COAGULATION OF SURFACE WATERS WITH PRE-HYDROLYSED IRON SALTS

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Abstract

The use of prehydrolized iron salts based coagulants as substitutes for aluminium based prehydrolized compounds for drinking water is a feasible alternative given the high removal efficiency of natural organic matter when treating water coming from various sources. By using prehydrolized coagulants, the removal efficiencies of the dissolved organic matter, (DOC), are 15-24% higher than in the case of using aluminium salts. On the other hand, as part of these experiments, the residual total organic carbon (TOC), is by 16.5% lower

when prehydrolized iron based salts are used. Each situation is assessed in order to set up the specific working conditions when substitution of iron salts for aluminum compounds is suitable given the fact that even extremely small amounts of residual iron can colour the treated water.

Keywords*:* drinking water, coagulation, prehydrolyzed iron salts

Introduction

Aluminum and iron salts are coagulants used in the treatment of drinking water [1-4]. The coagulation efficiency is directly proportional to the molecular weight coagulants species and is correlated with the acidity of the hydrolysed cations [5]. The pre-hydrolysed Al and Fe salts are a special category of coagulants. The hydrolysed compounds used in drinking water treatment are known as polynuclear salts. They contain a large amount of polymerized metal. The pre-hydrolysis species are more efficient in the reduction of the organic matter as compared to simple salts. Advanced hydrolysis causes the Al and Fe to polymerize as condensate hexametric ring forms [6]. In the past years, questions have been raised by the general public whether a connection between residual Al in the drinking water and certain health related issues, such as Alzheimer disease may be established. Consequently, the use of iron based coagulants in the treatment of water for human consumption has gained popularity. Pre-hydrolysed iron salts (PFC) represent, for the moment, a category of coagulants with a more restrictive applicability in comparison with pre-hydrolysed Al salts. The use of coagulants containing basic Fe polychloride or polysulphate in the drinking water treatment is less refered in literature. The replacement of Al based compounds with iron salts in the treatment of water for human consumption shall be done after a comprehensive analysis, considering all technical, economic, social and environmental impact related issues. Each case shall be assessed taking into account the international practices and results. The efficiency of the water treatment alternative solution consisting in the replacement of the coagulants containing Al with Fe salts is demonstrated for water samples taken from various sources. The data base currently available at international level is not sufficiently documented and requires additional studies. [7]. The analysis of the studies referring to the removal of organic matter from water for human consumption reveals an obvious tendency towards demonstrating the connection between the type of coagulant used, pH, optimal dosage and organic matter removal efficiency. In most of the cases, the Fe salts are associated with high removal efficiency rates. [2, 8]. The concentration of the Fe species coagulants is in equilibrium with the solid hydroxide, depending on the pH value. The adsorption of the Fe compounds on the surface during the coagulation process can influence the composition and concentration of the species present in the solution and also the surface properties. The adsorption on colloids can lead to formation of surfaces covered with complex compounds of pre-hydrloysed Fe species and hydroxy groups of the minerals. The Fe-surface bond may be an acid-base reaction, an ion exchange etc. A continuous surface process can result in adsorption/complexation compounds that finally precipitate. The development of precipitates on mineral surfaces highlights the increase in the density of

precipitated cations in the respective water, below saturation limit. The adsorption and precipitation of the coagulants containing metal species in natural water is a rather complicated process, due to the presence of humic substances. The Fe dosage is conditioned by the composition and concentration of the natural organic matter. [9,10] The humic acids are adsorbed to a greater extent than the fulvic acids, through a broad pH range, between 7 – 11, because the humic acids are more hydrophobic. Generally, the adsorption reduces as the pH value increases, because of the interaction of the electrostatic forces. Studies from the available data base on the removal of algae from synthetic solutions showed that the iron polysulphate was more efficient than the aluminium polychloride or the iron sulphate. But the appearance required by drinking water standards imposes limits on the concentration of the residual amounts of Fe up to 0.3 mg/l. Despite this, the use of Fe chloride at industrial scale, in the treatment plants is a rather complicated issue, due to the „red water" flowing at customers taps. [10]

