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Characteristic of Fulvic Acids Extracted from the Wastewater by Different Methods

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1. Introduction

Humic substances (HSs) are a major form of natural organic matter (NOM). They have different compositions and properties vary with the source of origin and the method of extraction (Litvin et al., 2015). Regardless of their origin and place of occurrence they always consist of: carbon, oxygen, hydrogen, nitrogen and sulphur. HSs are macromolecular compounds with a very complex and heterogeneous structure (Casassas et al., 1995). Their main functional groups are: carboxylic, phenolic, carbonyl, hydroxyl, amine and aromatic moieties, among others (Pena-Mendez et al. 2005). Discussed substances play many important roles in the environment, mostly in soils, although they are also uptaking toxic metals, anthropogenic organic chemicals and other contaminations from water (Pena-Mendez et al., 2005; Manzak et al., 2017). As reported by (Pena-Mendez et al., 2005; Manzak et al., 2017) ion modifiers based on the calcium humate could remove cadmium, iron, nickel, copper and mercury from water. HSs constitute a high percentage of total dissolved organic carbon (DOC) in the natural environment, they appear to be one of the most popular organic components of water (Boggs et al. 1985). Fulvic acids (FAs), as dissolved form of HSs are soluble in water under all pH conditions. There are many different methods of FAs extraction and it is difficult to compare the data reported by researchers (Kuwatsuka et al., 1992). Kuwatsuka et al. (Kuwatsuka et al., 1992) compared two methods of humic and fulvic acids isolation: IHSS Method and NAGOYA Method.According to the International Humic Substances Society (IHSS), it is not possible to define which one is the most effective. It may be the reason why the inconsistency of isolation methods hindered the development of humus studies. HSs are mainly extracted from soils, surface and groundwater and there is a shortage of information on the humification process taking place during wastewater treatment. According to Nissinen et al., (2001) chemical composition of wastewater indicated that they could affect forms of trace metals, salt and organic substances (including xenobiotics) concentrations which is higher in treated wastewater than in surface water. Also, humic acids (HAs) originated from the wastewater treatment had better complexing abilities than naturally occurring HSs. The authors (Polak et al., 2009) compared the humification processes at wastewater treatment plants (WWTPs) with different technological processes. The results showed that the sequence of wastewater treatment processes had a significant influence on the humification of sewage sludge and properties of extracted HAs. The next important thing was the order in which they were carried out at treatment plants. A lot of publications confirmed that HAs extracted from sludge were weakly humificated and they had low free radical concentrations (Polak et al., 2009). HSs stimulate biological processes, mainly nitrification. The authors (Yabing et al., 2019) investigated the potential influence of bio-refractory HSs on the reactor performance and a functional structure of microbial communities within anammox bioreactors. The results showed that the presence of HSs in wastewater did not significantly limit nitrogen removal in the anammox reactors. According to (Kochany & Lipczyńska-Kochany, 2008) the use of HAs would be beneficial for wastewater treatment plants supplied with leachate from landfills or industrial wastewater with inhibiting agents. This would allow improving their efficiency (mostly ammonia and phosphorus removal) without major modifications. On the other hand, HSs are generally considered to be irreplaceable or difficult to degrade during the wastewater treatment process, instead of biodegradation, the biosorption process is considered for their removal (Feng et al. 2008). Therefore, humification during wastewater treatment is a very important and interesting issue. It can determine the suitability of sludge for agricultural purposes and indicate changes that are needed to achieve this goal (Pajączkowska et al., 2003). Since large amounts of HSs can be found as by-products of different human activities (wastewater treatment plants and waste landfills) the authors (Anielak & Łomińska-Płatek, 2017) compared FAs extracted from the raw wastewater, sewage sludge and waste landfill leachates. The detailed analysis of the infrared spectrum (IR) indicated that discussed substances extracted from landfill leachates and treated wastewater had a convergent chemical structure. The degree of FAs aromatization depends on the time of their humification and a place of generation. In the environment, they undergo dynamic biochemical and chemical transformations and may have different content of inorganic matter (ash) depending on their origin (Anielak & Łomińska-Płatek, 2017).

Maximum use of treated wastewater e.g. to irrigation or in modern technologies purifying wastewater to drinking water standards is a very important problem.

In the work, the authors examined the content of FAs in the primary and secondary effluents. The main aim of the research was to compare isolated FAs using two different extraction methods.

2. Materials and methods

The samples were collected directly from the primary and secondary effluents at the WWTP and the obtained results were averaged. The WWTP treats mainly wastewater from individual users and industrial plants. The WWTP comprises mechanical and biological wastewater trains as well as sludge processing and biogas trains. The plant works as a three-stage Bardenpho system and operates five identical biological reactors.

