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Recovery of mixed acid and base from wastewater with bipolar membrane electrodialysis—a case study

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ABSTRACT

The current study simultaneously examined the treatability of wastewater by electrodialysis unit and recovery of ions removed as acidic/alkaline solutions. With a bipolar membrane electrodialysis process, the removed ions are stored separately in anolyte/catholyte solutions, and then turned into mixed acids and bases. After the treatment of the leachate using the BMED process, the molar concentration of H^+ ions in the acidic solution and the OH^- ions in the alkaline solution reached up to 0.095 and 0.048 M (conditions: 1 L wastewater and 1 L anolyte/catholyte solutions), respectively. When the ratio of wastewater to initial volume of anolyte and catholyte was ¼ (1 L wastewater and 0.25 L anolyte or catholyte solutions) at the end of a 360-min treatment period, 3.8- (from 0.01995 to 0.07586 M for $[H^+]$) and 3.98- (from 0.02344 to 0.09333 M for $[OH^-]$) times more intense acid and base concentrations were determined, respectively. This demonstrates that the process can be considered as a cleaner technology for the treatability of wastewater by obtaining more concentrated acid and base as recovered material and fewer byproducts.

Keywords: Electrodialysis; Bipolar membrane; Leachate; Desalination; Recovery

1. Introduction

The electrodialysis (ED) process has been widely used for many years in the recovery of process water [1–5]. Recently, ED has been used at wastewater treatment process, yet the studies are not sufficient [6–9]. The most common description of the ED process can consider the transport of ions by an electrical current [10]. Due to the removal mechanism, ED is known to be effective on ionic species. ED should be seen as an extremely effective treatment method, particularly for the ion removal processes [11].

Ionic pollutants have an important role in drinking water and wastewater, in terms of environmental pollution. However, particulate and other pollutant parameters can be treated easily, effectively, and economically. The removal of ionic pollutants is difficult

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and faces higher economic challenges [12]. Thus, the removal of ionic pollutants is very important, and this subject should be researched in greater detail.

In recent years, membrane processes have maintained their place within the scope of wastewater treatment, thanks to their removal efficiency and wide scope of use [13]. The ED process has a special place in membrane processes. The fundamental difference and main advantage of the ED unit from other membrane systems is the use of an electrical current as an ion transport system, not pressure. The ionic transport system using an electrical current has fewer costs than the system working with pressure, as in reverse osmosis. In addition, the removal efficiency is high, similar to the reverse osmosis system [14].

Another important issue is related to the portions of concentrate, which is the greatest drawback of the membrane processes. In particular, the ratio of the concentrated aliquot is approximately 25–35% for the reverse osmosis processes [15], and the highest ratio of the concentrated portion is water. This is an important problem for plants and the environment [16]. In contrast to ED, the separation of ionic species occurs through the membrane into the anolyte and catholyte parts, and therefore, no concentrated waste portion remains in the ED system as reverse osmosis. According to this perspective, the ED process comes to the fore in terms of less concentrated portion [17]. Indeed, waste quantity can be minimized by generating the ionic species at lower anolyte and catholyte volumes [18].

The ED process is divided into three types: ED, electrodeionization (EDI), and bipolar membrane electrodialysis (BMED). The electrode and the ion-selective membranes are used in each of the three methods. Ion exchangers are simultaneously used in the EDI process [19].

The BMED process has an important advantage compared to the conventional ED process. In this system, anions and cations are individually separated from the wastewater and combined with H^+ and OH^- ions, by means of bipolar membranes to form acidic and alkaline solutions. Therefore, while ionic species are removed from the wastewater, at the same time, pollutions are used to ensure acidic and alkaline solutions [20]. From this point, NaOH and HCl can be produced by means of using sodium chloride with BMED process [21]. The ED process can be used for this purpose [22,23]. The gathering of acidic and alkaline solutions from the ionic compounds is shown in Fig. 1.

