Coagulation of Surface Water using Simple and Prehydrolyzed Aluminium Salts

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This study investigated comparatively the performances of the coagulation stage of the drinking water treatment using Danube river water source, performed with two types of coagulation agents, a simple aluminium salt (alum) and a prepolymerized compound, alkaline aluminium polychloride (PACl). Jar-tests demonstrated that PACl as coagulation agent provided the best turbidity and natural organic matter (NOM) removal efficiency in comparison with alum usage. Under high turbidity conditions, the coagulation application using alum did not lead to the treated water quality that fit the standard requirements. A very high dissolved aluminium residual concentration was noticed when the coagulation was performed with alum, especial at low temperature. Also, it was found that PACl was less sensitive to low temperatures than alum in regard to both turbidity removal and the dissolved aluminium residual concentration.

Keywords: coagulation stage, drinking water treatment, coagulation agents, aluminium salt, alkaline aluminium polychloride

The most important component of water treatment technology is represented by coagulation-flocculation process, because it is responsible for the performances of the filtration and disinfection stages [1-3]. The coagulation is used to destabilize suspended particles and to react with dissolved organic material, which if it is not removed, can react with chlorine to reduce disinfection efficiency and form chlorinated organic species of health significance, e.g. disinfection by-products (DBPs). The performance of coagulation process depends on the diverse factors with respect to the efficiency of water purification, the coagulation agent playing the key role. In addition to the type of coagulant, these factors include the *p*H value, the coagulant dose, the temperature of water, the mixing operating conditions (fast and slow rate and time). The control parameter to determine the coagulation performance is residual turbidity. In the recent years, a deeper approach has been reported, by so-called advanced coagulation, which requires removing the total organic carbon (TOC) and thus, natural organic matter (NOM) from water. The effectiveness of the coagulation process for NOM removal is affected by NOM properties, e.g., size, functionality, charge and hydrophobicity [1].

Taking into account the various compositions and diversity of water, there is not a theoretical approach to establish the optimal conditions for the coagulation application in water treatment. Determining the optimal coagulant type and dosage is required to reach a high quality drinking water. The main problems appear for major changes in raw water quality in real time, especial for unusual condition characterized by a heavy rain and the storm water that brings high turbidity and NOM content to water source, and the treated effluent quality may be inferior to drinking water quality standards.

The best approach for determining the optimum parameters is Jar-test procedure. To establish the optimum *p*H and coagulant dose, which depends significantly on the raw water characteristics, an initial investigation into the variations in raw water quality from the source is required in the selection of the appropriate type of coagulation system to be used. Unexpected variations in raw water quality can led to the coagulation process disparagement, which cause the consequent problems in relation with the treated water quality.

The normal procedure for a jar test performing is to initially find the best performing coagulant and dose, and the performance is usually assessed based on the turbidity. As raw water conditions change, optimal coagulation dose rates also change and careful control is required to prevent overdosing and underdosing. In practice, the salts of aluminum and iron are mainly used as coagulants. Each type of coagulant features different behavior in various water compositions. The most commonly used aluminium-based coagulant has been alum ($Al_2(SO_4)_3$). However, the main disadvantage of the use of alum is the high aluminium residuals in the treated water, especially under cold temperatures and at low *p*H conditions, which can cause possible health hazard or distribution system fouling. [4-7].

In the recent years, prehydrolyzed aluminium coagulants by type of polyaluminium chloride (PACl), have been developed and researched [8-10]. PACl has been obtained by partially neutralizing $AlCl_3$ to different basicity ratios, being characterized by the neutralization degree (r). PACl contains highly charged polymeric aluminium species by type of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}^{7+}), which has been noted to be the most efficient Al-species for contaminant removal in the coagulation process [9, 11, 12]. The main advantage of the prehydrolyzed polymer coagulants have been reported as less temperature or *p*H dependence [11, 13-16]. However, the characteristics of the water to be treated, e.g., turbidity, NOM content and properties, play a major role in the choice of a proper coagulant [9, 10].

This study aimed at exploring optimum coagulant type and dose for a large spectrum of turbidity and temperature of surface water at the laboratory-scale. Aluminum sulphate (alum) and polyaluminium chloride (PACl) were tested as coagulation agents using Jar test method and the optimum coagulant type and dose were determined. For all studied conditions, the coagulation performance was assessed based on the treated water characteristics, e.g., turbidity, dissolved organic carbon (DOC), chemical oxygen demand (COD), dissolved aluminium residual.

