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Characterization of fulvic acids contained in municipal sewage purified with activated sludge

Anna Maria Anielak*, Małgorzata Kryłów, Dominika Łomińska-Płatek

Cracow University of Technology, Poland

*Corresponding author's e-mail: aanielak@pk.edu.pl

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Abstract: FA discharged from the wastewater treatment plant were extracted from purified effluents for the quantitative and qualitative analysis. The treated sewage from municipal treatment plants was acidified to pH <2 and extracted with ion exchange resins in a laboratory column. After desorption with NH_4OH, the fulvic acids were condensed under vacuum and tested for mass performance, UV-VIS light spectra, IR absorption spectra, elementary composition and other elements. Their structure was analysed and compared to FA present in surface waters and in sewage treated in other sewage treatment plants based on the authors' own research and the literature data. The concentration of FA in the treated sewage was 5.2 mg/L. There is a high interdependence between the IR spectrum analysis in the visible light and the elementary composition of FA extracted from different environments, confirming the conclusions pertaining to the structure and properties of the acids being tested. The longer sewage is subjected to a biological treatment process, the greater the degree of aromatic condensation and humus maturity of the FA contained within it. FA contained in the sewage treated in the three biological sewage treatment plants have the ratio A_2/A_3 (the ratio of the absorbance of light with the wavelength of 250 and 300 nm) equal to the value 1.7. There is a high interdependence between the IR spectrum analysis in the visible light and the elementary composition of FA extracted from different environments, confirming the conclusions pertaining to the structure and properties of the acids being tested.

Introduction

Humic substances (HS) are the most abundant and reactive components of soil organic matter. Humic acids (HA) and fulvic acids (FA) represent the major fraction of HS which features a colloidal, polydispersed, and polyelectrolytic character, and a mixed aliphatic and aromatic nature. The structure of humic substances depends on the time of humification, humidity, temperature and the type of substrate and the microorganisms, which take part in the process. A particle of a humic substance is believed to contain a hydrophobic nucleus with an aromatic structure and branched aliphatic chains with functional groups, such as hydroxyl, methoxy, methyl, methylenic, carboxylic, carbonyl, quinone, as well as amine-derived basic groups. (Palomino and Stoll 2013, Adani and Tambone 2005). Depending on their type, FA can contain carbon (38–54%), hydrogen (3–7%), nitrogen (0.6–9.5%) and oxygen (40–52%) (Kastelan-Macan and Petrovic 1996). In the case of HA the values range from 48 to 62% for carbon, from 2.9 to 5.3% for hydrogen, from 1.3 to 5.4% for nitrogen and from 29.4 to 40.7% for oxygen (See and Bronk 2005, Anielak and Świderska 2001). The capacity to bind metal ions is one of the most important physicochemical properties of HS. FA and HA are the most important reactive fractions of natural organic matter (NOM) in soils, sediments, surface water, and groundwater. HA, the initial focus of this research, are operationally defined as the fraction of HS that is insoluble in water at low pH (<2) and soluble at higher pH (>2). Land application is considered as the most environmentally safe, economically advantageous option for sewage sludge (SSL) disposal, based on the agronomic benefit of adding nutrients and organic matter to soil. However, relatively high levels of potentially toxic trace metals, including Cu, Zn, Pb, and Cd, which are typically present in SSL from heavily urbanized and industrialized areas, may pose a serious threat to the environment (Trubetskaya et al. 2013, Udom et al. 2004, Ye et al. 2014, Świderska-Dąbrowska et al. 2008).

The composition and structure of FA largely depend on the substrate and the conditions of their formation. These substances are resistant to biodegradation but are susceptible to archaea (Anielak et al. 2016). One of the main sources generating FA is crude sewage and the treatment plants where this sewage is processed. Therefore, an attempt was undertaken to examine FA from a biological sewage treatment plant in Płaszów (Cracow, Lesser Poland Voivodship) and analyze its structure compared to FA present in surface waters and in sewage treated in other sewage treatment plants based on the authors' own research and the literature data.

