

## COAGULATION CHARACTERISTICS OF ELECTROCHEMICALLY PREPARED POLYALUMINIUM CHLORIDE ON HUMIC ACID REMOVAL FROM WATER

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### ABSTRACT

The treatment of surface natural water for drinking water production goes through the degradation of humic substances. The increasing demand of more efficient coagulation water treatment, especially regarding the removal of natural organic matter (NOM), has led to the development of a new category of coagulants, the pre-polymerised inorganic coagulants, such as polyaluminium chloride (PAC). An alternative preparation procedure for PAC (pre-hydrolyzed aluminium chloride with general formula  $Al_m(OH)_nCl_{3n-m}$ ) is presented in this paper. Using the principles of coagulant preparation and of the electrolysis process, the proposed procedure is based on the use of a new method for the preparation of electrochemically obtained PAC (E-PAC) in an electrochemical reactor, equipped with plain-plate Al anodes and stainless steel cathodes, and  $AlCl_3$  aqueous solution as electrolyte, applied successfully in our laboratory. Coagulation behaviors of E-PAC and conventional coagulants as alum and commercial product PAC were compared, using the so-called „Jar test” procedure, in accordance with water treatment standards, to remove humic acid (HA) from deionized water with addition of 1mg/L of humic acid (commercial HA powder), selected for this study, due to the fact that it is a principal component of humic substances, which are typically the major component of NOM in water supplies. As part of the applied procedures, the level of residual turbidity, the amount of total organic carbon, the UV-254 absorbance and colour were evaluated, in order to assess the efficiency of the coagulation process in all situations (PAC, E-PAC and alum as coagulants). The results suggest that the electrochemically obtained E-PAC can be alternatively produced by electrolysis process easily controlled, resulting a product with better properties than the commercial PAC used for comparison to remove humic acid from synthetic water.

Keywords: Coagulation, Drinking water treatment, Electrochemical Polyaluminiumchloride (E-PAC), Humic acid

### 1. INTRODUCTION

The coagulation process typically includes promoting the interaction of particles to form larger aggregates. It is an essential component of conventional water treatment systems in which the processes of coagulation, sedimentation, filtration, and disinfection are combined to clarify the water for removal of natural organic material (NOM) and to remove and inactivate microbiological contaminants.

Optimizing natural organic matter (NOM) removal by coagulation is a crucial challenge in drinking water treatment. Indeed, the organic material remaining within the clarified water is involved in most problems encountered in the treatment process, such as

formation of carcinogenic chlorinated organic compounds during disinfection, taste and odor of the finished water, and biological regrowth in the distribution networks [2].

NOM consists of a huge variety of organic compounds including simple sugars, amino acids, organic acids, proteins and many others. In most cases, the so-called 'humic substances' are major components of aquatic NOM. They are classified according to their aqueous solubility, with fulvic acids being more soluble than humic acids [1].

It has long been known that humic substances can be effectively removed from water by hydrolysing coagulants and there have been many studies on this subject [1,2,3,6,7]. Enhanced coagulation has been proposed as the best available technology for NOM removal, and the regulation for percentage removal of NOM expressed in total organic carbon (TOC) was set up based on raw water quality.

The most common coagulant used in water treatment is alum  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-H}_2\text{O}$ , due to its effectiveness in treating a wide range of water types and relatively low cost. The use of preformed polymerized forms of Al has become more common as alternative coagulants, with polyaluminum chloride (PAC). These coagulants have the advantage of being more effective at lower temperatures and a broader pH range than alum. PAC contains stable preformed aluminum species that are thought to be more effective at charge neutralization than alum due to a higher charge density. The primary polymeric species is the tridecameric polymer  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})^{7+}$  referred to as the  $\text{Al}_{13}$  polymer [3].

At present, the commercial PAC solutions contain relative low content of  $\text{Al}_{13}$  (<50%) and there are still some limitations for other preparation methods to increase the  $\text{Al}_{13}$  content at high basicity [8].

