

THE REMOVAL OF IRON-ORGANIC COMPLEXES FROM DRINKING WATER USING COAGULATION PROCESS

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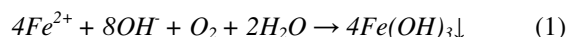
Abstract. The main problem of drinking water in Lithuania is high iron concentrations. Traditional methods can be used to remove iron from water; however, if drinking water contains organic matters, these matters have a negative effect on the process of iron removal from it. Because of the organic matters on the grain surface of screen filler, a membrane, which reduces the possibility of iron removal, is formed. There are also humus-iron complexes of organic origin that hinder iron removal. The article discusses the possibilities of removal of iron-organic complexes using the coagulant poly-aluminium chloride (PAC). During the investigation, different dose of coagulant was added into each drinking water sample; the process of coagulation was carried out, and then water was filtered. Measurements of concentration of total iron, permanganate index, pH and residual aluminium were conducted after the process of coagulation. The aim of this study was to establish the conditions under which the process of coagulation is most effective, iron organic complexes are removed from drinking water and its quality is maintained. The study established that water pH has the greatest impact on the removal of iron-organic complexes from drinking water. Iron-organic complexes are best eliminated from drinking water when its pH is from 6.8 to 6.5.

Keywords: drinking water, iron-organic complexes, permanganate index, coagulation, poly-aluminium chloride (PAC).

1. Introduction

32% of Asia, 75% of Europe, 29% of South America, 51% of North America, and 15% of Australia use groundwater for drinking (Klimas *et al.* 2002). Water utility companies supply only groundwater to the residents of Lithuania, which is rich in underground water resources (Klimas 2006). However, iron concentrations in 87% of groundwater resources exceed the permissible rate of hygiene (Diliūnas *et al.* 2006). Although iron does not have a significant impact on human health, the compounds should be removed from the groundwater because when soluble ferrous (bivalent) iron compounds interact with oxygen, insoluble ferric (trivalent) compounds, which fall into sediments, are formed. As a result water turbidity increases, water takes on an unpleasant metallic taste, and iron compounds provide water with a brownish color. Iron bacteria develop in iron accumulation and in the result sludge is formed. During water pressure fluctuation in the system more ferruginous sediments come from water taps (Potgieter *et al.* 2005; Vreeburg *et al.* 2007; Marjani *et al.* 2009). Due to these aesthetic matters the World Health Organization recommends that the maximum permissible iron concentration in drinking water should not exceed 300 µg/L. According to the European Union Council directive 98/83/EC total amount of iron should not exceed 200 µg/L.

Iron removal from groundwater is based on transforming soluble ferrous iron (by oxidation) into insoluble ferric iron compounds. Iron is oxidized with oxygen or other oxidants (potassium permanganate, ozone, chlorine), and with the use of bacteria that oxidise iron and manganese (Jankauskas 2004; Sakalauskas *et al.* 2007).



One of the problems with iron removal from groundwater is organic matters as they have a negative impact on the process of iron removal. Because of the organic matters on the grain surface of screen filler, a membrane, which reduces the possibility of iron removal, is formed. Assessing the concentration of organic compounds in accordance with the permanganate index (PI), the process of iron oxidation decelerates when PI > 3 mgO/L. There are also humus-iron complexes of organic origin that hinder iron removal. (Sakalauskas *et al.* 2007). Organic matters, namely, fulvic (FR) and humic (HA) acids, prevent iron removal from groundwater. (Diliūnas *et al.* 1998; Крайнов *и др.* 2001; Valentukevičienė and Rimeika 2004; Diliūnas *et al.* 2006).

