Removal of fluoride ion from fertilizer industry wastewater to recover ammonium and phosphate using a five-compartment electrodialysis system

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Abstract. Wastewater from the fertilizer industry contains high concentrations of ammonium and phosphate ions, up to 3,395 mg.L^{-1} and 12,725 mg.L^{-1}, respectively. These ions can be recovered as struvite precipitates. However, 1,158 mg.L^{-1} of fluoride ions contained in the wastewater may influence the struvite formation. Therefore, experiments using a laboratory-scale of five-compartment electrodialysis batch reactor were performed to remove fluoride ion and subsequently recover ammonium and phosphate ions. Electrical currents of 0.05, 0.1, and 0.15 A were applied constantly to the electrodes. The initial pH of wastewater was adjusted to 5, 7, and 9. The highest removal of fluoride ion was obtained at 0.1 A, i.e. decreased to 376 mg.L^{-1} and 486 mg.L^{-1} at pH 5 and pH 7, respectively. At the same conditions, the final ammonium concentrations at pH 5 and 7 were 2,127 mg and 2,185 mg, respectively. Similarly, 7,878 mg and 10,669 mg phosphate ions were recovered at pH 5 and pH 7, respectively. The energy consumed for fluoride removal at pH 5 was higher than pH 7, i.e. 4 Wh.g^{-1} F^{-} vs. 7 Wh.g^{-1} F^{-}. Nevertheless, the suspended solid formation at pH 5 was higher than pH 7, suggesting that pH operational at 7 is preferable for application with less possibility of scaling formation.

1. Introduction

The growing demand for fertilizer in the agricultural market drives fertilizer industries to increase their productivity. The wastewater generated during the production of fertilizer has likely become larger in its quantity as well as more complex in its characteristics. In general, the fertilizer industries generate wastewater containing high concentrations of phosphate and ammonium ions. Although the industries have applied wastewater treatments, the effluents may still contain an abundant amount of phosphate and ammonium ions. Therefore, if the wastewater is not properly treated, those substances will be highly accumulated in the discharge point, i.e. the aquatic environments. This leads to the high possibility of eutrophication occurred in the aquatic environment, interfering living organisms surrounding. Nitrogen and phosphate are macronutrients needed by plants. Besides, both of them hold important roles in the growth and development process in plants. On the other hand, as macronutrients, a high concentration of ammonium and phosphate in wastewater offers the opportunity to be recovered and reused as other valuable products.

Several common methods in recovering ammonium ion and phosphate ion have been developed, i.e., biological treatment, chemical precipitation, adsorption, and crystallization. From those developed technologies, chemical precipitation is preferable due to high efficiency [1]. One of the precipitation techniques is direct precipitation using magnesium chloride (MgCl$_2$) to form magnesium ammonium

phosphate ($MgNH_4PO_4.6H_2O$) precipitate or known as struvite. Aside from the two ions, the wastewater contains other ions that will interfere with the struvite formation. The ion with the third highest concentration after ammonium and phosphate is fluoride ion (F^-). Fluoride ion can interfere with struvite formation if the concentration is more than 600 mg.L^{-1} [2]. Therefore, a pre-treatment of the wastewater is required to separate and take ammonium ion and phosphate ion as much as possible with a low concentration of interfering ion.

Some technologies for ion separations are chemical precipitation, adsorption, ion exchange, reverse osmosis and nanofiltration, electrocoagulation, and electrodialysis. Among those technologies, one of them with less residue and does not need chemical addition is electrodialysis [3]. Electrodialysis is an ion separation technology where the ions are transferred through membranes due to the difference in electrical potential given [4]. When the difference in electrical potential is given to solution containing ions, the positive-charge ion (cation) will move to the negative-charge electrode (cathode) while the negative-charge ion (anion) will move to the positive-charge electrode (anode) [5]. The uncharged molecules will not be affected by the different electrical potential, thus the electrically-charged components will be separated from the uncharged components. Electrical-charged membranes are used to control ion transfer. Cation exchange membrane (CEM) let cations passing through, whereas anion exchange membrane (AEM) lets anions passing through. This ion transfer causes the ions to be concentrated in the product compartment [6]. By using electrodialysis, therefore, ammonium ion and phosphate ion are expected to be separated and taken at as high concentration as possible with a low concentration of interfering ion.

