Systematic Studies Regarding the Introduction of a New Product in the Flow of Drinking Water of an Atypical Surface Source

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Polyaluminium chloride is a new coagulation reagent recommended for water treatment. This paper presents a study regarding water treatment from the storage lake Stîmtori – Firiza with this new coagulation reagent in comparison with the classic method currently applied. The classic method uses cake of alum (aluminium sulfate) and hydrated lime. In the case of atypical waters having low temperatures, low alkalinity and variable turbidity, the classic method has poor results. The main purpose of the experimental studies is to establish the adequate doses of coagulation reagent for obtaining drinking water according to present legislations.

Keywords: water treatment, quality of drinking water, polyaluminium chloride, cake of alum (aluminium sulfate)

In water treatment, the coagulation process is used to increase aggregation, which leads to the transformation of a stable suspension in an unstable one. In a watery solution, there is mutual electrical repulsion among colloidal particles because of the formation of same poles coats. These repulsive forces lead to the stability of the suspension [1-2]. The particles, which stayed in the lake for months or even years, can become aggregates in an hour or less through the process of coagulation. The coagulation process must be carried out so that the aggregation degree could be modified and controlled. Generally, this is done by addition of some substances called coagulants [3]. By introducing these coagulants in water there is no more electric repulsion among the colloidal particles, which allows the formation of flocules. The flocules are then removed through settling and filtration. In addition, coagulation decreases the concentration of organic substances [4], since a part of these are adsorbed at the surface of the formed flocules.

A good coagulant must lead to an efficient water clarification, it must decrease the organic substances’ concentration and it must be found in concentrations as small as possible in the drinking water, in the optimum work conditions.

Because of the complex composition of each raw water sources, and also because of the change in time of the chemico-physical composition, the water treatment problem and the finding of an efficient coagulant for a water with a specific composition is not that simple. Systematic studies are necessary both in laboratory and also at an industrial pilot level.

Raw water sources have a complex and time-dependent chemico-physical composition and each source has its own peculiarities. Therefore, systematic tests for efficient coagulants both at the laboratory and at the industrial pilot levels are needed to solve the water treatment problem.

Alum with the chemical formula Al(SO₄)₃·18H₂O and a content of 8,1% Al, is generally an efficient coagulant, but for the raw waters with low turbidity, temperatures and alkalinity, the results are unsatisfactory. In this case, the hydrolysis velocity is low, the quantity of dosed cake of alum and the waste aluminium concentration are high and, in consequence, the efficiency of the coagulation process is reduced [5-6].

The polyaluminium chloride with the chemical formula Alₙ(OH)_{m}Clₙ-m is a coagulation reagent partially hydrolysed, based on aluminium chloride, where m and n-1 are associated with the mole ratio Al:Cl. As the chlorine content of the product decreases, the degree of neutralization or basicity (m) increases.

Unlike the cake of alum, the polyaluminium chloride is made from polymers of various sizes, which contain aluminium ions connected through oxygen atoms. One prevalent polymer is Al(OH)₃⁺ [7]. Polyaluminium chloride is liquid (density = 1,27 kg/dm³ and a 10% Al content), an acid product, which is diluted and then it can be dosed to be used in installation.

The storage lake Stîmtori – Firiza is a part of the Runcu Firiza hydrotechnics system and is currently the main source of water supply for the city of Baia Mare. Generally, the quality of water is good. However, for 4-5 months every year, a higher turbidity is registered because of the snow melting, rainfalls and of debris wash from the slopes.

Experimental part

In this paper the water treatment with cake of alum and hydrated lime was compared with water treatment with polyaluminium chloride and with hydrated lime. To establish the efficiency of these two techniques, experimental studies in laboratory and at the industrial pilot level (Micro plant) were done. The “Micro plant” is a component of the Drinking Water Treatment Plant.

