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Recovery of Alum Sludge by Using Membrane-Based Electrochemical Process

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ABSTRACT

The use of aluminum sulfate (Al_2SO_4) coagulant in water treatment plants generates large amount of sludge residues containing the alum hydroxide precipitates and organic matter. Due to its amphoteric characteristic, this sludge by-product offers alum coagulant recovery by using electrochemical process, before safe disposal to the environment. This study is aimed at evaluating the efficiency of membrane-based electrochemical processes to recover aluminum from the filtrate of the acidified sludge. The dried alum sludge was acidified using sulfuric acid at pH 3, and then centrifuged to obtain the filtrate. Organic content of the filtrate was measured by means of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD), i.e., 295.8 mg/L and 9,666.7 \pm 942.81 mg/L, respectively. In addition, the concentration of Al, Fe, Cu, and Cr was 1,194 mg/L, 515 mg/L, 0.559 mg/L, and 0.217 mg/L, respectively. The two-compartment electrochemical reactor was separated by using Cation Exchange Membrane (CEM) and Anion Exchange Membrane (AEM), and operated in a batch system for 10 hours with an electrical current of 300 mA. The results showed that the use of CEM in electrolysis with the electrodes distances of 1 cm increased the aluminum recovery up to 66.74% with the TOC removal of 24.04% compared to the use of AEM. An electrochemical process using CEM can be suggested to obtain organic-free recovery stream containing higher recovery of alum.

Keywords: Alum recovery; electrochemical process; ion exchange membrane; organic contaminant; water treatment sludge.

INTRODUCTION

In conventional water treatment process, an aluminum-based or iron-based coagulant is widely used to remove organic contaminants, colloidal particulates, and dissolved materials from the raw water through coagulation-flocculation, followed by the sedimentation process. This process generates a large amount of sludge by-product as residues containing high concentrations of Al^{3+} or Fe³⁺ precipitates and organic compounds (Ippolito et al., 2011). The direct disposal of the sludge without proper handling and treatment may cause river siltation, risk to the human health, and disturb the life of river biota (Muisa et al., 2011; Tantawy, 2015; Ahmad et al., 2015). Commonly, the alum sludge handling involves landfill disposal after the dewatering process by sludge drying bed and/or filter press as a low cost option in water treatment plants (Keeley et al., 2014). However, the accumulation of the sludge in a landfill requires larger area and leads to a potential release of the Al-bonded compounds as landfill leachate, which may pose environmental impacts (Ippolito et al., 2011).

A number of studies focused on to the reuse of water treatment sludge as materials for building construction or soil improvement (Rodriguez et al., 2011; El-Didamony et al., 2014; Fan et al., 2014). However, another alternative is to recover the alum from the sludge and reuse it as a metal ion coagulant due to its amphoteric characteristic (Diaz et al., 2014; Nair and Ahammed, 2017). In addition, the recovery of alum as coagulant is likely more beneficial due to the decreasing amount of bauxite, so that this approach may limit the consumption of alum products (Keeley et al., 2014). The aluminum residual sludge can be recovered as alum coagulant for further water/ wastewater treatment or as adsorbent for other removal of contaminants (Hong et al., 2005; Diaz et al., 2014; Cherifi et al., 2016; Nair and Ahammed, 2017). The water treatment sludge can be recovered as coagulant through several methods, including acidification as the commonly applied, alkalinization, ion exchange, and membrane processes (Prakash and Sengupta, 2003; Xu et al., 2009; Keeley et al., 2016; Evuti and Lawal, 2011). Acidification is carried out by adding a substantial amount of acid to reach pH 2-4, thus obtaining a soluble aluminum metal complex ion as a reusable coagulant from the residual sludge (Xu et al., 2009). This process is commonly followed by chemical precipitation and physical separation. However, since the residual sludge contains organic compounds and the dominant hydroxide precipitates of heavy metals, the acidified recovered coagulant also contains other redissolved heavy metals (such as chromium, lead, copper, etc.) and inorganic ions (such as calcium, silica, etc.), which then act as impurities (Barakwan et al., 2019). High concentration of organic impurities in the recovered alum coagulant may lead to the high formation potential of trihalomethane during the final chlorination stage of further water treatment (Sarkar et al., 2010; Keeley et al., 2016). Therefore, in order to minimize impurities of the recovered alum coagulant, a membrane separation process can be applied, which can be driven by external pressure or electricity.

