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CONSIDERATIONS ON THE RELATIVE EFFICACY OF ALUMINUM SULPHATE VERSUS POLYALUMINUM CHLORIDE FOR IMPROVING DRINKING WATER QUALITY

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ABSTRACT. This study presents the evolution of specific parameters of raw water quality from the Strâmtori-Firiza Lake, which is the raw water source of the water plant in Baia Mare town, Romania. Parameters such as temperature, turbidity, oxidability were recorded over a four years interval. A comprehensive database on the evolution of these water parameters was thus created showing the tendency of these parameters across time. The possible correlations among the parameters were investigated. Positive correlations were found for oxidability and Al content and also for turbidity and oxidability. Temperature and turbidity were found to be highly variable (2-17°C, 3-53 NTU) across seasons. In order to improve the turbidity of treated water, two coagulants were tested: basic polyaluminum chloride (PAC) and aluminum sulphate (SA) evaluating the efficiency of the two treatment methods. While the traditionally used aluminum sulphate was found to be effective only when the temperature and turbidity were high: temperature >10ºC, turbidity >10 NTU (nephelometric turbidity unit), PAC emerged as an efficient clarifying agent even at low temperature and turbidity.

Keywords: *treatment, drinking water, polyaluminum chloride, coagulation*

INTRODUCTION

The quality of raw water sources used for drinking water production must comply with strict requirements [1,2]. High quality drinking water is essential for optimal survival of human beings [3]. There are some important issues related to the drinking water sources: increasing of drinking water demand, shrinking water resources, more stringent water quality goals,

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concerns related to the water disinfection by-products [4,5] and the presence of the organic micropollutants in drinking water sources and as well as in finished drinking water [6,7,8].

Aiming to provide high quality drinking water brings about huge challenges and guides the evolution of water supply systems [9,10,11]. The main source of raw water for drinking purposes is surface water. Lake water is preferred as a source for drinking water production because usually it contains less suspended and colloidal materials and its temperature is more constant than that of river water [12].

Several natural phenomena generate high turbidities of the raw water, leading to large amounts of colloidal substances. Such phenomena include melting of snow, alluvial deposits from the lake surrounding versants, abundant rainfall, lake water destratification and gathering of the mud deposited on the lake bottom during the time periods when the lake volume is low.

These colloidal substances that contribute to turbidity have the specific gravity similar to water and practically stay in suspension for a long time [13]. This phenomenon is due to their stability in aqueous solutions. It consists of the formation of a layer having electric charges with the same sign around these colloidal particles which determines them to repel each other, so their deposition is delayed for a long time or doesn't happen [14].

Due to the complex and highly variable physical and chemical composition and of the particularities of each raw water source, the problem of water treatment and the use of an efficient coagulant is not an easy one. Systematic studies should be conducted in the laboratory as well as at industrial scale [15]. The most commonly used coagulation agents for water treatment are aluminum and iron compounds, used especially as chlorides and sulphates [16].

The aluminum sulphate having the chemical formula $Al_2(SO_4)_3$* $18H_2O$ and containing 8,1 % Al, is an efficient coagulant in most cases, but in the case of natural water with low turbidities, temperatures and alkalinity, the results are not satisfactory due to low flocculation velocities [17]. Polyaluminum chloride (PAC) represents an alternative product for aluminum sulphate used in the treatment of residual and drinking water [18,19]. PAC is composed of polymers having different dimensions which contain aluminum ions bound by oxygen atoms [20]. The basic polyaluminum chloride is an acid product in a liquid form which can be dosed in diluted solution in the installation.

