

Removal of Humic Substances in Water by Granular Activated Carbon

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Abstract. The basic characteristics of humic substances and their negative influence on water quality and its treatment are described. The paper presents the results of removing humic substances from water from the Hriňová (Slovakia) water reservoir with the addition of humic substances using granular activated carbon (GAC) from two producers (Chemviron, Cabot) at three different pH levels of water. The results of static experiments involving the removal efficiency of humic substances using TOC parameters and the instantaneous water adsorption capacity, which uses materials at the contact time of the water with GAC material, was calculated.

The results show that the pH of the water had no significant effect on the change in the efficiency of removing humic substances from water. A high level of efficiency (50%) and the lowest value of TOC are obtained at a pH of 6.5. The GAC adsorption capacity of humic substances, depending on the contact time with the water, ranged from 0.17 mg/g for one hour to 0.56 mg/g for eight hours of contact time. The most effective material was Filtrasorb F400.

Keywords: drinking water, water treatment, humic substances, adsorption, GAC.

Conference topic: Water engineering.

Introduction

Humic substances (mainly humic acids and fulvic acids) are present in almost all natural waters and often represent a major proportion of organic pollution (known in the literature as natural organic matter – NOM) (Filella 2009).

Humic substances are complex high molecular weight organic compounds, with an aromatic-aliphatic character, that contain carbon, oxygen, hydrogen, nitrogen and sulfur. The relative molecular mass of humic substances ranges from a few hundred to tens of thousands. The factors that determine the composition of humic substances are location dependent and include the source of the organic matter, the water chemistry, temperature, pH, and biological processes (Leenheer, Croué 2003). The elementary composition of humic substances is shown in Table 1 (Schnitzer, Khan 1972).

Table 1. Common properties of humic acid (HA) and fulvic acid (FA)

Property	HA	FA
Elementar composition (% by weight)		
Carbon	50–60	40–50
Hydrogen	4–6	4–6
Oxygen	30–35	44–50
Nitrogen	2–4	1–3
Sulfur	1–2	0–2
Functional group distribution (% of oxygen is indicated in functional groups)		
Carboxyl (–COOH)	14–45	58–65
Phenol (–Ph)	10–38	9–19
Alcohol (–R–OH)	13–15	11–16
Carbonyl (–C=O)	4–23	4–11
Methoxyl (–O–CH ₃)	1–5	1–2

Humic substances are characterized by the presence of carboxylic acid and the hydroxy (phenol, alcohol), methoxy, and carbonyl groups. These groups and the aliphatic side chains are bound to the nucleus (Uyguner-Demirel, Bekbolet 2011; Snoeyink, Jenkins 1980). Aquatic humic acids are larger than fulvic acids, but fulvic acids have more

carboxylic groups and oxygen; hence, they have less carbon on a mass basis than humic acids. FA are also more soluble in water, because they have more polar groups per unit mass than HA; therefore, natural water contains an average of 87% fulvic acids.

The structure of humic substances cannot be fully identified. Different, essentially hypothetical formulas are attributed; their task is to capture the particular positions of COOH and OH in a molecule, which significantly influences the properties of humic substances (Nriagu, Coker 1990; Peña-Méndez *et al.* 2005). Figure 1 and 2 shows the model structure of humic acids and fulvic acids.

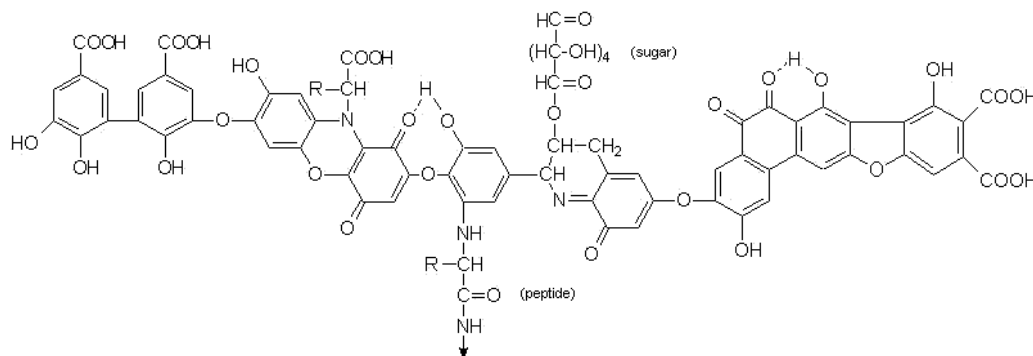


Fig. 1. Model structure of humic acid (Stevenson 1982)

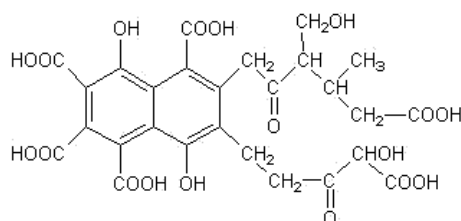


Fig. 2. Model structure of fulvic acid (Buffle *et al.* 1977).