Experimental part

The research study was carried on 2 simulated water types, T1 and T2. The samples were prepared using surface water from natural sources, with different chemical characteristics, treated with additional amounts of 8 mg/l FLUKA humic acids. The two water types were treated with simple and pre-hydrosed coagulants. All water samples (raw and treated) were characterised through conventional parameters, such as pH, turbidity, A436 or colour, (absorption in the visible spectrum of 436 nm wavelength), COD (chemical oxygen demand) and TOC (total organic carbon) and unconventional chemical parameters such as DOC (dissolved organic carbon), A254 (UV absorption at 254 nm wavelength), the DOC/TOC ratio, and SUVA (specific UV absorption). [11-12]. pH was measured using a Thermo Orion pH-meter at 25 °C and turbidity was measured using a HACH 2100 Turbidimeter. COD, (Chemical Oxygen Demand parameter gives an overall evaluation of almost all organic compounds, which can be fully oxidized to carbon dioxide with oxidising agent under acidic conditions.) TOC and DOC (dissolved organic carbon for filtrated water samples trough 0.45 µm filter) was measured using a Multi C/N 2100S TOC analyzer Analytik Jena; The A254) and A436 (colour), absorbance were determinate using a Specord 205 UV/VIS spectrophotometer Analytik Jena in a 1 cm quartz cuvette. Calculated parameter SUVA= A254/DOC x 100($Lm^{-1}mg^{-1}$) [11-12] and DOC/TOC ratio. Residual metals were measured using a Varian Spectra AAS spectrophotometer. The coagulant agents used are: Alum, $Al_2(SO_4)_3$*$18H_2O$ reagent, provided by Chimopar Bucuresti and poly-ferric chloride, PFC. PFC is characterized by r = 2.4 and was obtained by reaction of ferric salts with a base under carefully controlled conditions. They are typically characterized by degree of neutralisation or alkalinity, expressed as "r" which is the ratio OH/Fe total. Jar Test method: 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 minutes at 25 rpm and last settling for 30 minutes, without pH correction. The supernatant was analyzed.

Results and discussions

Table 1 shows the characteristics of T1 and T2 water, prepared from surface water treated with humic acids. The T1 and T2 water featured the following values for the conventional parameters: a high initial turbidity which falls in the range of 25–32 NTU and an initial COD value between 11.31–14.02 mg O_2/L. The initial TOC value was higher than 10 mg C/L.

Table 1. Characteristics of simulated waters treated with humic acids

No crt.	Parameters	Water supplies	
		T1	T2
Conventional parameters			
1	Turbidity [NTU]	25.00	32.00
2	pH	6,92	7,00
3	COD [mgO_2/L]	11,31	14.02
4	Colour A436 [cm^{-1}]	0,048	0,096
5	TOC [mgC/L]	10,40	13,30
Unconventional parameters			
6	Humic acids [mg/L]	8,00	8, 00
7	DOC [mgC/L]	8,48	11,57
8	A254 [cm^{-1}]	0,351	0,601
9	SUVA [L/mg·m]	4,13	5,19
10	DOC/TOC	0,81	0,86

The unconventional DOC parameter value falls in the range of 8.48 - 11.57 mg C/L. The DOC/TOC ratio in this case is high, for both water types, with values of 0.81–0.86. The DOC/TOC ratio in this case, considering the natural water as the referred media indicated a high amount of undissolved compounds present in water as fine particle and colloidal systems. The study of the spectrophotometric parameters revealed two times higher values for the absorption intensity in T2 as compared to T1 water, for both considered wavelengths of 254 nm, A254, respectively 436 nm, colour (A436).
The SUVA value exceeds 4, which indicates that the organic matter present in both water types is predominantly hydrophobic and the DOC removal efficiencies are above 50%, in accordance with SUVA indications.
Table 2 and 3 show the characteristics of the water samples treated with optimal dosage (OD) of coagulation agents. The optimal doses of the coagulation agents – the simple and pre-hydrolysed salts – are the same, in case of the T1 water. For the T2 water, the PFC, OD is by 14% lower than the alum OD