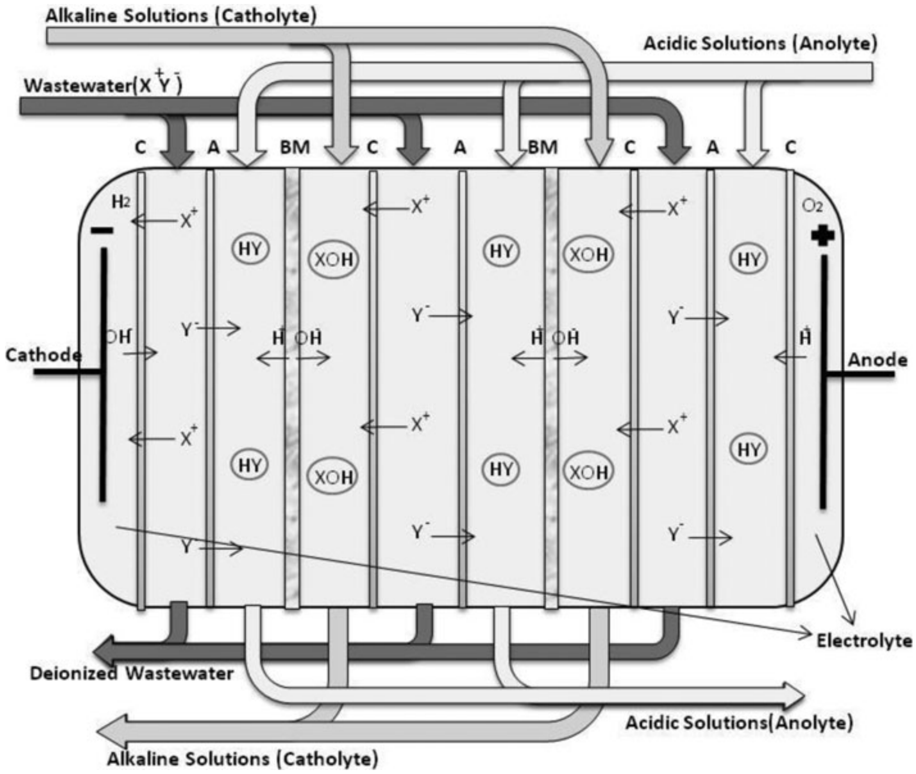

Fig. 1. Basic mechanism of bipolar membrane electrodialysis process (C: cation exchange membrane, A: anion exchange membrane, BM: bipolar membrane, and X^+, Y^-: ionic pollutants).

In this study, ions were obtained from the wastewater and used to generate mixed acidic and alkaline solutions. These mixed acid and base solutions can be used for some processes that do not require high quality or pure acid and base products. In this manner, the acid and base byproducts can be reused. Moreover, making some certain changes to the ED operating conditions, the desired levels of quality and quantity, and the impurity levels of the acid and base can be improved.

2. Methodology

2.1. Wastewater

In this experimental study, a high-strength ionic pollutant including leachate was used as wastewater. The leachate was taken from the Odayeri Landfill in Istanbul. The Odayeri Landfill was founded in 1995 and has served as a 75 ha area for 8,000 tons of municipal solid waste per day since it was first opened. The properties of the leachate were analyzed, and average values were given in Table 1. As is apparent in the table, the leachate required pretreatment before using it for the ED process. Because of the particulate matter and hardness of the leachate, ion-selective membranes of the ED process could be blocked. Therefore, an ultrafiltration process was used as pretreatment to remove particulate matters and a cationic ion exchanger was used to remove the same ions, particularly calcium and magnesium, to prevent calcification on the membrane surface prior to exposure to the ED unit. Raw and pretreated leachate changes are shown in Table 1. As expected, the sodium concentration was higher after processing with the sodium-based cation exchanger. This condition is desirable to generate the basic product during the ED process. For that reason, Cl^- was not removed in order to generate acidic solution in the anolyte.

2.2. Bipolar membrane electrodialysis process

In this study, a PCCell ED 64-4 unit and BMED 1-3 bench ED pump unit supplied by PCCell GmbH, Germany was used. The specifications and operating parameters of the cell and bench ED pump unit are

Table 1
The characterization of leachate from Odayeri Landfill

		Raw leachate			Pretreated leachate		
Analysis	Units	Young	Middle aged	Elderly	Young	Middle aged	Elderly
pH	–	8.1	8.1	8.4	8.8	8.5	8.6
COD	mg/L	17,760	14,400	3,550	15,985	7,200	3,375
BOD_5/COD	–	0.68	0.51	0.12	0.65	0.52	0.13
Ammonia-N	mg/L	2,295	2,910	3,865	545	1,790	1,010
Sodium	mg/L	3,510	3,620	3,840	9,980	9,430	8,120
Chloride	mg/L	3,960	4,010	3,790	4,285	4,370	3,895
Potassium	mg/L	1,620	1,685	1,700	1,690	55.25	193.5
Calcium	mg/L	187	195	202	10.9	12.50	23.90
Magnesium	mg/L	128	134	136	3.70	0.70	15.40
Conductivity (at 20°C)	mS/cm	31.10	39.80	38.70	22.00	14.61	26.40

