Removal of THM Precursors by Adsorption, Coagulation and UV Irradiation

Jan Ilavsky 1, Danka Barloková 1, Michal Marton 1, Ondrej Kapusta 2

1 Department of Sanitary & Environmental Engineering, Faculty of Civil Engineering, Slovak Technical University, Radlinského 11, 810 05 Bratislava, Slovakia
2 The Central Slovak Water Company, Partizánska cesta 5, 974 01 Banská Bystrica, Slovakia

Abstract. The general characteristics of humic substances (HS) and their negative effect on water quality and its treatment are described. The paper presents the results from the removal of humic substances from the Hriňová (Slovakia) water reservoir using 1) granular activated carbon (GAC) from two producers (Chemviron, Cabot) at three different pH levels, 2) by coagulation with two coagulants (aluminum sulfate and ferric sulfate), and 3) by an advanced oxidation process using UV radiation with the addition of the oxidizing agent hydrogen peroxide. The effectiveness of the removal of humic substances (expressed by the TOC parameter) from water with adsorption by GAC, depending on the contact time with the water, ranged from 14% for one hour to 50% for eight hours of contact time. The calculated GAC adsorption capacity of the humic substances ranged from 0.05 mg/g for one hour to 0.19 mg/g for eight hours of contact time. The pH of the water had no significant effect on the level of efficiency. A high level of efficiency (50%) and the lowest value of TOC are obtained at a pH of 6.5. The humic substances remain in the water though the optimal dose of the coagulant was used. The ferric sulfate coagulant is more suitable for removing of humic substances from water as aluminum sulfate. A dose of 16 mg/L of 1% solution Fe2(SO4)3, which is the equivalent of 4.47 mg/L Fe3+, is sufficient for the reduction of humic substances below 1 mg/L. The effectiveness of the removal of humic substances with coagulation using iron sulfate was 83% for a parameter of HS and 50% for TOC or CODMn. The iron sulfate has the influence on a reduction in pH of water, therefore pH of water should be adjusted after coagulation. A laboratory study of removal of humic acids from surface water by UV radiation and addition of hydrogen peroxide in order to increase the oxidation of organics are presented. The results showed that UV radiation and addition of H2O2 during the first few minutes of irradiation increases the concentration of the humic substances, CODMn and TOC in water. After 3 minutes of exposure to UV radiation, these values were reduced to baseline, and in the next irradiation phase the values of the monitored parameters decreased. The highly reactive OH radicals with a high oxidation potential oxidize humic substances to various intermediates (a lower molecular weight substances). After 20 minutes of irradiation, a decrease in the parameters of approx. 39% for TOC, 62% for CODMn and 37% for humic substances was observed.

1. 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” or NOM) [1].
Humic substances (HS) are complex high molecular weight organic compounds with an aromatic-aliphatic character; they 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 [2]. The elementary composition of humic substances is shown in Table 1 [3,4].

Humic substances are characterized by the presence of carboxylic acid and the hydroxy (phenol, alcohol), methoxy, and carbonyl groups. These groups are bound to the benzene nucleus or to the aliphatic side chains [5,6]. 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. Fulvic acids are also more soluble in water, because they have more polar groups per unit mass than humic acids; therefore, natural water contains an average of 87% fulvic acids.

| 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     |
| Metoxyl (–O–CH₃) | 1-5      | 1-2      |

The structure of NOM 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 [7-9].

The negative effect of humic substances on water quality and its treatment is follows:
- increase the intensity of the color of water,
- increase the acidity of water,
- increase the aggressiveness of water on metals and building materials,
- 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 organo-halogen 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 [10-12]. 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 (a molecular mass of 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 coagulation earlier in the range pH 4-6; they form large and well-separated units [13].

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) [14-22].

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 [5]. 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 (there are 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 [23].

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 the 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 [14].

The determination of humic substances in drinking water is not present in Slovak Regulation No. 247/2017 on Drinking Water. It is based on the value of the CODMn, the absorbance (A254), or the color of the water. Exceeding the limit values is the reason for a decision to determine the amount of humic substances.

In the older 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 in 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).

The lowest concentration of humic substances is found in groundwater (up to 0.1 mg/L). The average concentrations of humic substances in Czech drinking water was 0.63 mg/L [24]. The surface water concentration was on the order of unit mg/L. Some typical values for the most abundant aquatic systems are given in (Table 2) [25]. The concentration of humic substances in surface water and water treated by a few water treatment plant (WTP) in Slovakia are shown in 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 2. Typical ranges for dissolved organic carbon concentrations (DOC) and humic contribution in selected aquatic systems [25]

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

Table 3. Concentration of humic substances (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\textsubscript{Mn} (mg/L) | HS (mg/L)   | COD\textsubscript{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                      |

Advanced oxidation processes (AOPs) are known to be one of the most effective methods of removing organic compounds from water [26]). These methods include UV radiation either with or without the addition of an oxidizing agent (e.g., hydrogen peroxide). UV radiation is used for the disinfection of drinking water too. UV radiation as a disinfectant has several generally required advantages over chemical disinfection means [27,28]. Its popularity is growing rapidly, even in water management. However, when assessing the merits of this method of water treatment and disinfection, the various effects of UV disinfection upon live matter are only rarely mentioned. That is why it is necessary to discuss these undesirable effects and potential risks as well as their minimization. This means assessing the effects of UV radiation as a complex undertaking and searching for all possibilities for its optimum utilization.