In electrodialysis process, there are some factors that can affect the ion separating effectivity, e.g. pH and electrical current [7]. The pH value of wastewater affects scaling formation [8]. Mineralization process of inorganic solids on membrane surface or membrane scaling interferes the effectiveness of ion transfer process. The second factor, higher electrical current leads to the higher current density. The increasing current density creates maximum ion transfer per membrane area. However, if the current density exceeds the limit, it may result in the decreasing efficiency of the electrodialysis process due to the increasing resistance in solution [7]. Therefore, this study aims to investigate the effect of pH and electrical current in recovering ammonium ion and phosphate ion, as well as removing fluoride ions using an electrodialysis system.

2. Materials and methods

2.1. Sample preparation
Sample of wastewater effluent was obtained from local fertilizer industry in the phosphate unit plant, ammonium unit plant, and chemicals unit plant. The sample was also obtained from the point in which all effluent from the three units disembogued, which was called Point L. Phosphate unit plant produces phosphate fertilizers. Ammonium unit plant produces ammonia in liquid form, CO_2 gas, and urea fertilizer. Chemicals unit plant produces phosphoric acid, sulfuric acid, aluminium fluoride, and cement retarder. Characteristics of wastewater sample are detailed in Table 1.

Table 1. Wastewater characteristics.

Source	Parameter	Unit	Result
Point L	Ammonium (NH_4^+)	mg.L^{-1}	3,395
	Phosphate (PO_4^{3-})	mg.L^{-1}	12,725
	Fluoride (F^-)	mg.L^{-1}	1,157
	pH	-	3.2
Ammonium Unit Plant	Ammonium (NH_4^+)	mg.L^{-1}	3,895
	pH	-	9.0
Phosphate Unit Plant	Phosphate (PO_4^{3-})	mg.L^{-1}	11,275
	pH	-	2.0