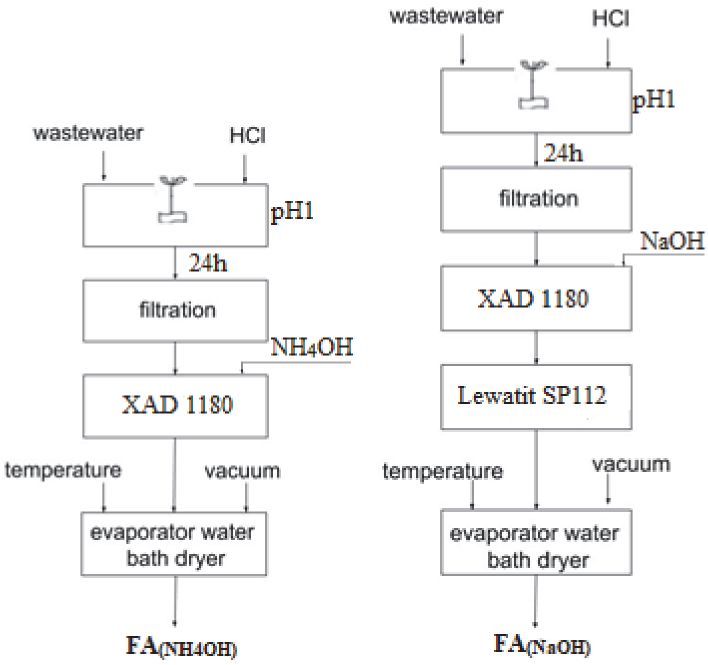
2.1. Extraction of FAs with the NH_4OH and NaOH methods

Isolation of FAs was carried out using two methods: 1) with NH_4OH, according to the work (Pempkowiak et al., 2008) and 2) with NaOH following the method presented by International Humic Substances Society (IHSS) with a small modification. Samples were acidified with HCl to pH = 1. After 24 hours, wastewater was filtered on a medium thickness filter with glass beads of diameter < 0.5 cm and then passed through a glass column (ϕ = 25 mm, h = 1000 mm) filled with polymeric adsorbent resin - Amberlit XAD 1180 at a rate of about 1 L/hr. In the first method, FAs were eluted with 0.5 mol /L NH_4OH (Fig. 1a) while in the second 0.5 mol/L NaOH (Fig. 1b) and then FAs eluent with an excess of NaOH from the first column was directed to the II-nd ionic column (Lewatit SP112 cation H^+). Next, FAs eluent from the II cation exchange column and from the I column with an excess of NH_4OH were concentrated in a vacuum evaporator at 85°C under a vacuum of 350 mbar. After evaporation bath at 85°C, the sample was dried to obtain a dry FAs residue.

2.2. Analysis of FAs properties

The analysis of carbon, hydrogen and nitrogen contents was performed using combustion technology with a chromatographic detection of evolving gas products (elemental analysis). The determinations were made on an elemental analyzer Flash 2000 Thermo. Oxygen was determined via mass balance 100% –(C% + H% + N%+ S%) for FAs on the ash-free basis (Łomińska & Anielak, 2017).

Analysis of the trace element content was performed using X-ray fluorescence (XRF), model S8 Tiger, Bruker apparatus. Discussed technique involves the excitation of characteristic X-rays using radiation from an X-ray tube or currently a synchrotron. X-ray fluorescent radiation has the same nature and wavelengths as the characteristic X-ray radiation of the corresponding element. The analysis was carried out in a vessel for analyzing powders on a 4 μm Prolen film. Elements such as Cl, Si, Ca, K, Mg, P, Br, Mn, Ce, Ti, I, Al, B and Sr were analyzed.



a) b)

Fig. 1. Elution of FAs with NH_4OH (a) and NaOH (b) method

Fourier transform infrared spectra of FAs were obtained in a Thermo Nicolet FTIR-is10S spectrophotometer. The spectral range was: 650-4000 cm^{-1} at a resolution of 1 cm^{-1}, the number of scans was 32. The IR absorption spectra were run to analyse the structure of extracted substances. FTIR spectroscopy allows determining characteristic vibrations for groups occurring in FAs. This method provides valuable information on oxygen-containing functional groups. Since there are many deforming and stretching vibrations within one molecule the full analysis of the IR spectra for FAs is quite difficult (Zhu & Ryan 2016).

3. Results and discussion

All measurements were carried out in three repetitions and then averaged. The concentration of the FA is given as dry residue.