Metal recovery can also be conducted by using the electrochemical processes. The mechanism of metal ion separation can be obtained at a higher purity without the addition of chemicals (Cherifi et al., 2016). The efficiency of metal recovery can be improved by applying an ion exchange membrane. This membrane is often used in desalination and chemical recovery applications. The use of membranes may improve the reduction and oxidation in the electrochemical process (Varcoe et al., 2014), so that the ion selectivity and pH can be adjusted. Furthermore, electric current could optimize the performance of ion exchange membranes by keeping the conductivity of the solution and become the driving force for the membranes (Sarkar et al., 2010). An ion exchange membrane is a semipermeable membrane that transports

certain dissolved ions (Varcoe et al., 2014). For example, a cation exchange membrane (CEM) is an electrically conductive semipermeable membrane that transports the dissolved cations while blocking other ions and neutral molecules. On the other hand, an anion exchange membrane (AEM) is a semipermeable membrane, generally made from ionomers, and designed to pass the anions, while being impermeable for gases such as oxygen or hydrogen (Varcoe et al., 2014).

The objective of this study was to determine the optimum technical configuration (i.e., electrode distance) and evaluate the efficiency of the membrane-based electrochemical processes (anion and cation exchange membrane) to recover the alum coagulant from the sludge. The distance between electrodes affects the energy potential reduction and rate of electron transfer between the anode and cathode. Energy potential reduction (E^0) is a measure of the ability of the solution to conduct the electro-deposition at the cathode. Therefore, the migration of ionic compounds during the recovery of the dewatered alum sludge using the membrane-based electrochemical process was discussed. This creates an opportunity to implement an alternative method in the water treatment system.

EXPERIMENTAL METHODS

Sludge sampling, preparation, and characterization

The study was performed using the alum sludge generated from several effluents of clearator (clarifier unit after coagulation-flocculation process) in Surabaya Water Treatment Plant. The sludge samples were dried at 105°C for 24 hours. The dried sludge samples were composited, mixed thoroughly, crushed using mortar, and finally sieved (~10 mesh sieves). The sludge was then characterized to analyze the organic content measured as total organic carbon (TOC), biochemical oxygen demand (BOD), and chemical oxygen demand (COD). These measurements were followed by the analyses of metal compounds (i.e., Al, Fe, Cr, and Cu).

Acidification

The dewatered sludge in the amount of 200 g was diluted with 1 L of distilled water and acidified

using sulfuric acid to adjust the pH of the sludge solution to pH 2, 3, and 4. The acidified sludge was then homogenized using a magnetic stirrer (C-MAG HS 7) with 800 rpm for 2 hours. Finally, the acidified sludge solution was separated from the solid fraction by using centrifugation (IEC 11210922 CL40) in 4000 rpm for 30 minutes and then filtered by using 0.45 μ m filter paper. The acidified solution was used as electrolyte in the electrochemical process.

Electrochemical configuration

The electrochemical process was performed in a laboratory scale using a batch recirculation reactor with two compartments (Fig 1). The anode and cathode compartments were separated by an ion exchange membrane, i.e., AEM type AMI-7001S or CEM type CMI-7000S, which was obtained from Membrane International, Inc. In each reactor, set-up, two distances of the electrodes were evaluated, i.e., 1 cm and 0.2 cm. In the CEM configuration, the acidified alum filtrate was pumped into the anode compartment, whereas the buffer solution containing Potassium hydrogen tartate ($KHC_4H_4O_6$) under acidic conditions (pH 3) was pumped into the cathode compartment. In the case of the AEM configuration, the acidified alum filtrate was pumped into the cathode compartment and the same buffer solution was pumped into the anode compartment. Both the 1-L feed tank of acidified filtrate and the buffer solution were continuously recirculated into the reactor using a peristaltic pump with a flow rate

