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HUMIC SUBSTANCES AS BY-PRODUCT PRECURSORS GENERATED DURING OXIDATION AND DISINFECTION – REVIEW OF THE LITERATURE

SUBSTANCJE HUMUSOWE JAKO PREKURSORZY UBOCZNYCH PRODUKTÓW UTLENIANIA I DEZYNFEKCJI – PRZEGLĄD LITERATURY

Abstract

Humic substances (HS), including soluble fulvic acids (FA), are commonly occurring pollutants, particularly in surface waters. HS were considered as substances, which are harmless for humans until now. They were mainly removed from the water because of turbidity, color and as a source of odor. HS in the process oxidation and disinfection are precursors of carcinogenic and mutagenic substances. Because of this, an analysis has been conducted, discussing their construction, properties and methods used of their disposal.

Keywords: humic substances, fulvic acids, water treatment, wastewater treatment

Streszczenie

Do powszechnie występujących zanieczyszczeń, szczególnie wód powierzchniowych należą substancje humusowe (SH), w tym rozpuszczalne kwasy fulwowe (KF). SH dotychczas uważane były za substancje zupełnie nieszkodliwe dla człowieka, a usuwane były z wody głównie ze względu na mętność, barwę oraz jako źródło przykrego zapachu. W procesach utleniania oraz dezynfekcji SH są prekursorami substancji kancerogennych oraz mutagennych. Ze względu na ten fakt przeprowadzono analizę studialną ich budowy oraz właściwości, a także stosowanych metod ich unieszkodliwiania.

Słowa kluczowe: substancje humusowe, kwasy fulwowe, uzdatnianie wody, oczyszczanie ścieków

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1. Introduction

Along with an increasing number of people and their standard of living, the demand for water also increases, which is a natural environment for the occurrence of many substances and living organisms. It is worth noting that, in water, there are a lot of pathogenic organisms, such as: viruses, bacteria, fungi and their mold spores, protozoan cysts and worm eggs, which are parasites that live in the human digestive tract. The occurrence of the above-mentioned pathogens can lead to many diseases and even death. Disinfection can be used to destroy or inactivate them and prevent their redevelopment in the water supply system. Physical methods of disinfection of water can include: cooking, pasteurization of water, ultrasound or ultraviolet radiation [1].

The relatively new, but also costly physical method, is disinfection by means of thermal techniques. Compared with the chlorination method, it is much less effective in preventing the formation and development of bacterial environments [2].

Chemical methods are used much more often. They are based on adding strong oxidizing agents to water, such as: chlorine, chlorine dioxide, sodium hypochlorite, chloramines and ozone less bromine or iodine. These substances react with the compounds present in water, leading to the creation of new compounds, which are known as disinfection by-products (DBP) [1].

Water treatment leads to the removal the majority of impurities. Purified water should meet the rigorous standards of both international – European Directive and national – Regulation of the Minister of Health. Humic substances, including soluble fulvic acids, are commonly occurring pollutants, particularly in surface waters.

2. Characteristics of humic substances

Humic substances exist in soils, rivers and lakes. They are usually aromatic and acidic in nature [3]. These substances are formed by humification, i.e. the microbiological decomposition of plant and animal residues, such as lignin, proteins, pectins, polysaccharides, and tannins [4]. They are biogenic, heterogeneous substances, belonging to organic compounds [5]. HS are commonly known as the most widespread and ubiquitous components, which belong to natural organic matter (NOM) [6].

According Górnjak, humic acids (HA) constitute up to 70% of the soil's organic matter, and up to 80% soluble organic carbon. HA has an unspecified structure [7]. These substances can be formed "in situ" in "aquatic ecosystems, but mostly are supplied from soil drainage areas [8].

