

Article

Humic Substances—Common Carriers of Micropollutants in Municipal Engineering

Anna M. Anielak ^{1,*}, Katarzyna Styszko ², Aneta Kłeczek ¹ and Dominika Łomińska-Płatek ¹¹ Faculty of Environmental Engineering and Energy, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland² Faculty of Energy and Fuels, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

* Correspondence: aanielak@pk.edu.pl; Tel.: +48-12-628-3069

Abstract: Research over several years has shown that municipal engineering is an important source of humic substance formation (HS). Effluents from municipal landfills and digested sludge, due to high concentrations of organic pollutants, including HS and inorganic pollutants, are discharged to a biological treatment plant, where their largely non-biodegradable pollutants constitute a burden on the activated sludge and generate problems related to wastewater treatment. To demonstrate that humic substances, primarily soluble acids, are the carriers of micro-pollutants, their isolation was carried out from samples taken at different municipal management sites. The following analyses were performed: elemental composition, and the content of inorganic micropollutants, including heavy metals. In addition, the sorption affinity of pure HS to selected pharmaceuticals was investigated. The sorbed pharmaceuticals were Diclofenac and Estrone. HS commonly found in municipal engineering have been shown to be carriers of inorganic and organic micropollutants, including pharmaceuticals. Based on the study data, surface water's primary source of micropollutants is treated municipal wastewater and fulvic acids are the transfer agent. To demonstrate the locations of HS occurrence within municipal engineering and the micropollutants they carry, their isolation was carried out from samples taken at different municipal management sites. Fulvic acids were studied due to their high mobility. Extraction was carried out according to the method recommended by the International Humic Substances Society (IHSS) with the author's modification. The following analyses were performed: elemental composition (N, C, O, and H); the content of inorganic micropollutants, including heavy metals; and the IR spectrum. In addition, the sorption affinity of pure HS to selected pharmaceuticals was investigated. The sorbed pharmaceuticals were Diclofenac and Estrone. The study confirmed the occurrence of HS in municipal landfill effluents, activated sludge, excess and digested sludge effluents, and treated wastewater. At the same time, HS commonly found in municipal engineering have been shown to be carriers of inorganic and organic micropollutants, including pharmaceuticals.

Keywords: humic substances; micropollutants; municipal engineering

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1. Introduction

According to the generally accepted definition, micropollutants are persistent and hazardous substances present in water at low concentrations from pictograms to micrograms (p/L–μg/L) but higher than natural background levels. The characteristics of micropollutants are persistence, resistance to biodegradation, and high biological activity [1,2]. These include substances such as pharmaceutical actives intimate hygiene products, sweeteners, stimulants, X-ray contrast agents, industrial chemicals, pesticides, heavy metals, and others. Antibiotics and other antimicrobial drugs excreted by humans and animals, due to only partial removal in wastewater treatment plants, are emitted into the environment and persist at levels ranging from a few pg/L to μg/L. [3,4]. Steroid hormones such as estrogen,

progesterone, and norgestrel have been observed in water bodies and surrounding areas at lower concentrations [4–6]. Consequently, as global studies have shown, micropollutants are now a global surface water quality problem [7,8]. It has been known for more than 20 years that these substances can only partially be removed by conventional wastewater treatment methods, including tertiary treatment [9,10]. As a result, wastewater treatment plants are the main points of entry for micropollutants into surface waters [11]. In addition, studies [12] have shown that birds and insects can transfer dissolved and suspended pollutants from water to terrestrial ecosystems, which explains the significant occurrence of micropollutants in coastal areas [12].

To reduce micropollutants in the aquatic environment, advanced treatment technologies have been investigated for many years, e.g., using algae [4], chlorination [13], UV radiation [11,14,15], membrane processes [11,16], ozonation, activated carbon filtration [17], biophenolic resin obtained from a mixture of Kraft black lye and condensed tannin [18], advanced oxidation processes, and (bio)electrochemical technologies [11,19,20]. Also, favorable results were obtained for the isolated *Pseudomonas aeruginosa* KS2002 strain capable of degrading high concentrations of triclosan [21]. Methane fermentation of Diclofenac confirms its resistance to biodegradation. Only its partial cometabolic degradation occurs. 25–40% is subject to biotransformation, 6% adsorbs in the solid phase, and 55–70% remains in the liquid phase [22].