The experimental studies done in laboratory where carried out on a 6 month period in order to determine the proper dose and conditions of coagulation for cake of alum and polyaluminium chloride. In this experiment, raw water with a turbidity between 10 UNT and 90 UNT was used. For the best coagulation pH, hydrated lime was used as a reagent of pH correction [8]. To establish the proper
coagulation conditions a "jar-test" method was used. The coagulant doses, cake of alum (1.51-4 mg Al/L) and polyaluminium chloride (1.1-2.2 mg Al/L) were properly added in samples of 1 litre of raw water. After that the sample was stirred at fast speed (140 rot/min) for 2 min and then at a slow speed (40 rot/min) for 15 min. After 30 min of settling from the supernatant, treated water was sampled and the following parameters were established: turbidity, chemical oxygen demand (COD), alkalinity, pH and aluminium waste. According to the admitted legislation’s values for the mentioned parameters, the proper doses of coagulation for cake of alum and polyaluminium chloride were established. The studies at the Micro-plant were done during the period of installation’s technological testing. The best doses of coagulation obtained in the laboratory for cake of alum and polyaluminium chloride were applied in the technological flow, according to the corresponding turbidity of the raw water established during the period of study.

The technique of water treatment using cake of alum and hydrated lime has been applied for a month and then for another month using polyaluminium chloride and calcium hydroxide. To determine the exact indicators, the following techniques/equipments were used:
- turbidity: equipment to measure turbidity WTW 350 IR;
- pH: pH-meter Hanna;
- aluminium: molecular absorption spectrophotometer Hach DR 2000;
- alkalinity, chemical oxygen demand (COD): volumetric chemical methods.

<table>
<thead>
<tr>
<th>Turbidity, UNT</th>
<th>pH</th>
<th>Alkalinity, mval/L</th>
<th>Chemical oxygen demand (COD), mg/L O₂</th>
<th>Aluminium, mg/L</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.8</td>
<td>0.5</td>
<td>1.89</td>
<td>0.009</td>
<td>7</td>
</tr>
<tr>
<td>20</td>
<td>6.8</td>
<td>0.5</td>
<td>2.05</td>
<td>0.012</td>
<td>9.5</td>
</tr>
<tr>
<td>30</td>
<td>6.7</td>
<td>0.5</td>
<td>3.15</td>
<td>0.021</td>
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</tr>
<tr>
<td>62</td>
<td>6.6</td>
<td>0.45</td>
<td>3.78</td>
<td>0.033</td>
<td>14</td>
</tr>
<tr>
<td>90</td>
<td>6.5</td>
<td>0.45</td>
<td>4.4</td>
<td>0.031</td>
<td>15</td>
</tr>
</tbody>
</table>

Results and discussions

Experimental studies made in laboratory

The composition of the raw water during the laboratory study period has been established according to the standard methods, the results being presented in table 1. The coagulation process efficiency using as coagulation reagent the cake of alum in comparison with polyaluminium chloride

The efficiency of the coagulation process was carefully observed and the two coagulation reagents were compared.

In figure 1 are presented by comparison the proper doses of aluminium established experimentally in laboratory for the two coagulants: aluminium sulfate (AS) or cake of alum and polyaluminium chloride (PAC) and the samples of hydrated lime used for achieving the best pH precipitation, for raw water's turbidity of 10-90 UNT.

It can be observed (fig. 1) that in the case of the of alum's usage, the best doses are between 1.57-4.0 mg Al/L and 3.3-8.26 mg OH/L and are higher than those established for polyaluminium chloride which have values between 1.1-1.2 mg Al/L and 4.57 -6.89 mg OH/L.

In the case of use of cake of alum and hydrated lime, at the turbidity of raw water between 10-90 UNT, the treatment process is proper if it assures an alkalinity of 0.5 mval/L and a pH of 7.0.

In the case of polyaluminium chloride and hydrated lime, for the same turbidity of the raw water, the treatment process is proper if it assures an alkalinity of 0.6 mval/L and a pH of 7.2.