Their color depends on their origin, concentrations and pH of the solution; it may change from yellow to dark brown. The molecular weight of HS ranges from a few hundred to a few thousand Daltons [9]. Humic substances are natural macromolecules commonly found in the aquatic environment, soil, sludge etc. [8]. Humic acids occur in a dissolved, colloidal form, small dispersion connection with suspensions or in the form of very small particles. As it was mentioned, these substances are commonly found on the surface of the Earth. Typically, their concentration in the rivers can be about 6 mg/l, while in the water marsh, even above

18 mg/l. HS represent between 50% and 75% of the total organic carbon contained in the surface waters [10, 11]. Fulvic and humic acids are the largest group present in the aquatic environment. Natural organic matter sediments and seawater contains 10–80% humic substances [10, 11].

In a pure state, humic substances are natural pollution, harmless to humans, but as a result of the oxidation and disinfection processes, they undergo chemical changes and form carcinogenic and mutagenic products. It is worth mentioning that the content of HS in drinking water is not normalized [12].

According Li et al. [13] who extracted humic acids from digested sludge by alkaline treatment and ultrafiltration, humic acids (HA) were the major constituent of humic substances in digested sludge, and most of the humic acids had molecular weights higher than 50 kDa [13].

Although the structure of humic substances was studied for about 200 years and has yet to be recognized, there are many models of their structure [10].

Figure 1 shows a model structure of humic acids by Stevenson.

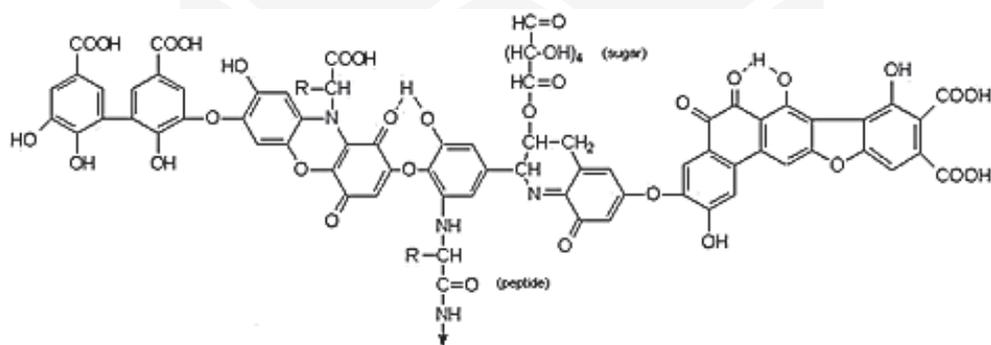


Fig. 1. Model structure of humic acid by Stevenson (1982)

Figure 2 shows a model structure of fulvic acid by Buffle.

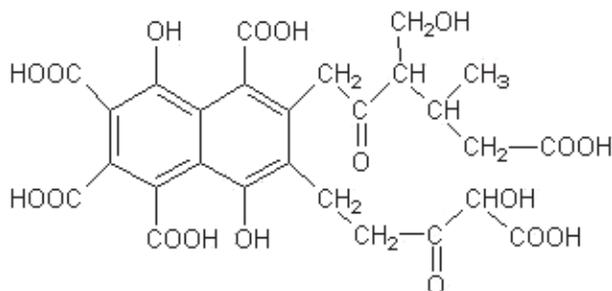


Fig. 2. Model structure of humic acid by Buffle [14]

One of the methods characterizing the construction of humic substances is the absorption analysis of infrared radiation. The absorption of the selected wavelength is suitable for the specific structural elements. For example, absorption bands of 3500–3000 nm are attributed to the amine groups and hydroxyl, which tend to form hydrogen bonds; the range of 3000–2800 nm is attributed to bonding between carbon and hydrogen in the methyl and methylene groups; 1500 nm – a carboxyl group and a secondary amine; 1430 nm – OH group in phenols; 1680–1650 nm aldehydes, ketones, and carboxylic acids as well as double bonds in the carbon chain aliphatic and aromatic rings [15].

According to most authors, HS are long-chain molecules, forming coils with elements of aromatic and aliphatic. However, in aqueous solutions, they create spherical forms [15].

