AMMONIUM ION REMOVAL FROM WATER BY COAGULATION USING AN ELECTROCHEMICALLY PREPARED POLYALUMINIUM CHLORIDE

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Abstract
As part of advanced technologies, water companies tend to use the most effective coagulants, which will produce higher quality for the final treated waters and greater reliability. Alum and prehydrolyzed aluminium chloride with general formula $Al_m(OH)_nCl_{3n-m}$ (PAC) have been widely applied as coagulants in water treatment technologies. Their hydroxyl aluminium polymers were recognized as the most effective components in Al coagulants.
Using the principles of coagulant preparation and of the electrolysis process, the method of electrochemical synthesis of the Polyaluminium chloride (E-PAC) has been proposed and carried out extensively in our previous research.
In this study the coagulation properties of electrochemically obtained PAC (E-PAC) on ammonium ion removal from water was evaluated in laboratory scale and it was compared with the performance of a commercially available PAC solution and classical aluminium sulphate (alum).

Introduction
Nitrogen is an essential element for life and undergoes many chemical and biochemical processes in water. It appears mainly as ammonium, nitrite, nitrate, gaseous nitrogen and fixed in organic compounds, groups between which there are continuous transformations / transits, forming the "nitrogen cycle".
The excess leads to eutrophication, contamination of aquifers, possible damage to human health: methemoglobinemia in children, gastric cancer, etc. The presence of ammonium ion in the composition of a surface water indicates a degree of its pollution.
Ammonium sources in waters are natural and anthropogenic. These "natural" sources are often indirectly also anthropogenic. "Direct" anthropogenic sources are pointful (wastewater discharges containing ammonium) and diffuse, mainly nitrogen compounds from agriculture, chemical fertilizers, and natural fertilizers.
The removal of nitrogen compounds from drinking water is expensive and complicated. Chemical (ion exchangers) and biochemical techniques have been experimented, mixing contaminated waters with others with a lower concentration of ammonium/nitrogens[1,2] .
Here are some aspects that were the basis for choosing the ammonium ion introduced as ammonium nitrate as a pollutant in a synthetic water in order to compare the efficiency of removing this type of pollutant through the coagulation-flocculation process with aluminum sulfate (alum), polyaluminium chloride (PAC) and a new electrochemically prepared polyaluminium chloride (E-PAC).

Experimental

Coagulants and water samples

For comparison purposes, commercially available PAC (8.8 % Al_2O_3, basicity 65, density 1.22 kg/dm^3) was a a Donau Chemie product (Austria). Alum stock solution was prepared from liquid aluminium sulphate (approximately 7.5% as Al_2O_3) obtained from a local Bega water treatment plant.

The synthetic model water consisted of a stock ammonium nitrate (NN) solution prepared by adding commercial ammonium nitrate powder (NN, Merck Company, Germany) into deionized water. After that, this stock solution was stirred for 5 min., at 300 rpm.

Electrochemical preparation of E-PAC

The electrochemical reactor (ECR) for E-PAC preparation [3,4] 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 (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 from our previous studies, respectively current density of 1.15 A dm-2, electrolysis time of 2 hours, current intensity of 1.5 A [5].

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 NN solution was added into the1000mL beaker. A measured amount of coagulant was added by a calibrated pipette (Multipette stream Electronic hand dispenser, Eppendorf, Germany) into the working NN solution under rapid stirring. The NN 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 mm 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 Spectrofotometer UV-VIS (UV-VIZ T90+, PG Instruments Ltd, SUA), using a 1 cm path length quartz cuvette.

Results and discussion

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 the introduced ammonium ion as ammonium nitrate from deionized water with addition of 10 mg/L of ammonium nitrate (commercial NN powder), selected for this study. The applied coagulant doses were the same 1 mg Al/L, for all three coagulants compared.

As part of the applied procedures, the level of residual turbidity, the amount of total organic carbon, the UV 254 absorbance and color were evaluated, in order to assess the efficiency of the coagulation process in all situations (E-PAC and alum as coagulants). Table 1 demonstrates the coagulation performance of all three coagulants.

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

| PARAMETER, **UNIT**	RAW WATER	ALUMINIUM SULFATE	PAC	E - PAC
Turbidity, NTU	0.697	0.540	0.605	0.412
pH	6.51	5.05	5.25	6.13
Temperature, °C	20	20	20	20
NH_4^+, mg/L	1.67	1.57	1.5	1.23
Colour, °Hazen	12	9	10	5
UV-254, m^{-1}	0.180	0.155	0.158	0.118
Conductivity, µS/cm	25.5	29.0	24.3	29.0

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

Figure 1. TOC results of raw water and treated water (1) with aluminium sulphate (2), PAC (3) and E-PAC (4).
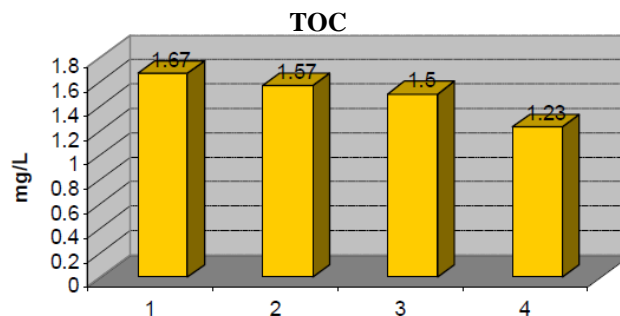
Scan Spectrum Curve for domaine 200-350 nm wavelength have been rendered with UV-254 nm absorbency, as shown in Figure 2.

Figure 2. UV absorbency spectrum curve
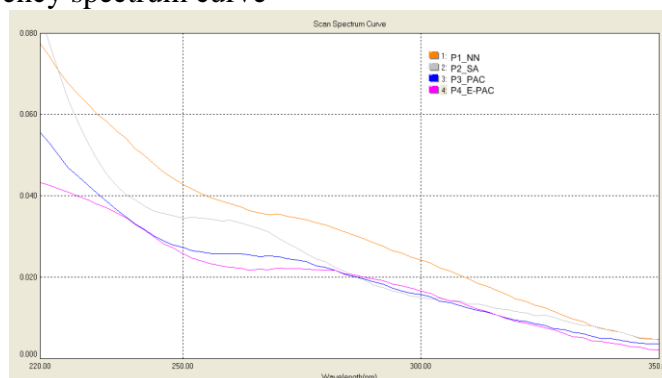
E-PAC seems to exhibit better coagulation performance than PAC and alum, especially in high coagulant dose (e.g. 10 mg Al/L). The superiority of E-PAC can be attributed to the higher Al_{13} content, than the respective values of PAC.

Conclusion

The results suggest that the electrochemically obtained E-PAC through a easily controlled electrolysis process, is a product with better properties than the commercial PAC used for comparison to remove the introduced ammonium ion as ammonium nitrate from synthetic water.

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