



Characteristics of fulvic acids generated in communes waste landfills

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Abstract: The leachate problem is important and difficult to solve in Poland and in the world. The composition and their properties leachates depend on the age of the landfill, type of waste, climatic conditions and the mode of operation of the landfill. A significant part of landfilled waste is subject to so-called humification. This process stabilizes organic substances in the landfill and creates humic substances that penetrate into the leachate. The leaks contain many toxic impurities, such as PAHs, pesticides, polychlorinated biphenyls and other substances hazardous to human health and life, which can be sorbed by humic substances. Leachates from three municipal landfills, differing in the characteristics of the stored waste, were studied. Fulvic acids (FAs) were extracted on the basis of affinity for specific solvents along with the use of sorption. The obtained acids were subjected to a qualitative analysis of the content of micro-impurities, essential elements forming the structure of the fulvic acid molecule, and their infrared spectra were tested. It has been noticed that with the age of waste deposited, the content of elemental carbon increases, and the amount of oxygen and hydrogen decreases. The degree of purity of fulvic acids was influenced by the time of waste storage, and the sulfur content depended on their characteristics. With the time of waste storage, the characteristics of the acids obtained were approaching humic acids, and the intensity of absorption bands clearly increased. The spectra obtained correlate well with those of fulvic acids available in the literature, and the findings provide scientific confirmation of the need for further research on the characteristics of fulvic acids.

Introduction

The beginning of 2020 in Poland, introduced two key changes regarding municipal waste. The first concerns changes in the principles of waste segregation, which should be divided into five fractions: metals and plastics, paper, glass, bio-waste and mixed waste. Until now, inhabitants have had a choice – to segregate waste and pay less or not to segregate and incur higher fees for municipal waste management. There is no choice now, and penalties for non-compliance are between two and four times of the basic rates. Everything is related to meeting increasingly strict recycling standards, which were included in two Directives 1993/31/EC on the landfill of waste and 2008/98/EC on the waste. The second change concerns the scope of records and reports to the waste database (BOD), whose task is to eliminate illegal garbage dumps and the gray economy in this industry. In 2019, there were 1,868 illegal garbage dumps in Poland, and 11,370 were closed (GUS, 2020). The amendment to the act introduces the obligation to keep records and report waste of a significant group of entrepreneurs. The obligation applies not only to large companies, but also to people conducting sole proprietorships (Journal of Laws 2020, item 150). The main purpose of the

introduced procedures is to improve the quality and reduce the arduousness of waste management in Poland, which every year increases the amount of generated waste subject to disposal processes.

Still, the most common practice in the field of solid waste management is landfilling (43% in Poland), which always causes a negative impact on the environment. Landfills pose a threat to employees, a significant nuisance for the local community, as well as cause pollution and/or degradation of soil, air and groundwater (Kalousek et al. 2020). It is well known that leachate from landfill contains many toxic substances in high concentrations, such as biodegradable and non-biodegradable organic pollutants, including humic and fulvic substances, microorganisms, heavy metals, chlorinated organic and inorganic salts (Ghosh et al. 2017, Islam et al. 2020). The composition and properties of the leachate depend on the age of the landfill, type of waste, climatic conditions and the operating mode of the landfill (Wang et al. 2016).

Currently, over 200 hazardous organic compounds found in leachate of landfills are identified (Khalil et al. 2020). One of them includes humic and fulvic acids, which have a high ability to bind heavy metals (Jin et al. 2018), and become their carriers (Zhang et al. 2016, Kjeldsen et al. 2002). The

results of tests carried out on the leachates from eight landfills in France indicate that they react with fulvic acids to form macromolecular complexes with them (Claret et al. 2011). The accumulation of waste after leather tanning, oil processing, metalworking, but also the storage of paints, pigments and asbestos release a huge amount of chromium compounds (potassium dichromate and chromate, chromium(VI) trioxide and other chromium compounds) into the environment. As a result of waste decomposition, chromium is transformed into hexavalent chromium compounds, which are highly carcinogenic, mutagenic and teratogenic (Elahi et al. 2020). Leachates from landfills, as a result of leaching pollutants from the landfill and infiltration into the soil, are a source of potential contamination of groundwater and surface waters. The research conducted on changes in groundwater quality around the municipal waste landfill in Jawaharnagar (India) suggests a significant impact of leachate on groundwater, which is the main source of drinking water for Hyderabad City. Groundwater was contaminated with dissolved organic and inorganic substances, as well as heavy metals such as Fe, Mn, Zn and others (Soujanya et al. 2020). This is also confirmed by other studies (Negi et al. 2020).

Leachate can therefore be divided into: young, medium and old. The old leachate is characterized by a high content of organic substances with significant resistance to biodegradation. They are substances with high molecular weight. Old leachate humic acids are characterized by a higher fluorescence intensity (Xiaol et al. 2012). Leachates from landfills are directed to biological municipal sewage treatment plants. The resistant humic substances contained in them, which do not undergo biochemical degradation, are partly adsorbed on activated sludge, partly undergo further humification, and eventually are discharged with treated wastewater into the surface waters alternatively to the soil. In water treatment plants, in the process of oxidation and disinfection, they are precursors of THM and other carcinogenic, mutagenic and teratogenic substances (Uyguner et al. 2004, Anielak et al. 2008, Anielak et al. 2018). That is why research on leachate purification is widely conducted. Good results are obtained using the Photo-Fenton method. The research shows that this method may increase the leachate biodegradability which is proved by the ratio of BZT₅/ChZT (from 0.18 to 0.39) and Zahna-Wellensa test (Dt>70%) (Welter et al. 2018). FA can be adsorbed using: goethite, magnetite, activated carbon with the addition of iron salts, whose cations form a bridge between FA and the adsorbent, increasing the efficiency of the process (Weng et al. 2006, Zhang et al. 2016). Other studies have shown (Esparza-Soto et al. 2003) that biosorption of high molecular weight humic substances on activated sludge is possible and should be considered as the initial stage preceding the breakdown of enzymatic hydrolysis.

Some methods for extracting HS from leachate are also known. For example, a yield of >94% can be achieved in a two-stage reverse osmosis process.