Table 1. Concentration and ash content of FAs isolated from primary (FA1) and secondary (FA2) effluent

Samples*	FA concentration ash free [g/m^3]	Ash content [%]
$FA1_{(NH4OH)}$	13.09	11.55
$FA1_{(NaOH)}$	15.20	41.53
$FA2_{(NH4OH)}$	4.69	9.74
$FA2_{(NaOH)}$	2.78	14.77

* primary effluent NH_4OH - $FA1_{(NH4OH),}$ primary effluent NaOH - $FA1_{(NaOH),}$ secondary effluent NH_4OH - $FA2_{(NH4OH),}$ secondary effluent NaOH - $FA2_{(NaOH)}$

The concentration of $FA1_{(NH4OH)}$ was 13.09 g/m^3 and $FA2_{(NH4OH)}$ was 4.69 g/m^3 for primary and secondary effluent, respectively. In the samples obtained using the NaOH method concentration was 15.20 g/m^3 for the primary effluent ($FA1_{(NaOH)}$) and 2.78 g/m^3 for the secondary effluent ($FA1_{(NaOH)}$) (Table 1). The highest amount of FAs was detected in the primary effluent sample isolated with the NaOH method. The results indicate that in the secondary effluent in $FA_{(NH4OH)}$ solution (I method) obtained in little more fulvic acids than in the method with NaOH. This may be caused by the application of a two-stage ion exchange, where more FAs remained absorbed by the ion-exchange grains resulting in their larger mass losses. Some differences in the isolated substances were observed in the primary effluent ($FA1_{(NH4OH)}$ - $FA1_{(NaOH)}$ = 2.11 g/m^3), which was richer in organic and inorganic constituents than the secondary effluent.

Regardless of the chosen method, the FAs concentration decreased in each subsequent stage of wastewater treatment:

$$FA1_{(NH4OH)} > FA2_{(NH4OH)}$$
$$FA1_{(NaOH)} > FA2_{(NaOH)}$$

The concentration of FAs extracted from biologically treated wastewater was similar to the data obtained previously (Pempkowiak et al., 2008). The concentration of HAs in the treated wastewater was 2.8 g/m^3 (Jamno WWTP) and 3.2 g/m^3 (Unieście WWTP). During the treatment process in selected WWTP the amount of FAs decreased over 2 times (in I method) and over 5 times (in II method). It can be concluded that the investigated WWTP discharges secondary effluents with a smaller concentration of discussed substances compared to primary effluents. This is particularly important because the secondary effluent is discharged directly to surface waters, serving as a water source to the water treatment plant. That is why their quality and composition is particularly important.

The ash content was much higher in the NaOH method ($FA1_{(NaOH)}$ = 41.53% and $FA2_{(NaOH)}$ = 14.77%), it may be related to the fact that sodium hydroxide is a stronger base than NH_4OH, therefore during ion exchange more cations were extracted together with FAs. The amount of isolated FAs in both methods were quite similar.

3.1. Elemental composition

A study of the elemental composition provided indications regarding a structure of isolated acids, an origin of their organic matter as well as a degree of aromatization and condensation. The results of the elemental composition were converted to the ashless mass. The analysis of the extracted FAs reveals that they are built primarily of carbon, oxygen, hydrogen and nitrogen, this is a characteristic feature for all of them, regardless origin (Łomińska & Anielak, 2017).

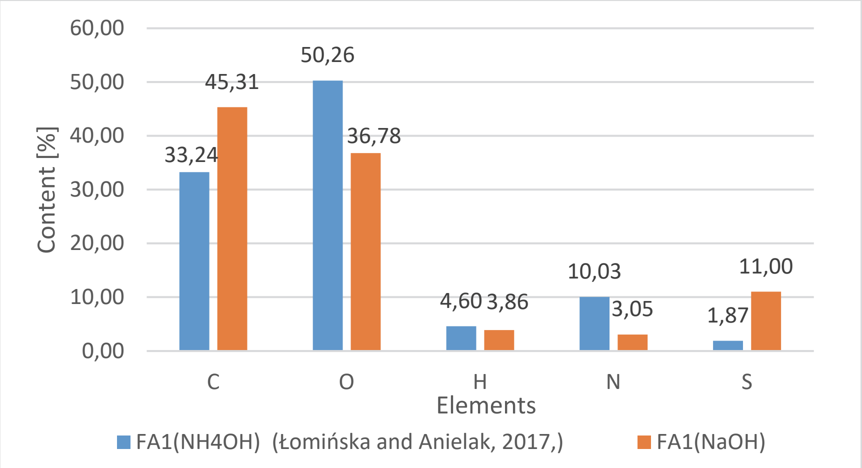


Fig. 2. Elemental composition of FAs extracted from the primary effluent by different methods

Carbon and Oxygen were the main elements found in the extracted FAs (Fig. 2 and Fig. 3). The content of C for $FA1_{(NaOH)}$ was bigger and amounted to 45.31% while in the $FA1(_{NH4OH})$ it was 33.24%. According to (Gomółka and Szaynok, 1997) FAs contain 43% to 52% of C. A higher content of this element means that the NaOH method resulted in the isolation of substances characterized by a higher degree of humification. The content of O for the first method was 50.26% while for the second one it was 36.78% and it is typical for FAs which usually contain from 42% to 51% (Litvin et al., 2015). High content of this element in their structure in the NaOH method may indicate a presence of carboxyl, carbonyl, methoxy, hydroxyl, alcohol, ester and eter groups (Grzegorczuk-Nowacka & Anielak, 2017). The content of H was similar for both samples (4.60% and 3.86%) and was typical 3.3-6.0%. Usually, FAs contain from 1.0% to 6.0% of N (Gomółka & Szaynok, 1997), since nitrogen compounds are removed as a result of biological nitrification and denitrification. It should be noticed that the content of N varied with the methodology used, the NH_4OH method generated more N (10.03%) than the NaOH method (3.05%). High nitrogen content is attributed to a large number of amino acids in the FAs structure (Łomińska & Anielak, 2017). FAs extracted by the I method had 1,87% of sulphur and it was almost 6 time less than by the II method.