The Strâmtori-Firiza storage lake is a part of the Runcu Firiza hydrotechnical system and is currently the main water supply for Baia Mare city. Raw water is treated in the water plant of the organization Vital SA. Baia Mare. The quality of raw and drinking water is monitored in the laboratory of the plant. The water treatment plant also includes an industrial pilot where new technologies of water treatment could be tested. Several analyses are performed in the central laboratory of SC Vital SA following the water quality control at its source, the potable water indicators, the monitoring program of the water quality in Baia Mare municipality and in county agencies. In addition, research studies aim to optimize the quality of drinking water whatever is the quality of raw water (even with high turbidity and low temperature) and to test new techniques of water treatment [12].

The water quality of the storage lake is influenced by the weather, having a pronounced seasonality. The hydrological and climatic parameters and also the water dynamics are ecological factors that impact the organisms living in or around the lakes [21]. The raw water quality was monitored during the 2011-2014 period.

Parameters of interest are temperature, turbidity, water oxidability and aluminum content. Temperature significantly influences the stages of the coagulation process by enhancing the rate of the hydrolysis process of aluminum compounds and diminishing the rate of their adsorption [22,23].

Turbidity is one of the most important indicators for the quality of drinking water and is a measure of its clarity [24]. Turbidity can provide food and protection for microorganisms. If not removed, turbidity can cause the multiplication of the pathogenic microorganisms in the distribution system, leading to waterborne disease outbreaks [25].

Water oxidability quantifies the amount of organic matters present in a liter of water that can be easily oxidized using a chemical oxidant such as potassium permanganate ($KMnO_4$). In aquatic ecosystems, such as a storage lake, natural organic matter comprises a heterogeneous mixture of organic compounds including high molecular compounds and small molecular substances: proteins, amino acids, lipids, polysaccharides and biopolymers [26-28].

Aluminum can occur in different forms in water: hydroxide species, colloidal polymeric solutions and gels, and precipitates. Also aluminum forms complexes with organic compounds like humic or fulvic acids [25].

Aluminum coagulants are widely used in water treatment plants to remove turbidity and the organic dissolved substances. Excessive aluminum in water is associated with adverse effects on human health and thus water plants concentrate their efforts towards controlling its concentration [22].

We created a comprehensive database that includes the variation of temperature, turbidity, water oxidability and aluminum content in order to establish the range of values for the registered parameters during four years, their tendencies across time and to investigate the possible correlation among the parameters. This database is useful in establishing the optimal coagulant doses for the treatment of raw water with varied compositions (oxidability, turbidity, pH, residual Al content etc.).

We aimed to find the best treatment method across all seasons and to maximize the quality of the drinking water in the treatment plant taking into account the significant variation of the parameters of raw water. The Strâmtori-Firiza storage lake is a water source with high turbidities and low temperatures during six months of the year when water treatment using aluminum sulphate was not efficient. The implementation of polyaluminum chloride as an alternative coagulation reagent in the case of Strâmtori Firiza raw water with highly variable temperature and turbidity needed extended studies in order to establish the optimum reagent doses. We performed a comparison with the coagulation method based on aluminum sulphate in the context of the variability of water parameters.

RESULTS AND DISCUSSION

This study was elaborated based on a mathematical calculation and on a database which monitors the values determined for the analyzed parameters. The monthly average values of the main parameters: temperature, turbidity, oxidability and aluminum content and their variation domains were determined in order to establish the evolution of raw water quality in the period 2011-2014. These data are presented in figures 1-3.

The monthly average turbidity (Fig. 1) of the raw water varied in the range 3.0-53.0 NTU according to the seasons: turbidities below 7.0 NTU are specific to winter periods while the ones below 20 NTU to the spring-autumn period. In particular, 2012 presented abundant rainfall and floods and as consequence higher turbidity levels were registered (about 50 NTU in May and around 30 NTU in August and September).