2.2. Experimental set-up

An electrodialysis reactor (internal dimension of 10 cm x 5 cm x 2 cm) was used in this study. The reactor consisted of 5 detachable acrylic compartments. Two anion exchange membranes AMI-7001S and two cation exchange membranes CMI-7000S (Membrane International, USA) were placed between the compartments as shown in Figure 1. A 1 mm-thick silver plate of 100% purity and a stainless steel plate (each 5 cm x 3 cm; projected active area of 15 cm^2) were used as anode and cathode, respectively. Each electrode was connected to a DC power supply. Frame-shaped rubber gaskets were located between acrylic and membrane to prevent leakage during the electrodialysis process. The experiments were conducted in a batch system at room temperature. Three different direct currents were applied i.e. 0.05, 0.10, and 0.15 A. The initial pH of wastewater was also adjusted to each experiment (i.e., 5, 7, and 9). A total of 1.2 L of Point L wastewater was continuously recirculated through the central compartment (C3) during 6 hours using a submersible pump with a rate of 11.76 mL/s. In the anode compartment, 1.2 L of ammonium unit plant wastewater was recirculated as anolyte. The pH of anolyte was maintained at pH 12.0-12.5 due to lowest solubility of silver in ammonium solution occurs in pH 12.0 [9]. In the catholyte compartment, 1.2 L of phosphate unit plant wastewater was recirculated as anolyte. There was no pH adjustment for catholyte.
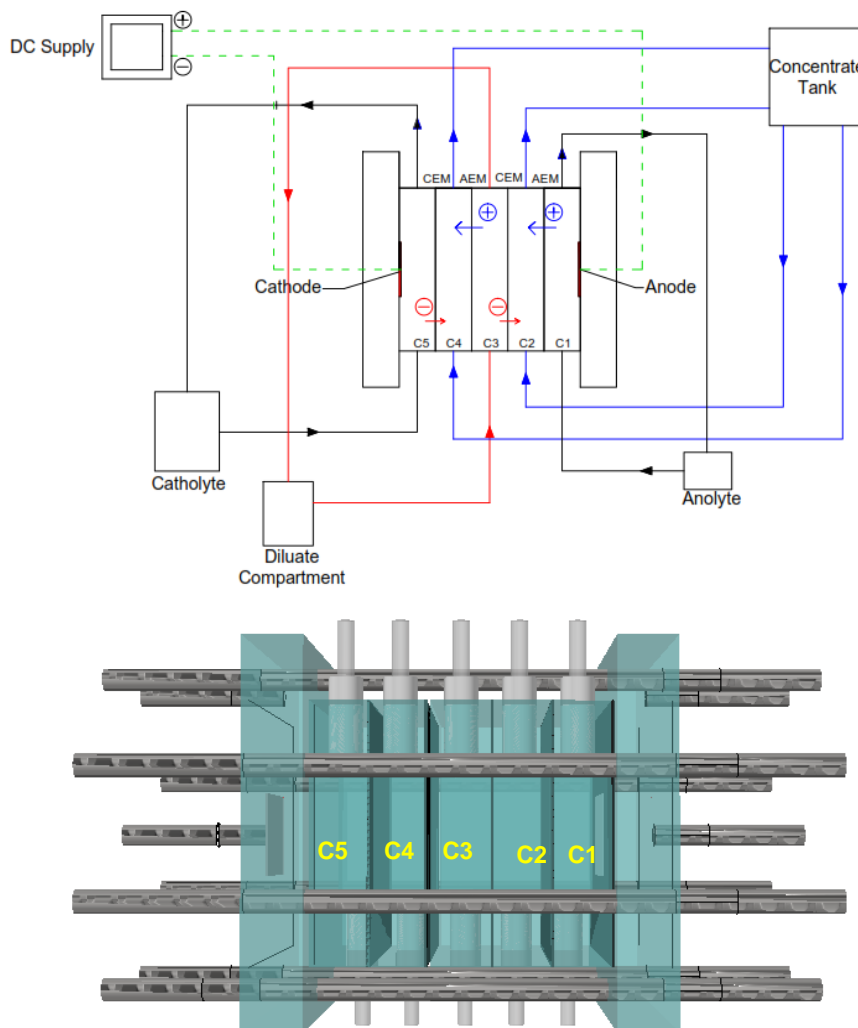

Figure 1. Experimental set-up (CEM: cation exchange membrane; AEM: anion exchange membrane; C: compartment).

2.3. Analytical methods
Samples (15 mL) were taken in all five compartments after 0, 60, 120, 180, 240, 300, and 360 min of the electrodialysis process. The pH, conductivity, concentrations of ammonium, phosphate, and fluoride were measured directly after sampling. The concentrations of ammonium, phosphate, and fluoride were measured using spectrophotometric methods. The remaining wastewater in the concentrate compartment was collected for suspended solids formation analyses. This result was to confirm the possibility of scaling formation.

3. Results and discussion

3.1. Ion transfer competition between phosphate ion and fluoride ion
Electrodialysis process was expected to produce a solution containing a high mass of phosphate ion and low concentration of fluoride ion. Since both ions were anions, they competed to pass through anion exchange membrane to the concentrate compartment. The transfer of fluoride ion and phosphate ion through the anion exchange membrane can be calculated using equation (1) as follows:

$$Ion\ transfer\ (\%) = \frac{(C_0 - C_t)}{C_t} x100\% \qquad (1)$$

where C_0 is the initial mass of ion in the feed water (mg), C_t is the mass of ion in the feed water at time t (mg).

Table 2. Comparison of ion transfer (%).

