



## Origin and characteristics of fulvic acids – precursors of oxidation and disinfection by-products

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### ABSTRACT

The work presents characteristics of humic substances (HSs), including water-soluble fulvic acids (FAs). FAs act as carriers of micropollutants and precursors of organic, carcinogenic, mutagenic, and teratogenic chloro compounds, during oxidation and disinfection of surface water. HSs can be found in the soils, peat bogs as well in surface and groundwaters. In the research, FAs was extracted from municipal wastewater (raw and treated) as well as from landfill leachates. Next subsequently subjected to qualitative and quantitative analysis. Their quantitative elemental composition included determination of O, C, H and N mass, O/C, H/C, and N/C atomic ratios, a micropollutant content, and an infrared spectrum. Based on a literature review and author's research, FAs characteristics, as well as, properties were presented and next compared with discussed substances originating from other sources, such as the waste landfill in Shanghai and Beijing in China, Antarctic soil, sewage sludge from Japan and the Suwannee River water. It was shown that municipal facilities, such as landfills and wastewater treatment plants, were important sources of the FAs formation. In Poland, approximately 15.6 tons of FAs/d (as dry solids) are discharged to surface waters. A detailed analysis of the infrared spectrum indicates that FAs extracted from leachates and treated wastewater has a convergent chemical structure. These are aromatic hydrocarbons with alkyl groups and carboxylic acid groups. The degree of FAs aromatization depends on their humification time and the place of origin. HSs undergoes a biochemical and chemical transformation in the environment. Their content of inorganic substances (ash) varies with their origin, the highest amount of microorganic impurities can be found in FAs extracted from raw sewage, sewage sludge, and landfill leachate.

*Keywords:* Fulvic acids; Humic acids; Humic substances; Leachate; Micropollutants

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### 1. Introduction

Humic acids (HAs) are one of the most common substances found in the natural environment, they were discovered even in deep underground locations. Depending on the environmental conditions, HAs can take either mobile and easily soluble forms (fulvic acids (FAs)) or become poorly soluble compounds (humic fractions) [1–3]. FAs is a typical

component of natural organic matter (NOM), they consist of the major part of humic substances (HSs) found in leachate.

They are heterogeneous macromolecular organic compounds with numerous functional groups that easily bind with impurities and thus affect the speciation and migration of micropollutants in the natural environment [4–6]. Due to their carboxyl and phenol groups, they have the ability to buffer and form complexes [2,7]. FAs – metal

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interactions take place mainly due to the presence of carboxylic and phenolic groups. Interactions of these substances with polycyclic aromatic hydrocarbons occur through a strong interaction of the *p-p* bindings [5,6]. However, mechanisms of interactions between organic compounds and FAs are still unclear due to the lack of appropriate research methods. The presence of FAs can also affect the accumulation of sulfonamide residues in the natural environment, especially in water, they stimulate the growth of antibiotic-resistant pathogens. Also, the speciation of sulfonamide residues is affected by FAs [6,8].

The formation of disinfection by-products is encouraged by a high content of NOM in surface waters [9]. The main source of NOM is humus, which is particularly abundant during the rainy seasons [10]. In natural waters, around 40%–80% of NOM are substances formed during various microbiological, chemical, and photochemical transformations [11]. Ozonation and chlorination of FAs can result in the formation of different intermediate oxidation by-products [12]. The concentration of trihalomethanes changes with seasons, a content of chlorides and organic substances as well as with pH and water temperature. Particularly significant changes are observed in waters with a temperature  $> 15^{\circ}\text{C}$  [13–17]. 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (MX), as a compound of high mutagenic activity is responsible for about 15%–57% of mutagenic activity of total water extracts and 50%–100% of HSs. The concentration of MX is determined by the pH of the chlorination reaction, most MX are formed at  $\text{pH} = 2$ . The MX concentration increases along with an increase of organic carbon, a  $\text{Cl}_2$  dose, and reaction time [18]. The studies show that more chloroorganic substances are formed in oxidized ocean waters than in surface or groundwaters. An increase in chloride concentrations results in an increased formation of xylenes. At chloride concentrations  $> 600 \text{ mg/dm}^3$ , the amount of all chloroorganic substances tested increases rapidly which proves a catalytic effect of chloride ions in the FAs oxidation process [19]. Until recently, HSs was considered as substances of a natural origin, formed as a result of plant humification and animals decaying, their main source is marshes, soil, and peatlands.