Unfortunately, the methods investigated so far, even with high efficiency, cannot be implemented due to the high investment and operating costs of a real-scale process. Moreover, the secondary use of treated municipal wastewater does not yield positive results. The uptake of micropollutants by plants depends on the physicochemical properties of a pollutant, plant habit, soil properties, and irrigation water quality. A variable, including a significant accumulation of micropollutants in plants, mainly in the root mass, has been demonstrated [11,23].

Most micropollutants show toxicity, such as endocrine disorders, chronic effects, and induction of mutations at the genetic level [3,4,6,24]. Some micropollutants are carcinogenic, mutagenic, and teratogenic. Humic substances are also present in surface waters and were initially thought to be of natural origin. Today, it is already known that a major source of these is municipal engineering. They can be found in municipal wastewater, treated wastewater, sludge effluents, and landfills [25–27]. They are resistant to biodegradation. Due to their aromatic-aliphatic structure, it is reasonable to believe that they are carriers of organic and inorganic substances. Previous studies have shown that they form soluble organometallic complexes that hinder water purification. Therefore, this study has been undertaken to investigate the role and ability of mobile fulvic acids in transporting organic (pharmaceuticals) and inorganic substances, including heavy metals, in the aquatic environment.

2. Materials and Methods

2.1. Materials and Sampling Points

The following raw materials were tested from the Płaszów sewage treatment plant in Cracow: (1) treated sewage, (2) excessive sludge, (3) digested sludge, and (4) leachate from the Barycz municipal landfill in Cracow. The tested samples contained fulvic acids the most. The places of sampling are marked in the diagram—Figure 1. The presented system shows that the tested FAs are practically in a semi-closed cycle. FAs, which are resistant to biodegradation, are partially adsorbed on the activated sludge and the remaining amounts are discharged with the treated sewage as micropollutants to surface waters.

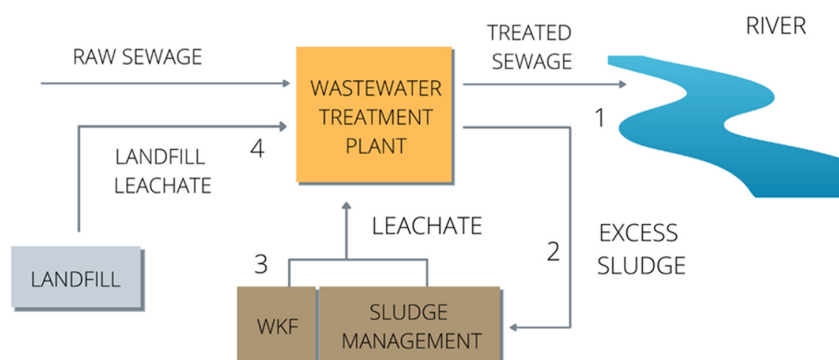


Figure 1. FA cycle in municipal engineering and sampling points: 1—treated sewage, 2—excess sludge, 3—digested sludge from fermentation chamber WKF, and 4—landfill leachate.

2.2. Procedure of HAs Extraction and Analytic

FAs were extracted according to the method of the International Humic Substances Society (IHSS), with a modification described in the article by Anielak et al. [26]. First, the samples that were collected from places described in point 2.1. were acidified with hydrochloric acid (HCl, A.C.S. 1:1) to a pH value of <2. After 24 h, the samples were centrifuged in a Thermo Scientific Sorvall Legend X1R centrifuge. The outflow from the centrifuge was passed through a hydrophobic bed of Amberlit XAD 1180 resin, with a speed of 1–0.5 L/h. Subsequently, acid desorption was performed with 0.1 n NaOH solution. The obtained desorbate was directed to the cation exchanger in the form of H^+ to execute the ion exchange process. The resulting leakage was concentrated in a vacuum evaporator at a vacuum of 350 mbar and a temperature of 80–60 °C. Then, the samples were evaporated and dried at 80–60 °C to obtain a dry residue of FAs.

