Simultaneous Reduction of Turbidity and Natural Organic Matter by Simple and Prehydrolyzed Aluminium Salts

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The study comparatively shows the efficiencies of the coagulation stage from the process of obtaining drinking water, performed with two types of coagulation agents, a simple aluminium salt and a prepolymerized compound, alkaline aluminium polychloride (PACl). The use of aluminium prepolymerized compounds led to improvement of the natural organic matter removal under conditions of similar coagulant dose, aluminium sulphate (Alum), mainly in surface waters characterized by turbidity and high ratio of dissolved organic matter.

Key words: basic aluminium polychloride, natural organic matter, coagulation, SUVA254 operational parameter

In general, coagulation is a process used to obtain drinking water referring especially to colour, taste and smell reduction and to the destabilizing of the suspended particles, that is the turbidity in the treated water [1-4]. A series of recent studies show the importance of the natural organic matter (NOM) composition and concentration from the water source on the efficiency of the treatment process and drinking water quality, respectively [5-7] and the importance of the chemistry of coagulants in the water to be treated [8-12].

Water source characteristics depend on the source of the natural organic matter (allochthonous or authochthonous sources), and also on the hydroclimatic conditions, such as during the drought season surface waters have a reduced load for turbidity, TOC (Total organic carbon) and DOC (Dissolved organic carbon – sample filtered through a 0.54 micron filter). Weather change during summer, characterized through torrential rains, rapidly modifies the water characteristics both as turbidity and TOC and DOC, respectively. Natural turbidity presence exercises in most cases augmenting effects on the coagulation process efficiency both for TOC and DOC reduction as well as for turbidity itself, but in some instances, it can have a reversed effect, hindering particles to aggregate [13, 14]. NOM influence the coagulation process through composition and concentration [14, 15]. From the SUVA operational parameter, determined for supplies water with the ratio A254/DOC, an estimation of the classic agent coagulation process efficiency can be made [16, 17]. For a better monitoring of the NOM throughout the technological process, the global parameters A254, A270, A365, A436, A664 are used, representing the absorbance of the organic compounds at wavelengths of 254, 270, 365, 436, 664 nm [16-19]. The coagulation process is an essential step in the water treatment, and, if well done, it contributes to solid, fine and colloidal suspension separation processes, together with NOM removal. The expected advantages are:reduction of the formation potential of the secondary disinfection products, reduction of the residual aluminium quantity in the treated water, advantageous prices for the whole water treatment process [1, 15-20].

An ineffective coagulation will determine flocculation phenomena and depositions in the distribution system and residual turbidity at the consumer [21, 22].

Prehydrolyzed metallic salt based coagulant use, such as polyaluminium chloride (PACl), determined the involvement in the coagulation processes of some species with augmented coagulation capacity, of the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$ (noted Al_{13}) type, as the main hydrolysis agent in solutions with alkalinity higher than 75 % [23-26].

The present paper proposes a comparative study over the coagulation process efficiency for two specific cases, the water type corresponding to a winter period characterized by low temperatures and abundant rains for long periods of times and snow thawing around the spring areas, and the type of water corresponding to a freezing period. The coagulation agents used are simple aluminium salts, aluminium sulphate and polyaluminium chloride with an alkalinity of 80%. This study referred to the comparison of the removal degree of the dissolved natural organic matter and of the fine and colloidal impurities from the supplies water using the two coagulant agents. In addition, the mechanistic aspects of the action of the two coagulants were discussed.

Experimental part

Materials

Two different water source types, selected to represent some of the common general types of winter water sources, sampled from Bega River surface water, Timisoara, were used for these treatment experiments.

Type 1- Two water samples (Water 1 and Water 2) were sampled between 10-18 January 2010, characterised by high turbidity and TOC, and SUVA254 = 2 - 4 $Lm^{-1}mg^{-1}$

Type 2 -One water sample (Water 3) was collected on February 2010, with low turbidity and TOC, and SUVA254 < 2 $Lm^{-1}mg^{-1}$.

Guidelines on the SUVA values and expected DOC removal present for water sources characterized by SUVA value maximum 2, the little effect of the coagulant dose for dissolved organic matter removal, (expected max. 25% DOC removal). For this water type, the NOM consisted of mostly non-humics hydrophobic and hydrophilic, with low hydrophobicity and low molecular weight [16, 17].