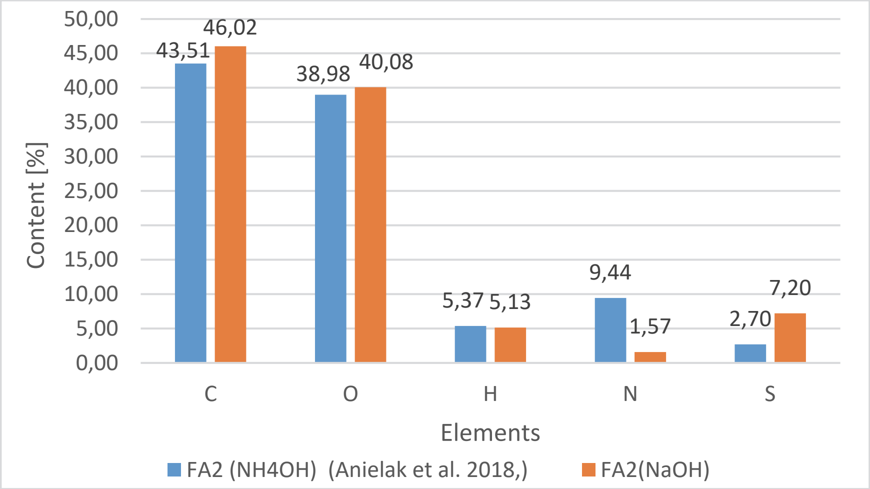


Fig. 3. Elemental composition of FAs extracted from the secondary effluent by different methods

The content of C in the secondary effluent (Fig. 3) was similar for both samples as it was 43.51% (NH_4OH) and 46.02% (NaOH), both values are characteristic for FAs (Gomółka & Szaynok, 1997). Slightly higher content of C in the NaOH method can indicate a higher degree of humification, but the difference is quite small. The same was true for O, its content was 38.98% and 40.08% for the first and the second method, respectively. Both these values are also characteristic of FAs (Gomółka & Szaynok, 1997). The content of H was similar for both samples (5.37% and 5.13%). As previously, the N content varied with the methodology. The NH_4OH method generated more N (9.44%) than the NaOH method (1.57%).

FAs extracted by the NaOH method had much more S in their structure - 11% and 7.20% (Figure 2) than the ones with using the NH_4OH method - 1.87%

and 2.7% (Figure 3). The content of S was similar in samples isolated with the same method. According to (Pempkowiak et al., 2008) various organic compounds like proteins and urea of natural origin are found in a primary effluent during biological treatment process, simple organic compounds (including monomer derived from proteins, such as amines) and others with nitrogen and sulphur in their structure are created (Pempkowiak et al., 2008). It can explain the high content of N and S in the isolated FAs. The high level of N and S (Fig. 2 and 3) may be attributed to the incorporation of protein decomposition products and sulphur-containing surfactant residues in the macromolecules (Senesi et al., 1996). Another source of N can be the aqua ammonia, which is used in FAs extraction. NH_4OH is easily broken down into water molecules and ammonia and is released into the atmosphere, in particular at elevated temperatures. However, small amounts of nitrogen may contaminate the extracted FAs (Pempkowiak et al., 2008). The remaining elements constituted a small percentage of the sample content.

Comparing the elemental compositions of extracted FAs with literature it can be seen that they have a similar structure.

3.2. Atomic ratios

Based on the elemental composition atomic ratios: C/O, C/H, C/N and O/H have been determined. Atomic percentages were calculated from the averages of the weight percentages determined from the elemental composition.

Table 2. Atomic ratios of FAs extracted from the different samples

Samples	Atomic ratios [-]			
	C/O	C/H	C/N	O/H
$FA1_{(NH4OH)}$	0.88	0.60	3.30	0.68
$FA1_{(NaOH)}$	1.64	0.98	14.86	0.60
$FA2_{(NH4OH)}$	1.49	0.68	4.61	0.45
$FA2_{(NaOH)}$	1.53	0.75	29.31	0.49