2. Material and Methods
The objective of experimental trials was to verify efficiency of different technological processes, which are used in water treatment for the removal of humic substances from water. The current water treatment technology in WTP Hriňová consist of UV radiation, dosing of CO\textsubscript{2}, dosing of coagulant (ferric sulfate), fast mixing using a hydro mixer, slow mixing, sedimentation, dosing of lime, filters with sand and disinfection with ClO\textsubscript{2}. To reduce of organic compound it is considered a design of filtration with activated carbon.

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 (Cabot Corporation, USA)
2. Filtrasorb F100 (Calgon Carbon, Belgium)
3. Filtrasorb F400 (Calgon Carbon, Belgium)

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

The experiments were performed in a laboratory using the static method. To prepare the model samples, 2.0 g of granular activated carbon (before the experiment it was washed in distilled water and dried at 105 °C) were added to 200 ml of raw (surface) water collected at the inlet to the Hriňová water
treatment plant (WTP). The removal efficiency of the humic substances from the water was monitored by TOC (the TOC analyzer was the Aurora Model 1030W from OI Analytical).

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         |
| Apparent density [kg/m³]             | 500    | 425    | 470        |
| Methylene blue [mg/g]                | 230    | 260    | 220        |
| Surface area (BET) [m²/g]            | 900    | 1100   | 1100       |
| Uniformity coefficient               | 1.9    | 1.7    | 1.6        |

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, along with the subsequent reextraction of a pentanol solution of NaOH, are recommended [23,29]. 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.

For the coagulation test the same surface water from WTP Hriňová and a device with five mixers with an adjustable speed and high-speed mixing was used. A liter of raw water was added to five flasks. The addition of a coagulant (a 1% solution) was followed by 3 minutes of rapid mixing (180 rpm) and 10 minutes of slow mixing (40 rpm). After the mixing, the sedimentation of the sample followed; it took 1 hour and was then filtered through filter paper. The prepared sample was then analyzed. The following parameters were monitored: pH, ANC₄,₅, Fe or Al concentration, turbidity, colour, TOC, COD₅, and the concentration of humic substances.

For the UV radiation a closed type 1 emitter T 5125 MVA 100 UVADEUS, produced by Holzli KG Austria (Figure 1) was used.

Figure 1. Equipment for UV radiation used during experiments

The maximum disinfection capacity of this device amounts to 3 m³ of water per hour. The radiation dose delivered to the water at a wavelength of about 254 nm amounts to approximately 15 W/h for a 25
W luminescent tube, a water layer of 3 cm, and a 50 cm high casing. The exposure time was measured in seconds up to minutes and calculated as follows:

\[ D = \frac{E \cdot t}{F} \left( \mu W \cdot s \cdot cm^{-2} \right) \]  

where \( E = E_0 - \alpha \cdot x \) (W), \( E_0 = 0.6 \times 25 \), \( F = \) irradiated area (cm), \( t = \) exposure time (s), \( x = \) depth of water layer in emitter, \( \alpha = \) absorption coefficient = 0.1.

Before the radiation, H2O2 (a dose of 1 ml/L 30% solution of hydrogen peroxide) was added to the samples. After the mixing, the water samples prepared in this manner were statically irradiated in the UVADEUS emitter, from which the samples were taken for chemical analyses after 0, 1, 3, 5, 10, 15 and 20 minutes.

3. Results and discussions

The experimental work, which was divided into 3 parts, was performed as follows:
- a) the removal of humic substances from water using GAC materials at different pH values of the water,
- b) the removal of humic substances from water using coagulation with two coagulants (aluminium sulphate and ferric sulphate),
- c) the removal of humic substances from water by an advanced oxidation process using UV radiation with the addition of the oxidizing agent hydrogen peroxide.

**The first experimental part** of this work was divided into 3 parts: 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 3.60 mg /L, at a pH of 7.5 (the pH of drinking water) and the TOC concentration of 3.62 mg /L and at a pH of 8.5 (adjusted by the addition of NaOH); the initial concentration of TOC in the raw water was 3.65 mg /L.

The effectiveness of the removal of the humic substances from the 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 Table 5. The values represent the average of two measurements.