of 0.3 mL/s. The reactor was made from acrylic with the dimensions of 5 x 20 cm and thickness of 2 cm, with a silver plate as the cathode and a carbon plate as the anode (2 x 5 cm). The thickness of the silver cathode and the carbon anode was 0.1 and 0.5 cm, respectively. The electrochemical process was conducted at a constant current of 300 mA for 10 hours using a DC power supply (Dekko PS – 305Q). The performance of electrochemical process was determined by sampling carried out every hour for 10 hours.

Analytical method

In accordance with the APHA Standard Method for the Examination of Water and Wastewater (2012), COD was measured using closed reflux and colorimetric method (Merck and Spectroquant NOVA 60A). TOC was measured using total digestion using TOC analyzer (Shimadzu). BOD₅ was measured using the Winkler method. A handheld pH meter and conductivity meter (Lutron) were used to monitor pH and measured total dissolved solid by means of electrical conductivity. The metal cations (Al, Fe, Cr, and Cu) were analyzed by *Inductively Coupled Plasma* (ICP) Agilent Technologies series 700 ICP-OES.

RESULTS AND DISCUSSION

Alum sludge characterization

Table 1 shows the initial characteristics of the water treatment alum sludge. The



Fig. 1. Electrochemical reactor design

Table 1. Characterization of the unacidified alumsludge* Decree of State Ministry for the Environmentof the Republic of Indonesia No. 5/2014 concerningQuality Standards of Wastewater

Parameter	Concentration (mg/L)	Effluent standards (mg/L)	
BOD	1,082.5±106.1	50	
COD	9,666.7±942.8	100	
TOC	295.8	30**	
AI	1,194	10**	
Fe	515	0.3	
Cr	0.22	0.05	
Cu	0.56	0.02	

** Environmental Protection Agency (EPA) in National Pollutant Discharge Elimination 6 System (NPDES) 2011.

concentration of BOD and COD of the sludge was 1,082.5±106.14 mg/L and 9,666.7±942.81 mg/L, respectively. The high concentrations of BOD and COD in the sludge may represent the accumulation of organic compounds in raw water source (from the surrounding activity) that redissolved at the similar pH solubility behaviour as in the targeted acidified alum (Keeley et al., 2016). In addition, the ratio of BOD/COD was 0.11, implying the dominant non-biodegradable organic compounds contained in the sludge. Therefore, the physicochemical method is preferable for the treatment of the sludge. The organic compound was also analyzed as TOC to support the COD measurement with less interference of the consumed $K_2Cr_2O_7$ by other contaminants in the acidified filtrate, such as ferrous ions (Dubber and Gray, 2010).

The highest metal concentration confirmed in the sludge was aluminum, i.e., 1,194 mg/L. This concentration exceeded the daily maximum limitation for aluminum of 10 mg/L, according to the National Pollutant Discharge Elimination 6 System (NPDES, USEPA). The high aluminum concentration was related to the use of aluminum salt $(Al_2(SO_4)_2)$ as a coagulant in the water treatment plant. Iron was the next highly prevalent element, with the measured concentration in the sludge of 515 mg/L. This can be explained by the fact that FeCl, was also added during the coagulation-flocculation as a mixture of the $Al_2(SO_4)_2$ coagulant, in case the higher turbidity of raw water was detected, e.g., during the rainy season. Furthermore, the soil sediments and silicate structures that were present in large quantities of hydroxide precipitates may also contribute to the

high concentration of iron in the sludge (Dahhou, 2017). Other metals detected in the sludge were Cr and Cu; their concentration amounted to 0.22 mg/L and 0.56 mg/L, respectively.

Metal solubility in alum sludge acidification

Acidification was carried out by adding sulfuric acid (H_2SO_4), because aluminum was dissolved faster and easier than in hydrochloric acid (Cheng et al., 2014). It was due to the chemical affinity between the SO_4^{2-} and Al^{3+} ions which was greater than between the Cl⁻ and Al^{3+} ions. In addition, the presence of abundant chloride ions may lead to the potential formation of chlorinated compounds during the electrochemical oxidation.