For water sources with SUVA254 = 2 - 4 $Lm^{-1}mg^{-1}$, the NOM consisted of mixture of hydrophobic and hydrophylic compounds and mixture molecular weights. The required coagulant dose increases with increasing NOM concentration and the effect expected is DOC removal of 25-50 % [16, 17].

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The coagulant agents used are alum $Al_2(SO_4)_3*18H_2O$ reagent provided by Chimopar Bucuresti, coagulant solution concentration of 1 mgAl/mL, and polyaluminium chloride that is characterized by r= 2,4. They are obtained by controlled reaction of aluminium salts with base under carefully controlled conditions [27]. They are typically characterized by the degree of neutralisation or alkalinity, expressed as total OH/Al. The coagulant solution concentration was 1mg Al/mL.

Raw and coagulated samples were filtered through 0.45 μm pre-rinsed filter of SPARTAN 3D/0.45 RC type, Whatman Inc. SUA for DOC, and A254, A365, A436 absorbance measurements.

The quantitative assessment of NOM was carried out as:

- TOC (total organic carbon) and DOC (dissolved organic carbon) using a Multi C/N 2100S TOC analyzer Analytik Jena;

- A254, A365, A436 represent the absorbances measured at 254 nm, 365 nm and respective, at 436 nm, using a Specord 205 UV/VIS spectrophotometer Analytik Jena in a 1 cm quartz cuvette.

A254 represents a quantitative measure of aromatic content of the organic carbon compounds (B and K band): aromatic sites substituted with oxigen containing functional groups i.e. -O-,-CH=O, $-COCH_3$, –COOH, -COO, $-CH=CH_2$, -OH [18, 19, 28].

A365 represents the assessment of other humic compounds with increased molecular size. A365 represents a measure for fraction of more pronounced aromatic character matter that consisted of polycondensed aromatic compounds. Some authors consider A365 as a measure of humic acids proceeded from dead vegetal matter, due to the fact that a series of N-based fractions exhibit signal at $\lambda > 300$ nm [19, 28].

- COD, Chemical Oxygen Demand parameter gives an overall evaluation of almost all organic compounds, which can be fully oxidized to carbon dioxide with an oxidising agent under acidic conditions and hence this is good comparison for TOC value.

- *p*H was measured using a Thermo Orion pH-meter at 25 °C and turbidity was measured using a HACH 2100 turbidimeter.

Calculated parameters:

- A2/A3 ratio (A254/A365) is a general index for monitoring the dissolved aromatic compounds with high weight expressed as A365 versus aromatics content of humic and fulvic substances with mixture of molecular weights compounds [19].

- SUVA254 is a specific ultraviolet absorbance, determined as the absorbance at 254 nm (cm^{-1}), A254, per unit of DOC (mg C/L), A254/DOC x 100 ($Lm^{-1}mg^{-1}$) [16, 17].

- DOC/TOC index for monitoring the dissolved organic carbon versus total organic carbon.

-TOC/COD was carried by comparing the TOC with the COD value.

Jar Test procedure

Coagulation and flocculation experiments were carried using Degremont Jar Test in 1L beakers. After the addition of the coagulants, the samples were subjected to rapid mixing for two minutes at 250 rpm, then flocculation for 10 min at 25 rpm and last settling for 30 min, without *p*H correction. The supernatant was analyzed.

Results and discussions

Table 1 shows the characteristics of the studied supplies waters.

Water 1and Water 2 were sampled in the first and second decade of January, a period of time characterized by abundant rains and snow thawing in the upper course of the surface water. The waters carry great quantities of suspensions that determine a turbidity of 95 – 120 °NTU. At the same time, the waters exhibit a high organic load

Characteristics	Water sources		
	Water 1	Water 2	Water 3
Water temperature, °C	5	7	3
Turbidity, ° NTU	120	95	12
pH	6.95	6.92	7.01
COD, mg O_2/L	10.04	12.26	3.2
TOC, mg C/L	11.2	12. 73	3.8
TOC/COD	1.12	1.13	1.19
DOC, mg C/L	7.93	8.04	2.83
DOC/TOC	0.67	0.63	0.74
A254, m^{-1}	15.98	16.2	5.5
A365, m^{-1}	5.2	7.6	3.45
A436, m^{-1}	2.25	2.93	2.17
A254/A365	3.1	2.13	1.73
SUVA254, L m^{-1} mg^{-1}	2.12	2.01	1.94
Predicted removal DOC vs. SUVA, %	25-50	25-50	< 25