The negative effect of humic substances on water quality and its treatment can be summarized in that they:

- increase the intensity of the color of water,
- increase the acidity of water,
- increase the aggressiveness of water on metals and building materials (mortar and concrete),
- affect the biochemical stability of water,
- influence the formation of metal complexes and increase the heavy metal content in water,
- influence the formation of THM in water chlorination,
- decrease the removability of the low molecular weight of fulvic acids that have coagulated,
- increase the consumption of coagulants and disinfectants.

Important precursors of organohalogen compounds in water are mainly fulvic acids and humic acids. Experimentally, it was confirmed that fulvic acids occur in approximately 60% more organochlorine compounds in comparison with humic acids (Rook 1974; Krasner *et al.* 2006). 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.

The most common and economically feasible processes to reduce NOM are coagulation and flocculation followed by sedimentation/flotation and filtration. Most of the NOM can be removed by coagulation, although hydrophilic, low molecular weight fractions of NOM (molecular mass up to 500) are apparently removed less efficiently (some fractions cannot be removed at all) than hydrophobic, high molecular weight compounds. Thus, low molecular weight fractions and hydrophilic NOM dominate the residual organic matter after coagulation. The best effect is achieved in the treatment of humic waters by clarification earlier in the acidic range (pH 4–6), which form large and well-separated units (Eikebrokk *et al.* 2004).

Other treatment options for NOM removal include magnetic ion exchange resin (MIEX®) techniques, activated carbon filtration, membrane filtration methods, electrochemical methods and advanced oxidation processes (AOPs) (Sillanpää 2015; Bond *et al.* 2011; Zhao *et al.* 2009; Ødegaard *et al.* 2010; Quinlivan *et al.* 2005; Cheng *et al.* 2005; Jacangelo *et al.* 1995; Jarvis *et al.* 2008).

Properties of aquatic humic substances and their behavior in coagulation, sorption on activated carbon, ion-exchange and membrane processes, and their reactions with ozone and chlorine have been detailed in books and journals (Suffet, MacCarthy 1989; Allard *et al.* 1991; Aiken *et al.* 1985; Ødegaard *et al.* 1999).

In practice, NOM is usually characterized by the measurement of its TOC, DOC, adsorption of UV light (UV254), or COD. NOM is also a major contributor to the brownish-yellow color in water; thus, measurement of color can provide some indication of the amount of NOM that the water contains (Uyguner-Demirel, Bekbolet 2011). Tests mostly provide information about the quantity of NOM, while offering limited information on its qualities.

Generally, a 2.5 mg/L concentration of humic substances corresponds to about 20 mg/L Pt to the color of water. However, color changes considerably with the pH of water (more colorful solutions with a higher pH). In addition, the color of the water depends on the composition of the humic substances, the size of the dispersed particles, etc., which may be different in various surface waters. Therefore, a universal linear relationship between the concentration of humic substances and the water color cannot be determined (Pitter 2009).

The specific UV-absorbance (SUVA) value (i.e., the UV254 absorbance in m^{-1} divided by the TOC or DOC concentration in mg/L) is a good indicator of water quality and the humic fraction of the TOC (DOC). A high SUVA value (4 L/mg.m or higher) indicates that the organic matter is largely composed of hydrophobic, high-molar mass organic material. A low SUVA value (less than 2 L/mg.m) indicates that the water contains organic compounds that are mainly hydrophilic, with a low molar mass and charge density. Due to their diverse properties, different NOM fractions respond differently to treatment by coagulation, coagulant demands, chlorine and ozone reactivity, and the formation of potential disinfection by-products (Sillanpää 2015).