The highest concentration of Al was 3,793.68 mg/L, measured at pH 2. At pH 3 and 4, the Al concentration was substantially lower, i.e., 298.06 mg/L and 237.06 mg/L, respectively (Table 2). This result was in accordance with the acidification reaction of aluminum hydroxide (Eq.1), showing the addition of acid creates reaction move to the right to produce more dissolved aluminum (Li et al., 2005).

$$2\text{Al(OH)}_3 + 3\text{H}_2\text{SO}_4 \leftrightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \quad (1)$$

As shown in Table 2, the highest concentration of iron was also measured at pH 2, i.e., 220.46 mg/L. This concentration was lower at pH 3, and pH 4, i.e., 213.72 and 203.53 mg/L. Likewise, the highest concentration of other metals (Cr and Cu) was detected at pH 2, although overall their presence was substantially lower than in the case of iron and the targeted Al, i.e., in the range of 0.09–1.32 mg/L. As most of the metal ions are likely dissolved at pH 2, Al and other metal ions have an elevated concentration in the acidified alum sludge (Xu et al., 2017). The concentration of metals ions was influenced by the pH values of supernatant, because each metal has different solubility at different pH. Therefore,

 Table 2. Metal concentrations in the acidified sludge solution

Metal compound	Concentration (mg/L)		
	pH 2	pH 3	pH 4
AI	3,793.68	298.06	237.06
Fe	220.46	213.72	203.53
Cr	0.64	0.09	0.09
Cu	1.32	0.14	0.24

this confirms that the aluminum in the sludge can be recovered through the acidification stage.

However, acidification is not a selective separation process, because in addition to the acidified/recovered aluminum ions, this process also dissolves other metals and organic content as impurities (Prakash and Sengupta, 2003). Therefore, the acidification process in the recovery of aluminum for coagulants must be followed by a further process for the separation of aluminum from organic content and other metals impurities. In the recent study, the acidification was conducted at pH 3, in order to evaluate the efficiency of membrane-based electrochemical in which the composition of alum and iron was in the equal concentration ratio.

ELECTROCHEMICAL PROCESS OF ACIDIFIED ALUM FILTRATE

Change of TDS during electrochemical process

It can be seen in Figure 2, in the CEM configuration, TDS in the cathode compartment was increased from 2.60 to 4.00 mg/L and from 2.33 to 4.92 mg/L at the electrodes distance of 0.2 and 1 cm, respectively. Conversely, in the anode compartment, the TDS was decreased from 4.50 to 0.60 mg/L and from 5.49 to 1.86 mg/L at the distances of electrodes of 0.2 and 1 cm, respectively. This indicates that the cations contained in the acidified filtrate in the anode compartment migrated to the buffer solution in the cathode compartment, i.e., passing through the CEM. Likewise, in the AEM configuration, the TDS in the cathode compartment was decreased from 2.16 to 0.73 mg/L and 3.92 to 1.00 mg/L for the electrode distance of 0.2 and 1 cm, respectively (Fig 3). TDS in the anode compartment was increased from 3.53 to 6.10 mg/L and 2.30 to 8.05 mg/L for the distance electrode of 0.2 and 1 cm, respectively.

Similarly to CEM, in the case of AEM, the decrease of TDS in the cathode compartment implies the migration of anions contained in the acidified alum filtrate to the anode compartment by passing through the AEM. However, the change of TDS was more substantially observed in the AEM configuration. This can be explained by the reduction process of metal ions at the cathode surface, forming electro-deposition. Moreover, the dissolved metal ions can also be precipitated as metal hydroxide as pH in the cathode is increased due to the electrolysis of water, forming hydrogen gas and releasing hydroxide ions.

