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REMOVAL OF HUMIC SUBSTANCES IN WATER BY COAGULATION

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Abstract: *Basic characteristics of humic substances and their negative influence on water quality and its treatment are described in the paper. Humic substances are unwanted therefore their removal is necessary. This can be done by coagulation which plays an important role in surface water treatment. This statement was confirmed in laboratory experiments. In order to remove humic substances from surface water of the water reservoir in Hriňová coagulation was used. As the coagulation reagent either ferric sulfate or aluminium sulfate was used as well. An optimum coagulant dosage was soughed. A treatment with ferric sulfate as well as aluminium sulfate can be sufficient if the acceptable limit for humic substances is 2.5 mg/L, our experiments showed. To reach a reduction of humic substance contents below its level of 1 mg/L dosage of 16 mg/L of 1% solution* $Fe_2(SO_4)_3$ *(Prefloc), which is the equivalent of 4,47 mg/L* Fe^{3+} *was sufficient.*

Keywords: *water treatment, humic substances, coagulation, drinking water, water analysis*

1. Introduction

Humic substances (mainly humic acids and fulvic acids) are present in almost all natural waters, which often represent a major proportion of organic pollution (in literature known as the natural organic matter - NOM).

Humic substances (HS) are complex high molecular weight organic compounds, with aromatic-aliphatic character, containing carbon, oxygen, hydrogen and nitrogen. Relative molecular mass of humic substances ranges from a few hundred to tens of thousands [1]. The elementary composition of humic substances, which are most commonly found in natural waters is shown in **Table 1** [2].

Table 1
Elemental composition of humic substances present in natural waters

Humic substances	composition (%)			
	C	O	H	N
Fulvic acid	43-52	42-51	3.3-6.0	1.0-6.0
Humic acid	52-62	30-39	2.5-5.8	2.6-5.1

Humic substances contain on average about 50% of organic carbon, followed by oxygen, hydrogen and nitrogen. Representation of oxygen in fulvic acids is significantly higher than in humic acids.

The humic substances are characterized by the presence of carboxylic acid, the hydroxy (phenol, alcohol) and also methoxy and carbonyl groups. These groups are bound to the nucleus, and the aliphatic side chains too. The average composition of functional groups of humic substances (with molecular weight in the range 1200 – 1600) is shown in **Table 2** [3].

Table 2
Average composition of functional groups in humic substances

Functional group	Humic acid	Fulvic acid
- COOH	4.4	8.1
- OH	3.3	3.9
- OH (R)	1.9	4.0
= C = O	1.2	1.4
$- O – CH_3$	0.3	0.4

The structure of humic substances could not be fully identified. These substances are attributed different, essentially hypothetical formulas, which is to capture the particular position of COOH and OH in the molecule, which significantly influences the properties of humic substances [4, 5].

The negative effect of humic substances on water quality and its treatment can be summarized as follows [2,3]:

- increase the intensity of the color of water
- increase the acidity of water
- affect the biochemical stability
- influence the formation of metal complexes
- influence the formation of THM in water chlorination

The presence of humic substances in waters is showed of their colouring, for example, fulvic acids are dependent on the concentration of light yellow to yellowish-brown color, humic acids are dark brown. Because of their origin it is the natural color of water. Generally, the concentration of humic substances 2.5 mg.l^{-1} corresponds to the color of water about 20 mg.l^{-1} Pt. However, color changes considerably with the pH of water (the colorful solutions with higher pH). In addition, the color of the water depends on the composition of humic substances, on the size of disperse particles, etc., which may be different in various surface waters. Therefore, it cannot get universal linear relationship between the concentration of humic substances and water color.

Humic substances are characterized by complexing properties [6,7,8]. Formation of complex is one of the causes leaching of heavy metals from soil humic substances (increasing their content in water) and cause increased concentrations of Fe and Mn in peat waters.

From a technological point of view, humic substances cause problems in water treatment [9,10], for example, increase consumption of coagulant and disinfectants, but mainly act as precursors of halogenated compounds.

Only high molecular humic acids can be removed from the water with coagulation, but for fulvic acids with low molecular weight (molecular mass to 500) is efficiency of removing smaller ones and some fraction cannot be removed at all.This is due to the size of molecules or particles. Larger molecules eventually particles are easily separated by coagulation, sedimentation and filtration processes in comparison with small molecules and particles. With increasing concentration of humic substances with increasing pH, the size of molecules or particles decreases, what makes worse the effect of separation. The best effect is achieved in the treatment of humic waters by clarification earlier in the acidic range (pH 4-6), which formed a large and well separable units.

Aggressive properties of humic waters have negative effect for metals and building materials (mortar and concrete), which cause not only acidity but also their ability to form complexes, in case of mortar and concrete to the aggressive leaching, which tends to increase the solubility of $CaCO_3$ and CaO.

