Forms of Aluminium Speciation in Electrochemically Prepared Polyaluminium Chloride as Coagulant

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The Polyaluminium chloride solution, a complex, dynamic mixture of positively charged polynuclear aluminium species, is used as primary coagulant in drinking water treatment. In order to maximize the active species content and optimize the species distribution, the method of electrochemical synthesis of polyaluminium chloride (E-PAC) has been proposed and carried out extensively in our recent research.

For obtaining as much as Al_{13} polymer by electrolysis process, optimum preparation conditions was selected. The aim of this paper is to evaluate the aluminium species distribution for the laboratory scale prepared E-PAC, using two analytical methods, the time-developed Al–Ferron complex colorimetry and [27]Al nuclear magnetic resonance spectroscopy method. The combined application of this methodes provides a better approach to investigate Al species distribution in polyaluminium chloride E-PAC solutions quantitatively, helpful in obtaining later a better explanation of the coagulation mechanisms, when it will be applied in water treatment process.

1. Introduction

In the drinking water treatment process the coagulation / flocculation is a mandatory and essential step, being today, after disinfection, the most common applied treatment, which destabilizes the colloidal particles and dissolved organic substances, followed by aggregation into larger flocs. These flocs can be effectively removed later on the sedimentation and/or filtration separation process.

To achieve a efficient coagulation treatment, it is important to select the best type of coagulant and coagulation conditions, in correlation with raw water and water treatment technology applied (Tchórzewska-Cieślak, 2012). As part of advanced technologies, water companies tend to use alternative coagulants, based on prehydrolysed forms of aluminium (and iron), more effective than the traditional coagulants, as aluminium sulphate in many cases, but their mode of action is not completely understood.

Much attention has been paid in the last two decades, with increasing demand, to the Polyaluminium chloride (PAC), also known as aluminium hydroxy chloride or basic aluminium chloride, with general formula $Al_m(OH)_nCl_{3n-m}$. PAC solution is a complex, dynamic mixture of positively charged polynuclear aluminium species. However, the superior performance of pre-polymerized coagulants is strongly determined by the species present during the coagulation process (Pacala, 2010). In fact, the hydrolysis is a complex process involving, apart from the hydrolysis reactions, parallel polymerization reactions which result in a great variety of polynuclear species (Zouboulis et al., 2007). The nature and extent of polymerization is not yet fully understood. Among the possible products, the dimmer ($Al_2(OH)_2^{4+}$), trimmer ($Al_3(OH)_4^{5+}$), tridecamer ($Al_{13}-AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{6,7+}$) and more recently $Al_{30}(Al_{30}O_8(OH)_{56}(H_2O)_{24}^{18+}$) have been determined through ^{27}Al-NMR and X-Ray Diffraction studies. It is suggested that a polynuclear species with up to 54 Al atoms ($Al_{54}(OH)_{144}^{18+}$) can be also formed. The most important reaction is regarded to be the one leading to $Al(OH)_4^-$ formation, because this aluminium anionic form is claimed to be the precursor for the polymeric Al_{13} creation (Zouboulis and Tzoupanos, 2010). Al_{13} with Keggin-like structure is claimed to be the most stable aluminium species in a partially neutralized Al solution and the improved coagulation properties of PAC are thought to be due to its existence, i.e. increased charge neutralization capability (coagulation) and increased molecular size and aggregation ability (flocculation)

(Zhou et al., 2006). Moreover, the decrease of monomeric Al in favour of Al_{13} and of the other polymeric compounds eliminates the hydrolysis reactions and therefore, results in a minor impact of the pH value after treatment. In order to maximize the active species content and optimize the species distribution, the method of electrochemical synthesis of PAC has been proposed and carried out extensively. In our recent research, the electrochemically PAC (E-PAC) was successfully generated in a electrochemical reactor, using three sheets of aluminium as anode, three sheets of stainless steel as chatodes, disposed in a mono-polar arrangement and $AlCl_3$ aqueous solution as electrolyte. For obtaining as much as Al_{13} polymer by electrolysis process, optimum preparation conditions was selected and process was carried out in galvanostatic conditions at high electric current densities (i = 1.15 Adm^{-2}). The aforementioned techniques were applied only in laboratory scale experiments and have not been evaluated the role of their physical properties, especially the content of active species, the stability of the active species, remains unclear, with particular importance in the behaviour and efficiency of E-PAC as coagulant.