Fig.1. The variation of the proper dose of aluminium and hydrated lime versus the turbidity of raw water (coagulants: cake of alum and polyaluminium chloride)
To evaluate the performance of the two coagulants, the waters were treated with proper doses of each. Parameters such as turbidity, aluminium waste and chemical oxygen demand (COD) (figs. 2-4) were analysed depending on the turbidity of the raw water.

From the data presented in figure 2 it can be observed that at the best doses, the residual turbidity of the treated water has approximate values for the two reagents, in the interval 2-5 UNT.

The aluminium waste has lower values in the case of the treated water with polyaluminium chloride than with those obtained through the treatment with cake of alum. The overflow of the maximum admitted concentration (0.2 mg/L) for the raw water with a turbidity of 10 UNT treated with cake of alum was registered (fig. 3).

In the case of the raw water with higher turbidity (90 UNT), lower values of the aluminium waste were obtained at the treated water with cake of alum, possibly because of the presence of clay particles, which favour the formation of flocules [9].

From the data shown in figure 4, in the case of polyaluminium chloride usage, a better reduction of the organic materials through coagulation than with the cake of alum can be observed.

Studies at the pilot industrial level:
The technological flow applied at the industrial pilot (Micro plant) includes the following steps: the raw water collection, the mixture of water with the coagulation reagent in the water mixing room, the finishing of the coagulation process in the reaction room combined with the lamellar settling tank, the filtration of water through filters under pressure, the water disinfection with sodium hypochlorite and the storage of the drinking water. The behaviour of the two coagulants in dynamic regime was closely observed and their performance regarding the reduction of the turbidity and of the organic materials from the raw water were registered and compared.

Further more, aluminium waste in treated water was observed, which in good conditions of work, did not pass over the legislation’s admitted value (Al= 0.2 mg/L).

The composition of the raw water during tests was established according to the standard methods and the results are presented in table 2.

In table 2 the data show that raw water is in accordance with the norms of quality necessary for the surface waters used in drinking water process. Therefore, it is a valid source of water supply [10-11].

Tests with cake of alum in the technological flow
The turbidity of raw water and of drinking water obtained during the period of study (a month), using the proper doses established in the laboratory for the initial turbidity smaller than 20 UNT, are presented in figure 5.

The data in figure 5 show that the turbidity of raw water is between 7 and 16 UNT and the turbidity of the drinking water is between 7 and 13 UNT, values over the limit admitted by the legislation (turbidity < 5 UNT) [12].

In figures 6 and 7 the variation of the aluminium waste concentration and the chemical oxygen demand (COD) during the period of study (a month) is presented.
Table 2
THE COMPOSITION OF RAW WATER

<table>
<thead>
<tr>
<th>No.</th>
<th>Determined parameter</th>
<th>U.M.</th>
<th>Obtained values</th>
<th>NTPA 013/2002</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>1.</td>
<td>Turbidity</td>
<td>UNT</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>2.</td>
<td>pH</td>
<td>pH units</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>3.</td>
<td>Alkalinity</td>
<td>mval/L</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>4.</td>
<td>Chemical oxygen demand (COD)</td>
<td>mg/L O₂</td>
<td>1.97</td>
<td>2.76</td>
</tr>
<tr>
<td>6.</td>
<td>Aluminium</td>
<td>mg/L</td>
<td>0.008</td>
<td>0.028</td>
</tr>
<tr>
<td>9.</td>
<td>Temperature, °C</td>
<td></td>
<td>6</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig 5. The variation of the turbidity of raw water and treated water during the study period (coagulant: AS)

Fig. 6. The variation of the aluminium waste during the study period (coagulant: AS)

From the data presented in figure 6, the values of the aluminium concentration are between 0.25 - 0.48 mg Al/L, that is over the limit admitted by the legislation (CMA Al<0.2 mg/L).

The chemical oxygen demand (COD) indicator, which does not pass over 5 mg O₂/L in the initial source, has values between 1.18-2.5 mg O₂/L in the treated water. Analysing the results, the reduced efficiency of the coagulation process in the case of cake of alum usage is observed. The residual turbidity and the concentration of aluminium waste were over the limits admitted by the legislation regarding drinking water.