Important precursors of organohalogen compounds in water are mainly fulvic acids and humic acids. Experimentally, it was confirmed that the fulvic acids occurs in approximately 60% more organochlorine compounds in comparison with humic acids [11]. Fulvic also have greater water solubility than humic acids, therefore natural water contains an average of 87% fulvic acids. To prevent the formation of chlorinated hydrocarbons it is necessary to reduce the content of humic substances in water or change the method of disinfection.

Due to these characteristics, the humic substances in drinking water and process water are unwanted.

In some industries, these substances (e.g. textile, paper) can impair the quality of the product color.

The determination of humic substances in drinking water is not present in Slovak Government Regulation No.496/2010 on Drinking water. It is based on the value of the COD-Mn, absorbance (A254), or color of water. Exceeding the limit values is the reason for the decision to determination of humic substances.

In the older standard for drinking water (STN 757111) humic substances were limited to value of 2.5 mg.l^{-1}. The excess value of 2.5 mg.l^{-1} indicates the possible presence of THM in water provided by chlorine. In the requirements for the quality of raw water for treatment of drinking water (STN 757214) humic substances are included in the cut-off value for the color of water (20 mg.l^{-1} Pt).

The lowest concentration of humic substances found in groundwater (up to 0.1 mg.l^{-1}). In year 1996, concentrations of humic substances in Czech drinking water was ranged from about 0.04 mg.l^{-1} up to 6.77 mg.l^{-1}, the average value 0.63 mg.l^{-1} [12]. The surface water concentration of the order of units mg.l^{-1}. In the waters of peat humic substances concentration fluctuates over a wide range, typically in the tens mg.l^{-1}. In some standing water can be determined the concentration of humic substances up to 500 mg.l^{-1} [13].

Tab. 3
Concentration of humic substances (HS) in the raw water (RW) and treated water (TW) from water treatment plant (WTP)

WTP	Inlet of RW		Outlet of TW	
	HS (mg/l)	COD_{Mn} (mg/l)	HS (mg/l)	COD_{Mn} (mg/l)
Stariná	4.5	2.08	2.9	1.76
Hriňová	4.9	4.72	4.7	1.92
Klenovec	3.3	2.32	3.6	1.76
Málinec	4.5	2.08	2.9	1.76

For the determination of the humic acids are recommended spectrophotometry methods in the visible zone at a wavelength of 420 nm or in the zone of ultraviolet light at a wavelength of 254 nm.We used spectrophotometric method, which uses extraction of humic substances at low pH in pentanol and subsequent reextraction of pentanol solution of NaOH [14,15]. The conversion of absorbance to concentration is using either an empirical coefficient (valid for peat water in Slovakia), or even commercial standard (Aldrich, Merck). Currently is used concentrating on various sorbents (XAD, Sephadex-DEAE) followed by desorption with NaOH solution. After removal of the inorganic forms of carbon is determined value of DOC (TOC).

The concentration of humic substances is obtained by multiplying the DOC mg.l^{-1} in two, because humic substances contain about 50% carbon. In literature [16] is present relation for humic substances COD-Cr ≅ DOC.

Indirect determination can be used for water, where in the organic matter dominate humic substances. Then content of humic substances is calculated by the concentration of COD-Mn, whose value is multiplied by an empirical factor of about 1.2 (valid for peat water in Slovakia).

Complicated determination of humic substances is the reason not to apply the results to their weight, but to the amount of organic carbon which is contained in them. Taking into consideration that humic substances contain about 50% organic carbon, is recommended to express the concentration of humic substances as DOC (TOC) in mg.l^{-1} [17].

2. Experimental

The experimental part of this work aime consists in removing the humic substances from water by coagulation. There were compared two coagulants, aluminum sulphate (Kemwater) and ferric sulphate - Prefloc (Kemifloc) to find the optimal dose for reduction of humic substances in surface water from water reservoir Hriňová.

2.1. Coagulation test

For the coagulation test was used device with five mixers with adjustable speed and high-speed mixing. Into five flasks were added per liter of raw water. After adding a coagulant (1% solution) followed by 3 minutes rapid mixing (180 rpm) and 10 minutes slow mixing (40 rpm). After mixing followed sedimentation of sample, which took 1 hour and then filtration through filter paper. Thus prepared sample was analyzed. The following parameters were monitored: pH, $ANC_{4,5}$, Fe or Al concentration, turbidity, color, TOC, and COD-Mn concentration of humic substances. Results of measurements are shown in the Table 4.

2.2 Determination of humic substances

Into separating flask 500 ml was added the 250 ml samples of water and 5 ml of concentrated H_2SO_4. After mixing, into banks was added 25 ml pentanol. After intense hand-shaking during 30 seconds and the separation of the layers (after two hours), was removed the aqueous layer. Into the separation flask was added 25 ml 0.5% solution of NaOH. Content of the flask was mixed (10 seconds). After 10 minutes part of the sample (about 3-4 ml) was took away (to clean the stem separating funnel) and the clear solution was added into a spectrophotometric cell (length 1 cm) and then the absorbance at a wavelength of 420 nm was measured. From the measured absorbance was read the absorbance of the blank of distilled water, which was made with the same procedure.