Many analytical instruments and experimental methods, such as potential titration, ^{27}Al nuclear magnetic resonance (NMR), X-ray powder diffraction (XRD), small angle X-ray diffraction and scattering, infrared and Raman spectroscopy, laser light scattering, electron microscopy, atomic force microscopy, Al-Ferron colorimetry and other wet chemical methods, have been employed in the study of Al speciation and the structural characterization of Al species. In spite of a great deal of literature, the chemistry composition in hydrolyzed Al solutions is not completely determined yet due to the complexity of the solutions (Chen et al., 2007). ^{27}Al NMR is an powerful method to describe chemical speciation distribution directly, which can measure quantitatively the chemical speciation in hydrolyzed aluminium solutions, including mononuclear (Al_m), oligomers (Al_2 even Al_3) and tridecamer Al_{13} Keggin, Al_{30} Keggin. As a limitation of ^{27}Al NMR are mentioned in the literature the difficulty to detect larger Al polymers, which may participate in coagulation, or that the Al_{13} cannot be detected in solutions of low Al concentration (<0.1 M), or low polynuclear species content (<30 %) (Wang and Su, 1994). All of these species can only be referred to the undetectable Al species (Al_{un}) in ^{27}Al NMR spectroscopy.

Based on the kinetic difference of the reactions between Ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid) with different hydrolyzed species, the speciation of Al solutions can be studied by the Ferron method, a timed colorimetric reaction. Mononuclear Al species (Al_a) react almost instantaneously and polynuclear species (Al_b) much more slowly. Colloidal or precipitated Al (Al_c) shows practically no reaction with ferron (Duan and Gregory, 2003).

In the present research, the aluminium species distribution in laboratory prepared E-PAC coagulant by an electrochemical process were quantitatively studied using high field ^{27}Al NMR spectroscopy and the time-developed Al-Ferron complex colorimetry. At the same time, if the quantities determinated are approximately equal, the ferron method offers a simple and inexpensive alternative to ^{27}Al-NMR analyses for identification and quantification especially for Al_{13} and Al_{30} species with Keggin structure distribution in electrochemically prepared polyaluminium chloride E-PAC solutions.

2. Materials and methods

In this study all chemical reagents used were analytically pure chemicals. Deionized water with conductivity lower than 0.5 µS/cm was used to prepare all solutions.

2.1 Electrochemical preparation of E-PAC

The electrochemically PAC (E-PAC) was successfully prepared by electrolysis process, in a electrochemical reactor (ECR) with aluminium as anodes, stainless steel as cathodes and $AlCl_3$ aqueous solution as the electrolyte (Pacala, 2010). It consisted on a D.C. Power Supply (HY 3000D, China), an electrolyzer made out of organic glass (rectangular size 76 x 51 x 70mm) equipped with 6 parallel plain-plate electrodes, 3 anodes and 3 cathodes disposed in a mono-polar arrangement with 10 mm anode-cathode distance. Three sheets of Al (95 x 50 mm) were used as anodes while the cathodes were three sheets of stainless steel plates (95 x 50 mm) (Pacala et al., 2009). The system is completed by the electrolyte (200 mL aqueous solution $AlCl_3$ 0.5M) and stirring apparatus (IKA, Germany), with degree of agitation selected of 600 rpm. An ammeter and a voltmeter were used for electrical characteristics control. Electrolysis was carried out in galvanostatic conditions at optimum conditions selected, respectively current density of 1.15 A dm^{-2} and electrolysis time of 2 hours.

A schematic view of ECR, the detailed coagulant E-PAC preparation and characterization methods can be found in our previous reports (Pacala et al., 2012).