HSs extracted from sewage sludge is mainly used in agriculture. Also, the discussed organic substances extracted from various sources can be used as adsorbents to remove heavy metals, form a matrix for the synthesis of various materials, as a binder in the pelletization process of titanium magnetite concentrates and others.

Recent studies have shown that large quantities of HSs come with effluents discharged from wastewater treatment plants and landfills. Therefore, the paper presents the quantitative and qualitative characteristics of FAs discharged from municipal plants at Cracow. This issue is very important because HSs has a significant influence on the environment. Thermal degradation changes in HSs chemical structure can reduce soil fertility and cause environmental damage to the carbon cycle [20,21].

He et al. [22] confirmed that aromaticity and humification degree, molecular weight, and HSs content of dissolved organic matter are important parameters influencing waste stability. What more increase in parameter values has led to an increase in organic matter resistance to biodegradation?

Dang et al. [23] that FAs contained in leachates decreased biogas production rates and organic degradation efficiencies.

## 2. Materials and methods

### 2.1. Analytical methods and extraction of FAs methodology

Both raw and treated wastewater was discharged from the “Płaszów” municipal wastewater treatment plant in Cracow and leachates from the “Barycz” waste landfill in Cracow were tested in the research. The samples were taken several times in the volume of 100–200 L and the given results are averaged. FAs was extracted from the wastewater and leachates according to the method described in the papers [24,25] with small modifications (Fig. 1).

Dried samples of FAs were subjected to qualitative analysis. The content of carbon, hydrogen, and nitrogen was determined using a combustion technique with chromatographic detection (elemental analysis) on a CHNS/O chromatograph manufactured by Thermo Scientific, (USA), Model Flash 2000. The weights of the samples were 5–10 mg. The analysis of other elements was carried out with the X-ray fluorescence (XRF) technique. The research was carried out in a powder analysis vessel on a  $4 \mu\text{m}$  Prolene foil. The FlashEA elemental analyzer by Thermo (USA) and WD-XRF spectrometer (model S8 Tiger) by Bruker (Germany) was used. The ash content was determined with a thermogravimetric method using the SDT Q600 apparatus by TA Instruments (USA). The heating rate was  $10^{\circ}\text{C}/\text{min}$  up to  $700^{\circ}\text{C}$  with an airflow of  $100 \text{ mL}/\text{min}$ .

## 3. Results and discussion

### 3.1. Characteristic of the wastewater and the leachate

On the basis of data obtained from the Płaszow WWTP and own research determined the parameters such as pH, chemical oxygen demand (COD), biochemical oxygen demand ( $\text{BOD}_5$ ),  $N_{\text{tot}}$  and  $P_{\text{tot}}$ .

The general characteristic of the wastewater and the leachate from which FAs was extracted was shown in Table 1.

The concentrations of COD in the urban raw sewage was  $320 \text{ mg O}_2/\text{L}$  in the purified urban sewage  $30.0 \text{ mg O}_2/\text{L}$ . The concentrations of  $\text{BOD}_5$  in the purified urban sewage

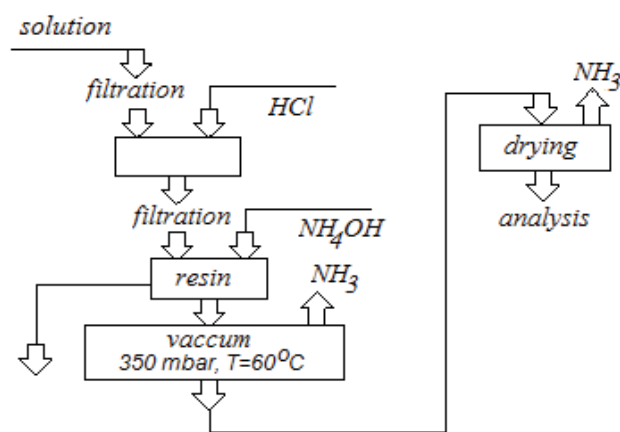


Fig. 1. Method of fulvic acid extraction.