Direct current (A)	pH	Ion transfer of PO_4^{3-} (%)	Ion transfer of F^- (%)
0.05		23.27	38.28
0.10	5	18.25	77.30
0.15		22.08	35.66
0.05		14.20	69.07
0.10	7	11.91	64.33
0.15		21.74	44.29
0.05		14.41	70.85
0.10	9	34.11	38.28
0.15		23.27	28.64

Table 2 shows the comparison of ion transfer from C3 to C2 in all experiments. The fluoride ion transfer ability was 2-5 times higher than phosphate ion transfer ability in all variations of pH value and direct current. The ability of fluoride ion transfer could reach up to 77.3% (1,171 mg.L^{-1}) from C3 to C2 when 0.10 A direct current was applied and the pH of wastewater was adjusted to 5. On the other hand, the highest value of phosphate ion transfer ability could only reach 34.11% (1,691 mg.L^{-1}) from C3 to C2 at 0.10 A and pH feed of 9.

The results confirmed that the ability of ion transfer was not only affected by electrical current. It was also affected by ion characteristics, initial concentration, electrolyte solution, and pH value of feed solution [10]. Monovalent ions have a smaller radius than the bivalent ion, so the ions can transfer through membrane pores and are not interfered by resistance in the membrane [11].

Besides the characteristics of ion, the value of pH also affected the ability of ion transfer. Fluoride ion has the highest mobility at pH 6 and the lowest mobility at pH 9 [12]. The result confirmed this theory. As shown in the result, when 0.10 A was applied, the ability of fluoride ion transfer in pH 5, 7, and 9 was 77.30%, 64.33%, and 38.38% respectively.

Table 3. Comparison of fluoride ion concentration.

Direct current (A)	pH	Concentration of F⁻ ion (mg.L⁻¹)
0.05		1,333
0.10	5	376
0.15		5829
0.05		1,150
0.10	7	486
0.15		6,713
0.05		781
0.10	9	1,334
0.15		1,578

The high ability of fluoride transfer resulted in a low concentration of fluoride ion in C3. Table 3 shows the comparison of fluoride ion concentration that remained in C3. The highest removal of fluoride ion occurred when 0.10 A electrical current was applied and the wastewater was adjusted to pH 5 and 7. The concentration of fluoride ion at pH 5 and 7 was 376 mg.L⁻¹ and 486 mg.L⁻¹, respectively. These values of fluoride concentrations could be accepted since both values were less than 600 mg.L⁻¹. If the concentration of fluoride ion was more than 600 mg.L⁻¹, fluoride ion would react with magnesium, forming magnesium fluoride (MgF_2) [2]. This condition would result in less quantity of struvite mineral formed. Besides, the morphology of struvite crystals obtained in the absence of the fluoride ions was columnar with smooth surfaces, whereas the shape of the crystals formed at fluoride concentrations of 600 mg.L⁻¹ and 1,500 mg.L⁻¹ gradually became irregular blocks with fine amorphous particles on their surfaces [13]. It showed that the existence of fluoride ion can affect the nucleation process and growth of struvite mineral that will result in different shapes of product.

Considering the ability of fluoride ion transfer was higher than phosphate ion transfer, it was recommended to choose C3 as the product compartment. In the C3, the phosphate ion transfer ability was low, thus, compared to other compartments, a higher concentration of ion phosphate could be obtained. On the other hand, the ability of fluoride transfer was so high, so the compartment contained a lower concentration of fluoride ion compared to other compartments. The variation of the electrical current selected based on the concentration of fluoride less than 600 mg.L⁻¹ was 0.10 A at pH 5 and 9. Thus, these two variations were investigated based on energy consumption and the possibility of scale formation to determine the effective pH value.

3.2. Transfer of ammonium ion
During electrodialysis process, ammonium ion migrated from C3 to concentrate compartment (C4). Based on the previous discussion about choosing C3 as the product compartment, the objective of investigating the transfer of ammonium ion was to ensure that the final concentration of ammonium ion remained in the C3 was still high. The investigation was implemented by comparing the migration of ammonium ion, which was affected by electrical current and pH of wastewater.

