



## Optimum conditions for the formation of Al<sub>13</sub> polymer and active chlorine in electrolysis process with Ti/RuO<sub>2</sub>-TiO<sub>2</sub> anodes

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### Abstract

A polyaluminum containing a high concentration of Al<sub>13</sub> polymer and active chlorine (PACC) was successfully synthesized by a new electrochemical reactor using Ti/RuO<sub>2</sub>-TiO<sub>2</sub> anodes. PACC can potentially be used as a dual-function chemical reagent for water treatment. The obtained results indicated that the formation of Al<sub>13</sub> polymer and active chlorine, were the most active components in PACC responsible for coagulation and disinfection respectively. These components were significantly influenced by electrolyte temperature, current density, and stirring rate. It was observed that high electrolyte temperature favored the formation of Al<sub>13</sub>. Increasing current density and stirring rate resulted in high current efficiency of chlorine evolution, thus favoring the generation of Al<sub>13</sub> and active chlorine in PACC. When the PACC (Al<sub>T</sub> = 0.5 mol/L, basicity = 2.3) was prepared at the optimum conditions by electrolysis process, the Al<sub>13</sub> polymer and active chlorine in product reached above 70% of Al<sub>T</sub> and 4000 mg/L, respectively. In the pilot scale experiment with raw polyaluminum chloride used as an electrolyte, PACC was successfully prepared and produced a high content of Al<sub>13</sub> and active chlorine products. The pilot scale experiment demonstrated a potential industrial approach of PACC preparation.

**Key words:** Al<sub>13</sub> polymer; coagulation; pre-oxidation; electrolysis; water treatment

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### Introduction

Coagulation is an essential process for the removal of various particulate and organic matters in water treatment. Aluminum salts are commonly used to coagulate small particles into larger flocs that can be effectively removed in the subsequent separation processes of sedimentation and/or filtration. Polyaluminum chloride (PACl) has been claimed by investigators (Edzwald, 1993; Sinha et al., 2004; Gao et al., 2009) to be superior to traditional Al coagulants (e.g. AlCl<sub>3</sub> and alum) in particulate and/or organic removal with inherent advantages of less alkalinity consumption, less sludge production, and less pH and temperature dependence. It is well known that PACl products contain cationic species, of which the most likely is Al<sub>13</sub> ([AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup>) species (Duan and Gregory, 2003; Lin et al., 2008; Hu et al., 2006b). Besides the characteristics of higher positive charge and strong binding ability to aggregates, it is temporarily resistant to hydrolysis before adsorption on particle surfaces. Many researchers believed that Al<sub>13</sub> species was the most active species in PACl responsible for coagulation or precipitation (Gray et al., 1995; Zhao et al., 2009). Thus they claimed that high content of Al<sub>13</sub> was the main aim of the research and production industry of PACl.

Active chlorine is widely used as a disinfectant and pre-oxidant in water treatment process. Besides decoloration, deodorization, and inactivating microorganisms, preoxidation can remove some inorganic matter (Haag et al., 1984), increase the biodegradability of organic matter (OM) (De Laat et al., 1991), aid the coagulation process (Zhang et al., 2009) and reduce the trihalomethane formation potential (Amy et al., 1991). Moreover, preoxidation with active chlorine could improve coagulation efficiency because active chlorine could change the surface charge characteristic of OM in water (Shen et al., 2011). The results of Ji et al. (2008) proved that PACl coagulation coupling with inter-chlorination exhibited higher removal efficiency of dissolved organic carbon and disinfection byproducts precursor than PACl coagulation coupling with pre-chlorination. It indicated that dual-function (i.e., coagulation and oxidation) chemical reagent might perform better to remove particles and OM from water, in comparison with the conventional two-unit system using pre-oxidant and coagulant.