Table 1
CHARACTERISTICS OF THE STUDIED WATER SOURCES

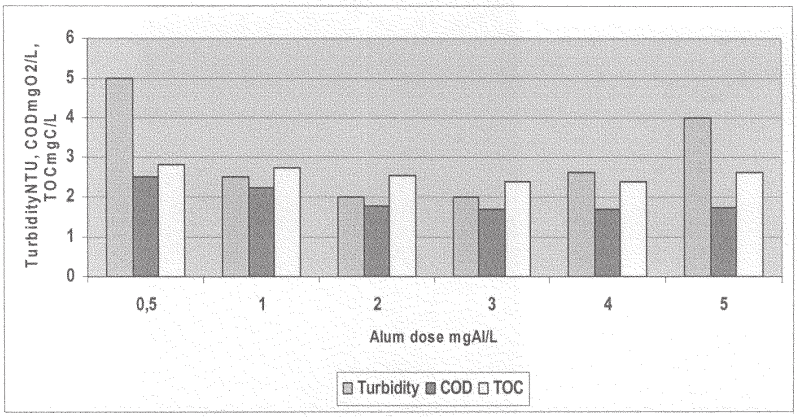

Fig. 1. Jar-Test Water 3. The results-effects of the Alum dosage on residual turbidity, COD and TOC

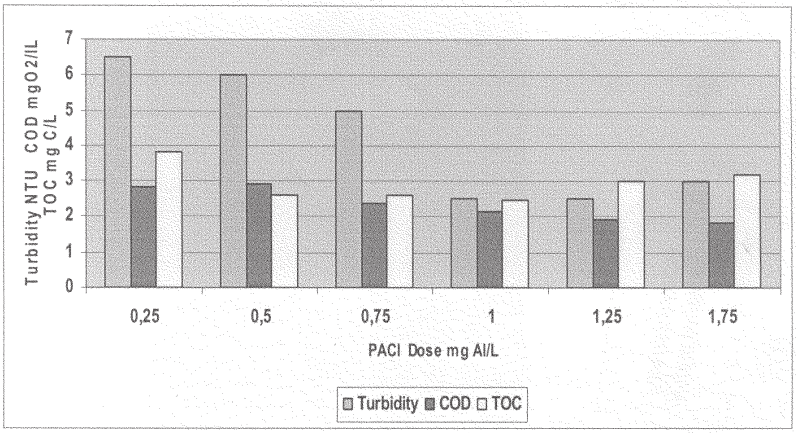

Fig. 2. Jar-Test Water 3. The results-effects of the PACl dosage on residual turbidity, COD and TOC

expressed as DOC parameter of 10.04 - 12.26 mg O_2/L and TOC parameter of 11.2-12.73 mg C/L. The quantity of the dissolved organic substances with carbon, DOC, is more than half of the TOC, which is DOC/TOC = 0.63 - 0.67. The absorbance of the substances from the filtered sample at the 254 nm wavelength is A254 =15.9-16.2 m^{-1}, of which the substances with high molecular weight absorbing at 365 nm represent 30-50 %. The values of A436 parameter, giving information on the water colour, ranged between 2.25 and 2.93 m^{-1}. The value of SUVA operational parameter is ranged within 2-4 $Lm^{-1}mg^{-1}$, therefore, an efficiency of DOC reduction between 25 to 50 % is expected in the aluminium sulphate coagulation step [16, 17].

Water 3, sampled in February, comes after a cold period, with air temperatures below 0 °C. Prolonged frost does not allow the water seepage from the surrounding areas, and, as a result, the turbidity is reduced, having a value of 12 °NTU. The matter content expressed by COD (Chemical Oxygen Demand) is 3 to 4 times less than in the case of the Water 1 and Water 2. Also, this type of water is characterized by a reduced TOC than that determined in the Water 1 and Water 2. Water 3 exhibits a different composition versus Water 1 and Water 2, because the dissolved organic matter quantity increases (DOC/TOC = 0.74). The A254 parameter is three times less than the Water 1 and Water 2, indicating a smaller quantity of aromatic character and double bond compounds compared to this type of water. This is because the allochthonous areas were not washed off and the metabolic activity which was slowed down, leading to the formation of such compounds. In such waters, the presence of the aromatic substances with high molecular weight, expressed through the A365 parameter is reduced, which was proved by value of A2/A3 ratio reduced at 1.73. This fact confirms that in this type of water reaches a smaller quantity of humic substances characteristic to soils, with polymerization levels greater than those of the aquatic ones. Natural water with higher A2/A3 ratio exhibits a lower degree of aromaticity [18, 25]. The SUVA operational parameter < 2 L m^{-1} mg^{-1} indicates that the Alum coagulation step reaches a DOC reduction efficiency of maximum 25 % [16-17].