Humic substances can be classified according to their solubility as: humic acids (HA), fulvic acids (FA), hymatomelanic acids and humin. Humic acids dissolve in an alkaline solution and precipitate in strongly acidic conditions ($\text{pH} < 2$). Fulvic acids dissolve in both alkaline and acid solution, while humin remains insoluble in acids and alkalis. Hymatomelanic acids (ulmine) dissolve in ethanol [9, 10].

Currently, the removal dissolved organic matter (DOM) from water includes coagulation, adsorption, nano-filtration (NF) and biological methods [16–17]. The most frequently used method mentioned above is adsorption [16–19]. Linnik and Vasilchuk [21], in their research, investigated the role of HS in the complexation and detoxification of heavy metals in Dnieper Reservoirs. The results of research showed that humic substances are the main component of dissolved organic matter (DOM) in Ukrainian rivers. The concentration of fulvic acids was 20–40 times higher than humic acids. Humic substances, and more specifically fulvic acids, preferentially bind heavy metals (HM). The content of metals bound into complexes with DOM depends on the season and reaches 70–100% of the total dissolved forms. The maximum content of HS is usually observed in spring, owing to the high water season [21].

3. Humic substances as by-product precursors of oxidation and disinfection

Fulvic acids were considered as harmless substances for humans and were removed from water mainly because of turbidity, color and as a source of odor.

The studies conducted in 1974 [22] showed that humic substances are precursors of carcinogenic and mutagenic compounds produced during oxidation and disinfection processes.

These substances are formed depending on the composition of the disinfectant and purified water. HS include substances such as: trihalomethanes (THM), haloacetic acids (HAA), halogeno-nitriles, halogeno ketones, trichlorophenol, trichlorobenzenes, hydroxi-furanes and others. This is the reason why humic substances should be investigated in the environment and eliminated from the water before sending it to treatment plants [22]. Trihalomethanes (THM) are the largest group of compounds generated during the chlorination of natural organic substances, such as HS [23]. The amount of trihalomethanes formed during the water chlorination process is affected by factors such as: temperature, pH, chlorine dose and duration of chlorination as well as the concentration of total organic carbon (TOC). The speed of their formation depends on the type of organic substances [24]. These compounds belong to the halogen derivatives of hydrocarbons. They have the general molecular formula CHX_3 ,

where X is atom fluorine, chlorine, bromine or iodine. The best-known representatives of trihalomethanes are: chloroform (CHCl_3), bromoform (CHBr_3) dibromochloromethane (CHClBr_2) bromodichloromethane (CHCl_2Br) [25].

Table 1 shows the acceptable concentration of THM in drinking water recommended by the World Health Organization (WHO) (1998) [26].

Table 1

**Allowable concentration of THM in drinking water
recommended by the World Health Organization
(WHO) [26]**

Substance	Concentration [$\mu\text{g/l}$]
Chloroform	200
Dichlorobromomethane	60
Dibromochloromethane	100
Bromoform	100

According to the data provided by the WHO, the risk of death from cancer caused by trihalomethanes is 1/100-1/1000 of the risk of death caused by bacteria present in the not disinfected water. There are ongoing studies on the effects of chlorine on the mass occurrence of various diseases, such as: heart attacks, cancer of the bowel and bladder, or the gradual loss of memory or arteriosclerosis. Because of the universality of disinfecting water with chlorine, these studies are difficult because, in highly developed countries practically, it is impossible to find people who were not exposed to chlorine for a long time. Another important issue is the intensity of the smell and taste of chlorine. According to the Regulation of the Minister of Health, the only criterion for setting forth the issue of taste and smell of water is to determine whether it is acceptable by the consumer, which, according to Komusińska [27], is debatable because it is hard to determine if this legal criterion is met. It is precisely this factor and more specifically the high concentration that has a significant impact on the negative opinion of Poles about water coming from the water supply. According to the author, the aroma of chlorine is so strong that even 10% content of it leads the users to conclude that the water is distasteful [27].