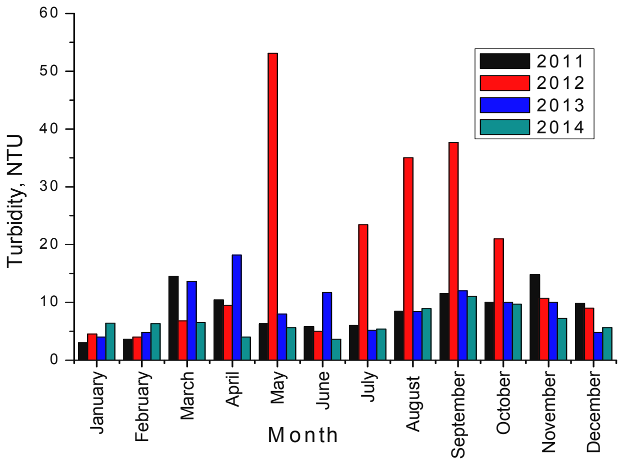

Figure 1. Average turbidity of the raw water during the period of the study

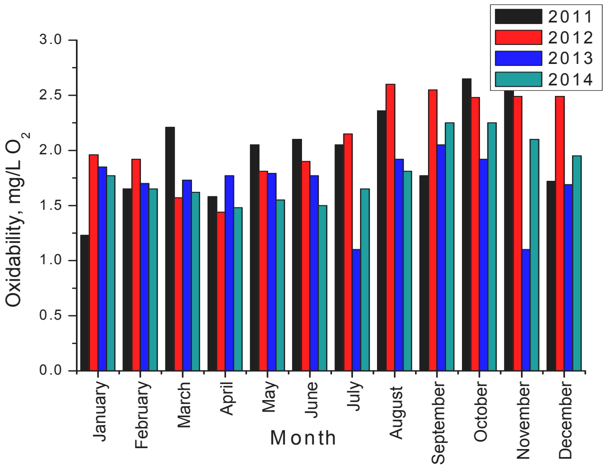

Figure 2. The average oxidability of the raw water during the period of the study

Figure 2 shows the dynamics of the oxidability parameter. During the period of the study, the organic matter that is globally quantified by the oxidability had monthly average values between 1.20 – 2.50 mg/L of O_2, with low values in the months characterized by low turbidity and with high values in the months of high raw water turbidity. Such a correlation between turbidity and oxidability is expected because the turbidity is higher especially in rainy days when there are leakages from the floods that flow in the lake from the versants that surround Strâmtori storage lake. The floods carry over the soil containing humic acids causing the increase of organic matter in raw water quantified by oxidability. Recent studies revealed the growing tendency of the natural organic matter content in the raw waters both in surface and ground waters [29].

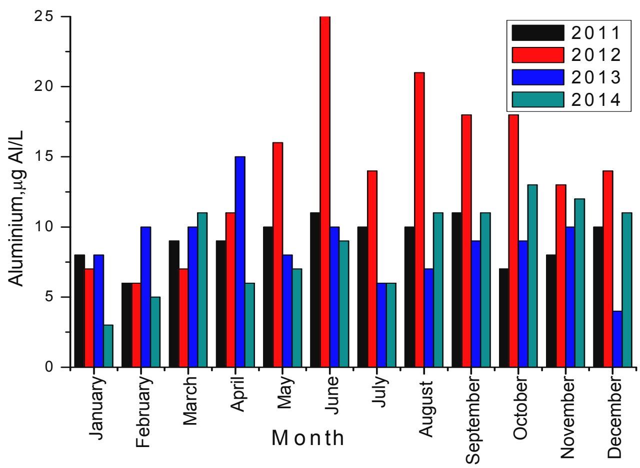

Figure 3. The average variation of aluminum in raw water during the studied period

Such two coagulation agents containing aluminum used for water treatment lead to differential increases of the aluminum content in the resulting drinking water. While research in this field is controversial, some studies claim that long-term excessive exposure to aluminum is related to the risk of Alzheimer's disease and dementia [30].

All other parameters equal, it is important to choose the coagulant agent that will result in the minimum residual aluminum content. The upper limit of aluminum content is set by Romanian legislation to 0.2 mg/L.

Table 1 shows the yearly average values and standard deviation of the studied parameters.