The optimal dose is considered the dose at which the residual values of conventional parameters (turbidity, COD and colour) meet the standard requirements. Figures 1 and 2 show as an example, the Jar test results obtained for both coagulant agents for Water 3. The optimal dose determined through conventional parameters cannot be considered as optimal dose in relation to the removal of organic matter that was characterized by TOC parameter, as showed in figures 1 and 2.

Table 2 shows conventional and non-conventional characteristics of the waters treated with optimal doses of Alum, determined by the Jar -Test. For Water 1 and Water 2, the optimal Alum dose corresponded to a residual turbidity of 3 °NTU allowed organic load removal, and the COD and TOC removal efficiencies of about 65 - 70.7 % and about 51.7 - 56.6 %, respectively, were achieved. For waters with low turbidity (Water 3), COD and TOC removal efficiencies of 30 % and 27.5 %, respectively, were reached.

DOC removal efficiencies of 29.4 - 39.4 % for the first type of water (Water 1 and Water 2) and 2.8 % for the second water type (Water 3) were achieved. The obtained removal efficiencies for both types of water are in accordance with the estimation given by the SUVA operational parameter. It has to be underlined that Alum coagulation allows an efficient removal of colloidal particles in comparison with dissolved ones, as can be seen in table 2 (DOC/TOC higher than 0.9).

The aromatic character substances are reduced for the waters with high turbidity, by 59 - 67.5 % and for those with low turbidity by only 21.8 %.

For Water 1 and Water 2, the use of Alum allows the removal efficiencies of 59-62.5% for compounds

Table 2
CHARACTERISTICS OF THE WATER TYPES TREATED WITH THE OPTIMAL DOSE OF ALUM

Characteristics	Treated water		
	Water 1	Water 2	Water 3
Optimal dose Alum, mg Al/L	3.5	5.0	1.0
pH	6.94	6.9	7.0
COD, mg O_2/L	2.94	3.94	2.24
COD Removal, %	70.7	65.0	30.0
TOC, mg C/L	4.86	6.15	2.675
TOC Removal, %	56.6	51.7	27.5
DOC, mg C/L	4.8	5.65	2.75
DOC Removal, %	39.4	29.4	2.8
DOC/TOC	0.98	0.91	0.98
A254, m^{-1}	5.19	6.45	4.3
A254 Removal, %	67.5	59.1	21.8
A365, m^{-1}	3.35	1.51	2.9
A365 Removal, %	55.9	79.0	15.9
A436, m^{-1}	0.25	0.25	0.12
A436 Removal, %	89.0	91.5	94.5
A254/A365	1.54	4.27	1.48
Turbidity, ° NTU	3	3	2.5

Table 3
CHARACTERISTICS OF THE WATER TYPES TREATED WITH THE OPTIMAL DOSE OF PACL

Characteristics	Treated water		
	Water 1	Water 2	Water 3
Optimal dose PACl, mg Al/L	3.5	5.0	1.0
pH	6.95	6.92	7
COD, mgO_2/L	3.05	4.8	2.16
COD Removal, %	60.6	57.4	32.5
TOC, mgC/L	4.5	5.35	2.45
TOC Removal, %	59.8	58.0	35.5
DOC, mgC/L	4.11	4.19	2.24
DOC Removal, %	48.7	47.5	20.8
DOC/TOC	0.78	0.78	0.91
A254, m^{-1}	5.5	6.2	2.5
A254 Removal, %	65.4	63.0	54.5
A365, m^{-1}	2.5	3.95	2.0
A365 Removal, %	67.1	48.0	45.2
A436, m^{-1}	0.25	0.12	0.08
A436 Removal, %	89.0	95.9	94.0
A254/A365	2.2	1.56	1.25
Turbidity, ° NTU	3.5	3.5	2.5

represented by A254, while for Water 3 a removal efficiency of only 21.8% was reached. Water 3 contains a higher amount of small molecular weight compounds with more hydrophilic character (SUVA<2), for which simple Alum salts exhibit reduced effect.