For sewage and digested sludge, the first extraction step was flooding the samples with 0.1 n NaOH for 24 h. Next, the solution was decanted, and the remaining part was flooded once more with the same amount of 0.1 n NaOH and left for another 24 h. Then, the sludge was centrifuged, and the effluent was acidified with HCl to a pH value of <2. Further treatment was in line with the extraction method described for sewage and effluent.

Determination of basic elements (carbon, hydrogen, and nitrogen) content is provided in the form of an ashless mass, with the use of a combustion method with chromatographic detection. Determination was executed with an elementary analyzer Flash 2000 from Thermo, a 5–10 mg sample was used for the test.

For FAs samples, the ash content was determined using the thermogravimetric method. Analysis was executed with a SDT Q600 thermogravimeter from TA Instruments, the samples were heated to 700 °C (10 °C/min) in the airflow of 100 mL/min.

The X-ray fluorescence (XRF) method was used to identify and determine the content of the remaining elements. The analysis was carried out with Bruker's ED-XRF spectrometer, Bruker's S8 Tiger spectrometer, and Thermo's EA Flash element analyzer, using a powder analysis vessel on 4 µm thick Proline film.

The heavy metal content was determined using the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) method. The test procedure was per the PN-EN ISO 17294-2:2006 standard.

The Fourier-transform infrared spectroscopy (FTIR) method with the Attenuated Total Reflection (ATR) attachment was used for the qualitative identification of obtained FAs. The analyzes were performed in the spectral range of 450–4000 cm^{-1} , with a resolution of 1 cm^{-1} , using the iS10 spectrometer from Thermo Nicolet and UART TWO from PerkinElmer.

2.3. Sorption Experiments with Pure HS and Selected Pharmaceuticals

Standards, Diclofenac, and Estrone were of >98% purity and were purchased from Sigma Aldrich (St. Louis, MO, USA). The derivatization reagent BSTFA + 1% TMCS was purchased from Supelco (Bellefonte, PA, USA). Methanol of GC grade was purchased from

Avantor Performance Materials Poland (Gliwice, Poland). Solutions of the compounds were prepared in methanol and diluted as necessary to prepare working solutions. Deionized water (<0.07 S/cm) used to prepare samples for the experiments was obtained from an HLP5 pure water system (Hydrolab, Gdańsk, Poland).

Batch experiments were conducted at 10 mg/L concentration of fulvic acid (commercial fulvic acids HumiAgra from Agraplant Kielce, Poland). 100 mL of solutions of fulvic acid in dark glass bottles, spiked with an appropriate working standard solution of compound to concentration 1 $\mu\text{g/L}$, were shaken for 4 h using a horizontal shaker at 50 rpm. Then, solutions were extracted by using 60 mg/3 mL Oasis HLB 3cc cartridges (Waters, Wexford, Ireland). The BAKER SPE 12G (J.T. Baker, Philipsburg, PA, USA) system was utilized for the SPE procedure. After elution with 4 mL of methanol, the evaporation of SPE extracts and derivatization were carried out with a thermo-block (AccuBlock Digital Dry Bath Labnet, Woodbridge, NJ, USA). After evaporation to dryness with a gentle stream of nitrogen, samples were redissolved in 200 μL of derivatization agent-Bis(trimethylsilyl)trifluoroacetamide + 1% Trimethylchlorosilane (BSTFA + 1% TMCS) and the silylation process was carried out at 60 $^{\circ}\text{C}$ for 30 min in the thermo-block.

For the samples obtained in this way, an analysis was performed using gas chromatography coupled with mass spectrometry (Thermo Scientific Trace 1310 gas chromatograph with a Tri Plus RSH autosampler, coupled with an ion trap mass spectrometer ITQ 900) [28].