The increase of TDS was higher when applying the electrodes distance of 1 cm than in the case of 0.2 cm, both in the AEM and CEM configurations (Fig. 2 and 3). This suggests that the closer the distance between the electrodes, the lower energy potential resulted in the electrochemical process. Therefore, the TDS values would be much higher due to the ions that have been reduced and oxidized faster (Kumar et al., 2015). On the other hand, the wider the distance between the electrodes, the slower movement of the ions resulted (Kumar et al., 2015). The decrease of TDS in the electrolyte is proportional to the decrease of electrical conductivity of ions. This is due to the oxidation and reduction reactions of the



Fig. 2. TDS values in the electrochemical process using CEM



Fig. 3. TDS values in the electrochemical process using AEM

ions, forming the O_2 gas at the anode and the H_2 gas as well as the deposited matter at the cathode (Scanell and Duffy, 2007).

The pH values in electrolysis

In both the CEM and AEM reactor configurations, pH was increased in the cathode compartment and reversely, it was decreased in the anode compartment. The pH of the electrolyte in the cathode compartments was increased from 3.70 to 11.00 and from 3.55 to 11.67 in the electrode distance of 0.2 and 1 cm for CEM configurations, respectively (Fig. 4). In the AEM configurations, the pH in the cathode compartments was increased from 3.22 to 8.35 and from 3.00 to 4.00 in the electrode distance of 0.2 and 1 cm, respectively (Fig. 5). The anode compartment in both AEM and CEM configuration shows a decrease of pH from approximately 3.5 to around 1.6–2.2. The high increase of pH in the cathode compartments at CEM reactor configuration was caused by the formation of OH⁻ ions (Eq. 2) and the accumulation of hydroxide ions in the cathode that would not be able to migrate to the anode due to the applied CEM (Rozendal et al., 2008). The decrease in pH occurred in the anode compartment due to the oxidation process that produces H⁺ (Eq. 5). The oxidation-reduction reactions that may involve in the electrochemical process by applying CEM can be written as follows (Chen et al., 2000):

Reactions in the cathode compartment:

$$2H_2O + 3e^- \rightarrow 2OH^- + H_2 \tag{2}$$

$$Al^{3+} + 3H_2O + 3e^{-} \rightarrow Al(OH)_3$$
(3)

$$Al(OH)_{3} + OH^{-} \rightarrow Al(OH)_{4}^{-}$$
(4)

Reactions in the anode compartment:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (5)

$$2\mathrm{SO}_{4}^{2-} + 2\mathrm{H}^{+} \to \mathrm{H}_{2}\mathrm{SO}_{4} \tag{6}$$



Fig. 4. The pH changes in the electrochemical process applying CEM



Fig. 5. The pH changes in the electrochemical process applying AEM

The formed precipitates were observed in small portion in the cathode compartment when applying CEM. Thus, the recovered aluminum was highly likely obtained in the form of concentrated solution. Aluminum hydrolysis causes a breakdown of the aluminum ions when reacting with H_2O_1 , so that it would present as $Al(OH)_4$ at high pH (pH>6) (MacCrehan et al., 2010). Equation 2 represents a reaction that leads to an increase of the pH observed in the experiments. The high availability of hydroxide ions (indicated by substantially increase of pH) leads to the formation of $Al(OH)_4^-$ (Eq. 4). In this metal ion form, $Al(OH)_{4}$ is highly soluble in the cathode compartment (Liu et al., 2010). Therefore, in the case of CEM application, alum was recovered as $Al(OH)_{4}$ and soluble $Al(OH)_{4}$ ion in the cathode compartments in all electrode distance set-up.

Similarly, the oxidation reaction in the anode compartment when applying AEM leads to the decrease of pH due to the accumulation of H⁺ (Eq. 10). A slight difference for the sulfuric acid formation in the anode, i.e., in the case of AEM, the sulfate ions migrated from the cathode to anode, whereas in the case of CEM, the sulfate ions were available from the acidified alum filtrate. On the other hand, the effect of electrode distance on pH increase in the cathode compartment was observed when applying AEM. Although both conditions intend to increase the pH, shorter distance of electrode leads to the increased reduction process at the cathode, and thus generating more efficient hydroxide ions and hydrogen gas (Eq. 8).

