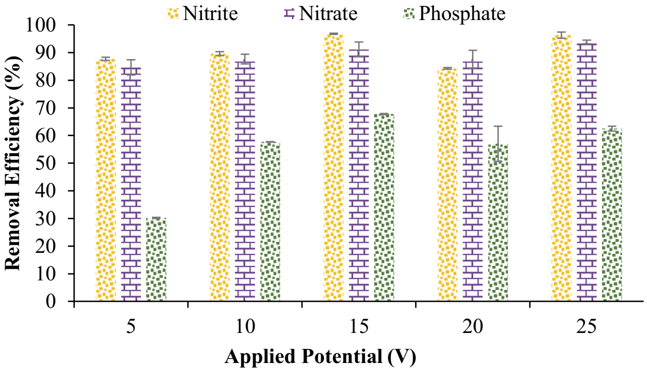

Fig. 8. Nutrient removal efficiencies in dilute compartments under different applied potentials.

3.3. Chemical oxygen demand

The chemical oxygen demand (COD) levels of the wastewater before and after treatment were investigated. Table 2 summarizes the COD at different levels of treatment.

The COD decreased with the preliminary treatments (filtration and ion-exchange), as well as after ED application. This is attributed to the fact that approximately 75% of the solids in DWW are suspended solids, and 40% of the filterable solids are organic [19]. Furthermore, charged organics have a capacity to migrate from the feed compartment to concentrate compartment with time [20]. Thus, the decrease in COD levels after the ED treatment can be attributed to the migration of some charged organics from the dilute compartment. In addition at pH 7.5, the major form of ammonia is NH_4^+ (ammonium ion), which is positively charged. The anion exchange membrane cannot allow the positive ammonium ions to migrate to the concentrate compartment, thus they remain in the dilute compartment. Table 3 illustrates characteristics of wastewater sample after applying ED.

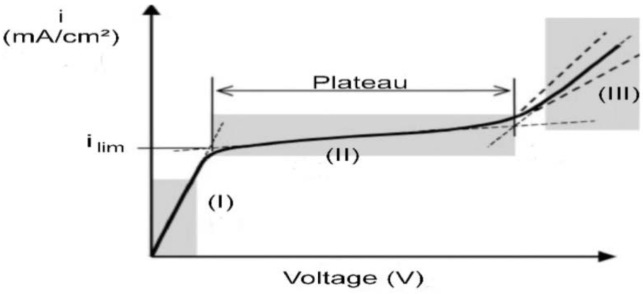

Fig. 9. Current–voltage curve graph [16].

Table 2
Concentration of Chemical oxygen demand

COD	Concentration (mg/L)
Raw wastewater	408
After filtration	373
After ion-exchange	329
After ED	178

3.4. Continuous flow experiments

Membrane technologies are affected by membrane fouling—hindering their performance. Therefore, continuous experiments were conducted to investigate the extent and capability of the ED to keep removing salinity and nutrient recovery. 1,000 mL of DWW was fed to the ED and the desalination performance was observed. Generally, after the second cycle, the desalination was fast for all the samples; it took around 20 min for each cycle to reach the target salinity levels as shown in Fig. 10. The longer time in the first two cycles might be attributed to concentration polarization effects.

Table 3
Characteristics of wastewater sample after applying Electrodialysis

Parameter	Concentration	unit
pH	4.33	–
Electrical conductivity (EC)	0.453	mS/cm
Chemical oxygen demand (COD)	178	mg/L
Nitrite (NO_2^-)	0.005	mg/L
Nitrate (NO_3^-)	0.022	mg/L
Phosphates (PO_4^{3-})	1.67	mg/L
Sulphate (SO_4^{2-})	6.84	mg/L

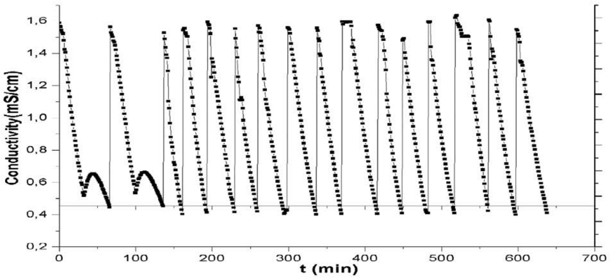

Fig. 10. Conductivity under continuous (flow-through) setup at pH 7 voltage 15.