The C/O ratio provides information on carbohydrate content and acid hydrophobicity (Table 2). FAs with a lower C/O have a lower content of carbohydrates. The more carbon, the greater the ratio and hydrophobicity of acids. The value of the ratio can result from biodegradation of protein, which are strongly present in both primary and secondary effluent. This fact is confirmed by a significant amount of nitrogen and sulphur in the structure of extracted acids (Fig. 4 and 5). Discussed atomic ratio determines the degree of oxidation, a high value indicates a low degree of oxidation and humification. It may be concluded that FAs from the primary effluent (NH_4OH), was the most hydrophilic and had many functional groups, such as hydroxyl and carboxyl. The atomic ratio was quite similar for all samples. An increase in the C/O value was observed in the following sequence:

$$\text{FA1}_{(NH4OH)} < \text{FA2}_{(NH4OH)} < \text{FA2}_{(NaOH)} < \text{FA1}_{(NaOH)}$$

The C/H ratio describes the aromatization and condensation of FAs (Table 2). A lower C/H value means an aliphatic characteristic of acids, while a higher one – their aromatic form. An atomic ratio was relatively small for all samples what means a low degree of aromatization. For $\text{FA1}_{(NH4OH)}$ it was 0.60 while for $\text{FA2}_{(NH4OH)}$ it was around 0.68, next for $\text{FA1}_{(NaOH)}$ 0.98 and for $\text{FA2}_{(NaOH)}$ 0.75. FAs extracted with the NaOH method were more aromatic. The differences between the samples were quite small.

$$\text{FA1}_{(NH4OH)} < \text{FA2}_{(NH4OH)} < \text{FA2}_{(NaOH)} < \text{FA1}_{(NaOH)}$$

The C/N ratio determines the degree of maturity (Table 2). It establishes direction and intensity of transformation of organic matter and nitrogen compounds, as well. The C/N ratio was quite small for 2 samples: $\text{FA1}_{(NH4OH)}$ 3.31 and $\text{FA2}_{(NH4OH)}$ 4.61 and it can be correlated with the extraction method (ammonia water). The higher the value of N, the lower the C/N atomic ratio according to the following sequence:

$$\text{FA1}_{(NH4OH)} < \text{FA2}_{(NH4OH)} < \text{FA1}_{(NaOH)} < \text{FA2}_{(NaOH)}$$

The O/H ratio determines the degree of humification (Table 2), this indicator is directly proportional to the atomic ratios. The higher O in the O/H ratio the higher the amount of oxygen-containing groups and a lower degree of humification. The O/H ratios were quite large for all samples. They were: $\text{FA2}_{(NH4OH)}$ 0.45, $\text{FA2}_{(NaOH)}$ 0.49, $\text{FA1}_{(NH4OH)}$ 0.68 and the biggest one $\text{FA1}_{(NaOH)}$ 0.60. It may be concluded that FA extracted from different samples had many oxygen groups. The higher loss of hydrogen than oxygen was observed in the NaOH method due to the humification process. An increase of the O/H value was observed in the following sequence:

$$\text{FA2}_{(NH4OH)} < \text{FA2}_{(NaOH)} < \text{FA1}_{(NaOH)} < \text{FA1}_{(NH4OH)}$$

3.3. The degree of inside oxidation

The degree of inside oxidation was based on the Żdanow formula (Becher et al., 2013; Boguta et al., 2016):

$$\omega = [(2O+3N)-H]/C \tag{1}$$

where:

O – the oxygen content, N – the nitrogen content, H – the hydrogen content,
C – the carbon content.

Samples	ω
$FA1_{(NH4OH)}$	1.51
$FA1_{(NaOH)}$	0.40
$FA2_{(NH4OH)}$	0.51
$FA2_{(NaOH)}$	0.07

Table 3. The degree of inside oxidation of FAs extracted from the primary and secondary effluents by different methods

According to the Table 3 ω was bigger for the primary and secondary effluents in the NH_4OH method. For primary effluent it was 1.51 $FA1(_{NH4OH})$ and 0.40 for $FA1_{(NaOH).}$ FA extracted from the secondary effluent had ω = 0.51 – $FA2_{(NH4OH)}$ and 0.07 for $FA2_{(NaOH)}$. The parameter is closely related to oxidation and degradation reactions. The degradation process involves the loss of CH_3 groups and partial oxidation, thus decreasing the number and length of aliphatic chains in HSs (Litvin et al., 2015). The high degree of oxidation means a high level of humification (Łomińska & Anielak, 2017; Pena-Mendez et al., 2005). Based on the results, it can be concluded that the extraction with a NaOH solution and a two-stage ion exchange process (hydrophobic ion-cation exchanger – H+) reduce internal oxidation of FAs. Soluble HSs extracted from the primary effluent had a higher level of humification in both methods. An increase in ω value was observed as below:

$$FA2_{(NaOH)} < FA1_{(NaOH)} < FA2_{(NH4OH)} < FA1_{(NH4OH)}$$

3.4. Trace elements content

The highest Cl content was found in the $FA1_{(NaOH)}$ (26,58%) while the other samples had the Cl content below 15%, in $FA2_{(NH4OH)}$ Cl was not found. The content of Si was similar for all samples, but in $FA2_{(NH4OH)}$ the element was not found. The lowest Na content was detected in the $FA1_{(NH4OH)}$ sample while all other samples had similar content of Na. The Na content was correlated with the extraction method, a higher content of this element could be related to the fact that NaOH was introduced to the column in the second method. The content of Ca and K was similar in three samples ($FA1_{(NH4OH)}$, $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$) while for $FA2_{(NH4OH)}$ the content of these elements was much higher (Ca – 8.8% and K – 2.5%). The content of Mg and P were similar (below 0,5%) in three samples ($FA1_{(NH4OH)}$, $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$) although in $FA2_{(NH4OH)}$ it was 1,6%. The highest content of Fe was in the $FA1_{(NaOH)}$ sample (18,76%), the other samples ($FA1_{(NH4OH)}$, $FA2_{(NH4OH)}$, $FA2_{(NaOH)}$) had the Fe content below 0,7%.

3.5. Infrared spectroscopy IR

The results of IR were compatible with the analyses of elemental composition and functional groups. The IR analysis showed some similar as well as different bands.

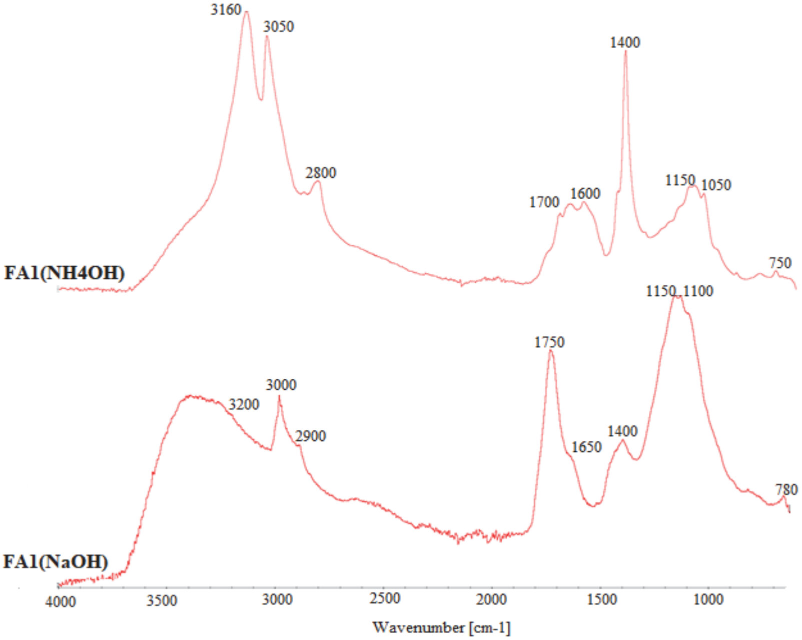


Fig. 4. The IR absorption spectra of FAs extracted by NH_4OH (Łomińska and Anielak, 2017) and NaOH method from the primary effluent

Quite broad peaks appeared around 3200^{cm-1} (FA1$_{(NaOH)}$) and 3160^{cm-1} FA1($_{(NH4OH)}$) (Fig. 4). They are usually attributed to O-H stretching from alcohols, phenols and carboxylic related groups and also to N-H stretching from amide and amine functional groups. The next quite intense peaks around 3050 $^{cm-1}$ (FA1$_{(NH4OH)}$) and 3000^{cm-1} (FA1$_{(NaOH)}$) are caused by C-H asymmetric and symmetric stretching of aromatic compounds. Peaks around 2900^{cm-1} (FA1$_{(NaOH)}$) and 2800^{cm-1} (FA1$_{(NH4OH)}$) may indicate the presence of alkanes stretching bonds C-H. Peaks around 1750 (FA1$_{(NaOH)}$), 1700^{cm-1} (FA1$_{(NH4OH)}$) and 1650^{cm-1} (FA1$_{(NaOH)}$), 1600^{cm-1} (FA1$_{(NH4OH)}$) can be attributed to the C=C and C=O stretching vibrations, coming from aromatic rings and carboxylic, ketone or ester groups, respectively. Peaks from 1400^{cm-1} to 1000^{cm-1} are probably due to C-O stretching and $-CH_3$ deformation vibrations (Zhu & Ryan 2016, He et al., 2011; Huo et al., 2008; Zieliński & Rajca. 2000; Huan et al., 2017).