Furthermore, the formation of precipitates were clearly observed in the cathode compartment, with AEM set-up. As for alum recovery, the precipitates can be formed through reaction as stated in Eq. 9, with aluminum hydride as the recovered Al products (Adhikari, 2008). Therefore, in the case of AEM application, alum was recovered in the cathode compartment as as $Al(OH)_3$, soluble $Al(OH)_4$ and AlH_3 precipitates. The formation of precipitates may also release protons, causing a decrease of pH. Overall, the oxidationreduction reactions that may occur in the electrochemical process with AEM were as follows (Chen et al., 2000, Adhikari, 2008):

Reactions in the cathode compartment:

$$Al^{3+} + 3e^{-} \rightarrow Al(s) \tag{7}$$

$$2H_2O + 3e^- \rightarrow 2OH^- + H_2 \tag{8}$$

$$2 \operatorname{Al} + \operatorname{OH}^{-} + 3\operatorname{H}_{2}\operatorname{O} \rightarrow \operatorname{Al}(\operatorname{OH})_{4}^{-} + \operatorname{AlH}_{3} \qquad (9)$$

Reactions in the anode compartment:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (10)

$$4\mathrm{H}^{+} + 2\mathrm{SO}_{4}^{2-} \rightarrow 2\mathrm{H}_{2}\mathrm{SO}_{4} \tag{11}$$

Aluminum recovery

The efficiency of aluminum recovery was determined by the percentage of aluminum deposited at the cathode and soluble aluminum in the cathode compartment (Fig. 6). In the electrochemical process applying CEM – 0.2 cm and 1 cm, the aluminum recovery was obtained at the cathode surface in the form of alum hydroxide precipitates, i.e., 13.2% and 16.61%, respectively (Fig. 6). In addition, the form of recovered aluminum as $Al(OH)_4^-$ complex compound was obtained as the solution in the cathode compartment after 10-hour electrochemical process (t-10), i.e.,



Fig. 6. Aluminum recovery in the electrochemical process

3.23% and 50.13% applying CEM with 0.2 cm and 1 cm electrode distance, respectively. The aluminum recovery in the electrochemical process applying AEM at both electrode distance of 0.2 cm and 1 cm was determined by the percentage of aluminum hydroxide and aluminum hydride deposited at the cathode, i.e., 7.96% and 24.95%, respectively (Fig. 6). In addition, the soluble aluminum in the cathode compartment was 1.91% and 13.50%, respectively.

In the electrochemical process applying CEM with 1 cm electrode distance shows that the recovery of aluminum was mostly formed as $Al(OH)_4^-$ because the pH of the electrolyte in the cathode compartment was up to 11.67 at the end of the process. Aluminum recovery as hydroxide precipitate at the cathode had a small portion due to the formation of the $Al(OH)_4^-$ ions that lead to the redissolved aluminum (Liu et al., 2010). The possible formation of aluminum hydride may also lead to redissolved aluminum as the $Al(OH)_4^-$ ions at higher pH (Adhikari, 2008). At high pH (pH> 6), aluminum dissolved as complex ions of $Al(OH)_4^-$ with higher solubility at alkaline pH (Adhikari, 2008; MacCrehan et al., 2010).

In the case of AEM, the recovery of aluminum dominantly in the form of hydroxide and hydride precipitates at the cathode, reaching up to 24.95% (Fig. 6). The pH increase in the cathode compartment only reached 4.5 at the end of the process, so that the dominant aluminum specification was in the form of Al^{3+} cations (Xu et al., 2017). Al^{3+} would react with OH⁻ to form $Al(OH)_3$ as the hydroxide precipitate. Nevertheless, the aluminum recovery efficiency using AEM was lower than CEM, due to the low final pH of the process caused the precipitate return back to dissolve ions (Sengupta, 2002). Furthermore, it can also be implied from Figure 6 that the electrode distance 1 cm showed more beneficial alum recovery than the shorter distance, i.e., 0.2 cm. This can be explained by the fact that the alum recovery through the cathode reduction process would be enhanced with less interference of the oxidation process, although membrane had been applied. Bulk reaction seems to be more preferable for alum recovery as soluble ion than the electro-deposition reaction at the vicinity of the cathode surface (Adhikari, 2008). However, the energy consumption needs to be considered when applying wider distance of electrode gaps since this lead to the increase of internal resistance of the process.