A novel dual-function water treatment reagent (PACC) was synthesized with a new electrochemical reactor, which used Ti/RuO<sub>2</sub>-TiO<sub>2</sub> anodes, Ti cathodes, and AlCl<sub>3</sub> or PACl solution as electrolyte (Hu et al., 2005). During the electrolysis, OH<sup>-</sup> homogeneously evolved on the surface of cathodes, leading to the formation of Al(OH)<sub>4</sub><sup>-</sup> (the

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precursor of  $Al_{13}$ ) (Parker and Bertsch, 1992) with subsequent formation of  $Al_{13}$  polymer. At the same time, chlorine was generated due to the chlorine evolution on the surface of anodes and partly dissolved into electrolyte. The active chlorine existed in PACC mainly by form of chlorine and hypochlorous. Finally, PACC contained high content of  $Al_{13}$  polymer and active chlorine, then combines together two distinct functions (viz. chemical coagulation and oxidation) and simultaneously showed high efficiency on removing particles and inactivating fecal coliforms in municipal wastewater (Hu et al., 2005, 2006c). Therefore, PACC shows a promising application in the near future in practical water treatment processes.

$Al_{13}$  polymer is an intermediate species in the processes of hydrolysis, polymerization, gelation and precipitation of  $Al^{3+}$  in aqueous solution. The operation conditions, such as base injection rate, temperature, and stirring rate, were very important in determining the relative distribution of Al species between monomeric and  $Al_{13}$  polymeric (Parker and Bertsch, 1992; Klopogge et al., 1992). In the electrolysis process of PACC preparation, current density ( $j$ ) determines the injection rate of base and chlorine into electrolyte through controlling the reaction rate of hydrogen evolution and chlorine evolution, and electrolyte is stirred to increase the mass transfer by a circulation pump. The extent to which the key parameters affect the generation of active chlorine and  $Al_{13}$  is still unclear. In the present article, the effect of current density, electrolyte temperature and stirring rate on the formation of  $Al_{13}$  species and active chlorine were investigated. The purpose of this investigation is to optimize the process for the  $Al_{13}$  polymer and active chlorine formation during the electrolysis process. A pilot scale experiment was conducted to seek the further information of operation conditions for producing PACC in practice.

## 1 Materials and method

### 1.1 Characteristics of electrochemical reactor

The schematic view of the electrochemical reactor is illustrated in Fig. 1. It consists of an electrolytic rectifier and an electrolytic cell made of organic glass. The volume of electrolytic cell is 0.25 L. Netlike sheets of Ti/RuO<sub>2</sub>-TiO<sub>2</sub> (50 mm × 65 mm) that are relatively cheap and widely used in chlorine-alkali industry was used as anode. Cathode was netlike sheets of Ti (50 mm × 65 mm). The

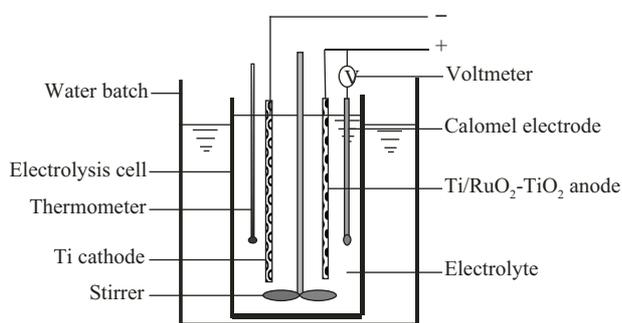


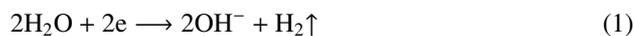
Fig. 1 Schematic view of electrochemical reactor.

distance between the anode and the cathode was 10 mm that was the optimal value. A stirrer (Caframo, BDC-1850, Canada) was used to circulate the solution to increase mass transfer. The temperature of electrolyte was controlled by a water bath.

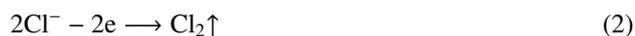
### 1.2 PACC preparation

Electrolyte was prepared by dissolving reagent grade  $AlCl_3 \cdot 6H_2O$  in deionized water. The electrolysis process was carried out at constant current. The main reaction on anode is chlorine evolution whose current efficiency is maximal when anode potential is about 1.5 V (Hu et al., 2005). Expected  $Al_T$  of PACC was 0.75 mol/L, and corresponding expected basicity value was 2.1, which is the optimal value for the formation of  $Al_{13}$  polymer at that  $Al_T$  (Zhao et al., 2009). Electrolytic time is decided by expected  $Al_T$  and basicity (the value of OH/Al molar ratios), the detailed method of calculation can be found in literature (Hu et al., 2005). When the electrolysis process is carried out at direct current in the electrochemical reactor, the hydrogen evolution and chlorine evolution will take place on the anodes and cathodes, respectively.