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Table 1
RAW WATER CHARACTERISTICS

No. crt.	Temperature / °C	Turbidity / NTU	COD / $mgO_2 \cdot L^{-1}$	pH	DOC / $mg \cdot L^{-1}$
1	6	5.65	2.65	7.95	4.12
2		26.87	3.29	7.98	5.32
3		165	5.89	8.01	6.29
4	14	5.70	2.53	7.97	4.13
5		25.32	3.11	7.96	5.11
6		160	5.73	7.98	6.1
7	25	5.85	2.62	7.98	4.22
8		25.63	3.36	8.01	5.23
9		172	6.21	8.08	6.63

Experimental part

The treatment processes of coagulation, flocculation and settling were simulated in the laboratory using a Jar-test procedure. Coagulation-flocculation studies were performed in a six-place conventional Jar-test apparatus, equipped with 6 beakers of 1000 mL volume. Raw waters were sampled from Danube river during different seasons to cover whole real situations range. Before coagulation/flocculation process, water sample was thoroughly shaken to avoid possibility of settling solids. The experimental process consisted of the initial rapid mixing stage that took place for 2 min at 160 rpm, the following slow mixing stage for 10 min at 50 rpm and the final settling step for 20 min. After 20 min settling period, samples were withdrawn from supernatant for analyses.

Process performance was monitored by using turbidity (T), disolved organic carbon (DOC), chemical oxygen demand (COD) and absorbance recorded at the wavelength of 254 nm (A_{254}). The optimum coagulant dose was considered to be the dose which produced a final turbidity of less than 5 NTU. Turbidity was measured on a Hach Ratio/XR model 43900 turbidity meter, pH was determined using a Radiometer PHM 95 *p*H/ion meter. DOC was measured using TOC\TN analyzer multi N\C 3100, Analytik Jena AG, and COD was determined in accordance with Romanian standardized method. A_{254} parameter was measured and recorded using SPECORD PC 205 - UV VIS Spectrophotometer, Analytik Jena AG. The dissolved aluminium concentration was determined using ZENIT 700 AAS spectrophotometer, Analytik Jena AG.

The raw water temperature and turbidity allowed classifying into the three levels of temperature and turbidity. The quality characteristics of raw water are gathered in table 1.

Aluminium sulphate (alum) and SACTHOKLAR polyaluminium chloride (PACl) with basicity of 45% were used as the coagulation agents. *p*H was adjusted using 30 % H_2SO_4 solution.

Results and discussion

*p*H is an important parameter for coagulation process since it affects some aspects responsible for the coagulation mechanism, i.e., coagulant solubility, surface charge of colloids, charge of NOM functional groups. For aluminium-based coagulants, the optimum coagulation pH is given by minimum coagulation solubility. Under water treatment conditions, alum and polyaluminium chloride (PACl) chemistry can be described by dissolved species in equilibrium with an amorphous solid phase ($Al(OH)_3$). The dissolved species are similarly for the both coagulation agents, i.e., Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_4^-$, except that PACl contain highly charged polymeric aluminium species, by type of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ [1]. Taking into account that the pH influence on effective treatment is different in relation with the various parameters (turbidity, COD, TOC, dissolved aluminium residuals) and that the minimum coagulant solubility belongs to *p*H ranged from 6 to 8 depending on the coagulant type, all coagulation experiments were performed at *p*H 7.5, selected as optimum *p*H.

The comparative coagulation experiments using alum and PACl coagulation agents were conducted to determine the optimum coagulant doses under various temperature and turbidity levels to cover the whole real range. The coagulant dose and process conditions are chosen considering the requirements to the treated water (turbidity, COD, the concentration of dissolved aluminum residuals). Also, taking into account that the presence of natural organic matter (NOM) influences the coagulation dosage, the absorbance recorded at 254 nm (A_{254}) and dissolved organic carbon (DOC) will be monitored.

Figures 1 and 2 show examples of the results of Jar-test applying under various temperatures to establish the optimal dose for alum coagulation agent under two extreme turbidity loading, i.e., very low (5.65 NTU, very close to maximum allowable concentration for drinking water) and very high (165 NTU, characteristics to the flood situation). The optimal alum dose was ranged between 0.75 and 1 mg $Al \cdot L^{-1}$ function of the temperature for low turbidity and 2.5 mg $Al \cdot L^{-1}$ for high turbidity independent on the temperature. As we expected, the low temperature influenced negatively the coagulation efficiency, the worst turbidity removal efficiency was reached for the lowest temperature. This effect is because the low temperature affects the solubility of the coagulation agent and delays the kinetics of the hydrolysis process, which is valid under high turbidity loading (fig. 2). It must be noticed that for high turbidity level, the application of alum coagulation agent does not meet the requirements for drinking water, and no turbidity lower than 5 NTU was reached. Also, under both turbidity conditions, the residual aluminium concentrations are above the maximum allowance concentration in drinking water in relation with Romanian Drinking Water Law, which can cause possible health hazard due to that the presence of aluminium in drinking water may pose a risk towards Alzheimer's disease [1].