Organic removal

The removal of organic was observed in both CEM and AEM reactor configurations. In the electrochemical process applying CEM with the electrode distance of 0.2 and 1 cm, TOC was decreased from 295.8 mg/L to 224.7 and 256.2 mg/L, respectively (Fig. 7). This implies the TOC removal of 24.04% and 13.39%, respectively. Conversely, the TOC removal was lower in the case of AEM, i.e., from 295.8 mg/L to 281.1 (4.97%) and 266.4 mg/L (9.94%) with the electrode distance of 0.2 and 1 cm, respectively (Fig. 7).

The decrease of TOC was enhanced when applying membrane since the reduction and oxidation processes occurred in two separated compartments (Sengupta, 2002). In the electrochemical process using CEM, organic contaminants, particularly the negatively charged organic contaminants, can not pass through the CEM, so that the



Fig. 7. Removal of TOC in electrochemical process

organic contaminants were oxidized in the anode compartment. In addition, since the carbon anode was applied, the electrosorption of organic contaminants may also occur. Thus, this explains the higher removal of TOC in the case of the CEM configurations. Nevertheless, the recovered aluminum was obtained in the cathode compartment, which were free from the organic contaminants.

In the case of the AEM configuration, the negatively charged organic contaminants may pass through the membrane, and then be possibly oxidized at the anode compartment. Since the alum filtrate was pumped into the cathode compartment, the decrease of TOC contained in the filtrate was dominantly due to the migration of negatively charged organic compounds. Nevertheless, as the recovered alum was collected in the cathode, the high conentration of organic remained in the filtrate can be seen as a drawback of the recovered alum products.

Acidification involved dissolving aluminum from aluminum hydroxide form in the sludge. This process was non-selective with the dissolved aluminum content as well as the dissolved natural organic matter like humates and fulvates (Sengupta, 2002). This process may still contain a considerable amount of organic compounds. If the recovered alum is used as coagulant, the potential formation of carcinogenic compounds, such as trihalomethane, is possible during the chlorination stage. Ion exchange membranes constitute one of the alternative methods to separate the DOC for alum recovery (Prakash et al., 2004). The other organic removal is by conducting electrochemical oxidation process (Barazesh et al., 2016). Therefore, this CEM configuration seems to be more beneficial for the alum recovery than the AEM reactor configuration.

CONCLUSIONS

The recovery of alum from alum sludge can be implemented as an alternative of sludge handling in water treatment plant. The impurities such as metal ions other than the targeted Al (i.e., Fe, Cr and Cu) as well as organic contaminants contained in the sludge requires membrane process to enhance the amount of the recovered product. An electrochemical process applying CEM or AEM creates a two-separated electrochemical cell that is able to enhance the oxidation and reduction processes required for the alum recovery. In both the CEM and AEM reactor configurations with 1 cm electrode gaps, 38.45-66.74% recovery of initial alum concentration was obtained after 10 hour electrochemical process of the acidified alum sludge. These results were higher than in the case of the electrochemical process in both the CEM and AEM with shorter electrode gaps (i.e., 0.2 cm) due to the interference of the reduction process by the oxidation process, i.e., 9.87-16.43% of alum recovery. Futhermore, although a slight removal of TOC was observed, i.e., up to 24.04%, the application of CEM seems to be more effective than in the case of AEM in order to obtain the recovered alum products (i.e., Soluble $Al(OH)_{4}^{-1}$ ions as well as Al(OH)₃ and AlH₃ precipitates), due to the organic-free recovery stream. Nevertheless, further process is required to separate the recovered alum with other metal ions, which may remain in the recovery stream.

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