2.2 Preparation of the simplified ferron colorimetric solution

Reagent A (0.2 %, w/v, ferron): under rapid stirring, 2 g ferron (8-hydroxy-7-iodo-quinoline-5-sulfonic acid, Sigma Chemical Co., U.S.A) was dissolved in deionized water (pre-boiled to remove dissolved CO_2), and then diluted to 1000 mL.

Reagent B (20 %, w/v, NaAc): 200 g sodium acetate (Chemopar, RO) was dissolved in 1000 mL of deionized water. Reagent C (1:9, v/v, HCl): 100 mL hydrochloric acid (37 %, Merck, Germany) was mixed with 900 mL of deionized water.

Each individual reagent mentioned above was filtered through pre-washed 0.45 µm membranes. The ferron colorimetric solution was obtained by mixing the above reagents A, B and C at a ratio of 2.5:2:1. The latter two were mixed prior to the addition of ferron. After preparation, the colorimetric solution was stored in refrigerator for later use.

2.3 Aluminium speciation using simplified ferron colorimetric solution

The total aluminium content (Al_T) of E-PAC solution synthesized (Al %w/w) were analyzed according to the methodology described by European standard EN (SR EN 1302, 2000) (Pacala et al., 2012). Aluminium species distribution was determined with the application of Al-ferron timed spectrophotometric method, which is based on the different reaction time of aluminium species with ferron reagent to form water soluble complexes at pH 5-5.2. These complexes absorb light with maximum at 364 nm, hence absorbance measurements at this wavelength allow the calculation of different species of aluminium. Specifically, absorbance increase were monitored for 120 min such that three fractions could be operationally defined: Al_a, Al_b, and Al_c, corresponding to monomeric species, medium polymer species and larger polymer species and/or solid phase $Al(OH)_3$, respectively. Monomeric Al_a reacted almost simultaneously (within 1 min) with ferron, while the intermediate polymeric species of aluminium reacted slower, i.e. at 120 min., represented (Al_a+ Al_b) and then three-dimensional species or sol-gel (Al_c) was obtained by Al_T minus (Al_a + Al_b).

The operation procedures are as follows: 20 µL test Al solutions and 5.5 mL ferron colorimetric solutions were transferred into a graduated glass tube; then diluted to 25 ml and homogeneous mixing. The reacting sample was quickly added to a 1-cm quartz cell, to avoid any unnecessary delay. The absorbance of the mixture were monitored automatically at 364 nm, from 60 s to cca 2 h until no detectable absorbance increase was observed. An UV–VIS spectrophotometer (T90+, PG Instruments Ltd) was used for this purpose. The reagents preparation and procedures of the colorimetric method can by found in reference (Parker, 1992).

2.4 ^{27}Al NMR spectroscopy

^{27}Al NMR spectroscopy was used to characterize the Al species in E-PAC solutions. More detailed instrumental parameters and methods for the quantities of ^{27}Al NMR determinations are found elsewhere (Qu and Liu, 2004). The intensities for [27]Al signals relative to the aluminate reference were used for calculating the Al concentrations corresponding signals. It has been generally accepted that for the Al_{13} complex, only the tetrahedrally coordinated Al at the center of the structure yields the signal at 63 ppm (Hu et al., 2005). The ^{27}Al-NMR spectra have been recorded at 104 MHz, on a Bruker Avance III 400 spectrometer, Germany, using a 10 mm direct detection broad band probehead. The instrumental settings and experimental conditions were: NS = 127, P1 = 20µs, solvent: D_2O and T = 298 K.

3. Results and discussion

A clear picture of the coagulation process has been limited by the complexity and diversity of natural organic matter (NOM) in natural water and aqueous coagulant Al species. There are still some uncertainties regarding the nature of the aqueous chemistry of metal coagulant, the polymer type (preformed and in-situ formed), and the effectiveness of particle size of hydrolyzed species, beyond the charge density parameters, for their application (Yan et al., 2008). Conventional ^{27}Al NMR spectroscopy in combination with time-developed Al–Ferron complex colorimetry improved with kinetic resolution can better explore the chemical speciation for hydroxyl-Al polymers in polyaluminium chloride as coagulant (Zhou et al., 2006).