For determining humic acids, spectrophotometry methods in the visible zone at a wavelength of 420 nm or in a zone of ultraviolet light at a wavelength of 254 nm, and the extraction of humic substances at a low pH in pentanol, a long with the subsequent reextraction of a pentanol solution of NaOH, are recommended (Pitter 2009; Eaton *et al.* 1995). The conversion of the absorbance to a concentration uses either an empirical coefficient (valid for peat water in Slovakia) or even a commercial standard (Aldrich, Merck). Currently, concentrating on various sorbents (XAD, Sephadex-DEAE) followed by desorption with a solution of NaOH is used. After removal of the inorganic forms of carbon, the value of the DOC (TOC) is determined.

The concentration of humic substances is obtained by multiplying the DOC mg/L by two, because humic substances contain about 50% carbon. According to the literature (Pitter 2009), the present relation for humic substances is $\text{COD-Cr} \approx \text{DOC}$.

An indirect determination can be used for water, where humic substances dominate the organic matter. Then the content of humic substances is calculated by the concentration of COD-Mn, the value of which is multiplied by an empirical factor of about 1.2 (valid for peat water in Slovakia) (Pitter 2009).

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, the absorbance (A^{254}), or the color of the water. Exceeding the limit values is the reason for a decision to determine the humic substances.

In the older Slovak technical standard for drinking water (STN 75 7111) humic substances were limited to a value of 2.5 mg/L. The excess value of 2.5 mg/L indicates the possible presence of THM in water treated with chlorine. In the requirements for the quality of raw water for the treatment of drinking water (STN 75 7214), humic substances are included in the cut-off value for the color of the water (20 mg/L Pt).

In aqueous samples, the concentrations of organic compounds are mostly expressed as total organic carbon (TOC) or dissolved organic carbon (DOC). Differentiation between both parameters is normally carried out by 0.45 μm membrane filtration. DOC concentrations of aquatic systems range from < 1mg/L in most groundwaters to several tens of mg/L in the brown water of swamps. Rivers typically show DOC concentrations of a few mg/L. The contribution of HS to the DOC as defined by specific isolation procedures can be found in the range between 40% to 70%. Some typical values for most abundant aquatic systems are given in Table 2 (Frimmel 2001).

Table. 2. Typical ranges for dissolved organic carbon concentrations (DOC) and humic contribution in selected aquatic systems

Source	DOC (mg/L)	HS (mg/L)
Sea water	0.2 ± 2.0	0.06 ± 0.6
Groundwater	0.1 ± 2.0	0.03 ± 0.6
River	1 ± 10	0.5 ± 4.0
Donau	1.7	1.0
Rhein	2.2	1.3
Lake	1 ± 50	0.5 ± 40
Bodensee	1.2	0.6
Starnberger See	3.2	1.5

In 1996, concentrations of humic substances (HS) in Czech drinking water ranged from about 0.04 mg/L up to 6.77 mg/L; the average value was 0.63 mg/L (Kratzer, Kožíšek 1997). The surface water concentration was on the order of units mg/L (Table 3). The concentration of humic substances in peat waters, fluctuates over a wide range,

typically in the tens mg/L. In some standing water, the concentration of humic substances can be determined to be up to 500 mg/L.

Table 3. Concentration of HS in the raw water (RW) and treated water (TW) from water treatment plant (WTP) in Slovakia

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	3.72	4.7	1.92
Klenovec	3.3	2.32	3.6	1.76
Málinec	4.5	2.08	2.9	1.76

The aim of this work was to investigate the effectiveness of removal humic substances from the surface water of Hriňová water reservoir with the addition of humic substances using granular activated carbon (GAC) from two producers (Chemviron, Cabot) at three different pH levels of water.

Experimental part

The experimental part of this work focused on removing humic substances from water using sorption with granular activated carbon from two different producers:

1. Norit 1240 (Calbon Carbot, USA);
2. Filtrasorb F100 (Chemviron Carbon, Belgium);
3. Filtrasorb F400 (Chemviron Carbon, Belgium).

The Filtrasorb F100 and F400 materials were delivered by the Jako, Ltd. Company; the Norit material was supplied by Vulcascot, Ltd. The basic properties of the GAC materials used are shown in Table 4.