Materials and methods

Preparation of the samples

The sewage to be tested was collected for 30 days from a discharge chamber in the Płaszów sewage treatment plant

in Cracow which operates in a three–stage Bardenpho system with pre-denitrification. With the total sample volume of 339 L, the treated sewage was characterized by a neutral reaction, the average content of organic substances, Chemical Oxygen Demand (COD) of 25.56 mgO_2/L, the content of nitrogen compounds NH_4^+ – 0.36 mg/L, NO_2 – 0.19 mg/L, NO_3 – 6.65 mg/L, N_{og} – 10.05 mg/L, and phosphorus compounds PO_4^{3-} – 0.16 mg/L. FA were isolated from the collected samples in accordance with the procedure (Aiken et al. 1979, Pempkowiak et al. 2008). The samples were acidified to pH < 2 with hydrochloric acid (1:1) and filtered through a glass bed. The resulting clear and transparent filtrate was subjected to sorption on the Amberlit XAD-1180 ion exchange bed with a 400 mm bed height and 25 mm column diameter and the flow velocity of 1 dm^3/h. FA were desorbed in 0.5 mol/L NH_4OH. The eluent was concentrated in a vacuum evaporator at the temperature of 80°C and the negative pressure of 350 mbar. The concentrated solution was evaporated on a water bath (80°C) and dried in an oven at the temperature of 110°C. The study (Drobnik and Latour 2011) showed that humus acids are characterized by a high resistance to elevated temperatures (80–121°C). High temperature (150–250°C) does not cause significant changes in their structure and the functional groups remain intact (Klimenko et al. 2008). A low 6.50% increase in the ratio of the absorbance of light with the 465/665 wavelength at the temperature of 121°C compared to the ambient temperature may indicate a slight decrease in the molecular weight, a drop in the polymerization of the aromatic nucleus of fulvic acids, and a reduction in the content of aromatic groupings with an increase in the aliphatic amounts (Drobnik and Latour 2011, Klimenko et al. 2008).

Analysis methods

The dried samples of FA were analyzed qualitatively. The analysis of the content of elements and the dry matter was performed according to the EkotechLAB (Poland) testing procedure. The contents of carbon, hydrogen and nitrogen were determined using a combustion technique with chromatographic detection (elemental analysis) by means of a Flash 2000 CHNSO chromatograph (Thermo Scientific). Sample masses were 5–10 mg. The analysis of the other elements was conducted using the X-ray fluorescence (XRF) technique. The tests were conducted in a vessel designed for the analysis of powders on the Prolen foil with the width of 4 µm. The tests used the Flash EA elemental analyzer (Thermo Scientific) and the S8 Tiger WD-XRF spectrometer (Bruker). The ash content was determined by thermogravimetry using the SDT Q600 analyzer (TA Instruments). The heating rate was 10°C/min up to 700°C with the air flow of 100 mL/min. 5–10 mg samples were used. The absorption spectrum of the dilute aqueous solutions of FA was examined in the ultraviolet and visible light range (UV/Vis) in the Specol UV/Vis spectrophotometer (Analytik Jena). In order to obtain samples with different concentrations of FA, they were diluted with demineralized water. Measurements were performed in quartz cuvettes with the optical path length of 1 cm. Infrared spectra were tested using FTIR with ATR. The spectral range was: 650–4000 cm^{-1} at 1 cm^{-1} resolution, number of scans – 32. The tests were performed on Thermo Nicolet's FT-IR iS10 spectrometer.

Results and discussion

Characterization of fulvic acids

The tests on the precipitation of FA with hydrochloric acid (1:1) at pH < 2 showed that the humus acids extracted from the sewage treated in the Płaszów plant in Cracow contain only fulvic acids. The content of FA in the treated sewage was 5.2 g/m^3. The extracted acids are called FA, which are the sum of both HA and FA. The extracted acids had a dark brown color, and the ash content in an amount of 9.74% indicates they are contaminated with inorganic substances.

The spectra in the infrared light

By analyzing the spectra in the infrared light, it is possible to conclude that even for relatively simple compounds with one functional group, the spectra consist of multiple absorption bands, not all of which can be interpreted. Therefore, a full analysis of the IR spectra for the FA is difficult (if not impossible) because there are many deforming and stretching vibrations within one molecule. FA contain various impurities, which are often a mixture of many organic compounds that have undergone a partial humification, as well as inorganic substances such as metals. Thus, the spectrum contains diverse bands corresponding to the vibrations characteristic of the occurring structural elements. Having a similar energy difference between the oscillating levels, various types of bindings absorb radiation with a characteristic frequency, producing a band with the same range independently of the other details of the molecule structure. This means that most of the functional groups (e.g. C=O, N-H, O-H) give characteristic absorption bands whose position in the spectrum is similar.