Sorption characteristics of humic acids make it easy to form soluble and insoluble salts, and complexes with organic and inorganic compounds (Calase 2001; Juodkasis *ir kt* 2003). Furthermore, when humic acids penetrate

into ground water sources, water has lower redox potential due to much lower solubility of O₂ than CO₂ in water. Therefore, iron and manganese compounds become soluble (Fajtl *et al.* 2002). It is difficult to remove iron from water with lower redox potential, because iron dissolved in water is already oxidized, i.e., Fe³⁺ ions that have formed complexes with fulvic acids, dominate here. Therefore, they cannot be hydrolyzed to Fe(OH)₃ compounds that easily form sediments (Klimas 2006). In addition, studies have shown that with the increase of fulvic acids concentration in groundwater particularly stable FeFR(OH)₂ complexes appear. They can be destroyed by heavily chlorinating or alkalinizing the groundwater. During the latter reaction, OH⁻ ion and fulvic acid are separated from Fe³⁺ ion. Then ferric iron is easily hydrolyzed and precipitated. The higher FR concentration in groundwater, the more alkalinizing it needs (not less than to pH 7.5) (Klimas 2006).

Since organic compounds are removed from water using coagulants (O'Melia, 1999; Cheng 2001; Zoubulis *et al.* 2004; Ødegaard 2010), and iron forms complexes with organic compounds, this research attempts to remove iron from water using coagulants.

Iron and aluminum salts are especially effective coagulants (Delgado *et al.* 2003; Cesiulis 2010). Aluminum salts remove organic matters from water well, if most of the organic matters are humic acids (Sung *et al.* 2005).

Zoubulis and others (2004) enumerated the conditions upon which the effectiveness of coagulation depends. Coagulation depends on:

1. The concentration of organic matters;
2. The nature of organic compounds;
3. The type of coagulant;
4. The dose of coagulant;
5. pH;
6. Ionic strength;
7. The duration of coagulation.

The aim of this study was to establish, using PAC, the conditions in which the process of coagulation, during which iron organic complexes are removed and drinking water quality is maintained, was most effective.

2. Materials and methods

Water samples for testing were taken from the water wellfields in Preila (Lithuanian coast side). Water quality indicators are presented in Table 1:

Table 1. Water quality indicators

Indicator	Value	Permissible rate 98/83/EB
pH	7.17	6.5-9.5
SEL, μS/cm	257	2500
Fe _{total} , μg/L	3210	200
Fe ²⁺ , μg/L	970	-
PI, mg O ₂ /L	12.4	5
Color, mg/L Pt	231	30

Poly-aluminium chloride (Al₂(OH)₅Cl) was selected to execute coagulation process. Poly-aluminium chloride

was in a liquid form, which contained ~ 0.9 g/L of aluminum. Five doses of coagulant were chosen: 5 mg/L; 10 mg/L; 15 mg/L; 20 mg/L; 30 mg/L (doses were calculated in milligrams of pure aluminum in a liter of water). After coagulation, water was filtered. Tests performed in the filtrate include determining a total iron (LST ISO 6333:1995) and aluminum concentration (LST ISO 10566:1998), water pH (LST ISO 10523:2008) and permanganate index (LST EN ISO 8467).

Analyzing the data, statistically significant differences in the assessment of the effect of the coagulant dose on pH, iron, permanganate index and aluminum concentrations were identified. The influence of coagulant doses was checked with the *Pearson Chi-Square* test (significance level $p \leq 0,05$). Values are presented as arithmetic averages of three independent measurements. The relative standard deviation S_R of water quality parameters (pH, iron, aluminum concentration and permanganate index) was not greater than 10%.

3. Results and discussion

Having performed drinking water treatment using PAC coagulant, and tested drinking water quality after its coagulation and filtration, the dependence of iron concentration and permanganate index efficiency reduction on the coagulant dose was composed. These data are presented in Figure 1.

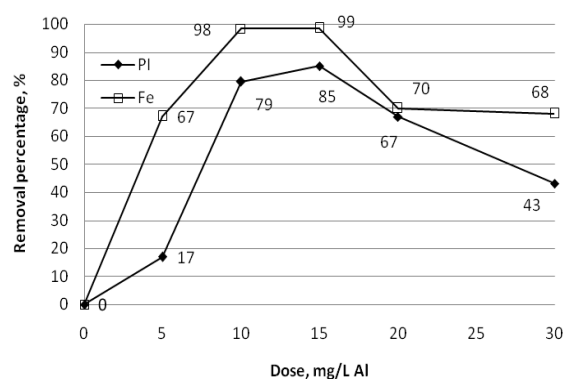


Fig 1. The effectiveness of iron concentration and permanganate index reduction using different coagulant doses