Figure 2 shows the migration of ammonium ion from C3 to C4 when 0.05 A was applied. At pH 5, the mass of ammonium ion migrated from K3 was the highest among the three pH values, reaching 1,159 mg (26.3% of ammonium ion mass eliminated from C3). The final mass of ammonium ion remained in the C3 was 3,241 mg. Meanwhile, the mass of ammonium ion migrated to C4 at pH 9 was the lowest, reaching only 705.4 mg (15.5% of ammonium ion mass eliminated). The final mass of ammonium ion remained was 3,834 mg.
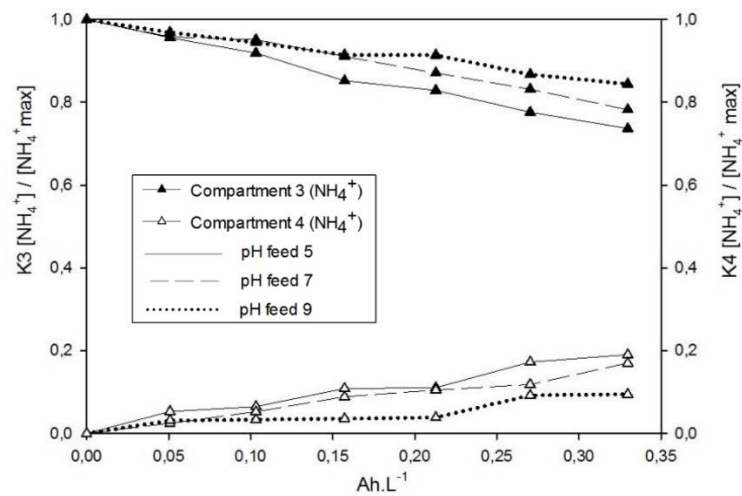
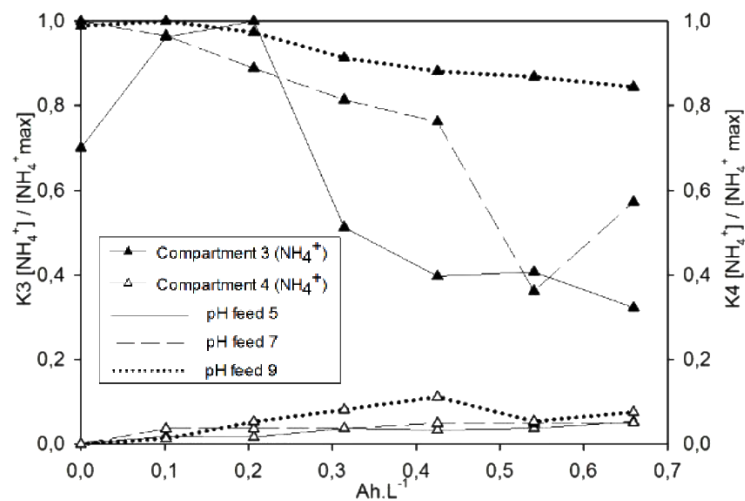**Figure 2.** Migration of ammonium ion from C3 to C4 when 0.05 A was applied.

Figure 3. Migration of ammonium ion from C3 to C4 when 0.10 A was applied.
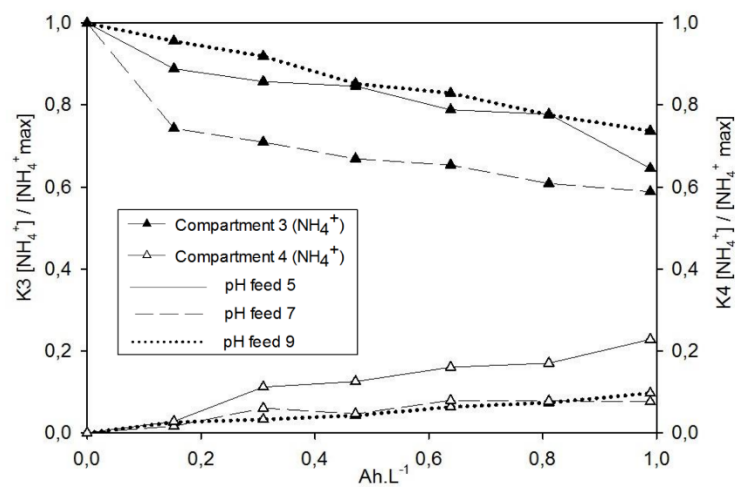

Figure 4. Migration of ammonium ion from C3 to C4 when 0.15 A was applied.