Table 1. The yearly average values of the main characteristics of raw water

Year/ Parameter	Temp., °C	Turbidity, NTU	Oxidability, mg/L O_2	Al, mg/L
2011	8.68±3.87*	8.62±3.81 *	2.01±0.45 *	9.17±1.53 *
2012	9.20±5.39	18.31±16.03	2.11±0.40	14.17±5.86
2013	9.03±5.24	9.22±4.27	1.70±0.30	8.83±2.69
2014	8.27± 5.47	6.68±2.21	1.80±0.28	8.75±3.22

*standard deviation of the average value

Table 2. Correlation coefficients between the studied parameters of raw water during the four years (Temp-temperature, T-turbidity, O-oxidability, Al content-Al)

	Temp	T	O	Al
Temp	1			
T	0.340	1		
O	0.340	0.376	1	
Al	0.411	0.578	0.426	1

Positive correlation coefficients were found for turbidity and oxidability and also for oxidability and Al content. These correlations indicate the likely sources of turbidity: organic matter derived from the runoff. The runoff contains both organic matter and Al in soluble and colloidal forms. The highest correlation coefficient was found for Al content and turbidity. Therefore it is a worthwhile pursuit to find an efficient way to reduce the Al dose of the coagulant by finding a coagulant that requires a lower Al dose to ensure a low turbidity, instead of good turbidity.

In order to obtain a better quality for drinking water (low turbidity and low aluminum content) basic polyaluminum chloride was tested during a month and compared with the classical coagulant aluminum sulphate.

Figures 4 and 5 present the comparison of the optimal aluminum doses experimentally obtained in the laboratory for the two coagulants: aluminum sulphate (SA) and basic polyaluminum chloride (PAC) and the calcium hydroxide doses corresponding for achieving the optimal precipitation pH for raw water turbidities of 10.0-200.0 NTU.

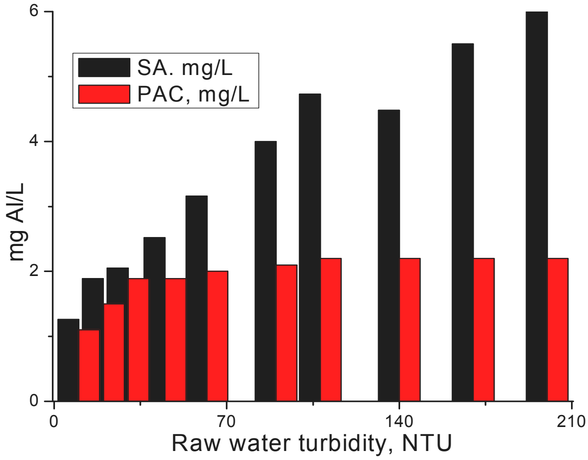

Figure 4. Optimal doses of aluminum depending on the turbidity of the raw water (coagulants: aluminum sulphate SA and polyaluminum chloride PAC)

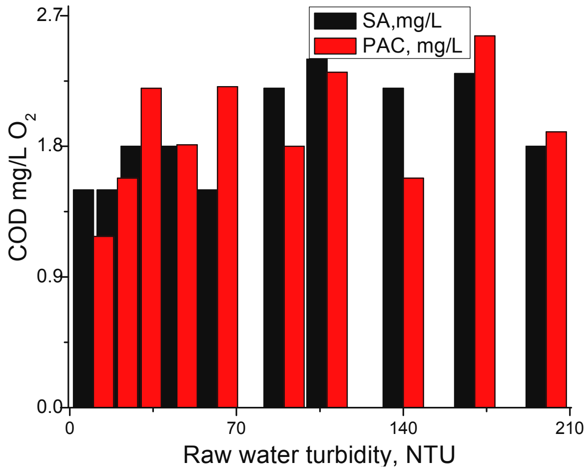

Figure 5. The treated water oxidability at optimal doses of Al depending on the turbidity of the raw water (aluminum sulphate SA, polyaluminum chloride PAC)