Control samples, without fulvic acid, with a concentration of 1 $\mu\text{g/L}$ of the tested compound were conducted in the same procedure as in the sorption experiments. Blank samples were included in each sample set. Absolute recoveries of analytes were determined by comparing the area of the peak of analyte in sorption samples to the area of the peak of control samples. Values of absolute recoveries were $74\% \pm 13$ and $70\% \pm 5$ for Estrone and Diclofenac, respectively. The quantification limits were 42.1 ng/L for Estrone and 11.4 ng/L for Diclofenac.

3. Results

3.1. Infrared Spectrum

The infrared (IR) spectrum provides the most information about the structure of an organic molecule. The atoms in a molecule are subject to constant oscillations, stretching, shrinking, and bond breaking. From the characteristics of the IR spectrum, it can be inferred whether the extracted substances have a spectrum typical of HS. The first two spectra (Figure 2: 1FA1, 2FA1) were obtained for two samples, 1 and 2, of treated wastewater discharged from the treatment plant into a surface watercourse. The samples were taken 1 year apart. In analyzing the spectra in question, a great similarity can be seen in their data. Absorption bands occur in the same areas, at 770, 1065–1050, 1100, 1400, 1650–1700, and 2800 cm^{-1} , and in the broad range of 3000–2800 cm^{-1} , with peaks at 3300 cm^{-1} and 2950 cm^{-1} of the 1FA1 spectrum, and 3280 cm^{-1} and 2996 cm^{-1} .

The absorption band of 770 cm^{-1} characterizes the deformation vibrations in NO_2 and NH_2 . The 1100–1065 cm^{-1} band in lignin-like material [2] characterizes C-O stretching vibrations in acids. The 1400 cm^{-1} band indicates O-H deformation, CH_3 bending, C-O stretching of phenolic OH, and antisymmetric COO- stretching. The 1700–1630 cm^{-1} region, especially the 1692 cm^{-1} and 1650 cm^{-1} bands, are notable for C=O and C=C double bonds (these are stretching vibrations) of acids, in aromatic rings (including lignin structures), C=N, and other amide groups (in proteins) containing nitrogen.

The spectra confirm the presence of an aliphatic carboxylic structure, consisting of a hydroxide part OH and a carbonyl group C=O. In the spectra, there are broad, intense bands within the 3300–2900 cm^{-1} region resulting from stretching vibrations of the O-H group and 1692 cm^{-1} and 1650 cm^{-1} bands of the carbonyl group.