Table 2 shows the chemical requirements for the trihalomethanes, which should correspond to the water on the basis of the Regulation of the Minister of Health from 2015.

The permissible concentration of THM in water intended for human consumption is subject to certain requirements and should be closely monitored. This is due to the mutagenic and carcinogenic influence of THM on living organisms. According to the Minister of Health of 13 November 2015 [27] regarding the quality of water intended for human consumption, the total value sum of THM concentration should not exceed 100 $\mu\text{g/l}$. This is due to the fact that the elevated levels of these substances lead to an increasing number of diseases – human tumor of the digestive system, urinary system and the number of increased risk of miscarriage in pregnant women. The most dangerous parameter listed in Table 3 THM is dibromochloromethane [25].

Table 2

Chemical requirements for the trihalomethanes, which should correspond to the water (Regulation of the Minister of Health of 13 November 2015 regarding the quality of water intended for human consumption, 7 Pos. 1989) [28]

Parameters	Maximum allowable concentration	Unit
Σ THM: trichloromethane, bromodichloromethane dibromochloromethane tribromomethane	100	[µg/l]
Σ THM – value is the sum of the concentrations of: trichloromethanes, bromodichloromethanes, dibromochloromethanes, tribromomethanes.		

Table 3 shows the allowable concentration of THM in drinking water in selected countries in the world.

Table 3

Allowable concentration of THM in drinking water in selected countries in the world [23]

Country	THM	CHCl ₃	Unit
Australia	250	–	[µg/l]
China	–	60	
France	–	30	
Japan*	100	60	
Korea	100	–	
Taiwan	100	–	
USA	80	–	
Poland	100	–	
WHO**	–	200	

* CHCl₂Br 30 µg/l, CHClBr₂ 100 µg/l, CHBr₃ 90 µg/l

** CHCl₂Br 60 µg/l, CHClBr₂ 100 µg/l, CHBr₃ 100 µg/l

Based on the above data table, it can be seen that the strictest standards for the concentration of THM in drinking water are in the USA (80 µg/l). In Poland, the allowable concentration is 100 µg/l and it corresponds to the requirements of the European Union. It is worth noting that the allowable concentration of THM in Australia is rather high at 250 µg/l.

Table 4 shows the index value THM quality of drinking water in Krakow in 2011 in four Water Treatment Plants: Raba, Rudawa, Dłubnia and Bielany.

Table 4

The indicator values THM quality of drinking water in Krakow in 2011 [27]

Indicator water quality	Unit	Water Treatment Plant				Regulation of the Minister of Health (2007 with amendments 2010)
		Raba	Rudawa	Dłubnia	Bielany	
Σ THM	µg/l	18	< 0.3	< 0.3	9.4	150 (100)

Based on the above table, it can be seen that the value of the concentration indicator THM in drinking water at the Water Treatment Plant Raba was 18 µg/l, at Bielany 9.4 µg/l, while in Rudawa and Dłubnia, it was below 0.3 µg/l. The values of these concentrations comply with the applicable legal requirements.

Haloacetic acids (HAA) are mainly formed during the chlorination of water with chlorine gas. These are organic substances that are present in water; they are largely known as humic substances, referred to as HAA precursors [29]. Haloacetic acids are another group of dangerous compounds. Haloacetic acids include acids, such as: bromoacetic acid, trichloroacetic acid, monochloroacetic and dichloroacetic [23]. The last two are the precursors of THM in water distribution networks [24].

Table 5 shows the permitted concentration for the sum of five haloacetic acids established by the United States Environmental Protection Agency (US EPA).