Table 4. Basic properties used materials GAC

Specification	F100	F400	Norit 1240
Iodine number, minimum [mg/g]	850	1050	975
Grain size [mm]	0.60–2.36	0.42–1.68	0.42–1.68
Effective size [mm]	1.6	1.0	0.7
Abrasion number, minimum [%]	75	75	78
Hardness	95	95	97
Moisture content [%]	max. 2	max. 2	max. 2
Apparent density [kg/m ³]	500	425	470
Methylene blue [mg/g]	230	260	220
Surface area (BET) [m ² /g]	900	1100	1100
Uniformity coefficient	1.9	1.7	1.6

Results and discussion

The experimental work, which was divided into 3 parts, was performed as follows:

1. The removal of humic substances from the model water at a pH of 6.5 (adjusted by the addition of HCl); the initial concentration of the TOC was 13.02 mg /L,
2. The removal of humic substances from the model water at a pH of 7.5 (the pH of drinking water) and the TOC concentration of 13.45 mg /L,
3. The removal of humic substances from the model water at a pH of 8.5 (adjusted by the addition of NaOH); the initial concentration of TOC in the raw water was 13.77 mg /L.

The effectiveness of the removal of the humic the substances from the model water samples with respect to the contact time of the water with the GAC materials and the different pH levels of the water are shown in Tables 5 to 7.

Table 5. The measured values of the first series experiments (at pH 6.5)

No.	GAC	0 hours	1 hours	2 hours	4 hours	8 hours
		TOC (mg/L)				
1	Norit 1240	13.02	11.34	10.11	8.74	7.47
2	Filtrisorb F100	13.02	11.78	10.7	9.39	7.92
3	Filtrisorb F400	13.02	11.29	9.79	8.04	6.3
		Absorbance A ²⁵⁴				
1	Norit 1240	0.148	0.129	0.124	0.116	0.096
2	Filtrisorb F100	0.148	0.132	0.125	0.118	0.102
3	Filtrisorb F400	0.148	0.146	0.129	0.121	0.103

Table 6. The measured values of the first series experiments (at pH 7.5)

No.	GAC	0 hours	1 hours	2 hours	4 hours	8 hours
		TOC (mg/L)				
1	Norit 1240	13.45	11.56	10.27	9.28	8.09
2	Filtrisorb F100	13.45	11.95	10.63	9.06	8.48
3	Filtrisorb F400	13.45	11.49	10.29	8.72	6.6
		Absorbance A ²⁵⁴				
1	Norit 1240	0.150	0.133	0.125	0.119	0.106
2	Filtrisorb F100	0.150	0.138	0.127	0.119	0.109
3	Filtrisorb F400	0.150	0.137	0.132	0.116	0.102

Table 7. The measured values of the first series experiments (at pH 8.5)

No.	GAC	0 hours	1 hours	2 hours	4 hours	8 hours
		TOC (mg/L)				
1	Norit 1240	13.77	12.41	11.09	9.69	8.75
2	Filtrisorb F100	13.77	12.45	11.22	9.7	8.38
3	Filtrisorb F400	13.77	12.29	10.89	9.17	8.15
		Absorbance A ²⁵⁴				
1	Norit 1240	0.151	0.139	0.130	0.121	0.101
2	Filtrisorb F100	0.151	0.139	0.131	0.122	0.106
3	Filtrisorb F400	0.151	0.144	0.132	0.124	0.117

From the TOC values determined in the experiments, the adsorption efficiency η (1) and the immediate adsorption capacity at (2) were calculated by the following formula:

$$\eta = \frac{(c_0 - c_m)100}{c_0} \quad [\%]; \quad (1)$$

$$a_t = \frac{(c_0 - c_m)V}{m} \quad [\text{mg/g}], \quad (2)$$

where: c_0 (mg/L) represents the TOC concentration before adsorption; c_m (mg/L) represents the TOC concentration after adsorption at the time t ; V (litre) represents the volume of the water solution of the pollutant; m (g) represents the weight of the adsorbent; η (%) is the adsorption efficiency; and a_t (mg/g) is the momentary adsorption capacity, i.e., the amount of the pollutant which is adsorbed by the mass unit of the adsorbent at a certain time.

The results of the adsorption efficiency η (in %) for the individual granular activated carbons at the different pH levels of the water are shown in Figure 3. The calculated values of the adsorption capacities (in mg/g) for the individual granular activated carbons are shown in Figure 4.