Figure 3 shows the migration of the ammonium ion when 0.10 A was applied. The highest migration of ammonium ion to C4 occurred at pH 5 where there was 2,497 mg of ammonium ion migrated from C3 to C4 (53.9% of ammonium ion mass eliminated). The final mass of ammonium ion remained was 2,127 mg. While the lowest migration of ammonium ion occurred at pH 9, reaching only 547 mg of ammonium migrated (14.6% of ammonium ion mass eliminated).

Figure 4 shows the migration of the ammonium ion when 0.15 A was applied. In this electrical current, the highest migration of ammonium occurred at pH 7, where the ion migrated was 1,965 mg (41.1% of ammonium ion mass eliminated). The final mass of ammonium ion remained was 2,812 mg. The lowest migration of ammonium ion occurred at pH 9, which only reached 1,159 mg of ammonium migrated (26.3% of ammonium ion mass eliminated).

Figure 2, 3, and 4 indicate that the electrical current affected the mass of ammonium ion migrated to the concentrated compartment. The mass percentage of ammonium ion at the same pH increased by the increase of electrical current, i.e. reaching 26.3% and 53.9% at 0.05A and 0.10 A, respectively. Besides, the value of wastewater initial pH also affected the ion migration. The highest mass of ion migration mostly occurred at pH 5, while the least mass occurred at pH 9. The value of pH affected the species of ions formed during the process. At pH 5, the ion species formed were 100% NH_4^+ ions [14]. While at pH 9, 70% of ions were in NH_4^+ ions form and 30% of them were in NH_3 form [14].

3.3. Energy consumption
The calculation of specific energy consumption (W) was related to specific electrical charge (Q) and specific electrical potential (V) [15]. The objective of this calculation was for consideration in choosing the effective electrical current. The calculation was done to variations selected in 3.1. The calculation was only done to calculate the energy consumed for the fluoride ion parameter since the only ion which was intended to be eliminated in this experiment was fluoride ion. Table 4 shows the result of calculating energy consumption for eliminating fluoride ion between pH 5 and pH 7 at 0.10 A electrical current applied. The energy consumed to eliminate fluoride ion from C3 at pH 5 was lower than pH 7, i.e. 4 $Wh.g^{-1}$and 7 $Wh.g^{-1}$, respectively. It can be pointed out that a higher pH value might affect the energy needed to migrate fluoride ion. The value of pH affected the mobility of fluoride ion, in which the mobility of the ion at pH 5 was higher than at pH 7 [12]. Due to the lower ion mobility, the energy consumed for migrating ion should be higher.

Table 4. Calculations of energy consumption for eliminating fluoride ion.

Variations	Specific energy consumption $(Wh.L^{-1})$	Mass eliminated $(g.L^{-1})$	Energy consumption/ mass eliminated $(Wh.g^{-1})$
pH feed 5 ; Electrical current 0.10 A	9.00	2.28	4
pH feed 7 ; Electrical current 0,10 A	8.88	1.22	7

3.4. The possibility of scale formation
The pH value of fertilizer industry wastewater is really fluctuate based on the units operating at the moment. When the ammonium unit plant is operating, the pH value of wastewater tends to be high. On the other hand, when the phosphate unit plant is operating, the pH value tends to be low. The pH values applied in this experiment were chosen based on the fluctuating pH value of wastewater. However, the pH value will affect ion species in the wastewater and there will be a possibility of precipitate formation. The precipitates are possible to cause scale formation on the membrane. Besides, the precipitates which are detected as Total Suspended Solids (TSS) can interfere with the ion transfer. Therefore, the analysis of TSS in product compartment C2 and C4 were conducted at pH 5, 7, 9 in 0.15 A. This variation of electrical current was selected since there was a possibility that the ion mobility occurred to be highest.