The study objective is to evaluate for the laboratory prepared E-PAC by electrolysis process (in optimum preparation conditions selected, before mentioned) the aluminium species distribution, by the Ferron assay and by high-field [27]Al nuclear magnetic resonance (NMR) spectroscopy method. Al species in the electrolyte were analyzed at the end of the electrolytic process.

3.1 Aluminium speciation in electrochemically prepared polyaluminium chloride evaluated by Ferron assay

In this study, a ferron assay was carried out for the quantitative analysis of the Al species in E-PAC. On the basis of the kinetics of the reaction between Al species and the ferron reagent, the hydrolyzed Al

species be categorized into three types: monomeric Al (Al_a), polymeric Al (Al_b) and colloidal Al (Al_c). The reaction kinetics of ferron with hydroxy-Al solutions are shown in Figure 1. The common characteristics of the kinetic curves can be seen: an initial rapid absorbance increase followed by a gradual increase, and then ending in a plateau. The initial absorbance increase is believed to be associated with the reaction of ferron with mononuclear Al species, and the following gradual increasing phases are related to reactions of ferron with various hydroxy-Al polymers. When all of the Al species mentioned above react completely with ferron, the kinetic curve of Al-ferron interaction would reach the plateau.
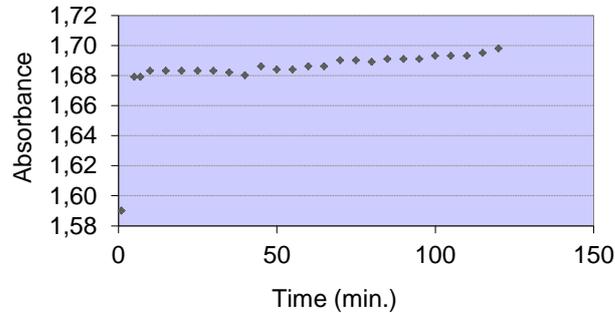
Figure 1: Al-Ferron reaction kinetics in E-PAC solution

Essentially, the colorimetric assay can only give indirect information about the speciation of hydroxy-Al solutions. The quantification of specific species depends on the interpretation of the reaction kinetics data. The Al species were quantified by the timed absorbances recorded at 364 nm (Figure 2). The absorbance recorded in the first minute and that recorded between 1 min and 2 h were assigned to Al_a and Al_b, respectively. The absorbance due to Al_c was obtained by subtracting the absorbances of Al_a and Al_b from the total absorbance.
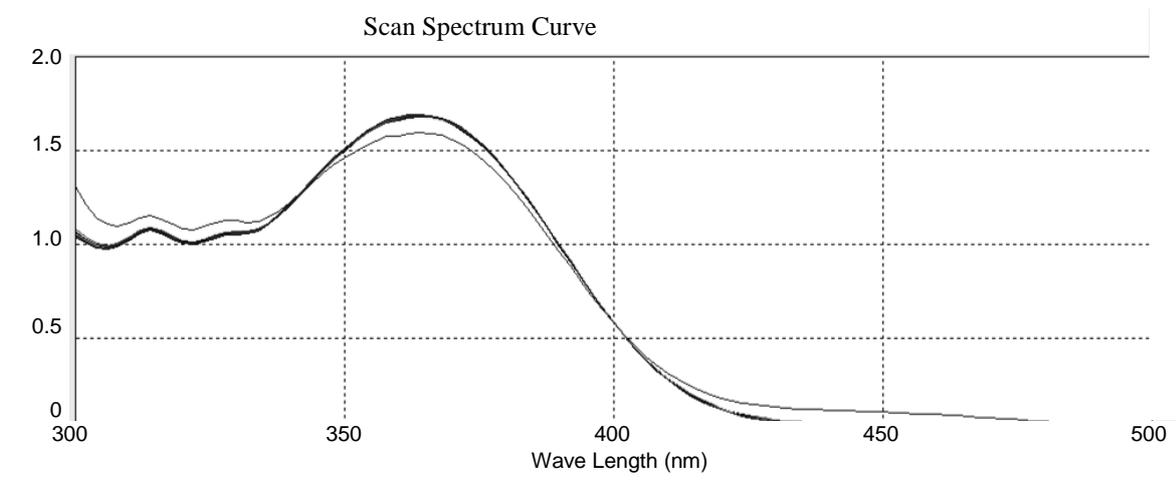
Figure 2: Absorbance spectra of Al-ferron complexes at different wavelength (300-500 nm), absorbance value detected in 2h in E-PAC solution