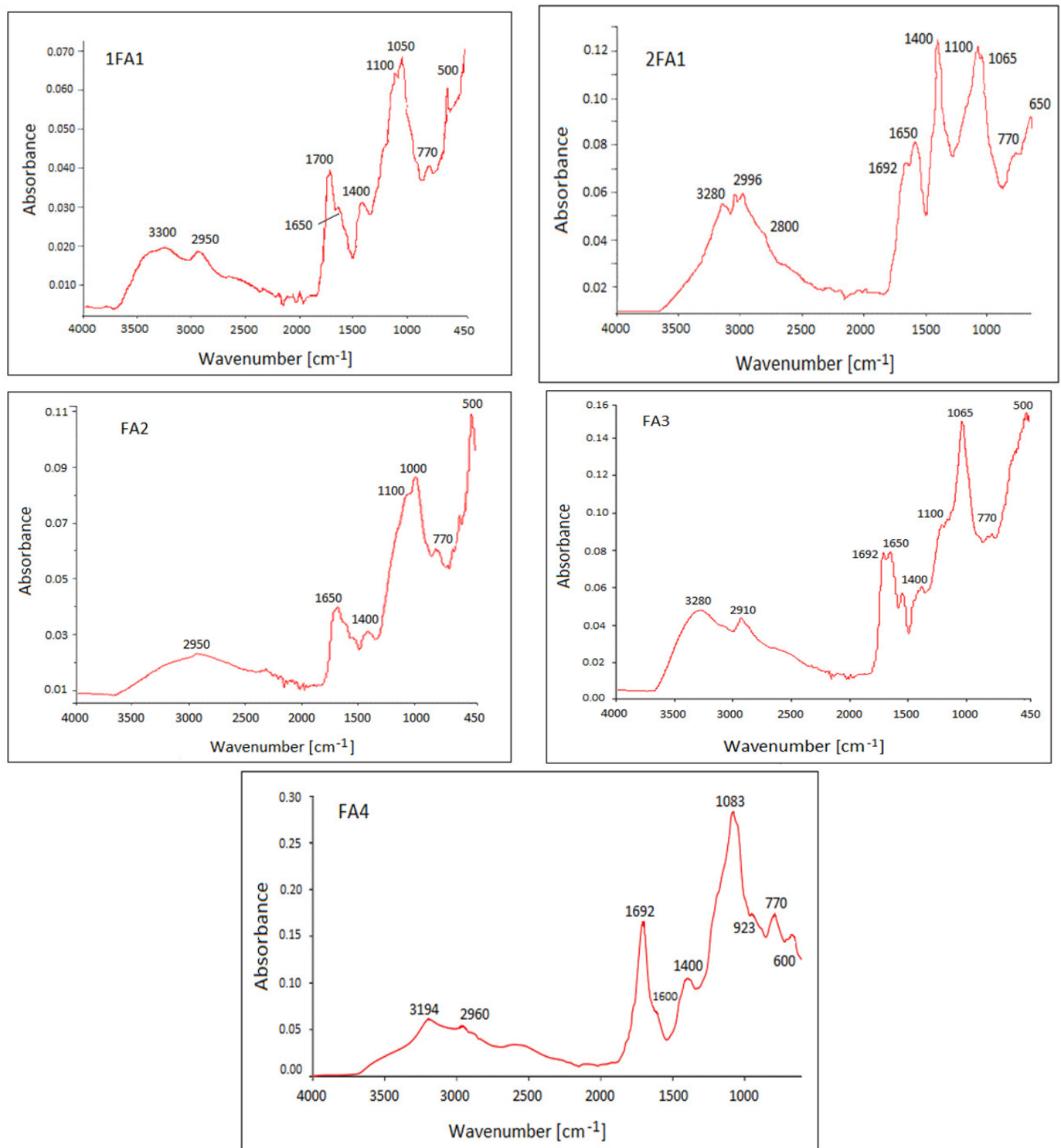


Figure 2. FTIR spectra of FA extracted from 1FA1, 2FA1—treated sewage; FA2—excess sludge; FA3—digested sludge; and FA4—landfill leachate (source: [29]).

The next two spectra (Figure 2: FA2, FA3) characterize substances extracted from sewage sludge: the FA2 spectrum—from excess sludge, after dephosphatization, denitrification, and nitrification; and the FA3 spectrum—from digested sludge. The infrared spectra of FA2 and FA3 differ from those obtained for fulvic acids from raw and treated sewage. However, these are humic substances, as confirmed by detailed analysis of the spectra.

The FA2 and FA3 spectra have absorption bands with peaks of 1100, 1400, and 1650 cm^{-1} , also present in the 1FA1 and 2FA1 spectra, as already described. In addition, they have a weak absorption band of 770 cm^{-1} and a broad one with a peak of 2950 cm^{-1} (FA2) and peaks at 3280 cm^{-1} and 2910 cm^{-1} (FA3). The bands show slight aberration compared to those found in the 1FA1 and 2FA1 spectra. Some differences may be due to the presence of a significant number of inorganic impurities in FA (FA2, 36.07% ash).

The bands present, the interpretation of which is presented above and in Table 1, confirm that fulvic acids have been extracted from the sewage sludge and digested sludge. The shape of the FA2 spectrum is similar to the FA3 spectrum. The spectra have absorption bands of 770, 1065–1100, 1100, 1400, and 1650 cm^{-1} and broad bands in the 2500–3300 cm^{-1} region.

Table 1. Characteristic absorption bands of fulvic acids.