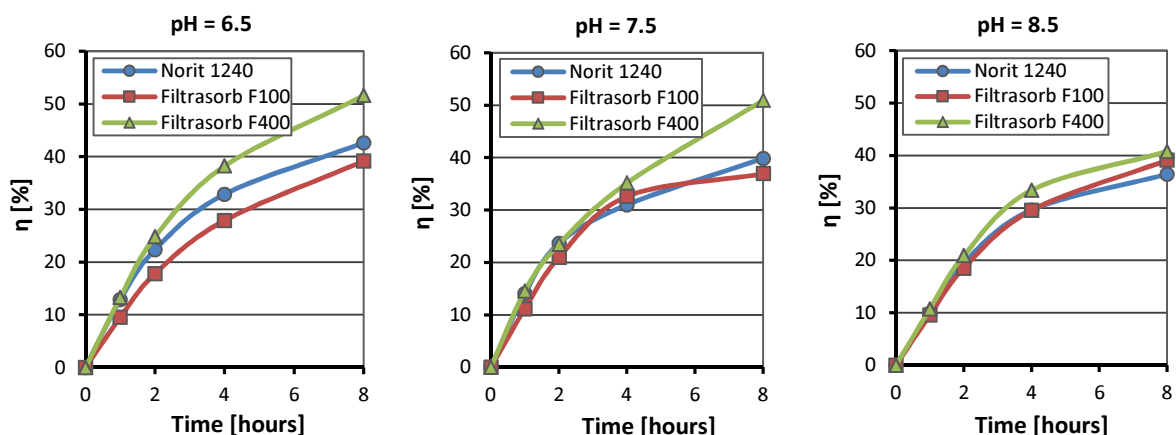


Fig. 3. The course of the adsorption efficiency of the granular activated carbons for the removal of the humic substances from the water at different pH levels of the water

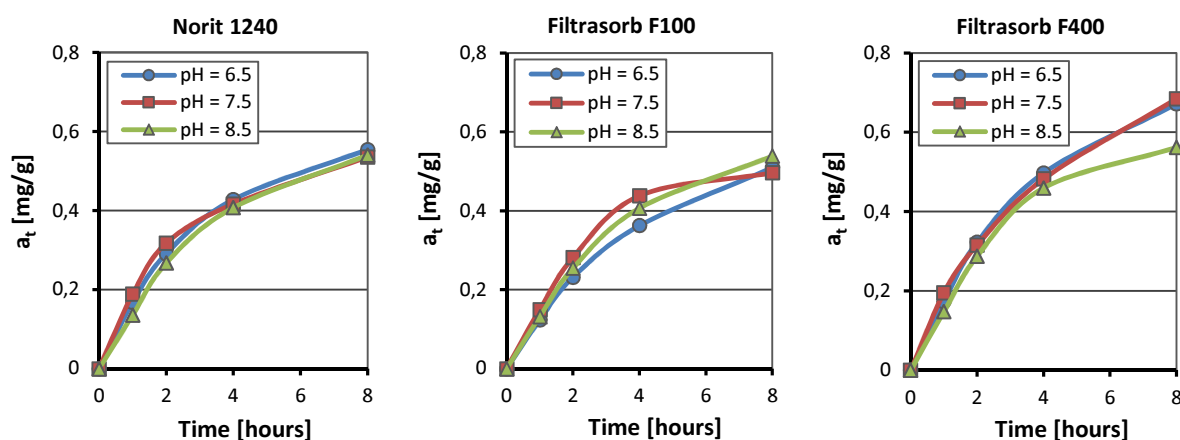


Fig. 4. The course of the adsorption capacities of the granular activated carbons for the removal of the humic substances from the water at different pH levels of the water

These results indicate that the pH of the water had no significant effect on the changes in the efficiency of removing the humic substances from the water. The highest efficiency and lowest TOC values were obtained at pH 6.5. The most effective material for the humic removal from the water was Filtrasorb F400.

Conclusion

The aim of this study was to monitor the effectiveness of granular activated carbon from different manufacturers in removing humic substances from water by laboratory static tests and to compare the adsorption capacity and adsorption efficiency of the materials used. The effect of the water quality (on the basis of the pH) on the effectiveness of the material was also studied.

The results indicate that the pH of the water had no significant effect on the change in the efficiency of removing the humic substances from water. The highest efficiency and lowest TOC values were obtained at pH 6.5. The most effective material for humic removal from water was the Filtrasorb F400.

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Contribution

J. Ilavský declare involvement in conception and design of the work and analysis. D. Barloková declare involvement in drafting the article, interpretation of data, revising the article. O. Kapusta declare involvement in interpretation of data and image processing.

Disclosure statement

The authors declare that they do not have any competing financial, professional, or personal interests from other parties.

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