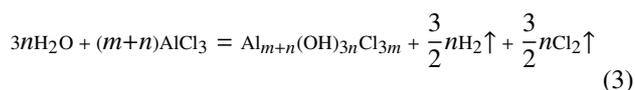
Cathode reaction:



Anode reaction:



Therefore, the complete electrochemical reaction can be expressed as:



### 1.3 Characterization of $Al_{13}$ species and active chlorine

$^{27}Al$  nuclear magnetic resonance (NMR) spectroscopy was used to characterize the Al species with  $^{27}Al$  NMR spectra obtained on a Varian UNITYINOVA (500 MHz) spectrometer (USA). Details of the operating approaches and parameters of the apparatus can be found in the literature (Liu et al., 2003). The  $^{27}Al$  NMR spectroscopy of PACls is shown in Fig. 2. The intensities of the  $^{27}Al$  signals relative to the aluminate reference were used for calculating the Al concentrations. The intensity at 0 resonance represented the quantitative determination of the monomeric Al. The

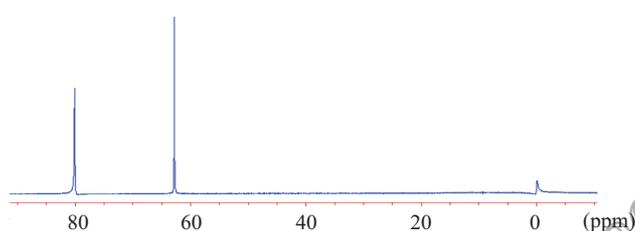


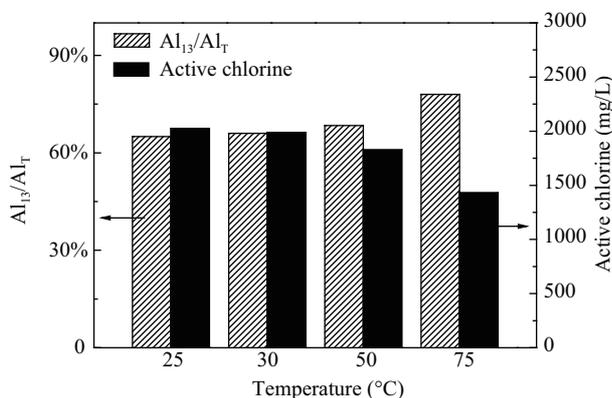
Fig. 2  $^{27}Al$  NMR spectra characterization of PACC sample.

monomeric and dimeric Al species were named together as Al<sub>m</sub>. The intensity at the 63 ppm resonance represented the quantitative determination of the Al<sub>13</sub> polymer in an Al solution. The 80 ppm resonance represented sodium aluminate. The concentration for the 63 ppm signal was multiplied by 13 to obtain the concentration of Al<sub>13</sub>. The difference between total Al concentrations (Al<sub>T</sub>) and [Al<sub>m</sub> + Al<sub>13</sub>] was an undetected part (Al<sub>u</sub>, i.e., larger polymer species and/or solid-phase Al(OH)<sub>3</sub>) by <sup>27</sup>Al NMR. The ferron colorimetric method was also used to analyze initial Al species distributions of PACC. The absorbance increase was monitored for 120 min such that three fractions could be operationally defined which included Al<sub>a</sub>, Al<sub>b</sub>, and Al<sub>c</sub>, corresponding to monomeric, medium polymer, and larger polymer species and/or solid-phase Al(OH)<sub>3</sub>, respectively. The reaction time of Al<sub>a</sub>-ferron was 1 min, and the Al species reacting with the ferron reagent before 120 min represented [Al<sub>a</sub> + Al<sub>b</sub>], then Al<sub>c</sub> was obtained by Al<sub>T</sub> minus Al<sub>a</sub> and Al<sub>b</sub>. Many investigations (Parker and Bertsch, 1992; Gao et al., 2009) proved that the Al<sub>b</sub> species could be regarded as the Al<sub>13</sub> species. Furthermore, the Al<sub>a</sub> and Al<sub>c</sub> species were approximately equal to the Al<sub>m</sub> and Al<sub>u</sub> species, respectively. Al<sub>T</sub> was determined using ICP-AES (Optima 2000, PerakinEimer, USA). Basicity value was determined by titrimetric methods (Standard method of the chemical industry of China). Active chlorine was determined by spectrophotometric method using N,N-diethyl-1,4-phenylenediamine (Standard Method of the Ministry of Environmental Protection of China).