Wave Number cm^{-1}	1FA1	2FA1	FA2	FA3	FA4 ¹	
3300–2500	X	X	X	X	X	Broad absorption, stretching vibration bands in carboxylic acids (forming O-H hydrogen bonds).
1700–1650	X	X	X	X	X	Intense stretching carbonyl band, C=O bond in acids, aromatic acids
Fingerprint region						
1400	X	X	X	X	X	Bending deformation of O-H, stretching of C-O and phenolic OH, and asymmetric stretching of COO-, acids
1100–1065	X	X	X	X	X	Stretching vibration of C-O in acids
770	X	X	X	X	X	Deformation vibration of δNO_2 , out-of-plane deformation of NH_2
650–500	X	X	X	X	X	Stretching vibration band of S-S in disulphides

source: [30–32]¹ source: [29].

The last spectrum characterizes fulvic acids extracted from municipal landfill effluents, FA4 [29]. The notable absorption bands present are 770 and 1400 cm^{-1} broad bands with peaks of 3194 and 2960 cm^{-1} , which, together with the 1692 cm^{-1} band, indicate the presence of carboxyl groups, with some aberration of the 1083 cm^{-1} band (2FA1, FA3—1065 cm^{-1} , and 1FA1—1050 cm^{-1}). As in FA3, the extracted FA4 also had high amounts of inorganic micropollutants (27.94%). All extracted FAs in the 1820–1650 cm^{-1} region are characterized by an intense carbonyl band, the 1100 cm^{-1} band (FAs of landfill effluents—1083 cm^{-1}) of stretching vibrations of C-O and broad OH absorption in the 3300–2500 cm^{-1} region. These data indicate that FAs have electronegative carboxyl and hydroxyl functional groups that show an affinity for cations.

3.2. Elemental Composition

When examining the elemental composition, the typical elements of humic substances (which are C, H, N, and O, contained in the ashless mass) were taken into account. Some authors include the proportion of sulfur in the elemental FAs molecule. Due to the industrial nature of the sampling sites and the presence of sulfur not bound to humic substances; this element was omitted from the analysis. However, it was included in the micropollutants of the extracted substances. In analyzing the values shown in Table 2, we can see the varying carbon percentage content of the individual fulvic acids. FA4 (derived from landfill effluents, 55.36%) and FA2 (derived from surplus sludge, 52.07%) have the highest C percentage content. The H percentage content of the acids tested ranged from 4.29 to 6.47%. A relatively large variation was obtained for the nitrogen content (from 1.07 to 9.44%). The

lowest percentage of nitrogen is in fulvic acids from landfill effluents and the highest in fulvic acids contained in treated wastewater.

Table 2. Elemental composition of extracted fulvic acids.

FA *	Elementals Content Ash Free (%)					Atomic Ratios (-)			
	C	H	N	O	Ash	O/C	H/C	C/N	O/H
1 FA1	46.02	5.13	1.57	47.28	14.77	0.77	1.34	34.20	0.58
2 FA1	43.51	5.37	9.44	41.68	9.74	0.72	1.47	5.41	0.49
FA2	52.07	6.07	7.12	34.74	36.07	0.50	1.41	8.51	0.36
FA3	44.83	6.47	5.23	43.47	14.66	0.97	1.72	10.08	0.56
FA4 ¹	55.36	4.29	1.07	43.42	27.94	0.59	0.93	60.66	0.63

* FA1, FA2, FA3, and FA4—fulvic acids, ¹ source: [29].

By comparing the O/C and H/C values obtained with the van Krevelen diagram [33], it can be concluded that the acids contained in the treated effluent are stable, mature fulvic acids. Comparing the FA1 fulvic acids with those extracted from the sewage sludge after the FA2 nitrification process, we found an increase in carbon and hydrogen percentile amount. Hence, it can be concluded that FAs with a higher number of functional groups enter the sludge—which are carriers of inorganic micropollutants and are therefore characterized by a high ash content of 36.07%—or in the sludge section of the bioreactor, humification of the organic sludge takes place. A H/C quotient of = 1.41 is typical for stable and mature FAs. The van Krevelen diagram and the values of the H/C and O/C quotients indicate that they are very similar to humic acids.