Table 1  
Characteristic of the urban raw and purified sewage from which FAs was extracted

Parameter	Urban raw sewage	Purified urban sewage
pH	7.5	7.6
COD (mgO <sub>2</sub> /L)	320	30.0
BOD <sub>5</sub> (mgO <sub>2</sub> /L)	240	5.0
N <sub>tot</sub> (mgN/L)	65	8.0
P <sub>tot</sub> (mgP/L)	6.4	0.3

was 5.0 mg O<sub>2</sub>/L. The concentrations of N<sub>tot</sub> in the urban raw sewage was 65 mg N/L in the purified urban sewage 8.0 mg N/L. The concentrations of P<sub>tot</sub> in the urban raw sewage was 6.4 mg P/L in the purified urban sewage 0.3 mg P/L. All indicators were in the range of permissible concentrations.

### 3.2. Analysis of the infrared absorption spectrum

Functional groups as well as other atomic groups most often absorb infrared radiation in the narrow wavenumber area. This is why infrared spectroscopy can be used to identify functional groups and other elements of a chemical compound. These relationships are characteristic for a specific structure of the compound which makes it possible to recognize and compare the examined organic substances.

Since there are different processes that take place at the waste landfill and municipal wastewater treatment plant, the infrared absorption spectra were determined for the extracted FAs to identify them as well as compare their absorption bands and chemical structures.

The tests (Figs. 2–4) show a large similarity of the infrared spectra of the FAs. Near area of 3,000 cm<sup>-1</sup> there are almost identical bands at 2,996 and 3,050 cm<sup>-1</sup> (treated sewage), at 2,995 cm<sup>-1</sup> (leachate) and at 3,050 cm<sup>-1</sup> (raw sewage). These are stretching vibrations of the aliphatic C–H group. The band for FAs coming from landfill leachates is small. In addition, there are 3,160 and 3150 cm<sup>-1</sup> absorption bands for FAs extracted from both raw wastewater and the effluent, which specify protein and amide residues. It should

also be noted that there are similar relative dependencies between heights of individual bands and areas of their base. Thus, the highest band was recorded for the wavenumber 1,400 cm<sup>-1</sup> (raw sewage and leachate) and 1,460 cm<sup>-1</sup> (treated sewage) and was associated with OH<sup>-</sup> bond deformation, CH<sub>3</sub> bending, C–O stretching in a phenol group and stretching in carboxylic groups COO and the presence of C–H bonds in methyl groups [3,27,28]. Then the observed bands include 1,590 cm<sup>-1</sup> (treated sewage, leachate) and two bands 1,630 and 1,650 cm<sup>-1</sup> (raw sewage, treated sewage), which are characteristic for double bonds C=O, C=C (stretching) of ketones, aldehydes, esters, and olefins. The spectra also include bands in the area of 1,100–1,065 cm<sup>-1</sup> (raw and treated sewage) and 1,050 cm<sup>-1</sup> (leachates), which characterize C–O bonds, originating from OCH<sub>3</sub>, COH and COC groups of organic compounds or related to a mineral fraction as well as with silicate impurities and stretching of S–O bonds [26–29].

The main difference between the three spectra is the presence of a 2,150 cm<sup>-1</sup> band for FAs extracted from landfill leachates since only a small group of compounds absorbs in this range. The band suggests the presence of triple bonds C<sup>o</sup>C, C<sup>o</sup>N, or systems such as ketenes, isocyanates, azides diazo compounds, and OH or N–H groups (amine salts). This highlights the uniqueness of FAs obtained from landfill leachates and the presence of organic micro-pollutants. For the given spectra similar widths of the base of absorption bands were observed. The smallest width was for the 1,400 cm<sup>-1</sup> area and a relatively large for the areas of 1,100–1,050 cm<sup>-1</sup> and 2,800–3,200 cm<sup>-1</sup>.