Figure 1 shows that having added the first coagulant dose permanganate index decreased by only 17%, while iron concentration decreased by 67% from the initial concentration. This higher decrease in the percentage of iron concentration, in comparison with the decrease in the percentage of permanganate index, can be explained by the fact that part of the insoluble iron compounds were simply filtered and the other part of iron was in soluble form. By increasing the dose of coagulant further, permanganate index decreased by 79%, and iron concentration decreased by 98%, which means that all organic compounds, which contained iron, had been removed during the coagulation and filtration processes. Increasing the dose of coagulant even further, iron concentration

practically did not change, the concentration of organic compounds decreased, and the effectiveness of permanganate index reduction reached 85%. Increasing the dose of coagulant further, permanganate index and iron concentration efficiency reduction decreased. Iron treatment efficiency decreases less rapidly than permanganate index. The decrease of water treatment efficiency can be explained by the decrease of water pH. When water becomes acidic, coagulation process is incomplete, therefore, the removal efficiency of organic compounds as well as iron decreases. However, part of insoluble iron is eliminated during the filtration process.

Since the permanganate index describes the presence of organic matters in water, and according to the analyzed literature, in which it is stated that when drinking water $PI \geq 3 \text{ mg/L O}_2$ and there are soluble iron compounds in water, then the iron removal process from water complicates. The paper examines the relationship between iron concentration decrease and permanganate index change depending on the coagulant dose. The change is illustrated in Figure 2.

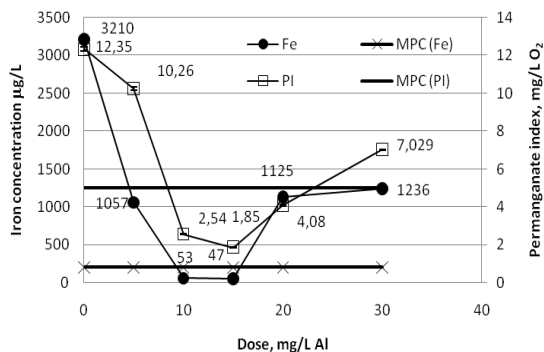
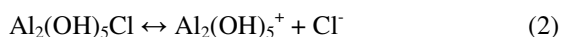


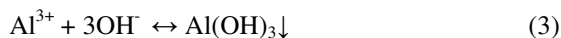
Fig 2. The change in iron concentration and permanganate index indicator using different coagulant doses

When we add the first coagulant dose, in which aluminum concentration is 5 mg/L, we see that iron concentration is still very high and exceeds the permissible rate. Permanganate index is 10.26 mg/L O₂. Increasing the coagulant dose (10 mg/L Al) further, permanganate index decreases even more; its value is lower than 3 mg/L O₂ and iron concentration no longer exceeds the permissible rate. Therefore, the claim that the iron is removed more easily when the permanganate index is lower than 3 mg/L O₂ is confirmed. Increasing coagulant dose (15 mg/L) even more, iron concentration continues to decrease, permanganate oxidation also decreases. Increasing the coagulant dose (20 mg/L Al) further, iron concentration and permanganate index increase.

The study uses aluminium based coagulant (Al₂(OH)₅Cl), therefore, it is necessary to follow that the residual aluminium concentration would not exceed the permissible rate (200 µg/L) in the treated water. Aluminium chlorides stimulate water impurities (iron compounds) to coagulate.



Newly arisen trivalent aluminium cations react with the substances in water. Particles of suspended impurities absorb part of the cations. The other part of the cations hydrolyses and sparingly soluble aluminium is formed:



Since aluminium hydroxide is insoluble, after filtration of water, it must retreat from it. Figures 3 and 4 demonstrate the evolution of concentration of iron and aluminium depending on the coagulant dose and water pH, and what happens to aluminium which becomes soluble and is able to get into drinking water.