The spectra of FA can be compared and, by analogy, appropriate conclusions can be drawn. The analysis of the IR absorption spectrum (Fig. 1) with the treated wavelength of 500–4000 nm of the FA extracted from the sewage in the Płaszów sewage treatment plant indicates that they have characteristics which are typical of sludge and sewage from a biological sewage treatment plant. The resulting bands with different absorbances for specific wavelengths were also typical of those obtained by other authors evaluating HA coming from sewage sludge. FA contained aliphatic groups (2996 cm^{-1}, 1461 cm^{-1}) with the existing C-H, O-H stretching vibrations (2996 cm^{-1}), that form hydrogen and scissoring bonds (1461 cm^{-1}) characteristic of organic compounds and proteinaceous and/or amide moieties (3280 cm^{-1}) (Boyd et al. 1998). The band at 1065 cm^{-1} represent material similar to lignin (Lawther et al. 1996), the band at 1692 cm^{-1} represent protein material and/or amide (Adani and Tambone 2005). The bands 1692 cm^{-1} and 1650 cm^{-1} are symptomatic of double bonds C=C and O=C (stretching bonds) and bonds of ketones, aldehydes, esters and olefins. Below 1500 cm^{-1} is the dactyloscopic range, where many of the vibrations are deformed.

The spectra in the ultraviolet and visible light UV/Vis

Another method used in organic compound structure testing is ultraviolet–visible spectroscopy (UV/Vis). The tests use the area of the electromagnetic spectrum 200–780 nm. The UV ultraviolet area extends from 100–380 nm. Far ultraviolet (100–200 nm wavelength) and near ultraviolet (200–380 nm wavelength) are distinguished. The range of the near ultraviolet (near UV) is important in organic chemistry, whereas the

far ultraviolet (vacuum UV) is accessible through the use of a vacuum (due to absorption of air in the area). The visible part of the spectrum extends from 380–780 nm. Fig. 2 shows the obtained spectra in the 190–305 nm range for FA from the sewage treated in Płaszów; the spectra are smooth.

Empirical indicators that characterize FA are the absorbance ratios at the wavelength of 465 nm and 665 nm A_4/A_6. The value of A_4/A_6 decreases with an increase in the condensation and aromatization of FA molecules. For FA from the Plaszow sewage treatment plant, the ratios A465/665 and A425/625 (Table 1) are 2.040 and 2.897, respectively. The ratio A465/665 was 7.930 for FA from the sewage treated in the Jamno sewage treatment plant (West Pomeranian Voivodship, NW Poland) and 6.560 for the Unieście sewage treatment plant (West Pomeranian Voivodship, NW Poland). In contrast, for FA obtained from the water of the Vistula River, the ratio A425/A665 exceeded those values and was equal to 9.060 (it was 2.897 for HA from Plaszow). The Jamno and Unieście treatment plants have simple technological systems. The sewage treated in the Jamno plant comes from Koszalin (West Pomeranian Voivodship, NW Poland). In this treatment plant, the biological treatment takes place in a three-phase system operating the A_2O technology. The Unieście treatment plant has a two-phase A_2O system. The Płaszów sewage treatment plant operates in a 3-stage Banderpho system with pre--de-nitrification and is more modern and complex than the Unieście and Jamno plants, and the FA generated there have the lowest value – of the ratio A_4/A_6.

The tested acids came from different environments. The greater the biochemical effects on the FA were, the lower the values of the ratio A_4/A_6, so there was an increase in the degree of their aromatization and dehydrogenation, with an increase in the molecular weight, polymerization of the aromatic nucleus, the number of aromatic groups, and a reduction in the number of aliphatic groups. The ash content of the FA depended on the efficiency of the sewage treatment process. The FA obtained