**Table 5.** The measured values of TOC (mg/L)

| No. | GAC          | 0 hours | 1 hours | 2 hours | 4 hours | 8 hours |
|-----|--------------|---------|---------|---------|---------|---------|
|     | pH = 6.5     |         |         |         |         |         |
| 1   | Norit 1240   | 3.60    | 3.14    | 2.79    | 2.42    | 2.06    |
| 2   | Filtrasorb F100 | 3.60 | 3.26    | 2.96    | 2.60    | 2.19    |
| 3   | Filtrasorb F400 | 3.60 | 3.12    | 2.71    | 2.22    | 1.74    |
|     | pH = 7.5     |         |         |         |         |         |
| 1   | Norit 1240   | 3.62    | 3.11    | 2.76    | 2.50    | 2.18    |
| 2   | Filtrasorb F100 | 3.62 | 3.22    | 2.86    | 2.44    | 2.28    |
| 3   | Filtrasorb F400 | 3.62 | 3.09    | 2.77    | 2.35    | 1.77    |
|     | pH = 8.5     |         |         |         |         |         |
| 1   | Norit 1240   | 3.65    | 3.29    | 2.94    | 2.57    | 2.32    |
| 2   | Filtrasorb F100 | 3.65 | 3.30    | 2.97    | 2.57    | 2.22    |
| 3   | Filtrasorb F400 | 3.65 | 3.26    | 2.89    | 2.43    | 2.16    |
From the TOC values determined in the experiments, the adsorption efficiency $\eta$ (2) and the immediate adsorption capacity at (3) were calculated by the following formula:

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

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

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; $\eta$ (%) 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 $\eta$ (in %) for the individual GAC at the different pH levels of the water are shown in Figure 2. The results of the adsorption capacities (in mg/g) for the individual GAC calculated using formula 3 are shown in Figure 3.

![Figure 2](image1.png)

**Figure 2.** The course of the adsorption efficiency of the GAC for the removal of the humic substances from the water at different pH levels of the water.

![Figure 3](image2.png)

**Figure 3.** The course of the adsorption capacities of the GAC 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 a pH of 6.5. The most effective material for the humic removal from the water was Filtrasorb F400.

The second experimental part of this work was aimed at removing the humic substances from water by coagulation. Two coagulants, aluminum sulphate (Kemwater) and ferric sulphate (Kemifloc) were compared to find the optimal dose for the reduction of humic substances in surface water from the Hriňová water reservoir. Twelve to 20 mg/L of Fe or Al in a 1% concentrated solution was added to the water. The results of the measurements are shown in Tables 6 and 7.

Table 6. The results of coagulation tests removal of humic substances with Fe$_2$(SO$_4$)$_3$

| The dose coagulant [mg Fe$^{3+}$/L] | pH    | alkalinity [mmol/L] | Fe [mg/L] | HS [mg/L] | COD$_{Mn}$ [mg/L] | TOC [mg/L] | turbidity [FTU] | color [mg/L Pt] |
|-----------------------------------|-------|---------------------|-----------|-----------|-------------------|------------|-----------------|----------------|
| 0                                 | 6.52  | 0.534               | 0.08      | 5.43      | 2.56              | 3.6        | 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 7. The results of coagulation tests removal of humic substances with Al$_2$(SO$_4$)$_3$

| The dose coagulant [mg Al$^{3+}$/L] | pH    | alkalinity [mmol/L] | Al [mg/L] | HS [mg/L] | COD$_{Mn}$ [mg/L] | TOC [mg/L] | turbidity [FTU] | color [mg/L Pt] |
|-----------------------------------|-------|---------------------|-----------|-----------|-------------------|------------|-----------------|----------------|
| 0                                 | 6.67  | 0.548               | 0.01      | 5.43      | 2.56              | 3.6        | 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            |

On the basis of the results shown in Tables 6 and 7, it can be concluded that the ferric sulfate coagulant is more suitable for removing humic substances from water than aluminum sulfate. These results should be confirmed by long-term monitoring, especially monitoring of changes in the water quality during the seasons. The highest efficiency of the coagulation versus the lowest value of the humic substances was reached at a dose of coagulant 16 mg/L (1% solution), i.e., 4.47 mg/L converted to Fe$^{3+}$, or 2.52 mg/L calculated for Al$^{3+}$. At optimal dose of coagulant the removal efficiency of humic substances was 83.6% using Fe$^{3+}$ coagulant and 73.6% using Al$^{3+}$ coagulant, respectively.

Because the effect of ferric sulfate, respectively oxide, reduces the pH value, it is necessary to adjust the pH after coagulation. The determination COD$_{Mn}$ and TOC conversion confirmed the relationship between these parameters and humic substances in the literature.