By using aluminum sulphate the values of the optimal doses are in the range of about 2- 4 mg Al/L being higher compared with the ones obtained in the case of basic polyaluminum chloride which are around 1 - 2 mg Al/L. Both coagulants need alkalinization with $Ca(OH)_2$ to obtain an adequate pH. The results of water quality monitoring during 2011-2014 period show that, except 3-4 months per year, when high values were registered for turbidity and oxidability, the quality of this source is appropriate to be used as drinking water source considering the main parameters. In order to evaluate the performances of the two coagulants, the characteristics of the treated water (turbidity) were compared with the optimal coagulant reagent expressed as Al doses and OH^- doses. In the case of PAC lower reagent doses were necessary for both Al and OH^-. Thus, at low turbidity the doses of reagent used for PAC were reduced with 30-50 % compared with those used for aluminum sulphate while at high turbidity the aluminum dose for PAC was approximately half of that used for the water treated with aluminum sulphate. That means lower reagent consumption and a lower residual Al in the drinking water.

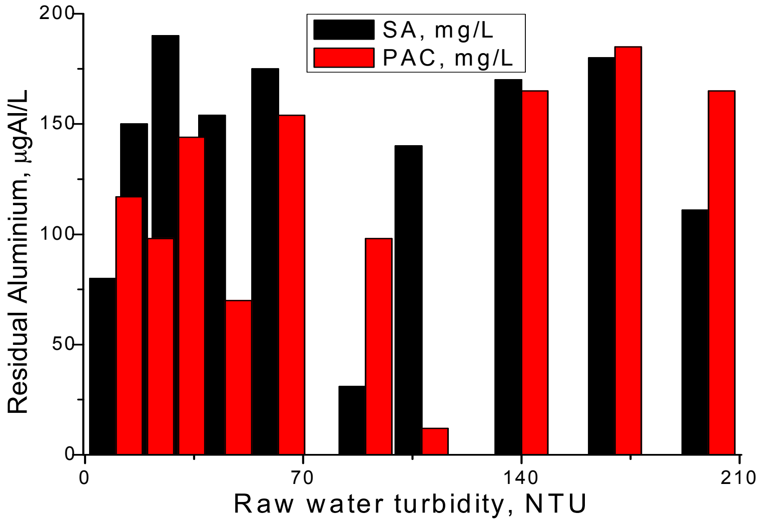

Figure 6. Residual aluminum content for treated water at optimal coagulant dose depending on the turbidity of the raw water for the two coagulation agents: SA-aluminum sulphate and PAC –polyaluminum chloride

Figure 6 shows the residual aluminum content of the treated water for different values of raw water turbidity when optimal doses of the two coagulants were used: PAC and SA. The Al residual content is lower in the case of PAC except for turbidity values higher than 170 NTU.

The turbidity of the treated water depending on the turbidity of the raw water was shown in figure 7.

It can be observed that, at the optimal doses, the remaining turbidity of the treated water has close values for the two studied coagulation reagents and these values are between 2.00 -5.00 NTU.

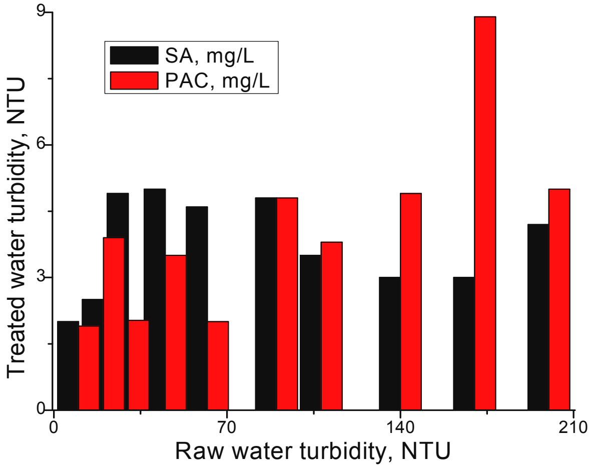

Figure 7. Influence of raw water turbidity on the treated water turbidity for the two tested coagulants