There are many studies on landfill leachates and methods of their treatment (Rani et al. 2020, Collado et al. 2020, Baettker et al. 2020, Luo et al. 2020, Gautam et al. 2019, Vithanage et al. 2014), but there is still no detailed characterization of humic substances, including fulvic acids (Qi et al. 2012, Tahiri et al. 2016). As it results from the previous analysis, humic

substances can pose a serious threat to human life and health, therefore learning about the behavior and characteristics of acids is extremely important and is the main focus of this work.

Research on humic substances has been conducted for a long time, but as confirmed by many publications, there is still no detailed characterization of these mysterious substances. On the one hand, they pose a serious threat to human life and health, and on the other hand, we are increasingly reading about the positive properties of humic substances, including their antioxidant, anti-inflammatory and antiviral activities, improving the growth and quality of meat in animals, improving plant yields, etc. The key is to understand humic substances in such a way as to clearly identify the factors influencing their positive properties, and thus eliminate or reduce negative factors.

Municipal waste landfills tested

The research concerning tests of leachates from three municipal landfills: “Barycz”, “Promnik” and “Kępný Ług”.

The „Barycz” municipal waste storage facility is located in the southern part of the city of Krakow, in the Swoszowice district, about 9.5 km from its center. Since 1974 wastes from the city of Krakow and Wieliczka have been deposited on the site of the Wieliczka Salt Mine. In this landfill, some processed municipal waste and non-hazardous waste is deposited, in quantities not exceeding 240,000 Mg/year (Frączek et al. 2009). The waste landfill is surrounded by an insulating green zone of a total area of about 16 hectares, which reduces the emission of noise and odors outside the site. The waste is deposited in layers, flattened by compactors up to a layer of about 2 m, disinfected with chlorinated lime and insulated with the layer of soil or fine debris, about 0.2 m thick. The municipal waste disposal facility in Krakow has an installation for degassing of the remaining waste. Water and leachate are captured through a drainage system. The collected leachate is directed via a sanitary sewage system to the Municipal Waste Water Treatment Plant Płaszow in Krakow (MPO 2010, Kłojzy-Kaczmarczyk et al. 2016).

The municipal waste landfill “Promnik” is located approximately 17 km north-west of the center of Kielce. Wastes in an amount not exceeding 122,000 Mg per year (Siemieniec et al. 2015) are deposited in layers, flattened by compactors to a layer of about 1.35–1.50 m and insulated with the mineral layer with a thickness of 0.15–0.20 m (Siemieniec et al. 2015). The landfill is degassed with a system of degassing wells, and the captured biogas is directed to a small power plant in order to obtain energy (Siemieniec et al. 2015). Waters and leachates are captured through a drainage system consisting of a perforated pipes and tanks for leachate, with a total capacity of approx. 800 m³ per year (Siemieniec et al. 2015).

At the “Kępný Ług” landfill, waste from the town of Włoszczowa and neighboring towns and villages has been deposited since 1992. In 2018, the functioning waste collection system collected a total of 2 267 Mg, including 1 727 Mg of the households waste. The waste is deposited in a layer of about 2.0 m, flattened by compactors and insulated with the mineral layer with a thickness of 0.15–0.3 m. The municipal waste disposal facility in “Kępný Ług” has an installation for degassing of the remaining waste. Water and leachate are collected via a drainage system by a main collector and

discharged into a 180 m³ storage tank, where the retention time is on average 2 months (PGKiM 2019).

The processed municipal waste and non-hazardous waste from group 19 are deposited at these landfills according to the waste catalog contained in the Regulation of the Minister of Climate of 2 January 2020 on the waste catalog (Journal of Laws 2020 item 10).

Material and methods

Samples were collected permanently from leachate tanks. It can be assumed that the collected sample represented leachate collected for at least 2 months. The total volume of the collected and averaged sample was 20 L.

Extraction and analysis of fulvic acids

FAs were obtained according to the method accented by the International Humic Substances Society (IHSS) with a slight modification (Anielak 2019, Anielak et al. 2018) – Fig. 1. The leachate samples were acidified with hydrochloric acid (HCl p.a. 1: 1) to a pH <2. After 24 hours, the leachate was filtered through medium thickness filters on which a layer of glass balls < 0.5 cm in diameter, was placed, serving as a filter material. The filtered leachate (20 L) was passed at a rate of 1L/h through Amberlit XAD 1180 hydrophobic bed (bed height: 1.0m, bed volume 2,83 dm³). The desorption of FAs was performed with 0.1 N NaOH sodium hydroxide solution. The obtained desorbate was directed to a strongly acidic H⁺ – form cation exchanger (Lewatit MonoPlus 112). The resulting leakage was concentrated in a vacuum evaporator at a vacuum of 350 mbar and a temperature of 85°C. The sample was evaporated in a water bath at 80°C and dried to obtain a dry residue of FAs.

Analysis of carbon, hydrogen and nitrogen contents was done using the combustion technique with a chromatographic detection (elemental analysis). For the analysis 5 to 10 mg of sample was used. The analysis of the remaining elements was done using X-ray fluorescence (XRF). The analysis was carried out in a powder analysis vessel on 4 µm thick Proline film. Brune's ED-XRF spectrometer, Bruker's S8 Tiger spectrometer and Thermo's EA Flash element analyzer were used. The ash designation was done by thermogravimetric method using the SDT Q600 Thermogravimeter from TA Instruments. The heating rate was 10°C/min to 700°C in the airflow of 100 ml/min. For the analysis 5 to 10 mg of sample was used. The identification of compound was made using FT-IR with ATR. The spectral range was 65–4000 cm⁻¹ at 1 cm⁻¹ resolution and 32 scans. The Thermo Nicolet FT-IR iS10 spectrophotometer was used.