Table 2 Characteristics of the T1 water samples treated with optimal doses of coagulation agents

No crt.	Parameters	Coagulation agent	
		PCF	Alum
0	*1*	*2*	*3*
	Optimal dose [mgMe/L]*	0.75	0,75

0	*1*	*2*	*3*
Conventional parameters			
1	Turbidity [NTU]	4.5	4,0
2	DOC [mgO_2/lL	3.62	3,32
3	Colour A436[cm^{-1}]	0,019	0,004
4	TOC [mgC/lL	4.88	5,33
5	Residual Fe [mgFe/L]	0.29	
6	Residual Al [mgAl/L]		0.183
Unconventional parameters			
7	DOC [mgC/lL	3.98	4.98
8	A 254 [cm^{-1}]	0,051	0,073

Table 3 Characteristics of the T2 water samples treated with optimal doses of coagulation agents

Nr. crt.	Parameters	Coagulation agent	
		PCF	Alum
	Optimal dose [mgMe/L]*	1,5	1.75
Conventional parameters			
1	Turbidity [NTU]	3,5	4,5
2	DOC [mgO_2/lL	2,9	4,65
3	Colour A436[cm^{-1}]	0,021	0,009
4	TOC [mgC/lL	4,52	5,41
5	Residual Fe [mgFe/L]	0.28	
6	Residual Al [mgAl/L]		0,09
Unconventional parameters			
7	DOC [mgC/L]	3,8	4,82
8	A 254 [cm^{-1}]	0,17	0,072

*Me- metal, aluminium or iron

The OD was established based on the turbidity residual value (5 NTU), A436 colour (that shall not affect the consumer at all) and COD (5 mg O_2/L) in accordance with the standard regulations in force. The tables indicate significant differences recorded in the values of residual parameters for the samples treated with OD of alum, respectively PCF For example, the residual TOC value for samples treated with alum OD is between 5.33 - 5.41 mgC/L, while for the samples treated with PFC OD, the TOC value is lower, between 4.52 - 4.88 mgC/l. For the DOC parameter, the residual values were by 20% smaller in PCF OD treated water samples as opposed to aluminium OD treated samples. Nevertheless, the presence of a residual iron amount in water, at the edge of the „red water" effect alters the real values of the A436, respectively A254 parameters for the samples treated with the OD of PFC coagulant A comparison of the removal efficiencies of the organic matter, expressed as conventional parameters is presented in Figures 1a and 1b, and as unconventional parameters in Figure 1c and 1d.