Table 5 shows that the highest TSS concentration formed at pH 9 in both compartments. While the lowest TSS concentration formed at pH 7 in both compartments.

Table 5. TSS concentration (mg.L^{-1}) formed at 0.15A after 6-hours operation.

Compartment	pH		
	5	7	9
2	4.19	1.60	80.25
4	2.24	0.24	11.03

This study sought to investigate the optimum pH for preventing scale formation. However, after 6-hours operating time, there was no scale formation yet and the mass of ions migrating to C2 and C4 (recovery of ammonium ion and phosphate ion) were still few. The scaling might happen when the recovery was high. Therefore, the calculation of operating time to reach 100% recovery was conducted using regression equation obtained by making linear graphs. The calculation was only done to compare TSS concentration formed at pH 5 and 7. However, further experiments are needed to confirm the operating time when scale formation occurred.
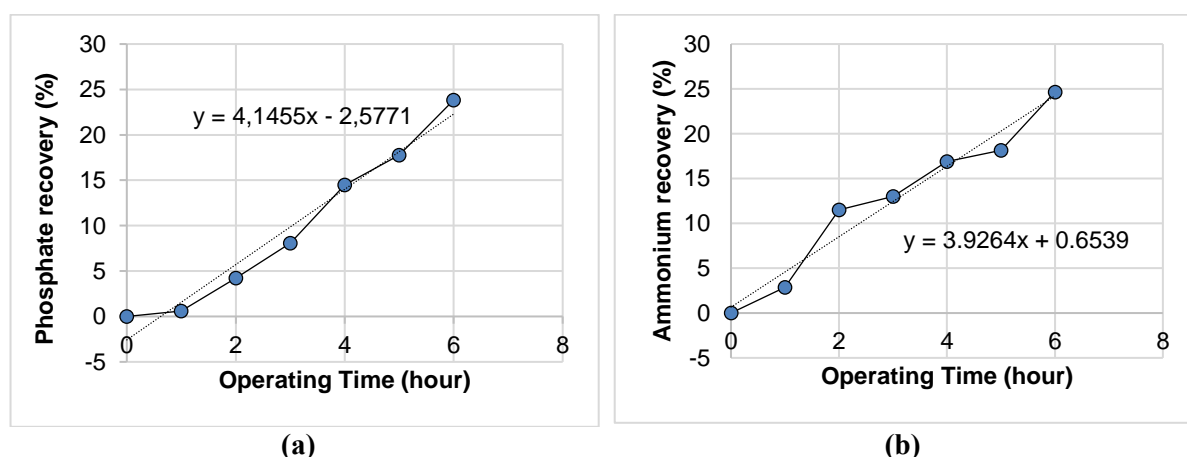

Figure 5. Relation between operating time and (a) phosphate recovery at pH 5 and (b) ammonium recovery at pH 5.

As shown in Figure 5, the recovery of ammonium ion and phosphate ion after 6-hours operating time were 24.7% and 23.8%, respectively. Using the regression equation from the figure, the operating time needed to gain 100% recovery was obtained. The calculations resulted in 30.14 hours and 24.74 hours needed for 100% recovery of ammonium ion and phosphate ion, respectively. The 30.14 hours operating time was chosen for predicting TSS formation due to the higher operating time.

The prediction of TSS formed after 30.14 hours was then conducted. After 6 hours operating time, the TSS formed in C2 and C4 were 4.19 mg.L^{-1} (4.25 mg) and 2.24 mg.L^{-1} (2.27 mg), respectively. Thus, the rate of TSS formed every hour in C2 and C4 were 0.71 mg.h^{-1} and 0.38 mg.h^{-1}, respectively. By multiplying the maximum operating time and rate of TSS formed, the prediction of maximum TSS formed was gained. The result showed that the predicted TSS formed was 32.74 mg, i.e., 21.34 mg in C2 and 11.40 mg in C4.