Results and discussion

Characteristics of stored waste

The amount and composition of municipal waste depend, among others, on technical infrastructure, the character of buildings and the standard of living of the inhabitants, technical and sanitary equipment of houses and the season (Leboda et al. 2002, Biedugnis et al. 2003). The amount of waste increases with the development of the country's urbanization and the increase in the standard of living. Table 1 presents the characteristics of municipal waste with the highest percentage by mass of waste for the studied landfills. The analysis shows that the stored waste is similar in quality and is typical mixed waste from human social and living existence, and the differences in the content of components result from the nature of the buildings. The "Barycz" landfill can be assigned to

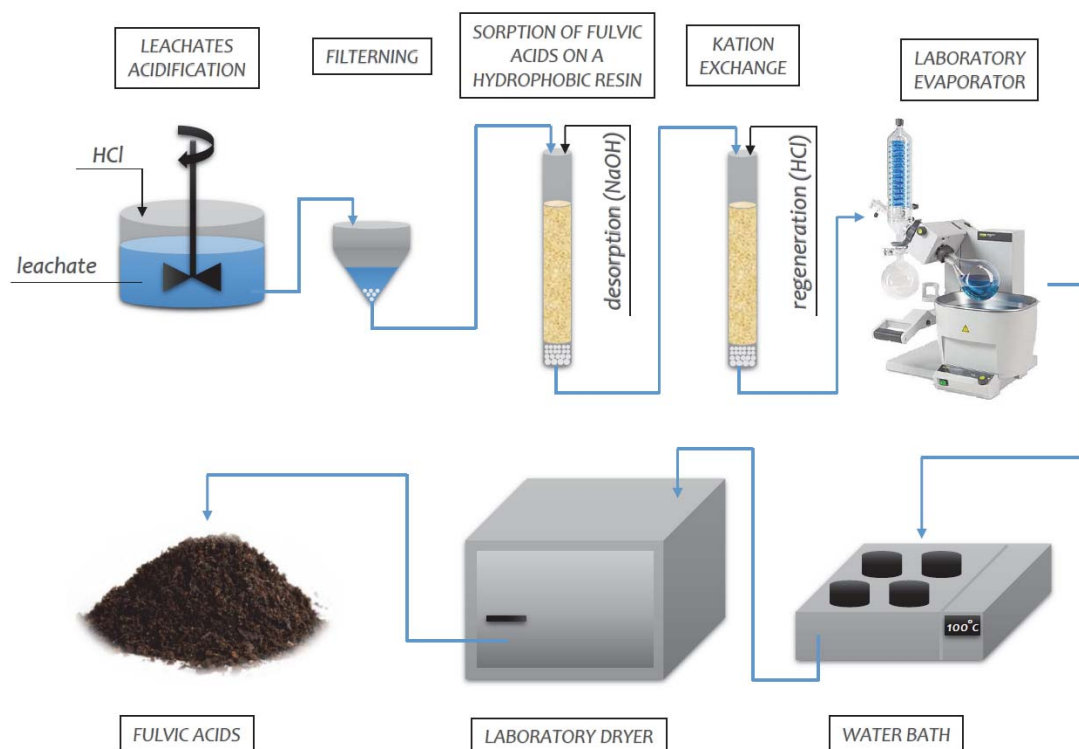


Fig. 1. Extraction scheme of fulvic acids from landfill leachate

a large city, “Promnik” to a small town, and “Kępnny Ług” to a rural area. The content of the ingredients is consistent with the typical characteristics of the amount of waste divided into large and small cities and rural areas (Biedugnis et al. 2003).

The only difference worth noting and affecting the quality of the tested leachate is the age of waste storage (Kapelewska 2018, Rosik-Dulewska 2020). With the age of the landfill, the contamination rates of the leachates change significantly (Kapelewska 2018). Young leachate (<5 years) shows very high values of BOD₅ and COD, with the product of these indicators within the range of 0.2–0.7. The ratio of parameters determines the high content of easily biodegradable organic substances (VFA) in waste. With time, the concentrations of the above-mentioned pollutant indicators decrease, reaching the BOD₅/COD ratio value ranging from 0.01–0.25 for old landfills (>10 years). Other indicators of pollution behave in a similar way – with the time of waste storage, the concentrations of substances in the leachate decrease (Kapelewska 2018).

The study investigated leachates from three landfills with different waste storage times. The oldest of them was the “Barycz” municipal waste landfill in Kraków, where waste has been stored since 1974. The second largest landfill was the facility in “Promnik”, where waste has been deposited since 1985. The youngest and the smallest landfill site was “Kępnny Ług” in Włoszczowa, operated from 1992. According to many studies (Kapelewska 2018, Rosik-Dulewska 2020), the objects “Barycz”, “Promnik” and “Kępnny Ług” can be considered old landfills (>10 years). However, it should be remembered that each of the discussed landfills is in continuous operation, which causes blurring of the clear boundaries between the age of the landfill. Therefore, a comparison of the extracted fulvic acids from landfill leachate is feasible.

Elemental composition and KF impurities analysis

The elemental composition of extracted KF from the leachate of the “Barycz” landfill in Krakow, “Promnik” in Kielce and “Kępnny Ług» in Włoszczowa is shown in Table 2. The composition of these acids did not differ from the acids extracted from the leachate of 6 landfills presented in the literature (Han et al. 2009). The carbon content ranged from 55.36 to 49.39%, hydrogen from 4.29 to 4.81%, oxygen from 36.50 to 38.27% and nitrogen from 1.07 to 3.79%. FA from the 46-year-old

“Barycz” landfill (55.36%) had the highest carbon content, followed by the 35-year-old “Promnik” landfill (50.89%). The youngest of the examined “Kępnny Ług” landfills generated FAs with the lowest carbon content (49.39%). There is a clear correlation between the age of the landfill and the carbon content of FAs from its leachate. Over the course of depositing waste, the degree of humification and carbon concentration increases. Analyzing the presented values, it can be seen the dependence of the entire elemental composition from the age of the landfill. The older the landfill, the more the relative carbon content increases in fulvic acids and leachates and the oxygen content decreases. As the waste storage time increases, the hydrogen content of the molecule decreases. The fullest amount of protons is in the FA from the “Kępnny Ług” landfill (4.81%), then from the “Promnik” landfill (4.54%) and the smallest is from the oldest landfill “Barycz”. Similar relationships were observed for the oxygen content (Fig. 2 and Table 2). In the humification process of humic substances, there is a degradation of oxygen functional groups (e.g. -COOH), which results in the loss of oxygen, nitrogen and hydrogen. The absolute amount of carbon is the same, but the relative value increases. The dependencies are linear and can be described by simple empirical functions:

$$O = 39.965 - 0.0621x, [\%] \quad (1)$$

$$C = 43.4258 + 0.2131x, [\%] \quad (2)$$

$$H = 5.2223 - 0.017x, [\%] \quad (3)$$

$$N = 5.8331 - 0.0875x, [\%] \quad (4)$$

in which x is the storage time, measured in years (from 25 to 55 years).