Effect of reaction duration adoption protocols on the speciation of hydroxyl-Al solutions

As mentioned above, many researchers calculate the content of Al species Al_a, Al_b and Al_c according to the absorbance value at 1 min and 2 h. This method is usually called Al-Ferron complexation timed spectrophotometry. But monomeric Al does not always react with Ferron reagent within 1 min, nor do Al_b species necessarily react in 2 h. Small variations in reaction time of Al_a - Ferron or Al_b - Ferron may lead to errors in Al_a, Al_b and Al_c calculations. This error cannot be avoided or modified by improving experimental technique. This flaw of the method calls for the development of another calculation method for Al species. Many researchers consider the complexation reactions of mononuclear-Al species in colorimetric test with Ferron could be completed immediately after mixing (Wang and Su, 1994). However, from experimental data obtained, the reactions takes 3

- 5 min for all species mononuclear-Al for the E-PAC solution analyzed. Thus, with the interpretation of the Ferron assay for E-PAC solution analyzed, obtained content of Al_b species represent 16.79 %.

3.2 Aluminium speciation in electrochemically prepared polyaluminium chloride evaluated by ^{27}Al NMR spectroscopy

^{27}Al NMR is the most powerful and exclusive way to describe Al speciation directly, which can measure the content of Al species quantificationally (Chen et al., 2007). There are six signals in the typical ^{27}Al NMR spectra. Two peaks are generally observed at 0 and 4 ppm. The chemical shift at 0 ppm is assigned to the monomeric form of aluminiu (Al_m) including $[Al(H_2O)_3]^{3+}$, $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$ (Yan et al., 2008). A low intensity broad peak at cca 4 ppm is assigned to Al oligomeric dimers or trimers. The resonance signals at $\delta = 80$ ppm are assigned to $NaAl(OH)_4$, respectively. The resonance peaks at $\delta = 62.5$–63.0 ppm and 70 ppm (broad peak) are attributed to central tetrahedral Al in Al_{13} and Al_{30}, respectively. The broad peak at $\delta = 10$–12 ppm is corresponded to octahedral Al of Keggin external shells in Al_{13} and Al_{30} with Keggin structure. Due to the overlapping of the peaks at $\delta = 4$ ppm and 10–12 ppm, areas of these peaks cannot be accurately integrated. In addition, there exist other polymeric Al species in hydrolytic polyaluminum solution which cannot be identified using current high-field ^{27}Al NMR, and these are undetected (Al_u). The concentration of Al_u was calculated by Al_T minus Al_m and Al_{13}.

Figure 3 shows ^{27}Al NMR spectra obtained for the same E-PAC solution previously analyzed by the Ferron technique. For each peak in ^{27}Al NMR spectroscopy correspond a specific species, as mentioned above, the integrated peak area of them corresponding with the quantitative distribution of the species.
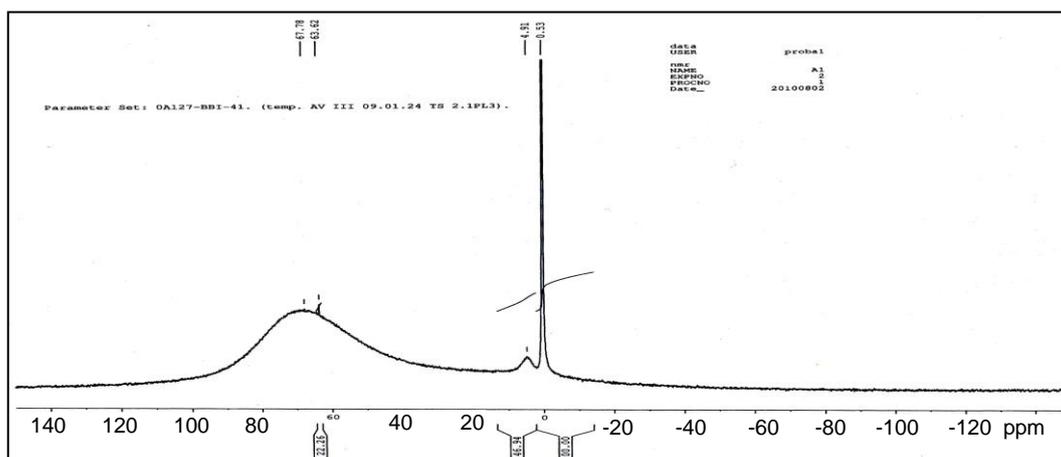
Figure 3: ^{27}Al RMN – E-PAC solution ($Al_T = 22.27$ gAl/L)