Table 2
The specifications of ED and bench ED pump unit

Specification/unit	ED unit 64-4	BMED 1-3 pumping unit
Membrane size	110 × 110 mm	–
Effective membrane area	64 mm^2 per membrane	–
Cell thickness	0.5 mm	
Nominal flow rate	4–8 L h^{-1}	Up to 1,500 L h^{-1}
Max voltage and ampere	30 V, 5 A	24 V/5 A
Medium contacting materials	PE	PP, PE
Max pumping height	–	4.2 m
Max system pressure	–	1.4 bar
Dimensions	165 × 150 × 190 mm^3	825 × 380 × 410 cm^3
Weight	3 kg	28 kg

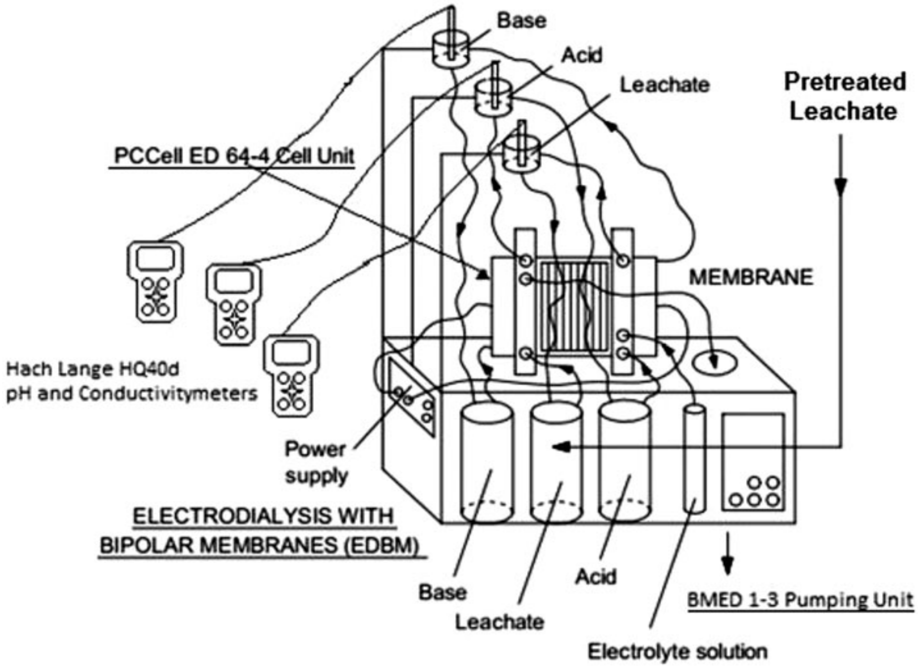

Fig. 2. Experimental setup.

listed in Table 2. The experimental set up used in the study is depicted in Fig. 2.

Cell pH and conductivity measurements of wastewater/anolyte/catholyte originating from ED were accomplished before feeding the samples to the feed tank. This process continued during the ED process. The process was terminated when it reached 2 mS/cm conductivity before considering 6-h working period. In contrast, if the 2 mS/cm level was not achieved, the study was terminated at sixth hour. During the process, some of the alkaline and acidic components, which are volatile, were released into the atmosphere.

2.3. Analysis

All of the experimental analyses were conducted according to standard methods [24]. Merck analytical quality chemicals were used in the preparation of reagents. All the runs were performed at room temperature and repeated twice. In addition, a multiparameter digital meter (Hach Lange HQ40d) was used to measure pH, temperature, and conductivity once per minute during the ED process.