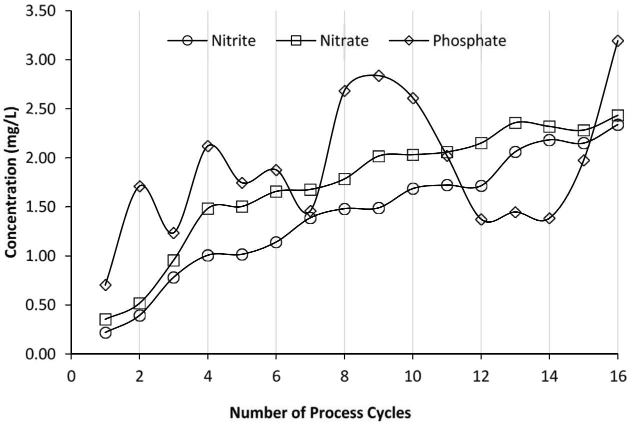

Fig. 11. Nutrient concentration in concentrate compartment under continuous setup.

3.5. Nutrient concentrating

A total of 16 cycles were done throughout the 638 min run time shown in Fig. 11. The ED nutrient recovery was evaluated to estimate the performance under continuous experiments. Table 4 summarizes nutrients concentration in ED compartments at the end of continuous flow set up. Nitrate and nitrite showed a linear increase, while phosphate showed an up-down tread. The phosphate recovery rate could not be optimized due to the pH changes that occurred due to concentration polarization. These changes in pH, causes the solubility of the phosphate to exceed the limit, thus precipitation [21]. Further evidence that asserts this theory is the white precipitates that were found on the cation membrane after the experiments were completed. This white precipitate that scaled the surface of the membranes is shown in Fig. 12b.

4. Conclusion

Electrodialysis was the main focus and was chosen as a method of further treatment in domestic wastewaters, performance in the desalination, nutrient removal and lastly their recovery from domestic wastewaters were evaluated. It was determined that ED is capable of achieving salinity levels below 0.469 mS/cm within 20 min which are salinity levels suitable for the majority of the crops. Also, under optimum conditions, 96.6%, 93.0% and 67.9% removal of nitrite, nitrate and phosphates, respectively, was achieved. Moreover, it was observed that concentrating certain nutrients was attainable by the end of continuous experimentation; however, phosphate was prone to precipitation.

The study further looked into the effect of certain parameters such as voltage and pH as the determiners of the overall performance of the ED system to desalinate, remove and recover nutrients as well. It was determined that pH affects desalination rate however has little to no effect on nutrient removal performance. While concentration polarization tremendously affects the rate of desalination and the quality of the final product, in terms of nutrients; phosphates were the most vulnerable and are affected the most by this phenomenon. In addition, some migration of what was attributed as charged organics were also observed as the COD concentration of the sample significantly dropped from 329 to 178 mg/L after ED was applied.

Under a discontinuous setup for this study, an ideal performance in both desalination, as well as nutrients removal, was determined to be under 15 V. To preserve the integrity of the final product, the study suggests termination of the experiment prior to drastic pH changes. The optimum conditions

Table 4
Nutrients concentration in ED compartments at the end of continuous flow set up

Parameter	Concentrate	Dilute	Unit
Nitrite (NO_2^-)	2.34	0.020	mg/L
Nitrate (NO_3^-)	2.43	0.038	mg/L
Phosphates (PO_4^{3-})	3.19	6.348	mg/L

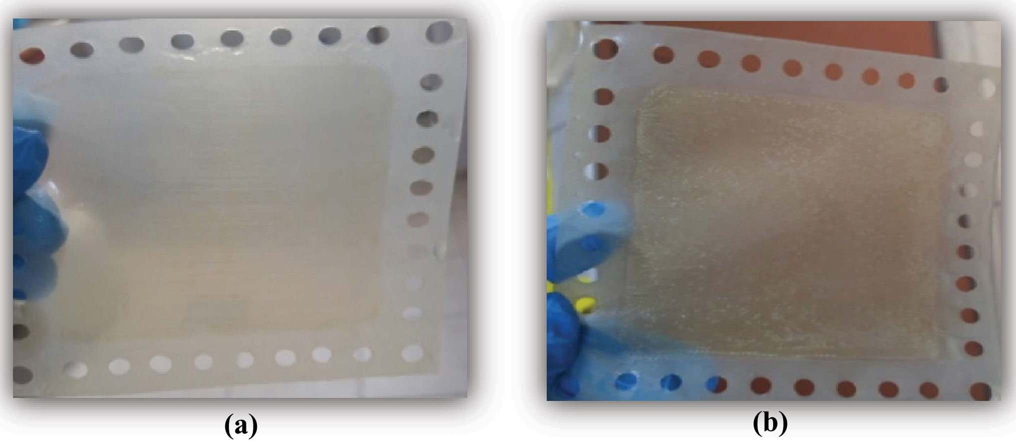

Fig. 12. Presentation of cation exchange membrane (a) before and (b) after running the ED process showing the precipitates.

under a continuing experiment need further investigations. In addition, since at pH 7.5, 99.15% of ammonia exists as positively charged ammonium ion, cationic separation of ammonia and its use for hydrogen production should be investigated.

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