Quite broad peaks (Fig. 5) appeared around 3200^{cm-1} (FA2$_{(NaOH)}$) and 3150^{cm-1} (FA2$_{(NH4OH)}$). They are usually attributed to O-H stretching from alcohols, phenols and carboxylic related groups and also to N-H stretching from amide and amine functional groups. The next peaks around 3000^{cm-1} – only for FA2$_{(NH4OH)}$ samples are caused by C-H asymmetric and symmetric stretching aromatic compounds. Peaks around 2970^{cm-1} ($FA2_{(NH4OH)}$) and 2950^{cm-1} ($FA2_{(NaOH)}$) may indicate the presence of alkanes stretching bonds C-H. Peaks around 1750^{cm-1} ($FA2_{(NaOH)}$), 1700^{cm-1} ($FA2_{(NH4OH)}$) and 1650^{cm-1} ($FA2_{(NaOH)}$ and $FA2_{(NH4OH)}$) can be attributed to the C=C and C=O stretching vibrations, coming from aromatic rings and carboxylic, ketone or ester groups respectively. Peaks from 1400^{cm-1} to 1050^{cm-1} are probably due to C-O stretching and $-CH_3$ deformation vibrations (Zhu & Ryan, 2016; He et al., 2011; Huo et al., 2008; Zieliński & Rajca, 2000; Huan et al., 2017).

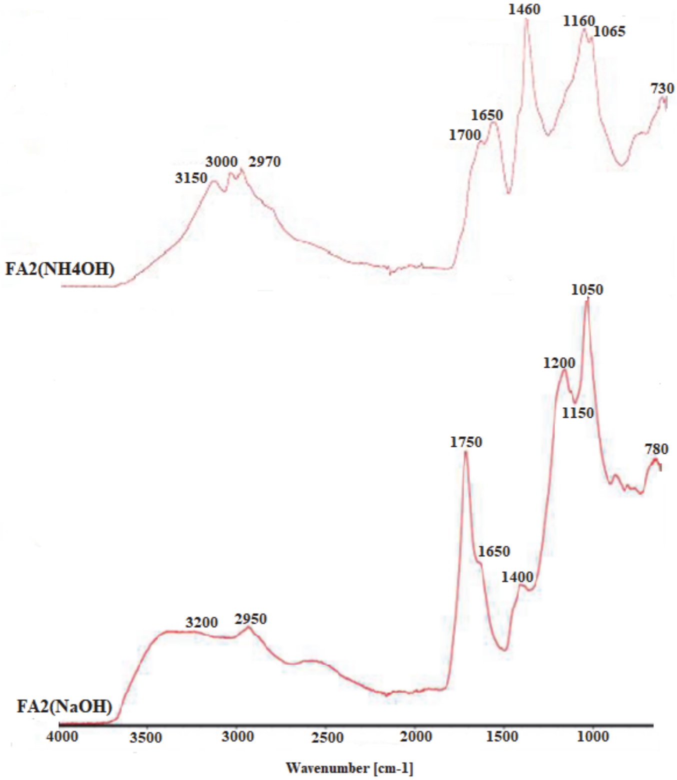


Fig. 5. The IR absorption spectra of FAs extracted by NH_4OH and NaOH methods from the secondary effluent

The bands of $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$ (Fig. 4,5) were broader than those of $FA1_{(NH4OH)}$ and $FA2_{(NH4OH)}$, it could indicate that H-bonded OH groups were formed during a wastewater treatment process.

4. Conclusions

The main objective of the study was to balance and assess the amount of FAs extracted by two different methods from the primary and secondary effluent. The studies have shown that the biggest concentration was received from the primary effluent using the NaOH method, moreover less inorganic impurities were removed in the secondary effluent. Based on the results, it can be concluded that the extraction with a NaOH solution with a two-stage ion exchange process (hydrophobic ion-cation exchanger – H^+) reduces the degree of internal oxidation of FAs. Discussed substances isolated from the primary effluent had a higher level of humification in both methods. Comparing an elemental composition of four samples, it can be noticed that a structure of FAs extracted with the same method is very similar for both primary and secondary effluent. But when two different methods are compared some small differences can be found. The content of C, O and H was similar in the secondary effluent, regardless of the chosen method. The significant difference was observed in the N content, which was in both methods higher for the primary effluent. FAs obtained from the primary effluent (NH_4OH) were the most hydrophilic and had many functional groups, such as hydroxyl and carboxyl. The C/H atomic ratio for all samples was relatively small and indicated a low degree of aromatization. The C/N ratio was quite small for $FA1_{(NH4OH)}$ – 3.31 and $FA2_{(NH4OH)}$ – 4.67. It can be correlated with the method of extraction using ammonia water. FAs isolated from different samples had many oxygen groups. The higher loss of oxygen than hydrogen was observed in the NaOH method due to the humification process. The IR absorption spectra showed that bands of $FA1_{(NaOH)}$ and $FA2_{(NaOH)}$ (Fig. 4 and 5) were broader than those of $FA1_{(NH4OH)}$ and $FA2_{(NH4OH)}$, it could indicate the formation of H-bonded OH groups during the wastewater treatment process.

Based on the research, it can be stated that the WWTP discharged less FAs compared to the input pollution load, regardless the method of extraction.