However, the sulfur content was higher (from 2.78 to 4.62%) in relation to the amount described in the literature (1.53–1.86%). Probably some of the sulfur is included in the elemental composition of fulvic acids, and some is its contamination, which has not been shown in Table 4. The largest amount of sulfur containing fulvic acids can be found in “Promnik” wastes, and the smallest in “Barycz”. Then it should be concluded that this dependency results from the type of waste deposited, and not from the time of storage.

At the same time, based on the results of the tests in Table 5 and Fig. 2, it can be observed that the age of the landfill affects

Table 1. Amount of generated municipal waste with the highest percentage by mass of waste for the areas of Kraków (“Barycz”), Kielce (“Promnik”) and Włoszczowa (“Kępnny Ług”), source: own study

| No. | Component name | Component content [%]* | | |
|-----|------------------------------------|------------------------|---------|------------|
| | | Barycz | Promnik | Kępnny Ług |
| 1 | Unsorted (mixed) municipal waste | 65.071 | 75.833 | 49.139 |
| 2 | Bulky waste | 3.894 | 3.561 | 0.263 |
| 3 | Biodegradable waste | 10.090 | 4.414 | 1.699 |
| 4 | Glass | 2.955 | 3.145 | 3.389 |
| 5 | Mixed packaging waste | 0.081 | 10.005 | 0.019 |
| 6 | Paper and cardboard with packaging | 0.409 | 0.054 | 3.927 |
| 7 | Plastics with packaging | 0.140 | 0.087 | 5.586 |

* for the total mass of municipal waste collected in the landfill

the degree of purity of fulvic acids. The lower the age of waste storage, the less fulvic acids are contaminated with inorganic substances, as indicated by the ash content. The youngest landfill site, “Kępny Ług”, showed the lowest ash content: 3.71%, and “Barycz” and “Promnik” had similar values, 27.94% and 27.15%, respectively (Table 5). The ash content can be related to the content of minerals in the deposited waste. This means that municipal waste from Kraków and Kielce is characterized by a high content of inorganic substances. Over time, the waste decomposes and releases inorganic impurities into leachate more easily.

By analyzing the molar ratios of individual structural elements, it is possible to present the exact characteristics of the extracted acids. Based on the H/C and O/C quotients and van Krevelen diagram (Anielak 2019) it can be seen that with the time of waste in landfills, fulvic acids become similar in characteristics to humic acids. The extracted acids have an H/C quotient in the range of 0.93–1.17, consisting of an aromatic nucleus and aliphatic chains. The test results confirm the relationship shown above that with the time of humification, the content of carbon increases in acids, and oxygen and hydrogen decreases. The O/C quotient is an indicator of the degree of oxidation of fulvic acid molecules, their content of oxygen-rich functional groups, e.g. carboxylic acid. The study results presented in Table 3 indicate that together with the age of the landfill, the degree of fulvic acid

oxidation decreases. In the case of fulvic acids contained in the leachate of the “Barycz” landfill, the O/C quotient corresponds to the values assigned by van Krevelen to humic acids. The time of waste storage changes the nature of humic acids and their degree of aromatization increases.

The qualitative composition of inorganic impurities depends on the type of deposited waste (Table 4) and the content of micropollutants decreases with the age of the landfill (Kapelewska 2018). The highest content was found in silicon (15.58% – “Promnik”), chlorine (4.47% – “Barycz” and 3.87% – “Kępny Ług”) and sodium (1.66% – “Barycz” and 1.56% – “Promnik”). The remaining elements tested constituted a small fraction of the total content of the sample.

Analysis of the IR spectrum of fulvic acids extracted from the leachate of the “Barycz” landfill in Krakow

Absorption spectra are used to identify functional groups, substitution types and double bond configurations because they are a characteristic of a given chemical. The authors distinguished four main ranges of the spectrum, characteristic of fulvic acid functional groups (Gong et al. 2020):

- hydroxyl functional group (3700–3000 cm^{-1}),
- aliphatic functional groups (3000–2800 cm^{-1}),
- oxygen function groups (1800–1000 cm^{-1}),
- aromatic functional groups (900–700 cm^{-1}).

Table 2. Elemental composition of FAs coming from leachate [%]

| Elemental composition (%) | Barycz (1974) | Promnik (1985) | Kępny Ług (1992) | Literature ^a Content [%] |
|---------------------------|---------------|----------------|------------------|-------------------------------------|
| C | 55.36 | 50.89 | 49.39 | 45.6–55.7 |
| H | 4.29 | 4.54 | 4.81 | 6.2–9.6 |
| N | 1.07 | 2.23 | 3.79 | 1.0–12.0 |
| S | 2.78 | 4.61 | 3.74 | 1.53–1.86 |
| O | 36.50 | 37.73 | 38.27 | 29.6–50.0 |

^a Based on 6 different landfills (Han et al. 2009)

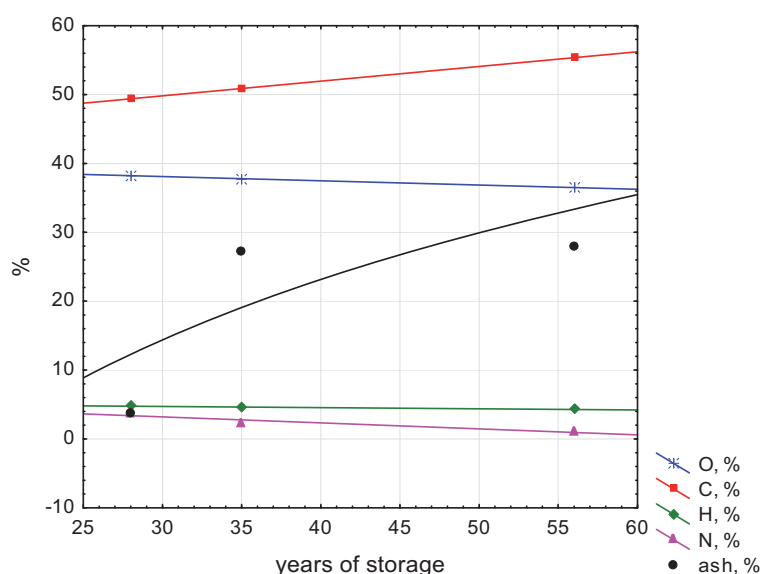


Fig. 2. The impact of waste storage time on the content of basic chemical elements included in fulvic acid extracted from leachate of above mentioned landfills

The infrared spectrum analysis of fulvic acids obtained from the “Barycz” landfill is shown below.