The infrared spectra of FAs extracted from leachate, raw and treated sewage, as well as FAs extracted by other authors [30], showed a similarity of isolated substances which indicates a slight variation in the chemical structure.

### 3.3. Changsha, China

#### 3.3.1. Qualitative analysis of FAs of different origin

A qualitative analysis of the FAs, extracted at three locations of the Cracow municipality (Tables 2 and 3) shows some correlations. FAs from landfill leachates (FA4) have

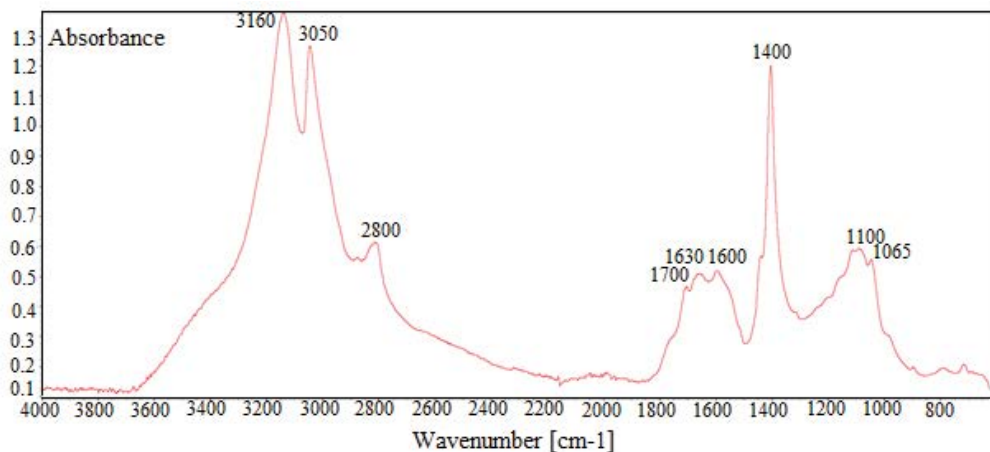


Fig. 2. The infrared spectrum of FAs extracted from the raw sewage.

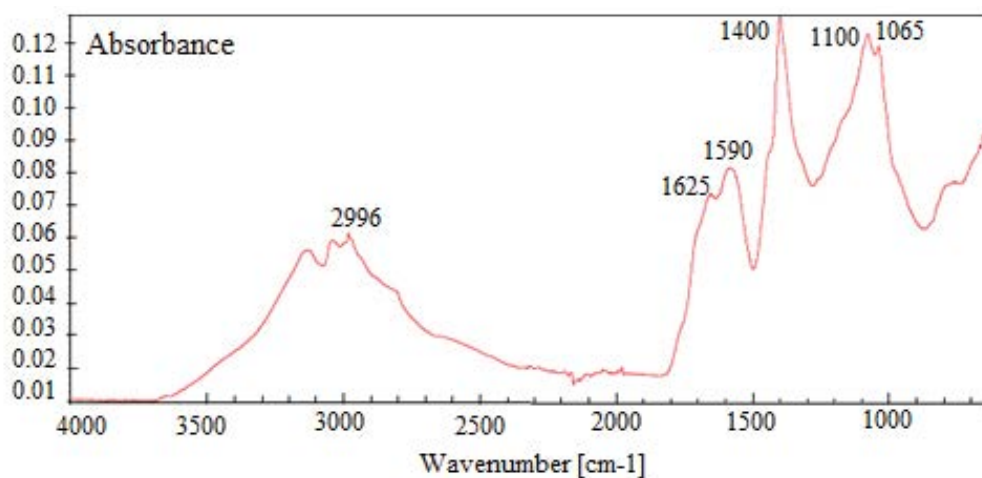


Fig. 3. The infrared spectrum of FAs extracted from treated sewage from the wastewater treatment plant in Cracow.