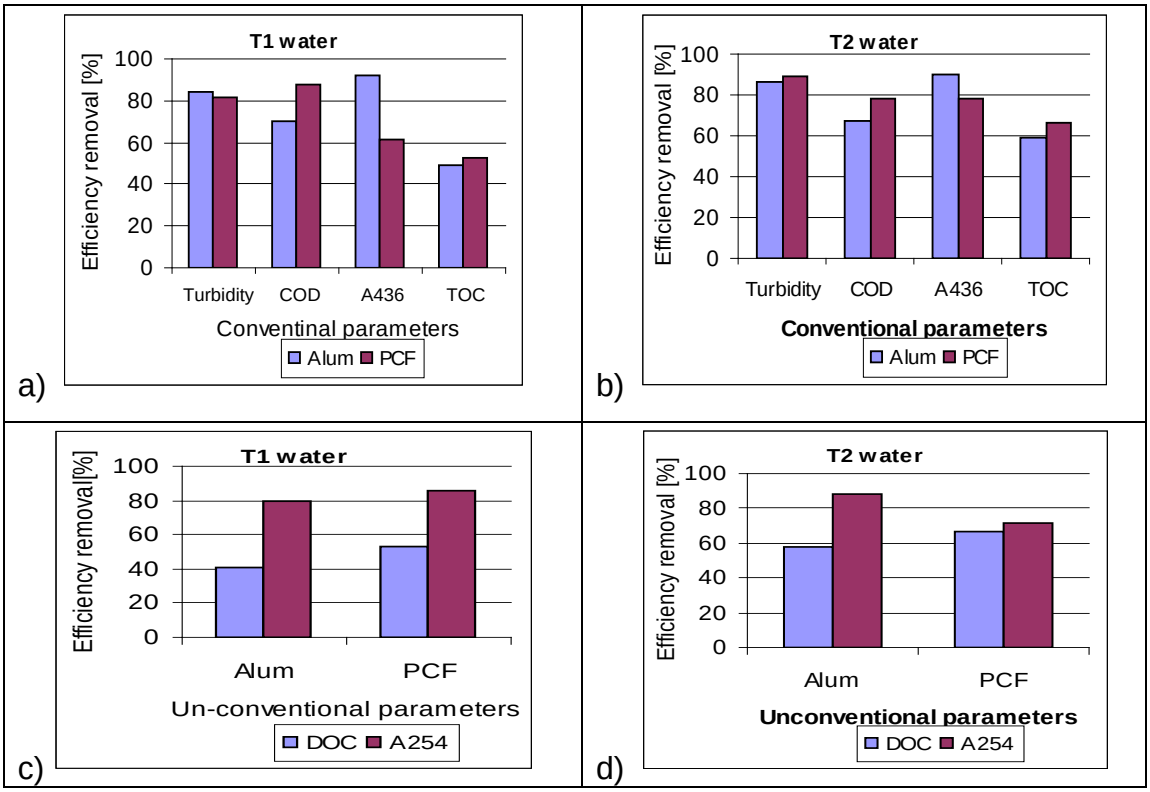

Figure 1 Removal efficient: a) conventional parameters T1; b) conventional parameters T2; c) unconventional parameters T1; d) unconventional parameters T2.

One can notice that the organic matter, expressed as COD, TOC, DOC and A254, was more efficiently decreased when treated with the OD of PCF, in both water types as opposed to treatment with alum. According to the SUVA value, the DOC removal efficiencies for both water types shall exceed 50%. For T1 water, the DOC removal efficiency at treatment with the alum OD is less than 50%.The SUVA was close to 4 in this case, which indicates the likely presence of a hydrophilic/ hydrophobic mixture, leading to efficiencies falling in the SUVA range of 2-4, that corresponds to estimated yields of 25-50%. On the other hand, the use of pre-hydrolysed Fe salts led to the increase in the DOC removal efficiency by 24%, at similar optimal doses, which is in accordance with the SUVA estimated range and proves an increased capacity for removal of the DOC. In case of T2, the SUVA estimations on the DOC removal efficiency are observed in both coagulants used. It is worth mentioning that the DOC reduction efficiency obtained is by 15% higher at treatment with the OD of pre-hydrolised iron based coagulant The alternative considered by this study to replace the Al based coagulants with Fe compounds was demonstrated by high removal efficiencies of the DOC, recorded in the treatment of two water types. The data obtained are not sufficient and require further investigations, for the improvement of the water appearance related issues.

Conclusions

The water types considered in this study contained a large amount of dissolved natural compounds, fine particles and colloidal systems. The DOC/TOC ratio fell in the range of 0.81-0.86 and indicated the prevalence of dissolved compounds present in water as colloidal systems and fine particles. The two water types considered in this study were treated with simple and pre-hydrolysed salts based coagulants. The optimal doses used for the simple and pre-hydrolysed salt based coagulants were similar or by 14% lower for the PFC coagulant. The SUVA > 4, which indicated a predominant hydrophobic character of the organic matter present in both water types, leads to DOC removal efficiencies above 50%, in accordance with the SUVA estimations. The alternative considered by this study, to replace the Al based coagulants with iFe compounds was demonstrated by higher removal efficiencies of the DOC, incurred in the treatment of both water types. The use of pre-hydrolysed Fe salts led to the increase in the DOC removal efficiency in both cases, in accordance with the SUVA estimated. The DOC removal efficiencies obtained when PCF compound were by 15-24% higher vs. treatment with Al salts.

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