In this paper, a new method for producing polyaluminium chloride PAC-electrolysis process (E-PAC) is applied, using the principle of coagulant preparation and of the electrolysis process [4,5,6]. Particularly, the purpose was to synthesize a product with similar properties to commercially available PAC. The aim of this work is to characterize the E-PAC prepared in optimum conditions in our laboratory by electrolysis process [6]. Its coagulation performance was evaluated in laboratory scale, using the so-called „Jar test" procedure, in accordance with water treatments standards, to remove humic acid (HA) from deionized water with addition of 1mg/L of humic acid (commercial HA powder), selected for this study due to the fact that is a principal component of humic substances, which are typically the major component of NOM in water supplies. Since we aim in particular to improve the treatment of Bega River as raw water source for potable utility of Timisoara town (Romania), we compared E-PAC with the performance of a commercially available PAC solution and classical aluminium sulphate (alum).

## 2. MATERIALS AND METHODS

### 2.1. Coagulants and water samples

All chemical reagents used were analytically pure chemicals. Deionized water with conductivity 2.54  $\mu\text{S}/\text{cm}$  was used in preparing all the solutions. For comparison purposes, commercially available PAC (8.8 %  $\text{Al}_2\text{O}_3$ , basicity 65, density 1.22  $\text{kg}/\text{dm}^3$ ) was a Donau Chemie product (Austria). Alum stock solution was prepared from liquid aluminium sulphate (approximately 7.5% as  $\text{Al}_2\text{O}_3$ ) obtained from a local Bega water treatment plant.

The synthetic model water consisted of a stock HA solution prepared by adding commercial Humic acid powder (HA, Agros Organics Company, Germany), used as the model organic matter, into deionized water. After that, this stock solution was stirred for 5 min., at 300 rpm and filtered for removing residual non-dissolved HA powder.

### 2.2. Electrochemical preparation of E-PAC

The electrochemical reactor (ECR) for E-PAC preparation [4,5] 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). The system is completed by the electrolyte (200ml aqueous solution  $\text{AlCl}_3$  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 from our previous studies, respectively current density of  $1.15 \text{ A dm}^{-2}$ , electrolysis time of 2 hours, current intensity of 1.5 A [6].

### 2.3. Experimental and analytical methods

Coagulation experiments were carried out at room temperature using jar test on a six-paddle gang stirrer, equipment manufactured by Velp Scientifica (Model FC6S, Italy). The 800mL working HA solution was added into the 1000mL beaker. A measured amount of coagulant was added by a calibrated pipette (Multipette stream Electronic hand dispenser, Eppendorf, Germany) into the working HA solution under rapid stirring. The HA solution was stirred rapidly at 150 rpm for 2 min after coagulant dosing, followed by slow stirring at 45 rpm for 15 min, which compares to current plant conditions at the Timisoara Waterworks. For 30 min after settling, supernatants were collected to measure residual turbidity using a Turbidimeter (HACH 2100N, USA). Total organic carbon (TOC) was analyzed after filtration through a 0.45  $\mu\text{m}$  membrane and were determined using a TOC Analyzer (TOC-V CPH, SHIMADZU, Germany). pH and conductivity were determined on a laboratory multi-parameter analyser (Consort C863, Consort, Belgium). Colour in Hazen units was measuring using a photometer SQ 118 Merck (Germany). The absorbance at 254 nm (due to the Natural Organic Matter/NOM content) was measured with a Spectrofotometru UV-VIS (UV-VIZ T90+, PG Instruments Ltd, SUA), using a 1 cm path length quartz cuvette.

## 3. RESULTS AND DISCUSSION

The coagulation behavior of the electrochemical PAC, obtained in our laboratory, conventionally named electrochemical - PAC (E-PAC), was evaluated in the (model) humic sample (with relatively low HA concentration level as 1mgHA/L), simulating contaminated surface water (see the previous §2.1) and compared with the coagulation behavior of a commercial PAC and with the traditionally applied coagulant aluminum sulphate ("alum"), used today in Bega water treatment process. The applied coagulant doses were the same 1mg Al/L, for all three coagulants compared.

Table 1 demonstrates the coagulation performance of all three coagulants. Removal of residual turbidity, conductivity and colour, the variation of pH, absorbance at 254 nm, TOC and NPOC of the suspensions after the addition of coagulant are presented.