Table 5

Concentration limits for the sum of five haloacetic acids established by the United States Environmental Protection Agency (US EPA) [30]

Type of haloacetic acid	The concentration limit of the sum of five acids	Unit
MCAA	60	mg/m ³
DCAA		
TCAA		
MBAA		
DBAA		

MCAA – monochloroacetic acid,

DCAA – dichloroacetic acid,

TCAA – trichloroacetic acid,

MBAA – monobromoacetic acid,

DBAA – dibromoacetic acid.

The United States Environmental Protection Agency (US EPA) has established a permissible value as a sum of the concentrations of five HAA, i.e. MCAA, DCAA, TCAA, MBA, equal to 60 mg/m^3 . Due to the fact that haloacetic acids are carcinogens and dangerous for humans, a reduction to 30 mg/m^3 is expected.

WHO guidelines for drinking water quality recommend limits of dichloroacetic acid to 50 mg/m^3 and trichloroacetic acid to 100 mg/m^3 . While the Regulation Minister of Health of 20 April 2010 defines the conditions to be met by water for drinking and domestic purposes, it refers only to a single acid – monochloroacetic. The maximum concentration may be 30 mg/m^3 [30].

Research conducted by Anielak, Grzegorzczuk and Schmidt [24] has shown that by oxidizing natural substances, which are safe for the environment, aliphatic and aromatic compounds with different values of MAC and LD50 are obtained, testifying to the toxicity of oxidation products. It was observed that, with increasing doses of the oxidant (NaOCl and H_2O_2), there were increases in the amount of organic oxidation products, including flavoring substances. During the oxidation of fulvic acids chlorite (I), sodium formed trichloromethane, or the main representative of THM [24]. It is widely believed that active chlorine compounds are formed in processes of oxidation of water with chlorine gas or compounds thereof. Therefore, ozone treatment, UV disinfection and primarily the use of safe oxidants and disinfectants are recommended [24].

Uyguner et al. [31], in their researches, tried to explain the relationship between formation potential (THMFP) and physicochemical properties of humic substances, UV-visible absorbance, fluorescence in emission and synchronous scan modes, and NMR spectra were measured for several aquatic fulvic and humic acids. For comparison, they examined soil fulvic acids using the same methods. Based on the tested methods, it was found that none of the results of analysis provided a good correlation with the THMFP values reported for the HS studied. According the authors, this means that earlier correlations between THMFP and color, size, or aromatic content as measured by different UV wavelengths do not hold for all types of aquatic humic substances [31–32].

4. The importance of humic substances for humans and other living organisms

Humic substances, like most of the compounds present in the environment have positive as well as negative effects on the processes of water purification.

HS due to the high content of functional groups and a high resistance to the biodegradation play an important role in aquatic and land environments. The occurrence of FA in groundwater may lead to the formation of soluble complexes $\text{KF} - \text{Fe}$ and K-Mn , which contributes to obstructing disposal of the water removal of iron and manganese [12]. Based on numerous studies, demonstrated a directly proportional relationship between the amount of generated THM and organic carbon content, so humic substances too. Highlighted the fact that this problem is particularly important during the chlorination of surface waters without forgetting the groundwater [12]. Miller, Randtke and Hathaway [12] conducted studies during which determined the potential to create already mentioned THM compounds in 50 different samples of groundwater. Groundwater contained organic carbon in quantities of $0.21\text{--}3.31 \text{ gCl}_2/\text{m}^3$.

It was found that during the process of purification underground water contaminated of various types of humus compounds, the chlorine can be dosed after removing THM precursors. This is particularly important as humic acids are the precursors of THM [12].

The role of humic substances present in the soil is closely linked with the stability of sorption processes of soil [33]. High content of humic substances in water restricts the access of light and leads to a reduction quantity of available micronutrients and in the result this helps to reduce the productivity of ecosystems [34].

Age occurrence of HS in some soils may be several thousand years. This is particularly important because of the negative character of their functional groups may promote accumulation heavy metals in aqueous environment and the formation of complex compounds.