3. Results and Discussion

Coagulation is an important process in the treatment of surface water. On the present surface water treatment is possible without the addition of chemical compounds only in sporadic cases. The advantage of coagulation is that addition of coagulants effects not only to colloidal and fine dispersion substances but to all others suspended solids which form flakes with high ability to settle. Iron, respectively aluminum salts are the most widely used coagulants.

Required dose of coagulant varies with the quality of raw water. The optimum dose of coagulant is possible to determine in the laboratory with coagulation test. The results of coagulation tests aimed at removing of the humic substances from surface water Hriňová dam (WTP Hriňová) are listed in Tables 1 and 2. The effectiveness of coagulation was monitored for two coagulants, aluminum sulphate and ferric sulphate.

On the basis of the results shown in Tables 4 and 5 it can be concluded that the ferric sulphate coagulant is more suitable for removing humic substances from water as aluminum sulphate (there are not wide differences between the used coagulants). These results should be confirmed by long-term monitoring, specially monitoring of changes water quality during the seasons.

The highest efficiency of coagulation, respectively lowest value of humic substances was reached at a dose of coagulant 16 $mg.l^{-1}$ (1% solution), i.e. 4.47 $mg.l^{-1}$ converted to Fe^{3+}, or 2.52 $mg.l^{-1}$ calculated for Al^{3+}.

The comparison of the removal efficiency of humic substances by different coagulants (Fe^{3+}, Al^{3+}) is shown in Fig. 1. Humic concentration of the raw water before coagulation was 5.44 mg/l.

Table 4
The results of coagulation tests removal of humic substances with $Fe_2(SO_4)_3$

The dose coagulant [mg Fe^{3+}/l]	pH	ACN$_{4,.5}$ [mmol/l]	Fe [mg/l]	HS [mg/l]	COD$_{Mn}$ [mg/l]	TOC [mg/l]	FTU [ZF]	color [mg/l]
0	6.52	0.534	0.08	5.44	2.56	3.4	3.0	11.0
3.35	5.90	0.276	0.06	1.22	1.92	2.5	< 2.0	9.0
3.91	5.54	0.241	0.05	1.08	1.76	2.4	< 2.0	7.0
4.47	5.05	0.076	0.08	0.89	1.28	1.9	< 2.0	5.0
5.03	4.62	0.034	0.08	1.46	1.26	1.8	< 2.0	4.0
5.58	3.91	0.0	0.06	1.63	1.38	2.2	< 2.0	4.0

Table 5
The results of coagulation tests removal of humic substances with $Al_2(SO_4)_3$

The dose coagulant [mg Al^{3+}/l]	pH	KNK$_{4,.5}$ [mmol/l]	Al [mg/l]	HS [mg/l]	COD$_{Mn}$ [mg/l]	TOC [mg/l]	FTU [ZF]	color [mg/l]
0	6.67	0.548	0.01	5.44	2.56	3.5	3.0	11.0
1.89	6.60	0.445	0.02	3.26	2.40	3.3	< 2.0	6.0
2.21	6.48	0.342	0.02	2.28	2.24	3.2	< 2.0	6.0
2.52	6.43	0.310	0.02	1.43	2.02	3.1	< 2.0	4.0
3.00	6.82	0.457	0.02	1.67	2.08	3.2	< 2.0	5.0
3.15	6.90	0.532	0.02	1.92	2.16	3.2	< 2.0	6.0

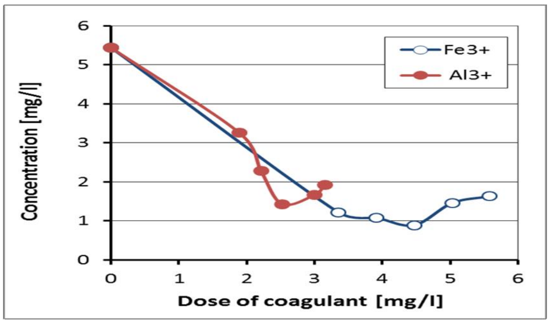

Figure 1. The removal of humic substances from water by coagulation

Because the influence of ferric sulfate, respectively oxide reduces the pH value, it is necessary to adjust the pH after coagulation. Determination COD-Mn and TOC conversion confirmed the relationship between these parameters and humic substances in the literature.

4. Conclusion

Laboratory tests with surface water from WTP Hriňová showed that coagulation using ferric sulfate (alum also) is the type of water sufficient method to remove humic substances from water (if we limit the comparison to humic substances 2.5 mg.l^{-1}). Already dose of 16 mg.l^{-1} of 1% solution $Fe_2(SO_4)_3$ (Prefloc), which is the equivalent of 4.47 mg.l^{-1} Fe^{3+} is sufficient for reduction of humic substances below 1 mg.l^{-1}. By the influence of iron sulphate to a reduction in pH should be adjusted pH of water after coagulation.

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