2.4. Anolyte, catholyte, and electrolyte solutions

As shown in Fig. 1, the BMED process has anolyte and catholyte solutions. There are electrolytes located between the electrodes and the first membranes. Ionic liquids seem to be the most appropriate liquid in anolyte and catholyte instead of using distilled water to achieve electrolytic reactions. Otherwise, the current value decreases to zero, which means much greater treatment time and cost. The ED process requires the addition of salt or acid/base to anolyte and catholyte compartment as an ions source for the electrolytic reactions. When salt is used, the impurities of the anolyte and catholyte solutions increase. For this reason, at the beginning of the study, the most appropriate solutions for the anolyte and catholyte were 0.01 M HCl and 0.01 M NaOH. The volume of the sample anolyte and catholyte was 1 L. It is considered to be a lower volume of anolyte and catholyte compared to the sample for full-scale applications, and as such, 0.01 L anolyte and catholyte volumes were studied to increase molarity of the anolyte and catholyte more effectively. In this manner, a decrease in the current value and impurities in the solutions were prevented. At the beginning of the reaction, the creation of partial ionic strength will avoid a decrease in the current value. To prevent oxidation of the electrodes, 0.01 M HCI was used as an electrolyte.

3. Results and discussion

The current study examined the deionization of the leachate, which has high ionic capacity, and the acidic and alkaline characterization of anolyte and catholyte solutions were analyzed. In addition, to determine the effect of the operating parameters on acidic and alkaline solutions, a working set was established. The number of membranes and the electrical voltage were considered as operating conditions in the working set. The current value and electrical reactions were expected to accelerate with an increase in the electrical voltage. The sample ED cell given in Fig. 1 is considered as a binary membrane set, due to its two bipolar membranes. Similarly, this set number can be upgraded to a triple membrane set by adding another bipolar membrane, a cation exchange membrane, and an anion exchange membrane. The increment of the membrane sets improves the treatment efficiency of the ED process. However, increasing the number of membranes causes higher resistance for the electric current and electrolytic reactions will slow down. For these reasons, both of these parameters should be optimized. The study for the proposed experimental setup is presented in Table 3. The study set was run for three different aged leachates, for an actual evaluation of 48 campaigns.

According to the results, there was an increase in ion transmission that was dependent on the time in the anolyte and catholyte zones. In addition to the transportation ions through the bipolar membrane, H^+ and OH^+ ion concentrations also increased and the molar fraction of the anolyte and catholyte changed.

Table 3
Experimental design and runs (Y: young leachate, MA: middle aged leachate, and E: elderly leachate)

Leachate type	Runs	Electrical voltage (V)	Membrane set
Y/MA/E	1	10	1
Y/MA/E	2	15	1
Y/MA/E	3	20	1
Y/MA/E	4	25	1
Y/MA/E	5	10	2
Y/MA/E	6	15	2
Y/MA/E	7	20	2
Y/MA/E	8	25	2
Y/MA/E	9	10	3
Y/MA/E	10	15	3
Y/MA/E	11	20	3
Y/MA/E	12	25	3
Y/MA/E	13	10	4
Y/MA/E	14	15	4
Y/MA/E	15	20	4
Y/MA/E	16	25	4

3.1. Anolyte solutions

The molar concentration of the anolyte solution increased through the electrolytic reactions during the campaigns. In this respect, the molar concentration change of the H^+ ion in the anolyte is presented in Fig. 3. The highest ion concentration changes over time during the campaign are shown in Fig. 4.

When Figs. 3 and 4 are analyzed, some fluctuations in the concentration of H^+ ions were observed. This variation is the same as the operating conditions. The main reason for this is the presence of organic acid content in the leachate. The volatility of these organic compounds changes the ambient acidic form. In this case, when the ambient is open air, the acidic level decreases. In fact, the odor emitted from the anolyte compartment demonstrates the presence of the organic