Interesting research were conducted by Navarrete et al. [35] HS are very good fertilizers and it was confirmed that in the presence of FA mineral ions are more evenly distributed in the leaves and flowers of vegetable. However it is worth noting that autoradiography small ions such as sodium was possible only in the absence of FA, it can be understood as HS showed evident selective qualities regarding toxic ions such as chromates or mentioned sodium. Moreover authors notes that so many curative properties that are attributed to FA deserve a closer look to them and a serious investigation [35, 36].

According Świdarska-Bróz [37] the largest complexes of humic acids with copper and lead is formed at a pH of 5–8. It is necessary to remove them from water treatment process, due to their adsorption properties of such organic compounds as: pesticides, polychlorinated biphenyls (PCBs) and phthalates [37, 38].

5. Disposal methods of humic substances

In order to effectively remove the by-products of oxidation and disinfection, their precursors have to be first removed. Water treatment, in which there are humic substances, requires the use of suitable unit processes, such as coagulation, filtration, adsorption on activated carbon, chemical oxidation, chemical precipitation or ion exchange and membrane processes. The most commonly used adsorbents for the purification of drinking water are activated carbons [34, 39–41].

According Dojlido and Taboryska [42], two methods can be used for the determination of humic substances: extraction-spectrophotometric method and the measurement of organic carbon. The extraction–spectrophotometric method consists of extracting humic substances amyl alcohol in an acid environment and then converting them to a solution of sodium hydroxide. It can be seen that the intensity of the alkaline aqueous layer is proportional to the concentration of humic substances. The second method involves the binding of humic substances on anionic cellulose at a neutral pH. Subsequently, HS is eluted with a solution of sodium hydroxide. Then, after acidification and removal of inorganic, carbon is indicated by the dissolved organic carbon (DOC) [42].

Humic substances are characterized by a high resistance to biodegradation. The new direction of research project fri. “Used archea and unconventional sources of carbon in the process of municipal wastewater treatment” [43] showed that fulvic acids inhibit the process

of municipal wastewater treatment with activated sludge. As a result of bioaugmentation sludge, archaea increased its activity and biodegradation resulted in fulvic acids. The efficiency of the process during the three days of observation was small and amounted to 21%. It must be concluded that it was not the result of sorption on the surface of activated sludge. In the presence of fulvic acids, the release of nitrogen occurred from the activated sludge; therefore, we should say that the FA adversely affect the denitrification process. Based on the research of molecular (PCR and RT-PCR), which formed part of the project, it has been shown that in the settlement, which was bioaugmentation, the archaea created a stable population that was able to develop [43].

6. Summary

Humic substances, like most of the compounds present in the environment, have positive as well as negative effects on the removal of organic pollutants. The role of humic substances present in the soil is closely linked with the stability of sorption processes of soil [33].

HS as natural organic acids constitute an organic carbon source for plants, microorganisms, and play an important role in the biogenic cycle; they participate in biochemical and nutrients. According to Ukrainian researchers, major contribution to the humic substances is represented by FA, the content of which may 81–95% of the total of HS [44, 45].

Along with a high content of humic substances in water, there is limited access to light, leading to the reduction of the quantity of available micronutrients, which contributes to reduced productivity of ecosystems [34].

In order to effectively remove by-products of oxidation and disinfection, their precursors have to be first removed. Water treatment, which includes humic substances, requires the use of suitable unit processes, which include: coagulation, filtration, adsorption on activated carbon, chemical oxidation, chemical precipitation or ion exchange and membrane processes. The most commonly used adsorbent for the purification of drinking water are activated carbons [34, 39–41].

To sum up, humic substances have a negative influence on living organisms and have the ability to transport metals and other pollutants. The analysis has shown that HA penetrate to the surface water and become precursors of oxidation and disinfection by-products at treatment plants. So, this is the reason why they should be removed from water directed to Water Treatment Plants.

This is particularly important due to the fact that, according to the World Health Organization (WHO), “up to 80% of all diseases of modern civilization are related to the quality of drinking water” [46].

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