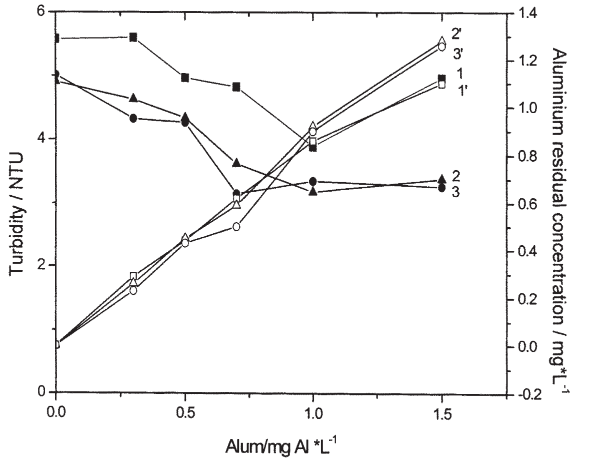

Fig. 1. Effect of alum dosage on the residual turbidity (curves 1, 2, 3) and aluminium residual concentration (curves 1', 2', 3') under various temperatures: 1-6°C; 2-15 °C; 3-25 °C; Initial turbidity of 5.65 NTU

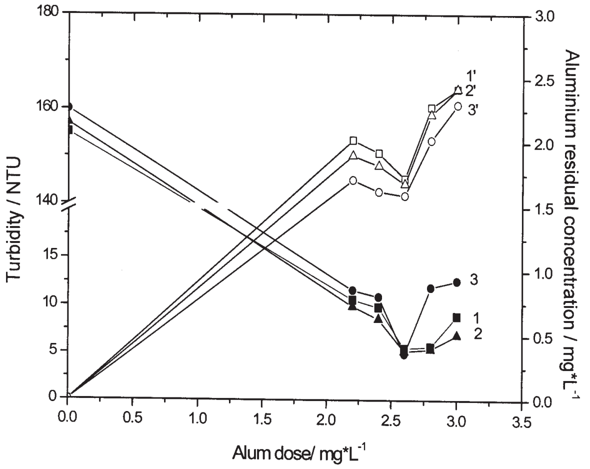

Fig. 2. Effect of alum dosage on the residual turbidity (curves 1, 2, 3) and aluminium residual concentration (curves 1', 2', 3') under various temperatures: 1-6°C; 2-15 °C; 3-25 °C; Initial turbidity of 165 NTU

The results of Jar-test applying under above-presented conditions using PACl coagulation agent are shown in figures 3 and 4. For low turbidity loading water, the optimal PACl dose led to the lowest residual turbidity of 0.3 mg $Al{\cdot}L^{-1}$ independent on the temperature. However, the temperature affected slightly the turbidity removal efficiency as for alum application. A major difference versus alum application is the dissolved aluminium residual concentration value at the optimal dose, which fits the drinking water requirements. For the water characterized by high turbidity, the residual turbidity below 5 NTU was reached at the optimal dose ranged from 0.75 and 1 mg $Al{\cdot}L^{-1}$, depending on the temperature. The aluminium residual concentration values were smaller than the maximum allowance concentration under all temperatures conditions.

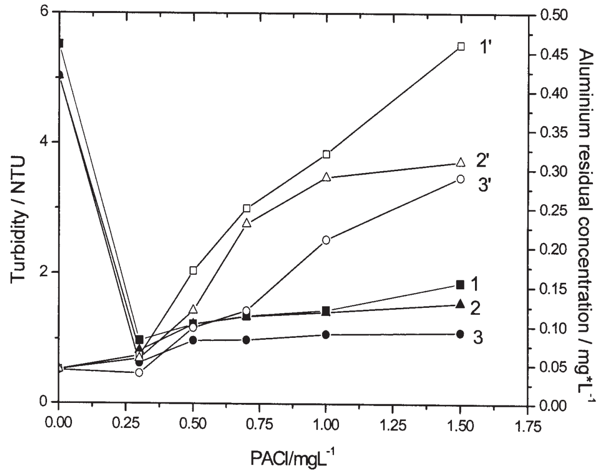

Fig. 3. Effect of PACl dosage on the residual turbidity (curves 1, 2, 3) and aluminium residual concentration (curves 1', 2', 3') under various temperatures: 1-6°C; 2-15 °C; 3-25 °C; Initial turbidity of 5.65 NTU