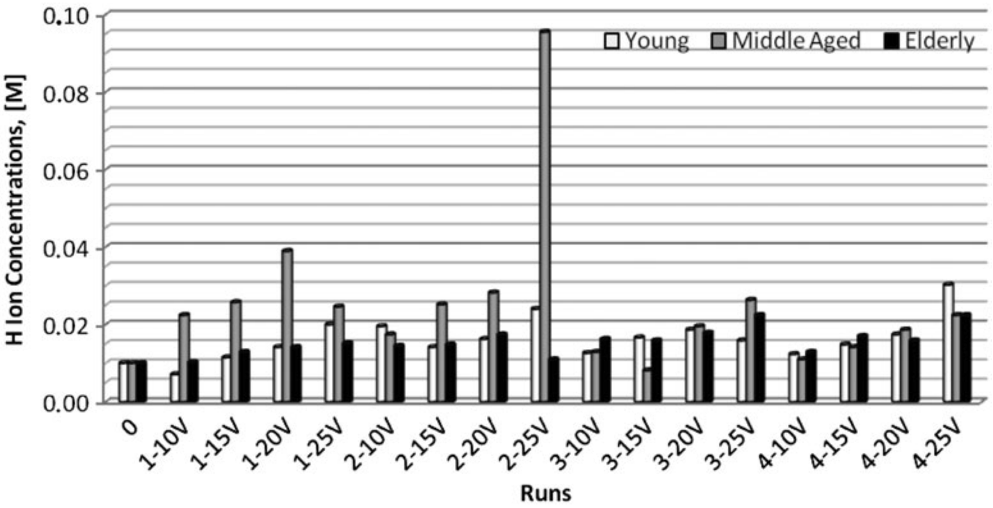

Fig. 3. Changes on molar concentration of H^+ during the working set in anolyte zone.

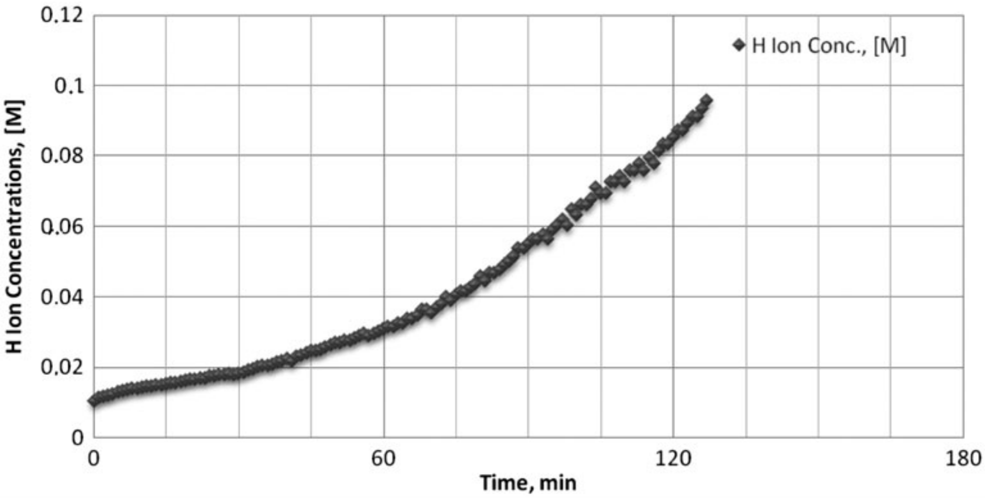

Fig. 4. Change of the highest H^+ ion concentration obtaining in course of time (Middle aged leachate, two membrane set, and 25 V).

acids. Volatile forms of wastewater, including organic and mineral acids, were collected separately at the end of the ED process.

3.2. Catholyte solutions

Data obtained for the catholyte solution are similar to the anolyte solution. During the study, cationic species were collected between the cation-selective membrane and the bipolar membrane (Fig. 1). Parallel to the number of bipolar membranes, the OH^- ion concentration increased in the catholyte zone. The molar concentration change of OH^- ions and the highest value of OH^- ions during the experimental runs are presented in Figs. 5 and 6, respectively (Table 2).

According to Figs. 5 and 6, some fluctuations of the molar concentration of OH^- ions were observed over time, which depend on the operating conditions. The main reason for this is the high ammonia content of the wastewater. The OH^- ion concentration increased with ammonia, but the OH^- ion concentration can decrease due to open air saturation over time.

3.3. Increasing molarity of acidic/alkaline

Figs. 3 and 5 show significant increase in H^+ and OH^- ion concentrations of anolyte and catholyte through the ED process. Nonetheless, the obtained results are not yet sufficiently high. The main reason is the high volume of anolyte and catholyte. This is