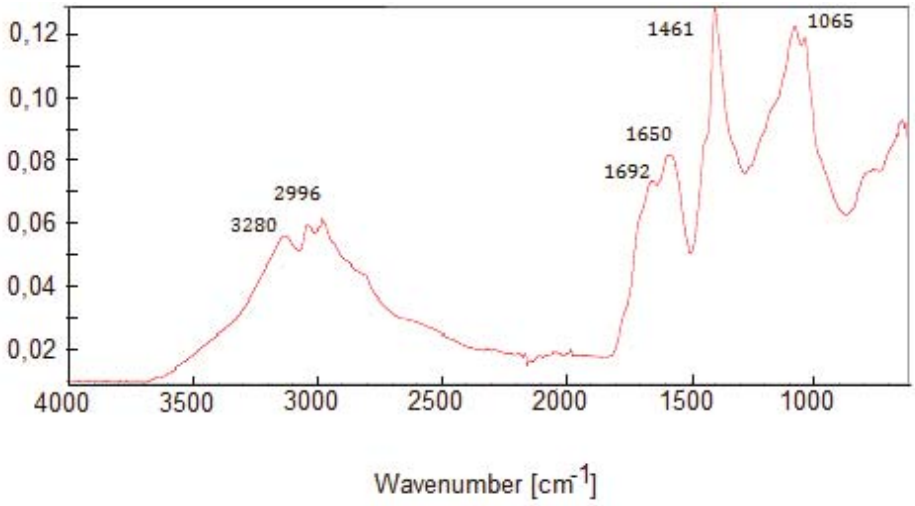

Fig. 1. The IR absorption spectra of fulvic acids separated from the treated wastewater (Płaszów in Cracow)

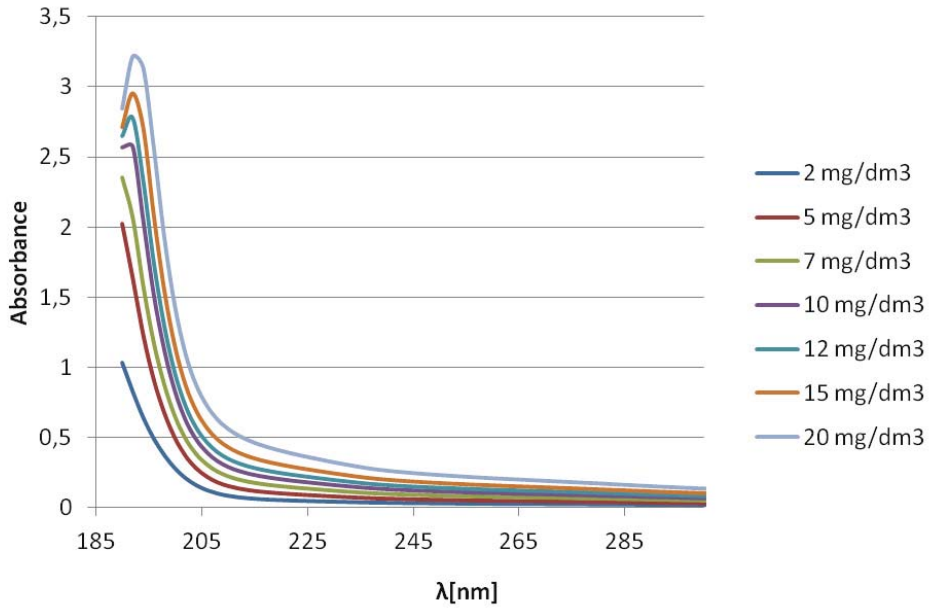

Fig. 2. Typical UV absorption spectra of FA separated from treated wastewater in Płaszów plant

from the sewage from the Płaszów plant contained 9.74% of ash, whereas the FA from the Jamno and Unieście plants contained 24% and 23%, respectively. This relationship was consistent with the quality of the treated sewage. The lower the quality of the treated sewage was, the more impurities their FA contained. The sewage treated in Jamno contained COD of 32.8 gO_2/m^3, 13.2 g/m^3 of total nitrogen, and 0.44 g/m^3 of total phosphorus. The sewage treated in Unieście contained COD of 32.2 gO_2/m^3, 17.9 g/m^3 of total nitrogen, and 0.93 g/m^3 of total phosphorus. In the case of the sewage from Płaszów, all the indicators had lower values: COD 25.56 gO_2/m^3, N_{og} 10.05 g/m^3, and PO_4^{3-} 0.16 g/m^3. The amounts of fulvic acids from the Jamno and Unieście sewage treatment plants were approx. 2.8 g/m^3 and 3.2 g/m^3, respectively (Pempkowiak et al. 2008).

Another indicator is the ratio A_2/A_3 (the ratio of absorbance of light with the wavelength of 250 and 300 nm) responsible for e.g. the size of the molecules. This indicator had similar values for all three types of fulvic acids: from Unieście – 1.7, Jamno – 1.7 and Płaszów – 1.7 (Table 4). It can therefore be assumed that the value of the ratio $A_2/A_3 = 1.7$ is symptomatic of FA (there were no humic acids in the sewage).