On the obtained spectrogram (Figure 3), several bands characteristic of fulvic acids are clearly marked. A wide peak (3194 cm^{-1} absorption band) was observed in the range of about 3000–3200 cm^{-1} , which means stretching O-H bonds of alcohols, phenols and carboxyl groups and vibration of the N-H bond from amides and amines (Han et al. 2009, Huo et al. 2008). These results prove the high proportion of aliphatic

structures in the structure of the studied fulvic acids (Rosik-Dulewska 2010).

A clearly marked signal in the band about 1703 cm^{-1} , proves the presence of C=O carbonyl groups in peptides, aldehydes and ketones and is associated with the occurrence of C=O double bonds and C=O stretching bond of carbonyl groups in ketones and quinones. The occurrence of C=O bonds confirms the high maturity of fulvic acids (Araujo et al. 2017, Han et al. 2009, Huo et al. 2008, Shuiqin et al. 2017).

Table 3. Atomic ratios of the FAs coming from leachate

| Atomic ratios Calculated as mole fraction | Barycz (1974) | Promnik (1985) | Kępnny Ług (1992) | Literature ^a |
|---|---------------|----------------|-------------------|-------------------------|
| H/C | 0.93 | 1.07 | 1.17 | 0.90–2.53 |
| O/H | 0.53 | 0.52 | 0.50 | – |
| O/C | 0.49 | 0.56 | 0.58 | 0.40–0.78 |
| C/N | 60.36 | 30.43 | 15.20 | 4.35–33.33 |

^a Based on 6 different landfills (Han et al. 2009, He et al. 2008, Qi et al. 2012)

Table 4. Micropollutants analysis of fulvic acid from leachate of landfill

| Element | Symbol | Content [%] | | |
|--------------|--------|---------------|----------------|-------------------|
| | | Barycz (1974) | Promnik (1985) | Kępnny Ług (1992) |
| Silicon | Si | 0.91 | 15.58 | 1.47 |
| Sodium | Na | 1.66 | 1.56 | 0.60 |
| Calcium | Ca | 0.36 | 0.60 | 0.83 |
| Chlorine | Cl | 4.47 | 0.42 | 3.87 |
| Phosphorus | P | 0.65 | 0.29 | 0.02 |
| Potassium | K | < 0.01 | 0.28 | 0.35 |
| Barium | Ba | < 0.01 | 0.14 | 0.23 |
| Iron | Fe | 0.07 | 0.12 | 0.27 |
| Aluminium | Al | 0.01 | 0.12 | 0.16 |
| Praseodymium | Pr | 0.05 | 0.11 | – |
| Scandium | Sc | 0.05 | 0.05 | – |
| Magnesium | Mg | 0.11 | 0.04 | 0.21 |
| Nickel | Ni | < 0.01 | 0.04 | 0.02 |
| Bromine | Br | 0.85 | – | 0.11 |
| Molybdenum | Mo | – | – | 0.03 |
| Zinc | Zn | – | – | 0.03 |
| Chromium | Cr | – | – | 0.03 |
| Copper | Cu | – | – | 0.02 |
| Strontium | Sr | – | – | 0.01 |
| Lead | Pb | – | – | < 0.01 |

Table 5. Total fulvic acids and ash content

| Element | Barycz (1974) | Promnik (1985) | Kępnny Ług (1992) |
|----------------------------------|---------------|----------------|-------------------|
| Fulvic acids [g/m ³] | 119.75 | 905.55 | 266.7 |
| Ash content [%] | 27.94 | 27.15 | 3.71 |

The 1617 cm^{-1} band indicates the presence of $\text{C}=\text{C}$ bonds in aromatic linkages and a $\text{C}=\text{O}$ bond found in quinones (Walenczak 2011).

The band in the 1402 cm^{-1} range is associated with O-H bond deformation, CH_3 bending, C-O phenolic OH stretching, and COO carboxylate groups. It also indicates the presence of C-H bonds in methyl groups (Araujo et al. 2017, Łabaz 2010).

The highest intensity of absorption bands was found in the area of 1083 cm^{-1} , which proves the stretching of C-O bonds from OCH_3 , COH and COC groups of organic compounds (Araujo et al. 2017, Huo et al. 2008, Walenczak 2011).

The band in the 950 cm^{-1} range confirms the bending vibrations of the C-H aromatic alkene compounds in the tested fulvic acids (Han et al. 2009). Clear peaks were observed at 792 cm^{-1} and 670 cm^{-1} . The first testifies to NH_2 plane deformation (Huo et al. 2008), while the second testifies to bending vibrations of the S-O bond (Huo et al. 2008).

Analysis of the IR spectrum of fulvic acids extracted from the leachate of the "Promnik" landfill in Kielce

The signal at the absorption band of 2942 cm^{-1} was assigned by symmetrical stretching of CH in $-\text{CH}_3$ and $-\text{CH}_2$ aliphatic

chains and indicates a high share of aliphatic structures in the structure of fulvic acids (Han et al. 2009, Linczar 1985).

Clearly marked absorption in the 1713 cm^{-1} band is associated with the presence of $\text{C}=\text{O}$ carbonyl groups in peptides, aldehydes and ketones, $\text{C}=\text{O}$ double bonds, and $\text{C}=\text{O}$ stretch bonding of carbonyl groups in ketones and quinones. The occurrence of $\text{C}=\text{O}$ bonds confirms the moderate and high maturity of fulvic acids (Han et al. 2009, Huo et al. 2008, Shuiqin et al. 2017).