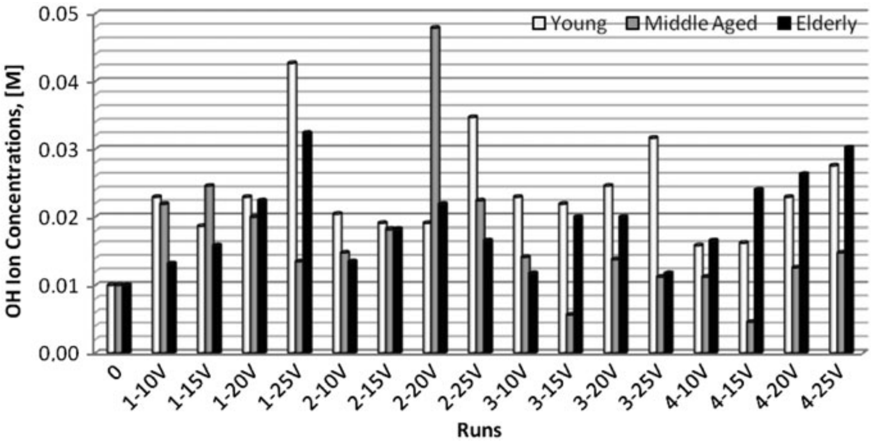

Fig. 5. Changes of molar concentration of OH^- during the working set in catholyte zone.

due to the fact that in the current study, the anolyte, catholyte, and wastewater volumes were the same. Experiments with lower volumes of anolyte and catholyte solutions result in concentrated solutions when compared to lower volumes of anolyte and catholyte solutions. To illustrate this fact, another study with different anolyte, catholyte, and wastewater volumes was conducted. The detailed results of this study are presented in Figs. 7 and 8.

In this study, the elderly leachate, which has the lowest removal efficiency, was used. Under these conditions, the efficiencies increased by fourfold. As shown in Figs. 6 and 7, the reduction rate of the anolyte and catholyte volumes to wastewater resulted in increasing concentrations of the acid and base. An initial concentration of 1,010 mg/L ammonia content, given in Table 1, decreased to 100 mg/L at the end of the ED process. In the meantime, the volatile form of ammonia caused a fluctuation of OH^+ concentrations in the catholyte. In this respect, this method can be considered as both a base separation and a recovery of ammonia from liquids containing high ammonia concentrations.

In Figs. 6 and 7, it is seen that the amount of reduction in the anolyte/catholyte solutions according to flow rate, led to concentration increment. In this manner, waste minimization is realized, and the reuse quality would be improved in full-scale studies. The NH_3–N amount in Table 1 could be reduced to 100 mg/L from 1790 mg/L after the ED process. Meanwhile, the generated NH_3–N occurs in the catholyte. Its volatile structure causes improper

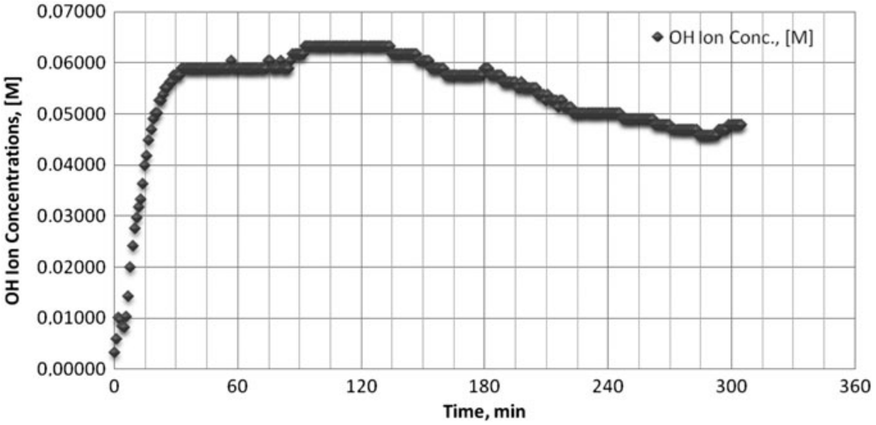

Fig. 6. Changes of the highest OH^- ion concentration obtaining in course of time in catholyte zone (middle aged leachate, two membrane set, and 20 V).