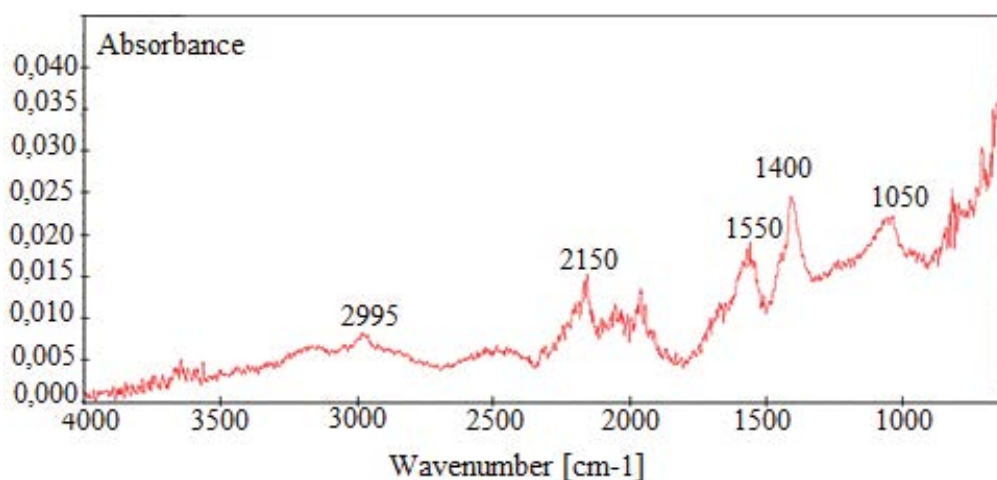


Fig. 4. The infrared spectrum of FAs extracted from landfill leachates at Cracow.

the highest content of micropollutants measured as ignition residue (17.55%) while FAs from raw sewage (FA0) also contains a large number of inorganic impurities (11.55%), the least pollutant content was recorded in FAs extracted from the wastewater plant effluent FA1 (9.74%). Similar results were obtained during the detailed analysis (Table 3). FAs in leachates are rich in chlorides, including NaCl (Na 33.7 mg/g, Cl 66.8 mg/g) and potassium (7.6 mg/g), calcium (5.5 mg/g) as well as silicon (3.3 mg/g) and magnesium (3.1 mg/g). FAs extracted from raw sewage have large amounts of silicon (15.5 mg/g) and sodium (14.5 mg/g) while in FAs extracted from the treated sewage silicon and sodium content were 2.58 and 1.74 mg/g, respectively. A similar relationship applies to the remaining micropollutants in FA, their amounts depend on the environmental conditions. Analysis of the elemental composition (Tables 2 and 4) indicates that for FAs extracted from raw wastewater the O/C ratio was higher than for FAs in the effluent ( $1.18 > 0.72$ ). The number of oxygen functional groups increases along with the increase of the O/C ratio, hence it should be

concluded that higher amounts of micropollutants result from their adsorption by the aliphatic groups of FA. During biological wastewater treatment with activated sludge, FAs are adsorbed on sludge via micropollutant bridging, lighter fractions with less aliphatic groups remain in the wastewater. Such an assumption is confirmed by the higher amount of molecular carbon in FAs extracted from the effluent. FAs extracted from landfill leachates have a high H/C ratio (1.99) and a small O/C ratio (0.57), so they are similar to HA [31]. They also show a low polarity of aliphatic groups.

After the qualitative analysis of the FAs extracted from three sources at Cracow (FA0, FA1, FA2), the results were compared with FAs originated from other sources, that is, from the landfill in Shanghai (FA3, FA4) and in Beijing (FA5), from the soil in the Antarctic (FA6, FA7), from sewage sludge in Japan (FA8) and surface water from the Suwannee River (FA9). The author's results and studies found in the literature are presented in Table 2. The data indicate that HSs found in different locations throughout the world are quite similar. In Table 2, the sums of elemental percentage

Table 2  
Elemental composition of FAs originated from selected environmental sites (%) and their atomic ratios