The band in the 1326 cm^{-1} range is associated with C-H deformation in the CH_2 and CH_3 groups, the asymmetrical stretch of the COO- groups and C-N stretch (Wang et al. 2016, Huo et al. 2008).

The highest intensity of absorption bands was found in the range of 1158 cm^{-1} and 1038 cm^{-1} , this proves the vibration of alcohol functions, stretching C-O-C carbohydrates, stretching C-O in polysaccharides, shaking C-H methyl vibrations connected with the S atom (Han et al. 2009, Mark et al. 2002).

Fulvic acids showed absorption in the range of $857\text{--}765\text{ cm}^{-1}$, due to N-O bonds with nitrogen esters, aromatic C-H bending, N-H vibration and non- NH_2 vibration (Han et al. 2009, Qi et al. 2012). The bands at 655 cm^{-1} are associated with

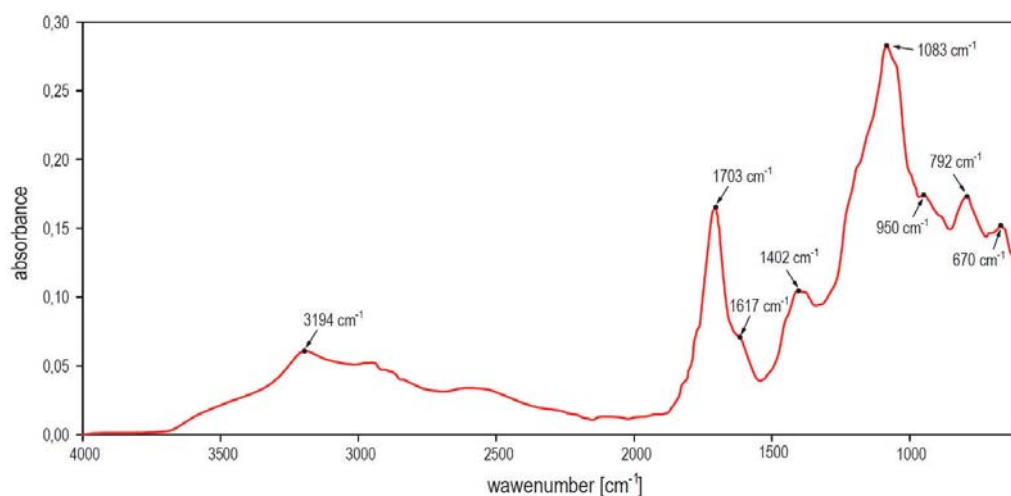


Fig. 3. Infrared spectra of fulvic acids from leachate of "Barycz" landfills

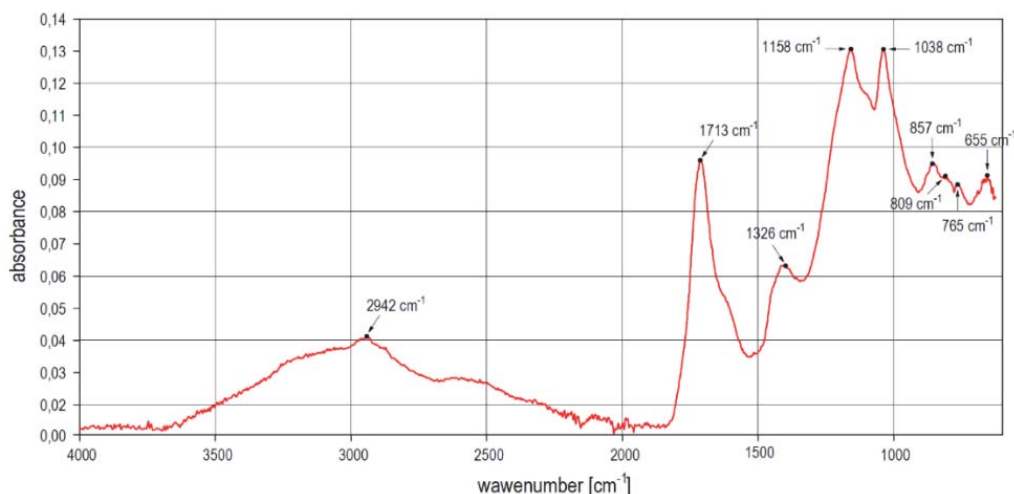


Fig. 4. Infrared spectra of fulvic acids from leachate of "Promnik" landfills

the occurrence of inorganic sulfates (bending and stretching S-O) and nitrite esters (Qi et al. 2012, Huo et al. 2008).

Analysis of the IR spectrum of fulvic acids extracted from the leachate of the “Kępnny Ług” landfill in Włoszczowa

The signal at the absorption band of 2940 cm^{-1} was assigned by symmetrical stretching of CH in $-\text{CH}_3$ and $-\text{CH}_2$ aliphatic chains and indicates a high share of aliphatic structures in the structure of fulvic acids (Han et al. 2009, Linczar 1985).

Clearly marked absorption in the band around 1703 cm^{-1} is associated with the presence of C=O carbonyl groups in peptides, aldehydes and ketones, C=O double bonds, C=O stretch bonding of carbonyl groups in ketones and quinones. The occurrence of C=O bonds confirms the moderate and high maturity of fulvic acids (Han et al. 2009, Huo et al. 2008, Shuiqin et al. 2017).

The band in the 1403 cm^{-1} range is associated with O-H bond deformation, CH_3 bending, C-O phenolic OH stretching, and COO carboxylate groups. It also indicates the presence of C-H bonds in methyl groups (Łabaz 2010, Araujo et al. 2017).

The highest intensity of absorption bands was found in the range of 1155 cm^{-1} and 1031 cm^{-1} , this proves the vibration of alcohol functions, stretching of C-O-C carbohydrates, stretching of C-O in polysaccharides, and shaking of C-H methyl vibrations connected with the S atom (Han et al. 2009, Mark et al. 2002).

Fulvic acids showed absorption at 779 cm^{-1} due to N-O bonds with nitrogen esters, aromatic C-H bending, N-H vibration and non- NH_2 vibration (Han et al. 2009, Qi et al. 2012). The bands at 666 cm^{-1} are associated with the occurrence of inorganic sulfates (bending and stretching S-O) and nitrite esters (Qi et al. 2012, Huo et al. 2008).