Based on the same consideration, the compounds characterized by A365 are better reduced (up to 79%) for Water 1 and Water 2 in comparison with Water 3, for which A365 removal efficiency is only 16%.

It can be noticed that A2/A3 ratio higher than 4.27 reflects a reduced content of compounds with more aromatic character reported to the total aromatic compounds (Water 2).

Table 3 shows the characteristics of the water types treated with PACl at the optimal dose, determined by the Jar Test. Control parameters of the Jar Test for determining the optimal dose refer to final turbidity, COD and colour, conditions under which the parameter reduction characterizing the organic matter is not the desired one.

For water characterized by low turbidity and load natural organic matter, the use of the polymerized coagulant agent – PACl shows the advantage of improving the coagulation efficiency, and DOC removal efficiency is higher by 7 times as compared to the results obtained for the coagulation with traditional agents, such as aluminium sulphate. In comparison with Alum effect, adding prepolymerized salt exhibit similar effect for the removal of compounds with aromatic character represented by A254 and A365 for Water 1 and Water 2, and for Water 3 the effect is improved by 2.5 times for both parameters.

In the case of waters characterised by high turbidity, even though the TOC is reduced to 4.86 - 6.1 mg C/L for the coagulation using aluminium sulphate, and to 4.5 - 5.35 mg C/L by PACl coagulation, these concentrations are yet too high and represent the potential for chloride compounds formation.

Also, waters characterized by initial TOC and DOC by 3 - 4 times lower and the removal efficiency under 25 %, exhibit high organic matter load, expressed by TOC and DOC values >2 mg C/L. Therefore, supplementary treatments are necessary in order to complete the coagulation to reduce the organic substances expressed as TOC value lower than 2 mg C/L, and to avoid the formation of the toxic chloride compounds in the drinking water.

The coagulation process mechanism is complex and consisted of: 1-charge neutralization, which can be achieved by *p*H variation by sorption of cationic particles on NOM surface; 2-interparticule binding of the polymers that adsorb more particles resulting flocons; 3-precipitate enmeshment, when formed precipitates retain colloids and adsorb dissolved matter. A possible interpretation is that the use of the aluminium polymer in the coagulation process allows that outside the main charge neutralizing and destabilizing mechanisms that the particles to manifest more intensely the mechanisms of adsorption of the dissolved organic matter, and its incorporation in the microfloccules formed, when separation through settable aggregates occurs.

Conclusions

The coagulation with simple salts compared to prehydrolyzed aluminium salts performed for surface waters characterized by a wide domain of organic and inorganic matters, solid and dissolved, deals to identify the operational conditions to reach high efficiencies of simultaneous removal of turbidity and organic load.

Rapid characterization of the water sources for drinking by the SUVA254 operational parameter allows the estimation of the dissolved natural organic matter reduction for applying the coagulation process.

Waters with turbidity higher than 95 °NTU, and a dissolved organic matter content DOC/TOC = 0.63 - 0.67, by coagulation with the optimal Alum dose remove TOC organic matter with yields of 51 - 56.6 %. The coagulation performance obtained for the removal of the dissolved natural organic matter DOC is ranged between 29.4 and 36.2 %, values that correspond with the prediction based on the SUVA254 parameter. The use of the aluminium prepolymerized coagulant agents allows that the DOC removal efficiency to reach the superior limit estimated based on the SUVA254 parameter, obtaining efficiencies of 47.5 - 48.7 % under conditions of similar conventional coagulant dose.

For the waters with low suspended matter content (turbidity = 12 °NTU and a high ratio of DOC/TOC = 0.74) for the optimal Alum dose, the removal efficiency of turbidity, DOC and colour is satisfactory, but the removal of the dissolved matter is minimal. By using PACl, the coagulation performance of dissolved organic matter removal is improved and the efficiency was higher by 7 times versus conventional coagulant under similar conditions.

The advantage of using the PACl as coagulant agent is confirmed in the case of the low turbidity waters, where the aromatic character compounds, identified at the A254 and A365, reduce in domain 45.2-54.5 %, which represents by 2.5-3 times than Alum use.

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