FA	Elemental composition				Ash content (%)	Literature	Atomic ratios		
	C (%)	H (%)	N (%)	O (%)			H/C	N/C	O/C
FA0	33.24	4.60	8.87	52.13	11.55	Own research	1.66	0.23	1.18
FA1	43.51	5.37	9.44	41.68	9.74	Own research	1.48	0.18	0.72
FA2	45.51	7.53	12.21	34.71	17.55	Own research	1.99	0.23	0.57

FA0 – urban raw sewage, Cracow; FA1 – purified urban sewage, Cracow; FA4 – waste landfill leachate, Cracow

Table 3  
Micropollutants in FAs extracted from the effluent from the wastewater treatment plant at Cracow and leachates from the Cracow landfill, mg/g (own research)

	Si	Na	Ca	K	P	Mg	I	Fe	Br	Ti	Zn	Cl	Cr	Co
FA0	2.58	1.74	0.93	0.37	0.28	0.29	wnf	0.04	wnf	wnf	0.087	13.62	wnf	wnf
FA1	15.50	14.50	8.80	2.50	1.60	1.30	0.70	0.60	0.20	0.10	0.087	wnf	wnf	wnf
FA2	3.30	33.70	5.50	7.60	1.0	3.1	wnf	0.4	0.067	0.1	wnf	66.8	0.084	0.052

FA0 – urban raw sewage; FA1 – purified urban sewage; FA4 – waste landfill leachate, Cracow  
wnf – was not found

Table 4  
Elemental composition of FAs originated from selected environmental sites (%) and their atomic ratios

FA	Elemental composition				Ash content (%)	Literature	Atomic ratios		
	C (%)	H (%)	N (%)	O (%)			H/C	N/C	O/C
FA3	36.80	3.96	2.28	56.46	4.33	[32]	1.29	0.05	1.15
FA4	43.49	5.05	2.88	48.58	5.31	[32]	1.39	0.06	0.84
FA5	44.70	7.26	4.72	43.32	–	[23]	–	0.09	0.73
FA6	50.73	4.79	5.95	38.53	5.74	[33]	1.13	0.10	0.57
FA7	51.80	5.37	5.20	37.63	2.05	[33]	1.24	0.09	0.54
FA8	44.83	6.52	7.50	36.43	16.44	[34]	1.74	0.14	0.61
FA9	52.60	4.28	–	42.00	–	[35]	0.98	–	0.6

FA2, FA3 – waste landfill, Shanghai; FA5 – leachate, Beijing, China; FA6, FA7 – soil, the Antarctic; FA8 – sewage sludge, Japan; FA9 – surface water, the Suwannee River, (USA)

composition for C, H, N, and O may be = 100%. In case when the authors additionally included sulfur in the calculations then the oxygen fraction was predicted.

The FAs samples from different sources can be ranked according to the carbon content in their ash-free mass:

$$C_{FA9} > C_{FA7} > C_{FA6} > C_{FA2} > C_{FA8} > C_{FA5} > C_{FA1} @ C_{FA4} > C_{FA3} > C_{FA0} \quad (1)$$

The highest amount of carbon is found in FAs from surface water (FA9) and the Antarctic soil (FA6, FA7), the lowest – in FAs extracted from raw sewage (FA0) and landfill leachate (FA3, FA4).

The carbon content in acids increased with the waste deposition time, that is, with the length of the humification process ( $C_{FA4} > C_{FA3}$ ). The O/C ratio is important since it indicates the presence of carbohydrates, carboxyl, and O-alkyl groups – acid functional groups. The rank of O/C ratio values is as follows:

$$\begin{aligned} O/C_{FA0} > O/C_{FA3} > O/C_{FA4} > O/C_{FA5} > O/C_{FA1} > O/C_{FA8} @ O/ \\ C_{FA9} > O/C_{FA2} = O/C_{FA6} @ O/C_{FA7} \end{aligned} \quad (2)$$

The more aliphatic functional groups, the smaller hydrophobicity of acids, hydrophobicity increases along with carbon content. Therefore, the highest hydrophilicity and the lowest carbon content are found in FAs extracted from raw sewage (FA0) and landfills (FA3, FA4). It may prove a short humification time of FAs substrates. Low carbon content and a hydrophilic character of FA3, FA4, and FA1 samples may result from their migration dynamics. At the same time, a relation of  $O/C_{FA3} > O/C_{FA4}$  is consistent with the landfilling age since as humification proceeds a number of oxygen and oxygen functional groups in FAs are reduced. The FA4 extracted from a landfill that was in operation for more than 6 y. During wastewater treatment HSs undergo transformations. They partially precipitate and are adsorbed on the activated sludge, so

only lighter fractions with fewer micropollutants pass to the effluent.