The low temperatures have an impact on the velocity of cake of alum’s hydrolysis reaction and also on the settlement velocity of the formed floccules, because of an increase in water viscosity. The increase of the coagulant dose in conditions of improper mixture activity (fast 2 min and slow 15 min), which influences directly the increase of aggregates formed and its settlement, does not lead to the improving of the efficiency of colloidal materials' coagulation - separation process.

Tests with polyaluminium chloride in the technological flow

Based on the results obtained in the laboratory for this technique of water treatment, concrete tests were made on the technological flow applied at the industrial pilot level. As in the case of alum, the main parameters studied during one month were: the drinking water turbidity, the chemical oxygen demand (COD) and the aluminium waste. The turbidity of the raw water and drinking water during the period of study are presented in figure 8.

The data presented in figure 8 show that the raw water turbidity is between 3.5 and 15 UNT, and the turbidity of the drinking water is between 0.01 and 2.1 UNT. Because polyaluminium chloride is a reagent of coagulation partially hydrolysed, the coagulation process assures high efficiency of turbidity reduction if the raw water is characterised by a turbidity smaller than 20 UNT, a lower alkalinity and a temperature under 10°C. In figure 9 the variation of the aluminium waste concentration from the treated water during the study period is presented.

It can be observed that the values of the aluminium waste concentration from the drinking water are between

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0.009 – 0.047 mg/L Al, that is under the limit admitted by the legislation (CMA Al<0.2 mg/L) [13].

Increasing the efficiency of the process of destabilization – separation of the colloidal substances minimizes the associated organic charge, determined by the chemical oxygen demand (COD) indicator (fig. 10).

From the experiment's data presented in figure 10 a significant reduction of the chemical oxygen demand (COD) can be observed, with the obtained values between 0.7-2.0 mg O₂/L. The use of polyaluminium chloride, leads to a long-lasting good quality of the treated water, in accordance with the norms imposed by the legislation.

Conclusions

In this paper a comparative study between the treatment of one atypical surface source (low temperature, turbidity and low alkalinity) with cake of alum and with polyaluminium chloride was presented. To establish the efficiency of these two techniques of water treatment, experimental studies were done both at the laboratory and at the industrial pilot levels. The purpose of the laboratory experimental studies was to establish the proper doses of aluminium for each coagulant in conditions of raw water turbidity changes between 10 and 90 UNT. From the experimental studies, the proper doses of aluminium for cake of alum were found to be between 1.51 – 4 mg Al/L, and are higher in comparison with those established for the polyaluminium chloride (1.1-2.2 mg Al/L).

The studies at the industrial pilot level were done at the Micro plant for implementing the mentioned treatment technologies, with the scientific support of the experimental laboratory studies. Each treatment technique was performed during one month, with the permanent monitoring of the quality of raw and drinking water at the main indicators (turbidity, alkalinity, pH, chemical oxygen demand (COD) and aluminium waste). The technique of water treatment using cake of alum and hydrated lime showed reduced efficiency. In this case, the indicators of the drinking water – turbidity and aluminium waste, were over the limit admitted by the legislation.
The use of polyaluminium chloride in the coagulation process led to the optimisation of the water treatment efficiency. In this case, all analysed parameters had values under the limit admitted by the legislation for the drinking water.

The polyaluminium chloride (a partial hydrolysed coagulant) assures a good removal of the turbidity and of the associated organic materials, with the aluminium waste concentrations under the standard value.

The studies performed represented an original contribution and led to the implementation of the promising studied techniques. At the station Micro plant – administrated by the SC VITAL SA Baia Mare, polyaluminium chloride and hydrated lime is currently used in the process of water treatment. The obtained drinking water is distributed to the inhabitants of Ferneziu neighbourhood, Baia Mare.

References
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11. *** NTPA-013 Norms of qualities which must be fulfilled the surface waters used as drinking water - annex no.1
12. ***NTPA-014 Norms regarding methods of measurement and frequency of sample and analyses of surface waters used for drinking water - annex nr.2

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