Elemental composition

The qualitative analysis of fulvic acids (Table 2) showed that they contained substantial amounts of silicon (15.5 mg/g), sodium (14.5 mg/g), calcium (8.8 mg/g), potassium (2.5 mg/g), phosphorus (1.6 mg/g), and magnesium (1.3 mg/g). Furthermore, the tested FA contained small amounts (< 1 mg/g) of iodine, iron, bromine, titanium, and zinc. Inorganic contaminants determined by the thermogravimetric analysis (Fig. 3), which form the so-called ash, were 9.74% of the total mass. It was only at 580°C that the mass of ash became stable and did not change, even after increasing the temperature to 700°C. The analysis of the elemental composition of FA showed (Table 3) that they contain 43.51% of carbon, 5.37% of hydrogen, 9.44% of nitrogen, 2.70% of sulphur and 38.98% of oxygen per the ashless mass. Depending on their type, FA can contain carbon (38.00–53.79%), hydrogen (3.35–6.78%), nitrogen (0.62–9.46%) and oxygen (40.01–51.43%), without the share of sulphu.[3] Thus, the contents of carbon, hydrogen, nitrogen, and oxygen in the tested samples were typical of FA.

The isolated acids were characterized by a large amount of nitrogen (9.44%) and sulphur (2.70%). The crude sewage contained various organic compounds e.g. proteins and urea of natural origin. The biological treatment process resulted in the biodegradation and humification and formation of simple organic compounds, including monomers derived from proteins, such as amines and others containing nitrogen and sulphur in their structure. This explains the high content of these elements in the extracted FA. Another source could be the aqua ammonia used to extract acids, which is easily decomposed into water molecules and ammonia that escapes into the atmosphere, in particular at elevated temperatures. Small amounts of nitrogen

Table 1. Characteristics VIS absorption spectra of the fulvic substances in aqueous solutions from treated wastewater (Płaszów in Cracow)

	Abs								
			A465/665			A425/625			A250/300
HS. mg/dm³	λ= 465nm	λ = 665nm		λ = 425nm	λ = 625nm		λ = 250nm	λ = 300nm	
2	0.004045	0.00301	1.343854	0.005009	0.002983	1.679182	0.028095	0.016974	1.655179
5	0.005295	0.002585	2.048356	0.007906	0.00259	3.05251	0.059734	0.035021	1.705662
7	0.009373	0.005464	1.71541	0.012856	0.005301	2.425203	0.086204	0.051183	1.684231
10	0.010994	0.006264	1.755109	0.015871	0.00549	2.890893	0.115264	0.06758	1.705593
12	0.014581	0.00662	2.202568	0.0204	0.007043	2.896493	0.141211	0.082946	1.702445
15	0.018944	0.010734	1.764859	0.025857	0.011196	2.309486	0.173524	0.100919	1.719438
20	0.019943	0.00731	2.728181	0.030011	0.007879	3.808986	0.231587	0.134852	1.717342
X			**2.035747**			**2.897262**			**1.705785**
SD			0.442066			0.670256			0.022327

Table 2. Trace elements content in fulvic acids (mg/g FA)

Si	Na	Ca	K	P	Mg	I	Fe	Br	Ti	Zn
15.500	14.500	8.800	2.500	1.600	1.300	0.700	0.600	0.200	0.100	0.087

Table 3. Elemental analysis and characteristic parameters of fulvic acids

	C	H	N	S	O	C/H	C/N	C/O
	(%)	(%)	(%)	(%)	(%)			
FA	43.51	5.37	9.44	2.70	38.98	8.10	4.61	1.11

may, however, contaminate the extracted acids. However, in order to compare the FA from the treated sewage with the acids extracted from the treated sewage in other biological treatment plants, the acid extraction method applied by the authors was reused (Pempkowiak et al. 2008).