As shown in Figure 6, the recovery of ammonium ion and phosphate ion after 6-hours operating time was 8.2% and 22.4%, respectively. The operating time needed for 100% recovery was calculated using the same steps above. The operating time needed for 100% ammonium ion recovery and phosphate ion recovery was 69.00 hours and 25.91 hours, respectively. The 69.00 hours operating time was then chosen for further calculation.
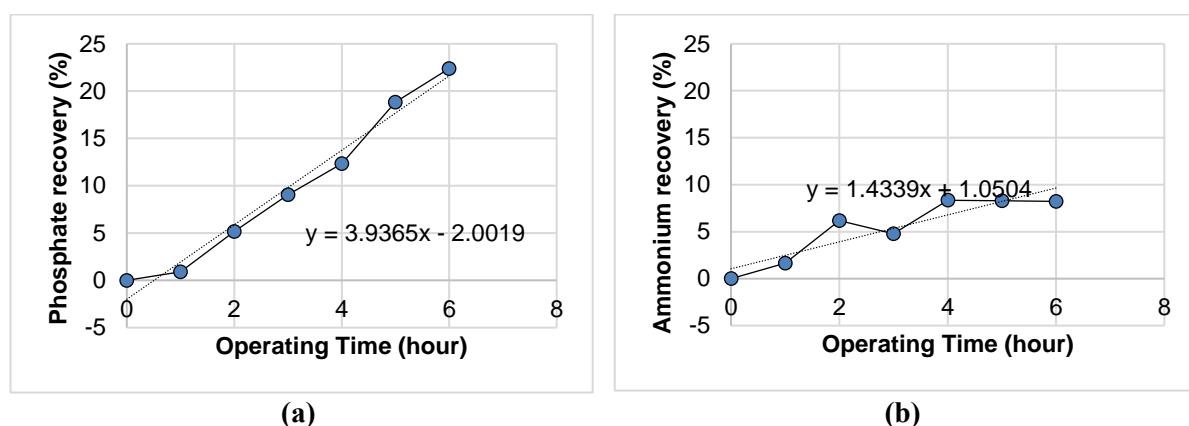
Figure 6. Relation between operating time and (a) phosphate recovery at pH 5 and (b) ammonium recovery at pH 7.

The prediction of TSS formed after 69.00 hours were then conducted. After 6 hours operating time, the TSS formed in C2 and C4 were 1.60 mg.L^{-1} (1.62 mg) and 0.24 mg.L^{-1} (0.24 mg), respectively. Thus, the rate of TSS formed every hour was calculated by dividing the TSS formed with operating hours, resulting in 0.27 mg.h^{-1} in C2 and 0.04 mg.h^{-1} in C4. The prediction of maximum TSS formed was gained by multiplying the maximum operating time by the rate of TSS formed. The result showed that the predicted TSS formed was 21.42 mg, i.e., 18.68 mg in C2 and 2.75 mg in C4.

4. Conclusions

Electrodialysis is one of the alternative methods to effectively separate ions nowadays since it generates less residue and limited addition of chemicals during the process. However, some factors need to be taken into account in order to obtain an optimum result. Two of the essential factors investigated in this study were pH value and electrical current using a laboratory-scale of five-compartment electrodialysis reactor. Subsequently, a prediction of scale formation for a longer operating time was performed to determine the optimum pH value while considering scale formation during the process. The main conclusions obtained from this study are as follows:

(1) Electrodialysis process with 0.1 A applied resulted in the highest removal of fluoride ion, i.e., decreased to 344 mg.L^{-1} and 486 mg.L^{-1} at pH 5 and pH 7, respectively.

(2) Despite the higher energy consumption for eliminating fluoride ion, pH operational at 7 is preferable for the application rather than pH 5 since the lowest suspended solid formation (21.42 mg) occurred at pH 7 compared with 32.47 mg formed at pH 5, which indicates a lower possibility of scale formation.

Acknowledgments

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