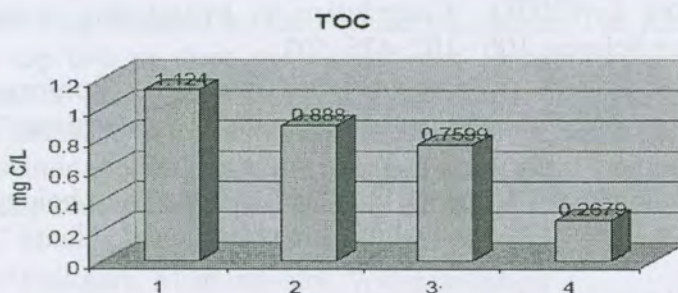
The mechanisms to explain the coagulation of humic substances include charge neutralization, precipitation, bridge-aggregation, adsorption and sweep-flocculation [7].

For turbidity removal, polymer bridging plays an important role, which is facilitated by high molecular weight polymers with relatively low charge density. For NOM removal, charge neutralization plays a dominant role.

**Table 1.** Water quality parameters of raw water and treated water with aluminium sulphate, PAC and E-PAC

| PARAMETER,<br>UNIT      | RAW<br>WATER | ALUMINIUM<br>SULFATE | PAC   | E - PAC |
|-------------------------|--------------|----------------------|-------|---------|
| Turbidity, NTU          | 2.08         | 1.29                 | 1.11  | 1.10    |
| pH                      | 5.26         | 4.96                 | 5.42  | 4.99    |
| TOC, mgC/L              | 1.124        | 0.888                | 0.759 | 0.268   |
| Colour, °Hazen          | 8            | 6                    | 7     | 6       |
| UV-254, m <sup>-1</sup> | 0.046        | 0.027                | 0.038 | 0.041   |
| Conductivity, µS/cm     | 8.77         | 24.6                 | 20    | 61.3    |

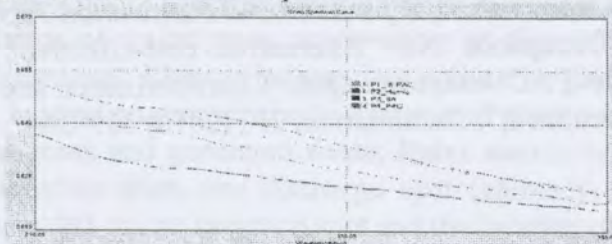
Generally, aqueous NOM is negatively charged and the coagulant demand for neutralizing the negative charge is much higher than the one for neutralizing the charge of mineral particles [4,5].

**Figure 1.** TOC results of raw water and treated water(1) with aluminium sulphate(2), PAC(3) and E-PAC(4).

Therefore, E-PAC proved to be the most efficient coagulant in terms of TOC and turbidity removal (Fig.1) on humic acid from synthetic water.

Scan Spectrum Curve for domain 200-350 nm wavelength have been rendered with UV-254 nm absorbency, as shown in Fig.2.

E-PAC seems to exhibit better coagulation performance than PAC and alum, especially in very low coagulant dose (e.g. 1 mg Al/L).The superiority of E-PAC can be attributed to the higher Al<sub>13</sub> content, than the respective values of PAC.

**Figure 2.** UV absorbency spectrum curve

This is an indication of higher coagulant charge, resulting in more effective charge neutralization, colloids destabilization and consequently, in better coagulation performance.

#### 4. CONCLUSIONS

- ▶ The results suggest that the electrochemically obtained E-PAC can be alternatively produced by electrolysis process easily controlled.
- ▶ Due to their improved properties, E-PAC show superior coagulation performance than the commercial PAC used for comparison, when applied for the treatment on humic acid removal from synthetic water.
- ▶ Our study suggests that the functional groups involved in the aggregation of humic substances change with the positively charged coagulants species.
- ▶ Optimum data regarding residual turbidity and concentration of organics compounds (TOC) were obtained when E-PAC has been utilized as coagulant.
- ▶ It can be estimated that the electrochemical production of polyaluminium chloride might be developed at a larger scale, to be used in surface water treatment for potabilization, but more research efforts can be devoted to this purpose.

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