Collective analysis of the IR spectrum

A summary analysis of the IR spectral bands for the fulvic acids tested is presented below in Table 6. The comparison of IR bands showed differences in functional groups, substitution types, and double bond configurations in fulvic acids. In addition, fulvic acids from “Barycz” and “Promnik” were characterized by the presence of bands not noticed in the other samples tested. Such absorption peaks in “Barycz” occurred

at 3194 cm^{-1} , 1083 cm^{-1} and 950 cm^{-1} , which indicates a high proportion of aliphatic structures, OH bond deformation, bending of CH_3 , stretching of phenolic CO, OH, stretching in COO carboxylate groups, the presence of CH bonds in methyl groups and vibrations bending the bond of CH aromatic alkene compounds in the studied fulvic acids. Whereas, in fulvic acids from “Promnik”, characteristic peaks occurred at the wave number values 1326 cm^{-1} and 857 cm^{-1} , which is associated with CH deformation in the CH_2 and CH_3 groups, asymmetrical stretch of COO- groups, CN stretch, NO bonds with nitrogen esters, aromatic CH bending, NH vibration and non- NH_2 vibration. All peaks observed in fulvic acids from the “Kępnny Ług” landfill were also found in “Barycz” and “Promnik”.

Collective analysis of all observed bands indicates a similar structure of the obtained fulvic acids from “Barycz”, “Promnik” and “Kępnny Ług”, however with some characteristic differences. Probably the differences in the construction of fulvic acids result from the characteristics of the waste deposited there, its retention time and the methodology of landfill operation. It is worth noting that fulvic acid impurities could also cause spectral deformation and the formation of new bands, unnoticed in the other samples tested.

Figure 6 presents a summary of infrared spectra. Comparison of the spectra shows that there are significant similarities in the position of the absorbance bands. In all spectra, bands with similar wave number values were observed, differing in relative intensities. This means that the acids obtained were characterized by a similar structure with different amounts of bonds of a given type.

The highest absorbance intensities were shown by fulvic acids from the “Barycz” landfill in Krakow, and the lowest from the “Kępnny Ług” landfill in Włoszczowa. Significant differences in the absorbance of the bands should be associated with the characteristics of the waste, time of municipal waste storage and the method of landfill operation. Most of the organic substances in the “Barycz” landfill, also hard to decompose, underwent a process of humification within 46 years. Waste storage for 28 years in Włoszczowa is much shorter, which means that the absorbance of the bands is correspondingly lower. The analysis shows a certain relationship related to the absorption of IR spectra – the longer the period of municipal

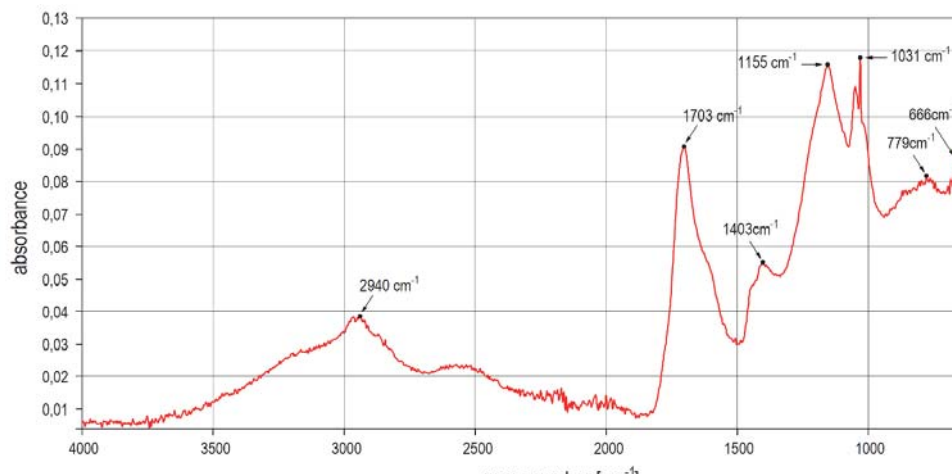


Fig. 5. Infrared spectra of fulvic acids from leachate of “Kępnny Ług” landfills

waste storage, the more double bonds present there. The longer humification period causes significantly higher maturity of fulvic acids.

The intensity of fulvic acid bands from the Kielce landfill is similar to the intensity of the fulvic acid bands from Włoszczowa. This demonstrates similar characteristics of landfills, i.e. landfills show similarities in the characteristics of the waste, the age of storage and the way the deposit is exploited.

There is also no doubt that all three samples obtained are fulvic acids because the band distribution is characteristic to typical fulvic acids.

Application of fulvic acids

Fulvic acids are widely used in many areas of life, especially in agriculture and medicine, due to their specific chemical and physical properties depending on the molecular weight (Gong et al. 2020). Characteristic functional groups provide fulvic acids with antioxidant and immunostimulating activities, anti-inflammatory and antiviral properties (Mao 2019). Fulvic

acids have an antidiarrheal effect in animals and humans (Yi et al. 2019), they can be used as a therapeutic factor in the treatment of cancer (Jayasooriya et al. 2016), and finally as a good painkiller and anti-inflammatory agent (Klößing et al. 2005). FAs also participate in the metabolic pathways of plants and microalgae, regulate hormone levels, improve crop quality and root development, increase drought resistance and salt tolerance (Gong et al. 2020, Li et al. 2019). Li et al. emphasize the beneficial effect of fulvic acids in improving the remediation efficiency of contaminated soil. The use of acid dosing increased the remediation efficiency by 2 to 3 times (Li et al. 2020). In turn, Liu et al. investigated the effect of FA doses in the process of anaerobic ammonia oxidation (Anammox). The obtained results showed an increase in the activity of Anammox bacteria and a significant improvement in nitrogen removal (Liu et al. 2020). Fulvic acids can be successfully used as a medium for the production of graphene, which in the conducted study showed a complete absence of defects in the build of the structure and increased stability (Yang et al. 2019). It is worth mentioning the acquisition of humic substances