## 2 Results and discussion

### 2.1 Effect of electrolyte temperature on Al<sub>13</sub> and active chlorine formation

PACC samples were prepared at 25, 30, 50, and 75°C, respectively. The content of Al<sub>13</sub> and active chlorine in the three PACC samples (Al<sub>T</sub> = 0.75 mol/L, basicity = 2.1) were determined. As shown in Fig. 3, from 25 to 75°C, Al<sub>13</sub> fraction increased from 65% to 78%, while the content of active chlorine decreased from 2026 to 1430 mg/L. Al<sub>13</sub> content exhibited a positive correlation with electrolyte temperature. While in contrast, the content of



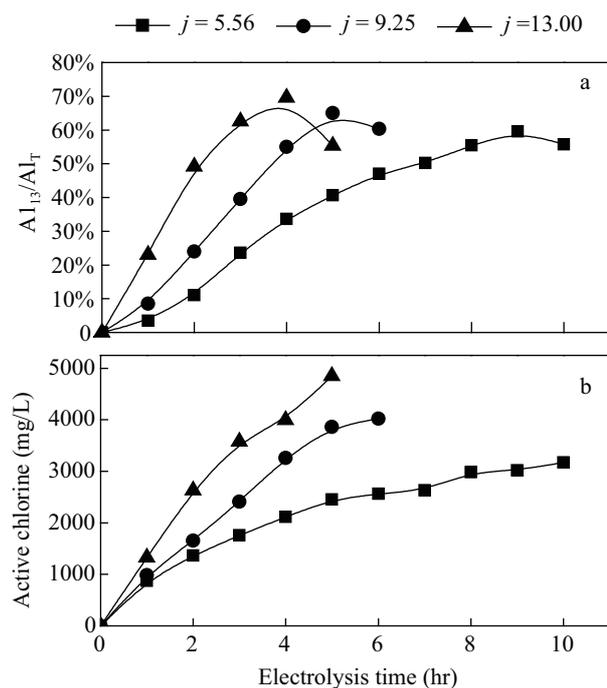
**Fig. 3** Effect of electrolyte temperature on the formation of Al<sub>13</sub> polymer and active chlorine. Total Al concentration (Al<sub>T</sub>) = 0.75 mol/L, basicity = 2.1, current density (*j*) = 5.56 A/dm<sup>2</sup>, stirring rate = 150 r/min.

active chlorine had a negative correlation with electrolyte temperature. This phenomenon about Al<sub>13</sub> formation at various temperatures agreed with result presented by Wang et al. (2003). They found that PACl synthesis at higher temperature resulted in a higher production of Al<sub>13</sub> polymer above basicity = 1.8. Increasing temperature favored the generation of Al(OH)<sub>4</sub><sup>-</sup> and small polymeric Al such as dimer and therefore enhanced the interaction between small polymeric Al and Al(OH)<sub>4</sub><sup>-</sup> to form Al<sub>13</sub>. Generally, the chlorine solubility in water decreases with the increase of water temperature. Furthermore, high temperature will accelerate the decomposition reaction rate of HClO in aqueous solution. The two reasons contribute to low yield of active chlorine in PACC at high electrolyte temperature.

### 2.2 Effect of current density on Al<sub>13</sub> and active chlorine formation

Effect of current density (*j*) on the formation of Al<sub>13</sub> and active chlorine was investigated at the electrolyte temperature of 30°C. As shown in Fig. 4, increasing *j* shortened the electrolysis time for the preparation of PACC (Al<sub>T</sub> = 0.75 mol/L, basicity = 2.1). Electrolysis time for the PACC preparation took about 9 hr at the *j* of 5.56 A/dm<sup>2</sup>, while only 4 hr were needed to reach the expected basicity value 2.1 of PACC at the *j* of 13.00 A/dm<sup>2</sup>. Moreover, the results indicated that the content of Al<sub>13</sub> and active chlorine increased with the increase of *j*. The maximal Al<sub>13</sub> fraction in electrolysis process at *j* of 5.56, 9.25, and 13.00 A/dm<sup>2</sup> accounted for 59.6%, 65.0%, and 69.6% of Al<sub>T</sub>, respectively. Corresponding content of active chlorine at final electrolysis process were 3170, 4021, and 4852 mg/L, respectively.