At landfill, lighter more mobile, and soluble fractions tend to migrate. In addition, as the research shows landfill age is an important issue. This is not the case for FAs extracted from FA2 leachates with a relatively high degree of aromatization. FAs extracted from the soil of the Antarctic have the highest hydrophobicity, which proves that they have remained at this location for a long time.

This relationship is confirmed by the H/C ratio, which shows the degree of aromatization and condensation of FAs for which the rank of values is as follows:

$$\frac{H}{C}_{FA2} > \frac{H}{C}_{FA8} > \frac{H}{C}_{FA0} > \frac{H}{C}_{FA1} = > \frac{H}{C}_{FA4} \cong \frac{H}{C}_{FA3} > \frac{H}{C}_{FA7} > \frac{H}{C}_{FA6} > \frac{H}{C}_{FA9} \quad (3)$$

FA9, FA6 and FA7 samples with the highest carbon content show the lowest hydrogenation, whereas FA2 and FA8 samples with the highest aromatic condensation have the highest hydrogenation.

The analysis of the data presented in Table 3 confirms that FAs constitutes the carriers of various inorganic contaminations. FAs extracted from raw sewage are more contaminated than the ones extracted from the effluent because of the contact time of HSs with the contaminants in wastewater and their concentrations. During wastewater treatment, biochemical and physicochemical processes occur, FAs availability for solutes increases and hydrolysis, ion exchange and adsorption take place, consequently, the amount of contaminants transported by organic matter decreases. The research results indicate that there are different anthropogenic sources of FA. Since according to the research, the FAs content in the plant effluent can amount to 5.2 g/m<sup>3</sup>, and about 3 million m<sup>3</sup>/d of wastewater is treated in Poland, so approx. 15.6 tonnes of FAs/d is discharged to the surface waters, as calculated on the dry matter basis. Only this simple analysis proves the necessity to dispose of HSs in municipal facilities, wastewater treatment plants, or waste landfills. It should be emphasized that the amount of discussed substances discharged with a single leachate volume unit is much higher than the one discharged with 1 m<sup>3</sup> of the plant effluent. Most often, leachates are directed to biological wastewater treatment plants where they do not undergo biodegradation. A lot of HS, especially FA, were absorbed on the mineral. They are just partially adsorbed on activated sludge while lighter fractions with smaller amounts of micropollutants pass to the effluent. Unfortunately, so far it is impossible to carry out a quantitative analysis of HSs discharged with landfill leachates.

#### 4. Conclusions

The precursors of oxidation and disinfection by-products are formed mainly at municipal facilities, such as landfills and wastewater treatment plants. In Poland, approximately 15.6 tonnes of FAs/d (as dry matter) is discharged to the surface waters with the treated wastewater. In addition, FAs is carriers of many organic and inorganic pollutants of different toxicity. The detailed analysis of the infrared spectrum shows that FAs extracted from landfill leachates as well as raw and treated wastewater has a similar chemical

structure. They are aromatic hydrocarbons with alkyl and carboxylic acid groups. The more aliphatic groups are in the acids, the more micropollutants they comprise. At the same time, micropollutants serve as a bridging element in their adsorption. The degree of FAs aromatization depends on the time of their humification and the place of origin. HSs undergoes dynamic physicochemical transformations in the environment. Depending on their origin, they may have different content of inorganic matter (ash). The largest share of inorganic contaminants was found in FAs extracted from raw sewage, sewage sludge, and landfill leachate, that is, places with a large pollution load.

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