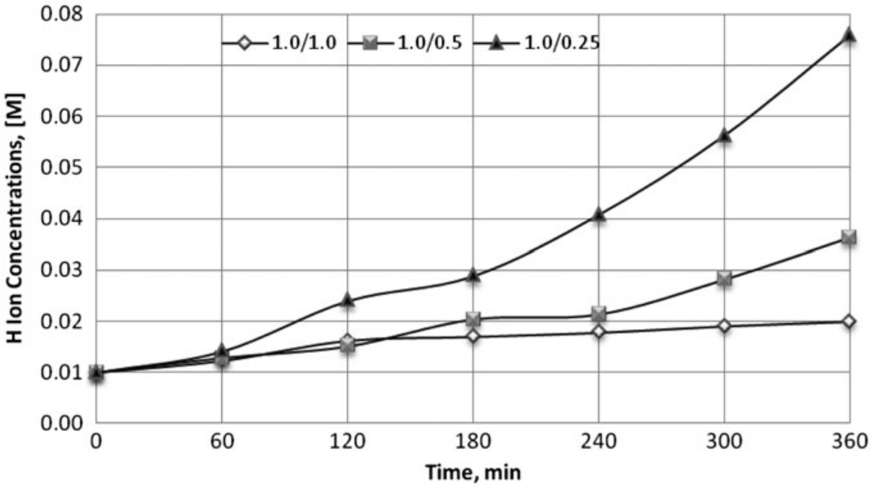

Fig. 7. Changes of H^+ ion concentrations for different anolyte/wastewater ratio (wastewater/anolyte).

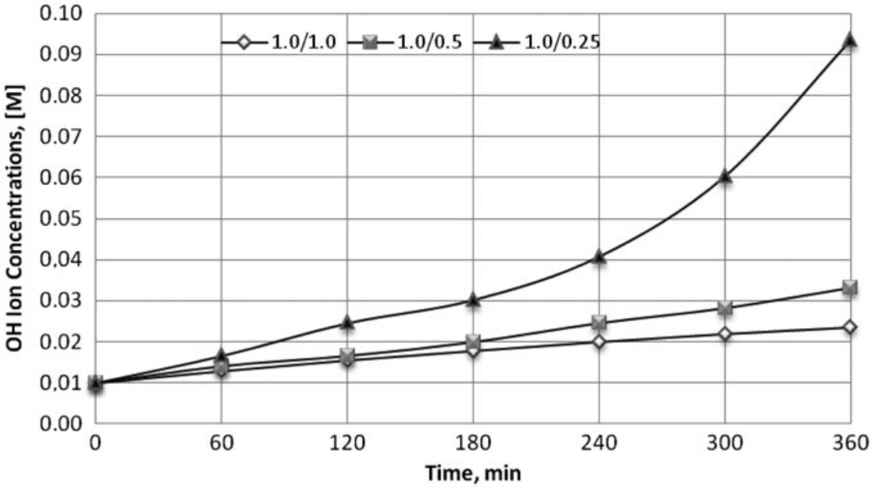

Fig. 8. Changes of OH^- ion concentrations for different catholyte/wastewater ratio (wastewater/catholyte).

concentrations. From this perspective, this method can be used in ammonia reclamation from high ammonia-containing liquids and mixed base separations.

3.4. Utilizing of waste mixed acid/base

The obtained acid and base solutions were used successfully in some applications through laboratory studies. This acid/base mixture can be used for neutralization, as well as different chemical treatment processes in terms of pH adjustment. Forthcoming studies should examine the purification of the obtained mixed acid/base solution.

4. Conclusion

The current study examined the treatment of three different aged leachates that have different characterizations. In addition to the treatment process, anolyte and catholyte solutions were evaluated. The obtained results and future recommendations are given below:

- Firstly, the treatability of three different aged leachates were studied and successful results are obtained.
- The utilization of bipolar membrane from electrolysis process yields a significant income.
- After treatment, the reclamation of waste ions can be achieved by separate collection.
- Anolyte/catholyte solutions will not be regarded as waste anymore due to their acidic/alkaline properties. They can be used as new products. From this perspective, it can be emphasized that it is not a waste-producing process.
- Different operating conditions and acidic/alkaline solution change were measured.
- Fluctuations during the process were due to organic acid in the volatile form and ammonia.
- It was observed that organic acids and mineral acids can be collected separately. Furthermore, it was discovered that in high NH_3-N containing wastewaters, ammonia can be collected separately. This yield can be used in the production of pure ammonia.
- Acidic/alkaline molarities increased by shifting the amount of anolyte/catholyte solutions. In this manner, in full-scale studies, anolyte/catholyte amounts could be reduced, and the quality of the obtained acidic/alkaline solution could be improved.
- The problems that were encountered and their solutions are presented in this study.

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