Increasing *j* can increase the current efficiency of chlorine evolution and inhibits the oxygen evolution (Chen,



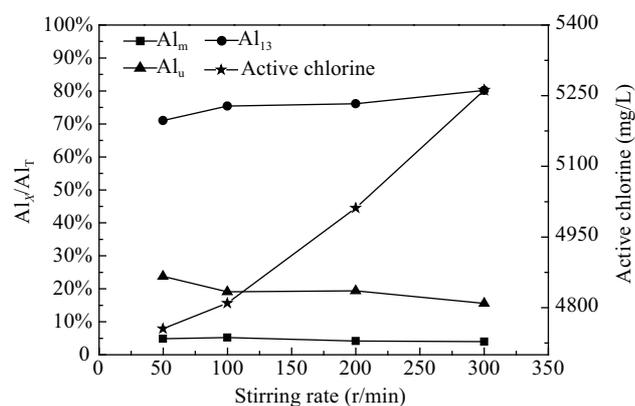
**Fig. 4** Effect of current density on the formation of Al<sub>13</sub> polymer (a) and active chlorine (b). Al<sub>T</sub> = 0.75 mol/L, basicity = 2.1, electrolyte temperature = 30°C, stirring rate = 150 r/min.

1993), which is the side reaction on anode in PACC preparation and generates  $H^+$  that neutralizes the injected  $OH^-$  from hydrogen evolution on the cathode. With the high current efficiency of chlorine evolution, the  $OH^-$  added into bulk solution can more effectively interact with  $Al^{3+}$  to form  $Al(OH)_4^-$ , which is the  $Al_{13}$  precursor. Therefore, the  $Al_{13}$  content increased with the increase of  $j$ . Although the same electric capacity was consumed for the preparation of the three PACC samples, the actual base injection volumes were not equal because of the difference in current efficiency. When the electrolysis process was carried out at the highest  $j$  (13.00 A/dm<sup>2</sup>), the largest base volume was added into electrolyte for the highest current efficiency of chlorine evolution. The solubility of active chlorine in PACC is positively correlated with the pH value of sample. Consequently, the content of active chlorine in PACC prepared at the largest  $j$  (13.00 A/dm<sup>2</sup>) was the highest.

### 2.3 Effect of stirring rate on $Al_{13}$ and active chlorine formation

The circulation of electrolyte in the electrochemical reactor was adjusted by a stirrer. The effect of stirring rate on  $Al_{13}$  and active chlorine formation was investigated at the  $j$  of 5.56 A/dm<sup>2</sup> and the temperature of 30°C. Four PACC samples ( $Al_T = 0.75$  mol/L, basicity = 2.1) were prepared at the stirring rate of 50, 100, 200, and 300 r/min, respectively. The results showed that the content of  $Al_{13}$  and active chlorine increased with increasing stirring rate (Fig. 5).

In the electrolysis process, high stirring rate causes high mass transfer rate, which can increase the collision opportunity between  $Al(OH)_4^-$  and small polymeric Al in electrolyte. On the contrary, at low stirring rate, the injected base will be very concentrated near cathode owing to poor dispersal, which will result in greater generation of colloidal Al rather than  $Al_{13}$  polymer. As a result, cathode



**Fig. 5** Al species distribution and the content of active chlorine as a function of stirring rate.  $Al_T = 0.75$  mol/L, basicity = 2.1,  $j = 5.56$  A/dm<sup>2</sup>, electrolyte temperature = 30°C.

passivation may occur for the sedimentation of colloidal Al on cathode. High mass transfer rate leads to high current efficiency of chlorine evolution, and thus favors the formation of  $Al_{13}$  and active chlorine in electrolysis process.