The efficiency of coagulation process is quantified by the relation Efficiency = ($T_{raw\ water}$ –$T_{treated\ water}$) * 100 * $T_{raw\ water}^{-1}$ (T is the turbidity). Raw water turbidities and potable water turbidities resulting during the study period (one month), using the corresponding doses of aluminum sulphate and polyaluminum chloride established in the laboratory for initial turbidities< 20 NTU are presented in figures 8 and 9.

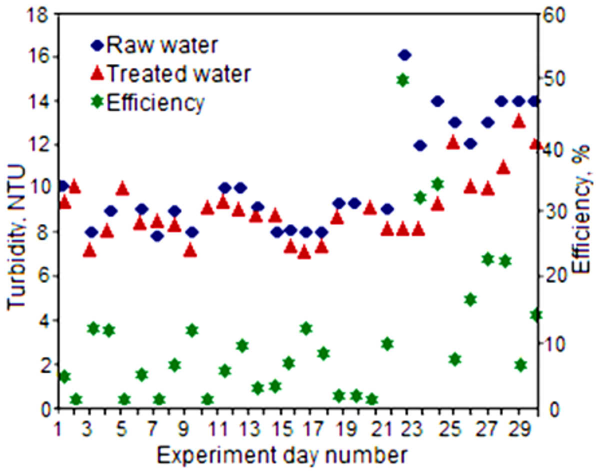

Figure 8. Raw water, potable water turbidity and the coagulation efficiency during the study period; coagulant: aluminum sulphate

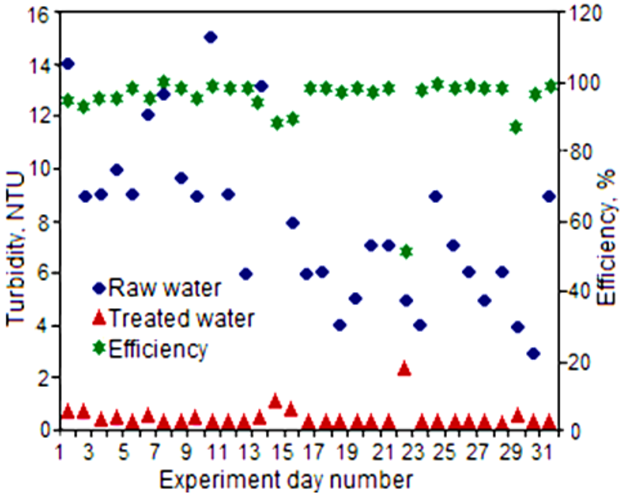

Figure 9. Raw water, potable water turbidity and the coagulation efficiency during the study period; coagulant: polyaluminum chloride (PAC)

Analyzing the data presented in Figures 8 and 9, one can observe that water treatment using basic polyaluminum chloride and calcium hydroxide presents high efficiency compared with the water treatment using aluminum sulphate and calcium hydroxide

Considering the aluminum sulphate, the low temperatures affect the rate of the hydrolysis reaction and of the flakes sedimentation due to a high water viscosity [24]. Increasing the coagulant dose (SA) and not providing the optimal conditions for the mixture process (fast for 2 minutes and slow for 15 minutes) that influences directly the flakes formation and their sedimentation, does not improve the efficiency of the coagulation-colloidal material separation process. On the other hand, the coagulation process with polyaluminum chloride and calcium hydroxide ensures high efficiency in the turbidity reduction even if the raw water shows turbidity values under 20 NTU, low alkalinity and a temperature below 10ºC because the basic aluminum polychloride is a partially hydrolyzed coagulation reagent [16].