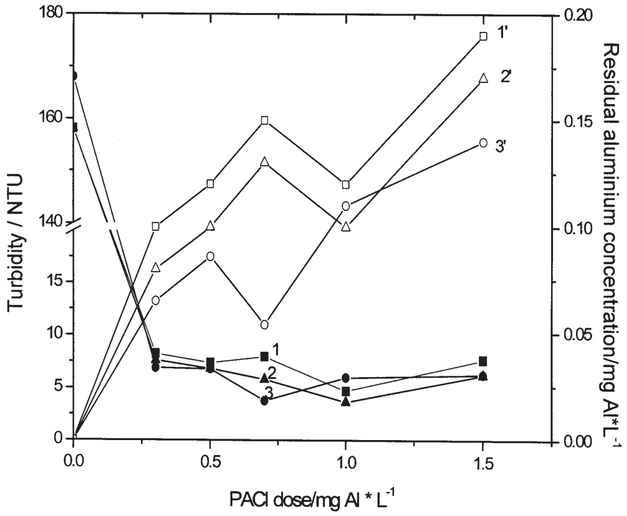

Fig. 4. Effect of PACl dosage on the residual turbidity (curves 1, 2, 3) and aluminium residual concentration (curves 1', 2', 3') under various temperatures: 1-6°C; 2-15 °C; 3-25 °C; Initial turbidity of 165 NTU

Besides turbidity, other parameters characteristic to the treated drinking water quality were monitorized during Jar-test to achieve the best selection of the coagulation agent. In table 2 are gathered the comparative results of the turbity, COD and DOC parameters in comparison with the dissolved aluminium residual concentration after the Jar-test application for high loading water using both alum and PACl coagulation agents. For all parameters studied, PACl coagulation agent exhibited a better performance for their removal. Also, the dissolved aluminium residual determined in the treated water claim the superiority of PACl coagulation agent.

The influence of the NOM presence on coagulation demand is checked by operational parameter, Specific UV Absorbance (SUVA), which offer a simple characterization of the nature of NOM based on the measurements of UV absorbance and TOC. SUVA value, defined as ratio between A_{254} and TOC concentration , determine the NOM character. High SUVA value indicates that the organic matter is largely composed of hydrophobic and low SUVA value indicates that water contains mainly hydrophilic organic compounds, characterized by low charge density [17-19]. In accordance with the literature [1], for SUVA lower than 2, NOM will not control the coagulant dose, but for SUVA higher than 2, an excess of coagulation dosage will be required to remove

Coagulation agent type	Coagulation agent dose/ $mg \cdot L^{-1}$	Turbidity/ NTU	COD/ $mgO_2 \cdot L^{-1}$	DOC/ $mg \cdot L^{-1}$	Aluminium residual/ $mg \cdot L^{-1}$
Alum	0.0	165	6.10	6.75	0.00
	2.2	10.6	5.88	6.24	1.72
	2.4	9.8	5.86	6.25	1.92
	2.6	5.5	5.84	6.23	1.72
	2.8	5.7	5.86	6.24	2.28
	3.0	8.9	5.88	6.25	2.42
PACl	0.0	165	6.10	6.75	0.00
	0.3	8.21	5.23	5.95	0.10
	0.5	7.96	5.02	5.35	0.12
	0.7	7.36	4.76	5.11	0.15
	1.0	4.7	4.50	4.80	0.12
	1.5	7.6	5.20	5.40	0.19

Table 2
JAR-TEST RESULTS FOR HIGH LOADING RAW WATER; TURBIDITY=165 NTU; COD=6.20 mg $O_2 \cdot L^{-1}$, DOC=6.82 $mg \cdot L^{-1}$

NOM from water. During the coagulation process, A_{254} followed the same trend as the turbidity. Reductions of A_{254} were usually between 25 and 75 % at the optimal Alum doses and between 50 and 95 % at the optimal PACl dose, function of the temperature and NOM character. For water characterized by SUVA lower that 2, the prediction for DOC removal is lower that 25 %, and for water characterized by SUVA higher than 4 the presence of NOM controls the coagulation process, and the prediction for DOC removal is higher. As it can be seen from table 2, DOC removal efficiencies at the optimal coagulation agent dose fit the SUVA prediction. In our study, for all situations, SUVA value was lower than 2, NOM is characterized by low hydrophobicity and the maximum DOC removal efficiency was 7.7% for Alum and 28.8% for PACl. Compared to DOC, UV254 has been noted to reduce more, suggesting that aromatic materials are removed more effectively than other NOM fractions [20-22].