This ^{27}Al NMR spectra represent quantitative determination of monomeric and dimers aluminium species (Al_m) in the E-PAC solution, 46.94 % respectively and the resonance of 63 ppm (range 63.67-67.78 ppm) represent quantitative determination of polymer Al_{13} in solution, 22.26 % respectively. The difference between $[Al_m + Al_{13}]$ represent the undetectable species (Al_u, or the larger species of polymer and/or a solid phase $Al(OH)_3$) and this concentration is 30.8 %, from total aluminium content (Al_T).

3.3 General discussion

Therefore, using the Ferron method to determine the Al species distribution for the laboratory prepared E-PAC solution by electrolysis process, may introduce errors when monomeric and polynuclear Al (Al_a and Al_b) do not react with Ferron reagent within 1 min and 2 h, respectively. Kinetics curves provide a more accurate method of identifying the Al speciation and include information about all phases of the Al-Ferron reaction. With help of the [27]Al spectroscopic measurements, the monomeric and Al_{13} polymer concentrations can be established directly. But the small polymer, the larger polymeric components including colloidal precipitate and other precipitated Al phases which are derived from the conventional Al_c fraction of the ferron assay, are not observable by the ^{27}Al NMR method. On the other hand, because some signals are very broad, the concentrations calculated from NMR spectra are semiquantitative.

For the E-PAC solution analysed, by comparing obtained results with the Ferron method and with the NMR technique, we obtained a difference of only approx. 6 % for the Al_b species (planar oligomeric medium polymeric species) content. The Ferron method applied provide a rapid and inexpensive alternative to [27]Al-

NMR analysis, which has previously been viewed as the only unequivocal method of detection, and may thus prove useful in water treatment applications.

4. Conclusions

The following conclusions can be drawn:

(1) The electrolytic method can provide the best conditions to generate more Al_{13} and get the E-PAC which contains the highest Al_{13} content. The E-PAC preparation by electrolysis is a simple process and easily controlled.

(2) The empirical approaches to the speciation of hydroxy-Al in E-PAC solutions using the simplified ferron colorimetric solution were investigated. Theoretically, the kinetic curve of ferron with hydroxyl-Al solutions can be divided into different phases according to the evolution of reaction rates, and each phase can be assigned to certain specific Al species. Due to the limitations of actual operation, it is hard to distinguish the reaction end times of mononuclear and oligomeric Al species.

(3) Through ^{27}Al NMR analysis, the aluminum species distribution in electrochemically prepared polyaluminium chloride as coagulant can be well described.

(4) For the E-PAC solution analyzed, our results of ^{27}Al NMR method almost corresponded with that of the ferron method for the Al_b species (planar oligomeric medium polymeric species) content. Therefore, we suggest that Al_b could be used to represent the Al_{13} content indirectly.

Thus the combined application of Ferron assay with NMR spectroscopy provides a better approach to investigate Al species distribution in polyaluminium chloride E-PAC solutions quantitatively, especially for Al_{13} and Al_{30} species with Keggin structure, helpful in obtaining later a better explanation of the coagulation mechanisms when it will be applied in the water treatment process. However, more detailed information about the aluminium speciation in the E-PAC solutions needs further studies using more sophisticated analytical methods in the future.

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