### 2.4 $Al_{13}$ and active chlorine formation in electrolysis process at optimum conditions

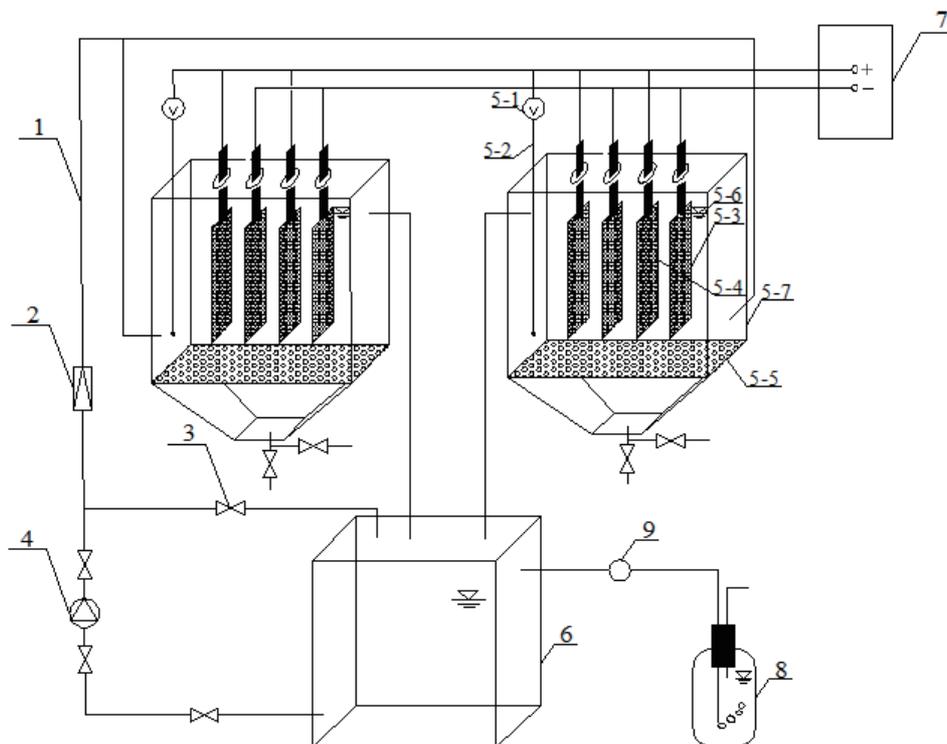
According to the above results, the PACC (expected  $Al_T$  and basicity were 0.5 mol/L and 2.3, respectively) was prepared using the following parameter: 250 mL  $AlCl_3$  aqueous solution (0.5 mol/L) in electrolysis reactor was electrolyzed for 2.15 hr under  $j$  13.00 A/dm<sup>2</sup>, stirring rate 300 r/min, and electrolyte temperature 30°C. At the final of electrolysis process, the PACC solution was yellowy suspended solution because of the existence of a little colloidal Al and chlorine. Because of the precipitation of dissolved Al and the release of chlorine, the PACC solution became clear along with aging time. The characterization of PACC is illustrated in Table 1. After 3 days aging, the  $Al_T$  increased from 0.48 to 0.52 mol/L, and  $Al_{13}$  fraction increased from 78.3% to 82.5%. Some colloid Al re-dissolved into PACC solution might contribute to the increase of  $Al_{13}$  and  $Al_T$ . At the same time, the content of active chlorine decreased from 4800 to 4463 mg/L due to the decomposition of active chlorine. Our previous research (Hu et al., 2006a) indicated that the preoxidation of active chlorine in PACC could improve the  $Al_{13}$  coagulation efficiency if the water possessed the characteristics of relatively low OM content and high hardness.