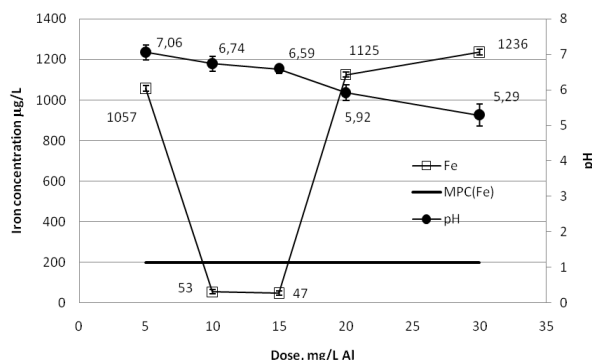


Fig 3. The change of iron concentration and water pH using different coagulant doses

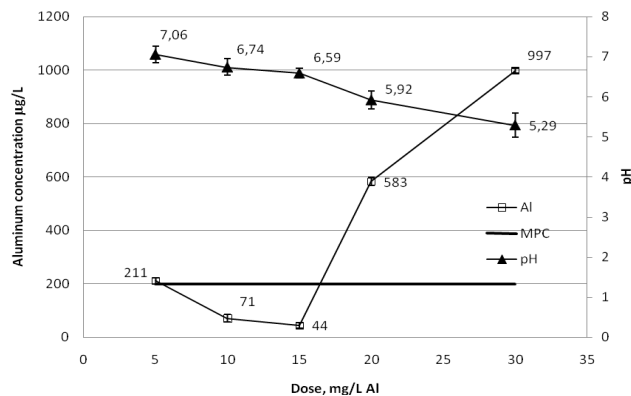


Fig 4. The change of aluminium concentration and water pH using different coagulant doses

Figures 3 and 4 show that when we added the first coagulant dose into the sample of drinking water, the process of coagulation was not fully. This means that sufficient number of insoluble aluminium hydroxide, which did not form flakes and did not remove the organic complex compounds of iron from water, had not been formed yet. Iron concentration value still exceeds the permissible rate, and aluminium concentration also slightly exceeds the permissible rate. Increasing the coagulant dose (10 mg/L Al) further, iron concentration decreased significantly and does no longer exceed the permissible rate. Aluminium concentration also does no longer exceed the permissible rate. Water pH equals 6.74.

This indicates that coagulation has occurred; insoluble aluminum hydroxides, which produced flakes and absorbed iron compounds, were formed and filtered. Increasing the coagulant concentration further, coagulation successfully continues, iron and aluminum concentrations do not exceed the permissible rate. Increasing coagulant dose even more, water pH decreases and is approaching to pH 6.0. Aluminium concentration in water slightly increases, iron concentration also increases. This means that the medium becomes acidic, and while reducing water pH, the aluminum becomes soluble and does no longer produce insoluble aluminum hydroxide, coagulation does not take place, therefore, the iron organic complex compounds are not removed. Residual aluminium concentration increases in water.

The literature has mentioned that coagulation is highly dependent on water pH. Aluminum hydroxide dissociation is minimal when water pH is from 6.5 to 7.5. When water pH is below 6.5, particles of aluminum hydroxide acquire a positive charge, when more than 7.5 – a negative charge. When water pH is less than 5.0 and greater than 8.0, almost all aluminum hydroxide disassociate, i.e., it is transferred to the ion state. The figures 3 and 4 show that coagulation is most effective when water pH is between 6.74 and 6.59. Increasing the coagulant dose further, the water becomes acidic, aluminium begins to melt and coagulation process does no longer take place.

4. Conclusions

1. The research showed that having added 10 mg/L and 15 mg/L of aluminum, iron removal efficiency from water has reached 98-99%. Further increase of coagulant dose has negative effects on iron removal process.
2. Permanganate index is being gradually reduced by increasing coagulant dose. However, coagulation dose above 15 mg Al/L is not recommended, as efficiency does not increase.
3. Clear relationships between iron and organic matter removal were observed. If one of the parameters is removed, the removal of other pollutants can also be expected.
4. The residual aluminum concentration does not exceed the permissible level and iron concentration conforms to the tolerance limits when coagulant dose is 10 or 15 mg/L.
5. During coagulation process pH level should be monitored or regulated, because the coagulant reducing pH level. Therefore, if pH drops below 6,5, conditions for removal of iron and organic matters become unfavorable.

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