C/H, C/O and C/N are important indicators of the degree of the aromatic condensation and fulvic maturity of FA. The calculated values of the proportions are shown in Table 4. The ratio C/H = 8.10 is relatively large, indicating a substantial degree of aromatization of HA and is higher than that of the FA obtained from Unieście (C/H = 6.62) and Jamno (C/H = 6.61). At the same time, these relations are in line with the value A_4/A_6 obtained for acids from the three sewage treatment plants and the IR spectrum analysis (Fig. 1) of FA from the Płaszów sewage treatment plant, which indicates the presence of C=C bonds in the aromatic compounds. Once more, a relationship was demonstrated between the degree of aromatization of FA and the method of treatment of sewage from which the acids were extracted. The longer the sewage is subjected to a biological treatment process, the greater the degree of the aromatic condensation and fulvic maturity of the FA. The value of the ratio C/O equal to 1.11 obtained for the FA from Płaszów is low, indicating the presence of carbohydrates and a carboxyl structure. The value of this ratio can result from the biodegradation of the protein present in the crude sewage in large quantities, which is confirmed by a significant amount of sulphur (2.70%) and nitrogen (9.44%). Therefore, the ratios C/N = 4.61 and C/O are relatively small. In the treated sewage, the total nitrogen content is approx. 8.7 g/m^3. It can be concluded that the nitrogen is structurally linked to the HA to a large extent. Its high content in the HA molecule results from complex biochemical processes taking place in the biological reactor of the sewage treatment plant (pre-de-nitrification, dephosphatation, denitrification, 1st degree nitrification, and 2nd degree nitrification).

When comparing values with those presented in the work (Kučeríka et al. 2012) for waters of the Suwannee River, it can be observed that there are some differences in the elemental composition of the acids extracted from the water and the treated sewage. The carbon content in the FA isolated from water of the Suwannee was 52.60% (Kučeríka et al. 2012), while for the sewage treated in Płaszów it was 43.51%, so less by approx. 9.09%. The oxygen content was also lower in FA coming from the sewage – by approx. 3.02%. The ratio C/O informs us of the hydrophobicity of acids. The more carbon, the greater the ratio and the hydrophobicity of acids are. The ratio C/O for the Suwannee FA was 1.25, and for the sewage HA – 1.11. The difference is small, but it can be concluded that the acids from Płaszów are more hydrophilic and have more carboxyl functional groups.

Large ratio C/O characterizes FA contained in sewage sludge (Adani and Tambone 2005). Hydrophobic FA are more easily deposited on sludge, whereas hydrophilic ones

Table 4. Comparison of the properties of isolated fulvic acids

Source of HA	FA	Ash	A_4/A_6	C/H	C/O	C/N	C/S	Literature
	(g/m^3)	(%)						
WWTP Płaszów	5.2	9.74	2.04–2.90	8.10	1.11	4.61	16.11	–
WWTP Jamno	2.8	24.00	7.93	6.61	1.26	7.62	22.15	Pempkowiak et al. 2008.
WWTP Unieście	3.2	23.00	6.56	6.62	1.36	8.03	22.26	Pempkowiak et al. 2008.
Activated sludge (Giussago)				7.96	2.05	7.18	25.46	Adani & Tambone 2005
Wisła			9.06	–	–	–	–	Pempkowiak et al. 2008.
Suwanee				12.30	1.25	–	–	Kučerík et al. 2012

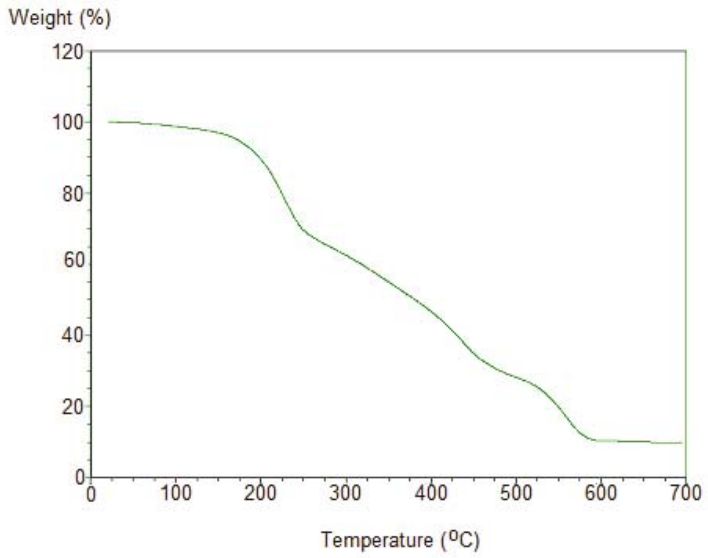

Fig. 3. Typical UV absorption spectra of FA separated from treated wastewater in Płaszów plant