### 2.5 Pilot scale preparation of PACC

According to the lab-scale reactor and optimal parameters, a pilot scale device (Fig. 6) was set up to produce PACC. The device consisted of an electrolysis system, circulation system, and gas absorption system. The electrolysis system (i.e. electrochemical reactor) is the core part of the device. The schematic view of the electrochemical reactor is illustrated in Fig. 6. It consisted of a power supply, working electrode, voltmeter and calomel electrode that were used to control the anode potential to get the maximum current efficiency for chlorine evolution (Hu et al., 2005). The optimal distance between the anode and the adjacent cathode was 6 mm, and the circuit was arranged in parallel to improve spatio-temporal productivity. The released chlorine gas from the electrochemical reactor was absorbed by aqueous alkali in the gas adsorption bottle. The volume of the circulation tank was 400 L, making his the largest component of the electrolysis system. The circulation rate of the electrolyte could reach 0.175 m/sec with an acid-resistant pump. The pilot scale experiment was carried out at a PACl manufacturing plant. To save on

**Table 1** Characterization of PACC electrochemically prepared at optimum conditions

Aging time (day)	$Al_T$ (mol/L)	Basicity	pH	$Al_m$ (%)	$Al_{13}$ (%)	$Al_u$ (%)	Active chlorine (mg/L)
0	0.48	2.35	4.65	0	78.3	21.7	4800
3	0.52	2.35	4.76	0	82.5	17.5	4463



**Fig. 6** Flow chart of the pilot scale device for PACC preparation. (1) circulation tube; (2) flowmeter; (3) valve; (4) pump; (5) electrolysis reactor; (5-1) thermometer; (5-2) calomel electrode; (5-3) Ti cathode; (5-4) Ti/RuO<sub>2</sub>-TiO<sub>2</sub> anode; (5-5) water distribution plate; (5-6) electrolyte; (5-7) electrolytic cell; (6) circulation tank; (7) power supply; (8) gas adsorption bottle; (9) vacuum pump.

**Table 2** Characterization of PACC electrochemically prepared by a pilot scale device

Product	Al <sub>T</sub> (Al <sub>2</sub> O <sub>3</sub> %)	Basicity	pH	Al <sub>a</sub> (%)	Al <sub>b</sub> (%)	Al <sub>c</sub> (%)	Active chlorine (mg/L)
Raw PACl	10.5	1.2	2.4	65.2	27.4	7.4	0
PACC	12.7	2.1	3.2	14.8	58.3	26.9	569.3

raw material cost and shorten electrolysis time, PACl with low basicity was used as an electrolyte. The electrolysis process was carried out at room temperature with  $j$  of 2.98 A/dm<sup>2</sup>. Although PACC was not prepared under the optimal conditions due to actual conditions, the electrolysis parameters were selected to be as close as possible to the optimal values.

After the electrolysis process, the quality of raw PACl improved greatly (Table 2). The basicity increased from 1.2 to 2.1. The monomeric Al that was the predominant species in raw PACl transformed into polymeric Al. The content of Al<sub>b</sub> (Al<sub>13</sub>) increased from 27.4% to 58.3%. The content of active chlorine in the final product reached 569.3 mg/L. Raw PACl turned into a high quality dual functional water treatment agent. Although there was no additional aluminum source in the electrolysis process, Al<sub>T</sub> (Al<sub>2</sub>O<sub>3</sub>%) increased from 10.5% to 12.7%, possibly resulting from the concentration effect of the electrolysis process.

### 3 Conclusions

The effect of temperature, current density, and stirring rate were investigated to determine their optimum conditions on the formation of Al<sub>13</sub> and active chlorine. It has been observed that high temperature favored Al<sub>13</sub> formation. Increasing current density and stirring rate resulted in high

current efficiency of chlorine evolution, and thus favored the creation of Al<sub>13</sub> and active chlorine in PACC by electrolysis process. When the PACC (Al<sub>T</sub> = 0.5 mol/L, basicity = 2.3) was prepared at the optimum conditions, the Al<sub>13</sub> and active chlorine products reached to above 70% of Al<sub>T</sub> and 4000 mg/L, respectively. Using a pilot scale device, raw PACl as electrolyte, PACC (Al<sub>T</sub> = 12.73 Al<sub>2</sub>O<sub>3</sub>%, basicity = 2.1) was successfully prepared, and the Al<sub>b</sub> and active chlorine products reached close to 60% and 600 mg/L, respectively. The pilot scale experiment demonstrated a potential industrial approach of PACC preparation. The optimal parameters in the PACC preparation process should be selected not only considering the maximum yield of Al<sub>13</sub> species and active chlorine but also control the consumption of electric energy. Increasing current density and stirring rate will increase the product cost. It is very important to reach a balance between current efficiency and production cost in PACC preparation process.

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