The third part of this work was aimed at the removal of humic substances from water by an advanced oxidation process using UV radiation with and without the addition of the oxidizing agent hydrogen peroxide (H$_2$O$_2$). The addition of an oxidizing agent increases the oxidation efficiency (formation of highly reactive OH radicals with a high oxidation potential) [30,31].
We monitored the effect of the removal of humic substances depending on:
- the dose of 1 ml 30% H$_2$O$_2$ as the oxidant,
- the exposure time of UV irradiation (0, 1, 5, 10, 15 and 20 minutes after addition of the oxidant with water),
- a temperature of 20 °C and pH value of the water of 7.5.

The results of this experiment are documented in Table 8. UV radiation during the first few minutes of irradiation increases the concentration of the monitored parameters (humic substances were decomposed to lower molecular weight substances by oxidize highly reactive OH radicals). After 3 minutes of exposure to the UV radiation, these values were reduced below the baseline; in the next irradiation phase, the values of the monitored parameters decreased. Twenty minutes of irradiation led to a decrease concentration in the observed parameters by approximately 39% for TOC, 62% for CODMn and 37% for humic substances.

| Sample                  | TOC (mg/L) | COD$_{Mn}$ (mg/L) | HS (mg/L) |
|-------------------------|------------|-------------------|-----------|
| 0 min                   | 3.60       | 2.56              | 5.43      |
| Dose of H$_2$O$_2$      | 3.54       | 2.51              | 5.38      |
| 1 min irradiation       | 3.72       | 2.67              | 5.52      |
| 3 min irradiation       | 3.57       | 2.53              | 5.38      |
| 5 min irradiation       | 3.45       | 2.41              | 5.17      |
| 10 min irradiation      | 2.96       | 2.01              | 4.65      |
| 15 min irradiation      | 2.41       | 1.50              | 3.98      |
| 20 min irradiation      | 2.18       | 0.98              | 3.40      |

4. Conclusions
The methods mentioned in this article are often used in water treatment, e.g., coagulation to remove humic substances, turbidity, color and microbiological organisms in surface water sources. Adsorption is used to reduce organic matter content or inorganic pollution in water, and UV radiation is used for water disinfection or as a method for advanced oxidation processes (AOPs) to remove organic substances from water.

The aim of this study was to compare the removal efficiency of humic substances from water with all these methods. The research conducted allowed us to draw the following conclusions:

1. The effectiveness of granular activated carbon from different manufacturers in removal humic substances from water by laboratory static tests and calculated the adsorption capacity and adsorption efficiency of the GAC materials for humic substances on concentration of 5.43 mg/L (TOC 3.6 mg/L) was investigate. The effect of the water quality (on the basis of the pH) on the effectiveness of the material was also studied.

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

3. The effectiveness of the removal of humic substances from water with adsorption by GAC, depending on the contact time with the water, ranged from 14 % for one hour to 50% for eight hours of contact time. The calculated GAC adsorption capacity of the humic substances ranged from 0.05 mg/g for one hour to 0.19 mg/g for eight hours of contact time.
4. The coagulation tests with the surface water from WTP Hriňová showed that coagulation using ferric sulfate (also alum) is a sufficient method to remove humic substances from water (if we limit the comparison to 2.5 mg/L of humic substances). A dose of 16 mg/L of 1% solution Fe$_2$(SO$_4$)$_3$, which is the equivalent of 4.47 mg/L Fe$^{3+}$, is sufficient for the reduction of humic substances below 1 mg/L. The iron sulfate has the influence on a reduction in pH of water, therefore pH of water should be adjusted after coagulation.

5. The humic substances (low molecular weight fractions with a molecular mass of up to 500) are apparently removed less efficiently and remain in the water even though the optimal dose of the coagulant was used. The effectiveness of the removal of humic substances with coagulation using iron sulfate was 83% for a parameter of HS and 50% for TOC or COD$_{Mn}$.

6. When using UV radiation at the beginning of the surface water treatment from the Hriňová water reservoir, an increase in the concentration of humic substances in water must be considered. UV radiation during the first few minutes of irradiation increases the concentration of humic substances, COD$_{Mn}$ and TOC in water. The highly reactive OH radicals with a high oxidation potential oxidize humic substances to various intermediates (a lower molecular weight substances). After 20 minutes of irradiation, a decrease in the parameters of approximately 39% for TOC, 62% for COD$_{Mn}$ and 37% for humic substances was observed. A determination of the optimum conditions (dose of oxidizing agent, irradiation time, pH, water temperature, etc.) on the total effect of the water treatment is needed.

Acknowledgment(s)
This article was created with the support of the Ministry of Education, Science, Research and Sport of the Slovak Republic within the Research and Development Operational Programme for the project "University Science Park of STU Bratislava", ITMS 26240220084, co-funded by the European Regional Development Fund. Experimental measurements were carried out with the financial support projects APVV-15-0379 and VEGA 1/0737/19.

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