Table 6. Interpretation of IR spectral bands of fulvovous substances from landfills

| Wavelength (cm ⁻¹) | | | Interpretation* |
|--------------------------------|---------|-----------|--|
| Barycz | Promnik | Kępny Ług | |
| 3194 | | | O–H vibrations of the hydroxyl groups of phenols, alcohols and carboxyl functions and N–H vibrations from amides and amines, NH ₂ stretch (2 bands) |
| | 2942 | 2940 | Symmetric CH stretching in –CH ₃ and –CH ₂ – of aliphatic chains |
| 1703 | 1713 | 1703 | C = O bonding of carbonyl groups in ketones and quinines |
| 1402 | 1326 | 1403 | CH ₃ bending, C–O stretching of phenolic OH, and COO– antisymmetric stretching |
| | 1158 | 1155 | Alcohol function vibrations |
| 1083 | | | C–O–C stretching of carbohydrates |
| | 1038 | 1031 | C–O–C stretching of carbohydrates; C–O stretching in polysaccharides; methyl C–H rocking vibrations connected with atom S; |
| 950 | 857 | | Out-of-plane bending of aromatic C–H |
| 792 | 765 | 779 | NH ₂ out of plane |
| 670 | 655 | 666 | S–O bends |

* source: (Han et al. 2009, Huo et al. 2008, Shuiqin et al. 2017, Wang et al. 2016, Dong-June et al. 2007, Zhang et al. 2014, Mark et al. 2002, Gong et al. 2020)

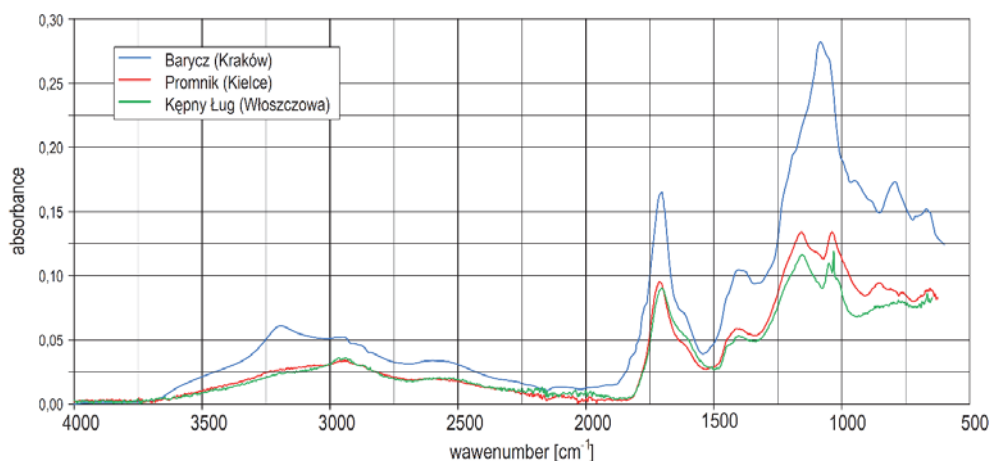


Fig. 6. Summary of Infrared spectra of fulvic acids from leachate landfills

for industrial purposes. The coloring of humic matter allows them to be used as a dye in the paint and ceramic industry (MacCarthy et al. 1994).

Summary

1. A clear correlation was noted between the age of the landfill and the carbon and oxygen content in FA. The older the landfill, the higher the percentage of elemental carbon, and the lower the oxygen and hydrogen contents.
2. The sulfur content in FA results from the type of waste deposited, and not from the time of storage.
3. The storage time of waste influences the degree of purity of FA – the shorter the age, the less FA are contaminated with inorganic substances.
4. With the time of waste storage, the degree of FA aromatization increases, oxygen function groups decrease, the relative carbon content increases, and FA characteristics approaches humic acids, O/H values increase, and O/C and H/C decreases.
5. All IR spectra of extracted acids had similar bands, differing in relative intensities. With the age of landfills, band intensity (absorbance) increases.
6. The relationship observed is that – the longer the period of municipal waste storage, the more functional groups, substitution types and double bond configuration are characterized by higher absorbance intensity.

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Charakterystyka kwasów fulwowych generowanych na składowiskach odpadów komunalnych

Streszczenie: Porównanie charakterystyk kwasów fulwowych wydobywanych z odcieków z trzech różnych składowisk komunalnych, różniących się charakterystyką składowanych odpadów, czasem ich unieszkodliwiania oraz sposobem funkcjonowania składowiska. Materiałem użytym do badań były odcieki z trzech różnych składowisk komunalnych. Kwasy fulwowe ekstrahowano na podstawie powinowactwa do określonych rozpuszczalników oraz adsorpcji na złożu jonitowym i kationitowym. Ilość kwasów fulwowych określono wagowo. Otrzymane kwasy fulwowe analizowano pod kątem składu pierwiastkowego i widm FT-IR. Zauważono wyraźną korelację pomiędzy wiekiem składowiska odpadów, a zawartością węgla i tlenu w badanych kwasach fulwowych. Zawartość siarki wynikała jedynie z rodzaju składowanych odpadów. Wraz z wiekiem składowania odpadów, czystość kwasów fulwowych maleje, rośnie stopień zaromatyzowania cząsteczki, a charakterystyka kwasów fulwowych zbliża się do kwasów huminowych. Wiek składowania znacząco wpływa na intensywność pasm absorpcji. Każdy z badanych odcieków zawierał znaczną ilość kwasów fulwowych, które były znacząco zanieczyszczone substancjami nieorganicznymi. Kwasy fulwowe wykazały wysoką aktywność chemiczną, co powoduje, że stają się nośnikami toksycznych mikrozanieczyszczeń. W typowych procesach zachodzących na oczyszczalniach ścieków oraz zakładach uzdatniania wody, kwasy fulwowe nie są usuwane, przez co stwarzają zagrożenie dla życia ludzi. Jedynie poznanie szczegółowej charakterystyki kwasów fulwowych, pozwoli na opracowanie zadowalających metod nie tylko usuwania i oczyszczania kwasów ale również wykorzystywania na przykład do nawożenia gleby. Nadal skład elementarny oraz charakterystyka budzi ogromne kontrowersje wśród badaczy. Dlatego niezwykle ważne są dalsze badania odkrywające każdą kolejną część tych zagadkowych substancji.