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Abstract

Fulvic acids (FAs) were isolated from the wastewater by two different extraction methods. The first one with ammonia water (NH_4OH) and the second with an ion exchange using a hydrophobic ion exchanger and desorbed using aqueous sodium hydroxide (NaOH). The samples were collected directly from the primary and secondary effluents at the WWTP and the obtained results were averaged. The WWTP treats mainly wastewater from individual users and industrial plants. The selected plant comprises mechanical and biological wastewater trains as well as sludge processing and biogas trains. The plant works as a three-stage Bardenpho system and operates five identical biological reactors. The main objective of the study was to conduct a mass balance and assess the amount of FAs in the primary and secondary effluent. The extracted acids were subjected to an analysis of their elemental composition, trace elements content and IR spectrum analysis. Based on elemental composition, atomic ratios: C/O, C/H, C/N and O/H, as well as a degree of inside oxidation, have been determined. The studies have shown that the highest amount of FAs was extracted from the primary effluent with the NaOH method and in the secondary effluent less inorganic impurities were removed. Based on the results, it can be concluded that extraction with NaOH solution and a two-stage ion exchange process (hydrophobic ion-cation exchanger-H+) reduces the degree of internal oxidation of FAs. Soluble HSs extracted from the primary effluent had a higher level of humification in both methods. Comparing an elemental composition of four samples, it can be noticed that a structure of FAs extracted with the same method is very similar for both primary and secondary effluent, but when two different methods are compared some small differences can be found.

Based on the research, it can be stated that the WWTP discharged less FAs compared to the input pollution load, regardless of the extraction method used.

Keywords:
humic substances, fulvic acids, wastewater treatment plant, extraction of fulvic acids, elemental analysis, spectroscopic characteristics

Właściwości kwasów fulwowych wyekstrahowanych ze ścieków za pomocą różnych metod

Streszczenie

Kwasy fulwowe (KF) zostały wyekstrahowane ze ścieków z wykorzystaniem różnych metod ekstrakcji. Pierwsza metoda z użyciem wody amoniakalnej (NH_4OH) natomiast druga oparta na procesie wymiany jonowej na hydrofobowym wymienniku jonitowym przy użyciu wodnego roztworu wodorotlenku sodu (NaOH). Próbki zostały pobrane bezpośrednio z mechanicznie oraz biologicznie oczyszczonych ścieków z wybranej oczyszczalni ścieków a podane wyniki zostały uśrednione. Oczyszczalnia ścieków (OŚ) odprowadza głównie ścieki od indywidualnych użytkowników, ale i również z zakładów przemysłowych. Wybrana OŚ składa się z części mechanicznej i biologicznej oraz osadowej i gazowej. W skład części mechanicznej wchodzą: kraty rzadkie, pompownia, kraty gęste, piaskowniki, osadniki wstępne, pompownia II stopnia. Część biologiczna składa się z reaktorów i osadników wtórnych. OŚ pracuje w układzie 3 stopniowym Bardenpho i składa się z 5 identycznych biologicznych reaktorów. Z kolei część osadowa to: zagęszczarki mechaniczne, stacja dezintegracji osadu, zagęszczanie grawitacyjne, prasy taśmowe, wydzielone komory fermentacji oraz ciąg generowania gazu. Oczyszczone ścieki trafiają do rzeki poprzez wylot kaskadowy.

Głównym celem badań był bilans masy oraz określenie ilości KF w mechanicznie i biologicznie oczyszczonych ściekach. Wyekstrahowane KF poddano analizie ich składu elementarnego, zawartości pierwiastków oraz przeprowadzono badanie absorbancji widma IR w podczerwieni. Na podstawie składu elementarnego określono ilorazy atomowe: C/O, C/H, C/N i O/H oraz wyliczono stopień utlenienia wewnętrznego. Wyniki badań pokazały, że największe stężenie KF wyekstrahowano przy użyciu metody z wykorzystaniem NaOH z mechanicznie oczyszczonych ścieków. Przy użyciu tej samej metody mniej zanieczyszczeń nieorganicznych usunięto z KF wyekstrahowanych ze ścieków biologicznie oczyszczonych. Na podstawie wyników badań można wnioskować, że ekstrakcja KF z użyciem roztworu NaOH podczas dwu stopniowej wymiany jonowej (hydrofobowy wymiennik jonitowy H^+) zmniejsza stopień utlenienia wewnętrznego (ω). KF wyekstrahowane ze ścieków mechanicznie oczyszczonych miały wyższy stopień humifikacji, w obu metodach. Porównując skład elementarny czterech próbek można zauważyć, że budowa KF wyekstrahowanych tą samą metodą jest bardzo zbliżona, ale kiedy porówna się ze sobą KF wyekstrahowane z tych samych ścieków jednak różnymi metodami zauważalne są małe różnice.

Badania wykazały, że wybrana OŚ odprowadza mniejszy ładunek KF w porównaniu do wprowadzanego, bez względu na rodzaj zastosowanej metody ekstrakcji.

Słowa kluczowe:
substancje humusowe, kwasy fulwowe, oczyszczalnia ścieków,
ekstrakcja kwasów fulwowych, analiza elementarna, charakterystyka spektroskopowa