Conclusions

Jar-tests demonstrated that PACl as coagulation agent provided the best turbidity and NOM removal efficiency in comparison with alum usage. Under high turbidity conditions, the coagulation application using alum did not lead to the treated water quality that fit the standard requirements. Also, a very high dissolved aluminium residual concentration was noticed when the coagulation was performed with Alum, especial at low temperature. According to this study, PAC coagulant exhibited a good performance to remove both turbidity and NOM, which was measured as DOC and A_{254}, being more effectively than alum. Also, it was found that PAC was less sensitive to low temperatures than alum in regard to turbidity removal. The best operational conditions determined in the Jar-test using plyaluminium chloride coagulation agent led to a good performance of the laboratory scale in terms of water quality.

References

1. MATILAINEN, A., VEPSÄLÄINEN, M., SILLANPÄÄ, M., Adv. Colloid Interface Sci., **159**, 2010, p. 189.
2. WU, G-D., LO, S-L., Eng. Appl. Artif. Intell., **21**, 2008, p. 1189.
3. LORENTSSON, A.V., CHERNOBEREZHSKII, YU. M., DYAGILEVA, A.B., Colloid J., **64**, no. 1, 2002, p. 87
4. CHOW, C.W.K., VAN LEEUWEN, J.A., FABRIS, R., DRIKAS, M., Desalination, **245**, 2009, p. 120.
5. UYGUNER, C.S., SUPHANDAG, S.A., KERC, A., BEKBOLET, M., Desalination, **210**, 2007, p. 183
6. MATSUKAWA, S., ITOHO, S., HABUTNU, S., AIZAWA, T., Water. Sci. Technol. **6 (4)**, 2006, p. 67
7. BÉRUB , D., DOREA, C.C., Water. Sci. Technol. **8(5)**, 2008, p. 505.
8. YAN, M., LIU ,H., WANG, D., NI, J., QU, J., Water. Sci. Technol. **9(1)**, 2009, p. 21
9. HU, J.C., LIU, H., QU, J., WANG, D., J. Environ. Sci. Technol. **40**, 2006, p. 325
10.YAN, M., WANG, D., YU, J., NI, J., EDWARDS, M., QU J., Chemosphere, **71**, 2008, p. 1665
11. DONGSHENG, W., HONG L., CHUNHUA, L., HONGXIAO T., Water Sci. Technol., **6(1)**, 2006, p. 59
12. YAN, M., WANG, D., NI, J., QU, J., CHOW, C.W.K., LIU, H., Water Res., **42**, 2008, p. 3361
13. IRIARTE-VELASCO, U., LVAREZ-URIARTE, J.I., GONZÁLES-VELASCO, J.R., Sep. Purif. Technol., **55**, 2007, p. 368
14. WANG, Y., GAO, B-Y., XU, X-M., XU, W-Y., XU, G-Y., J Colloid. Interf. Sci., **323**, 2009, p. 354
15. SHI, B., WEI, Q., WANG, D., ZHU, Z., TANG, H., Colloid. Surf. A., **296**, 2007, p. 141
16. YAN, M., WANG, D., NI, J., QU, J., NI, W., VAN LEEUWEN, J., Sep. Purif. Technol., **68**, 2009, p. 320
17. SHARP, E.L., PARSONS, S.A., JEFFERSON, B., Sci. Total. Environ., **363**, 2006, p. 183
18. SHARP, E.L., JARVIS, P., PARSONS, S.A., JEFFERSON, B., Colloid. Surf. A., **286**, 2006, p. 104
19. EDZWALD, J.K., TOBIASON, J.E., Water. Sci. Technol., **40(9)**, 1999, p. 63
20. UYGUNER, C.S., BEKBOLET, M., SELCUK, H., Sep. Sci. Technol., **42**, 2007, p. 1405
21. UYAK, V., TOROZ, I., J. Hazard. Mater. **141**, 2007, p. 320
22. UYAK, V., YAVUZ, S., TOROZ, I., OZAYDIN, S., GENCELI, E.A. Desalination, **216**, 2007, p. 334

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