CONCLUSIONS

The water treatment technique using aluminum sulphate and calcium hydroxide has a low efficiency, even the obtained water turbidities are in accordance with the law limit.

By using the basic polyaluminum chloride in the coagulation process the treatment efficiency was optimized and all the turbidities were below the law limit.

The originality and the importance of the study consist in the solving of an important problem: the establishment of the optimal doses of polyaluminum chloride for water treatment with different qualities and a high variability across the seasons.

The study brings new data about the seasonal variability of lake water and demonstrates that by using polyaluminum chloride as coagulant agent, drinking water with improved quality characteristics (high clearness and low residual aluminum content) can be obtain even for raw water with low alkalinity, low temperature and turbidity.

By using polyaluminum chloride as coagulant reagent high efficiencies in the turbidity reduction were obtained.

Future studies will focus on the treatment of the water with very high turbidity using polyaluminum chloride and polymeric organic flocculants.

EXPERIMENTAL SECTION

All the reagents used in chemical analysis were of analytical degree. Aluminum sulphate was a commercial product with 15.3 % of Al_2O_3. The polyaluminum chloride (PAC) used in the experiments was a commercially available product containing 18,9 % Al_2O_3, a basicity of 83% and density of 1.27 Kg/dm^3.

Sampling and analysis of raw water

The samples of raw water were taken at the entrance of the water treatment plant. Turbidity, oxidability and aluminum content of raw water were determined according to the Romanian standard methodology, adapted after the EU methodology.

Samples were taken daily and the month average values of the studied indicators were calculated and registered. Turbidity was measured using a turbidimeter (model 350 IR, WTW). The water oxidability was measured using the standard volumetric method.

To determine the aluminum content of water, a molecular absorption spectrophotometer Hach DR 2000 was used.

Coagulation tests

We assessed the efficiency of the coagulation process using as chemical reagents PAC and calcium hydroxide in comparison with the conventional aluminum sulphate and calcium hydroxide. Studies were carried out both in the laboratory of the water plant of SC Vital and in the microfactory (industrial pilot).

The experimental studies carried out in the laboratory took place during a 6 months period of time with the main objective of determining the doses and the optimal coagulation conditions for aluminum sulphate and for PAC. We used raw water with turbidity between 10.0 - 90.0 NTU. In order to obtain the optimum coagulation pH, the calcium hydroxide was used as a pH correction reagent. The determination of the optimal coagulation conditions was carried out using the „Jar-test" method.

The doses of the two coagulants used, were 1.51 – 4.00 mg Al/ L for aluminum sulphate and 1.10 - 2.20 mg Al/ L for PAC, correspondingly added to raw water samples of 1 liter. These samples were stirred rapidly (140 rotation/ min) for 2 minutes and slowly (40 rotation/ min) for 15 minutes. After 30 minutes of sedimentation, samples of the treated water were taken from the supernatant and the parameters of turbidity, oxidability and residual aluminum were determined. The optimum dose was established depending on the turbidity of the treated water. The studies carried out on the industrial pilot (microfactory) took place during the technological probation of the installation. The optimal coagulation doses experimentally obtained in the laboratory for the aluminum sulphate and for the basic polyaluminum chloride were applied in the technological flux depending on the raw water turbidity during the study period.

The water treatment technique using aluminum sulphate and calcium hydroxide was studied for one month and the water treatment technique using the basic polyaluminum chloride and calcium hydroxide was also studied for one month.

The technological flux applied on the industrial pilot consists of the following stages: collecting raw water, mixing water with the coagulation reagents in the water mixture room, coagulation process finishing in the reaction room combined with the lamellar decantation device, water filtration using under pressure filters, water disinfection using sodium hypochlorite and the potable water storage. Practically, the behavior of the two studied coagulants on the technological flux was followed and also their performances on obtaining turbidity values according to the Romanian legislation concerning drinking water quality [31] were registered and compared in the dynamic regime.

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