are soluble and remain in the solution. The ratio C/H is an indicator of the degree of aromatization and condensation of FA. The Suwannee water has the ratio C/H = 12.3. In contrast, FA from Płaszów have C/H = 8.1, so are characterized by a lower degree of aromatization and condensation than the Suwannee water FA (Table 4). Similarly HA of the sewage treated in the treatment plant in Jamno (C/H = 6.61) and Unieście (C/H = 6.62) have a lower degree of aromatization than the FA from Suwannee and Płaszów (Table 4). Fulvic acids from the activated sludge have C/H = 7.96, so they have a ratio similar to FA from Płaszów. So the degree of aromatzation is determined not only by the source of FA formation, but also by the duration of the process of humification, which is much longer in surface waters. The large variation of ratios may also arise from the fact that the elemental composition of FA isolated from the sewage took into account the presence of nitrogen and sulphur, i.e. the elements that are in the sewage in large quantities and are the elements forming amine and sulphonic functional and other groups (Kuĉeríka et al. 2012).

Conclusions

1) The longer sewage is subjected to a biological treatment process, the greater the degree of aromatic condensation and humus maturity of the fulvic acids contained within it.
2) C/H, C/O and C/N are important indicators of the degree of the aromatic condensation and humus maturity of fulvic acids. The dehydrogenation of FA grows with the increase in C/H. Hydrophobicity increases, solubility decreases, and the probability of the occurrence of FA in sludge increases with the rise in the value of the ratio C/O.
3) Fulvic acids contained in the sewage treated in the three biological sewage treatment plants have the ratio A_2/A_3 (the ratio of the absorbance of light with the wavelength of 250 and 300 nm) equal to the value 1.7.
4) There is a high interdependence between the IR spectrum analysis in the visible light and the elementary composition of FA extracted from different environments, confirming the conclusions pertaining to the structure and properties of the acids being tested.
5) The tests showed that the sewage treated in the Płaszów sewage treatment plant (Cracow, Lesser Poland Voivodship) contains 5.2 g/m^3 of FA.
6) Fulvic acids extracted from the sewage treated in the Płaszów sewage treatment plant have contents of carbon, nitrogen, hydrogen, and oxygen that are typical for FA.

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Charakterystyka kwasów fulwowych zawartych w ściekach oczyszczonych osadem czynnym

Streszczenie: W celu określenia jakościowej i ilościowej charakterystyki kwasów fulwowych odprowadzanych z oczyszczalni ścieków komunalnych przeprowadzono ich ekstrakcję ze ścieków oczyszczonych. Oczyszczone ścieki z oczyszczalni miejskiej zakwaszono do pH <2 i ekstrahowano żywicami jonowymiennymi w kolumnie laboratoryjnej. Po desorpcji roztworem NH_4OH, KF zatężano w próżni i badano ich suchą masę, widmo UV-VIS, widmo absorpcji IR, skład elementarny i inne pierwiastki. Na podstawie własnych badań i danych z literatury przeanalizowano strukturę otrzymanych kwasów fulwowych i porównano je z kwasami fulwowymi występującymi w wodach powierzchniowych oraz ściekach oczyszczonych w innych oczyszczalniach ścieków. Stężenie kwasów fulwowych w ściekach oczyszczonych wynosiło 5,2 mg/L. Badania wykazały, że istnieje duża współzależność między analizą widma IR, w świetle widzialnym i składem elementarnym ekstrahowanych kwasów fulwowych z różnych środowisk, potwierdzająca wnioskowania dotyczące budowy i właściwości badanych kwasów. Kwasy fulwowe wyekstrahowane ze ścieków miały zawartość węgla, azotu, wodoru i tlenu, typową dla kwasów fulwowych. Im dłużej ścieki poddawane są procesowi biologicznego oczyszczania, tym większy jest stopień kondensacji aromatycznej i dojrzałości humusowej zawartych w nich kwasów humusowych. Kwasy fulwowe zawarte w ściekach oczyszczonych w trzech różnych biologicznych oczyszczalniach mają iloraz A2/A3 (iloraz absorbancji światła o długości fali 250 i 300 nm) równy wartości 1,7. Istnieje duża współzależność między analizą widma IR, w świetle widzialnym i składu elementarnego ekstrahowanych kwasów humusowych z różnych środowisk, potwierdzająca wnioskowania dotyczące budowy i właściwości badanych kwasów.