3.3. Inorganic Micropollutants in FAs

Infrared spectral analysis indicates that fulvic acids have hydroxyl and carboxyl functional groups and should therefore be good carriers of metal and electropositive ions. An indicator of the number of inorganic micropollutants, mainly metals, is the amount of ash remaining after calcining the organic matter. The data in Table 2 show that fulvic acids contained in the activated sludge excess (36.07% ash) have the highest amount of inorganic micropollutants and the least in the treated effluent (9.74–14.77% ash). The relationship obtained was correct: in the wastewater treatment process, inorganic pollutants coagulate or adsorb on activated sludge flocs. Regarding humic substances, organic complexes are formed, which are adsorbed onto activated sludge. This relationship has been demonstrated by studies [25], which show that 26% of FAs that enter a treatment plant with raw sewage are discharged with the treated effluent into surface waters. Previous studies indicate that treated wastewater discharges an average of about 5 g FAs/m³. Based on the data in Table 3, it can be calculated that FAs in 1 m³ of treated wastewater transport between 0.74 and 0.49 g of inorganic micropollutants. If there were 1517 hm³ of biologically treated wastewater in 2019, the number of micropollutants carried by FAs into surface watercourses can be estimated at was 1123 tons. These included elements such as Si, Na, Ca, K, Mg, P, Br, Al, and heavy metals such as Cu, Cr, Zn, Ni, Pb, Cd, Mn, and Fe.

3.4. Organic Micropollutants in FAs

Organic HumiAgra humic substances obtained by hydrolytic-oxidative decomposition of lignosulphonate were used in this study. It was a mixture of predominant FAs and humic acids in the form of potassium salt. The commercial product was in solid form and soluble in water; the 10 mg/L solution had a pH of 7.33. According to the manufacturer, the pH of the solid product is between 8 and 10. HumiAgra was used for the study, assuming that this product did not contain organic micropollutants of anthropogenic origin—such as pharmaceuticals—which would affect the adsorption process, thus increasing the error of

the test results. Such an assumption was inappropriate for FAs extracted from sewage and sludge landfill effluents.

Table 3. Micropollutants in FAs mg/gAF.

Element	Concentration, mg/g _{FA}				
	1FA1	2FA1	FA2	FA3	FA4 ¹
Cl	nf	nf	58.5	60.8	4.2
Si	nf	15.5	5.54	nf	155.8
Na	nf	14.5	nf	18.4	15.6
Ca	nf	8.80	25.8	8.0	6.0
K	10.83	2.50	4.71	0.08	2.8
Mg	20.31	1.30	17.2	0.005	0.04
P	nf	1.60	207	16.3	2.9
Br	nf	0.20	nf	5.0	nf
Al	13.54	-	nf	-	-
Cu	0.0074	-	-	-	-
Cr	0.008	nf	0.16	0.02	nf
Zn	0.0468	0.09	1.66	-	nf
Ni	0.0038	-	-	-	-
Pb	<0.0001	-	-	-	-
Cd	<0.0001	-	-	-	-
Mn	4.69	-	-	-	-
Fe	0.11	0.6	18.3	4.3	1.2
Ash, %	14.77	9.74	36.07	14.66	27.94

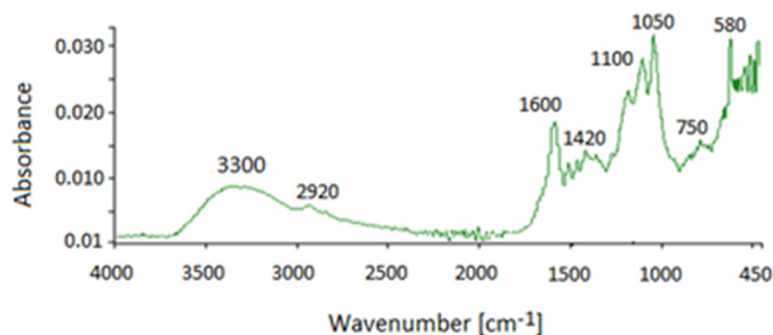
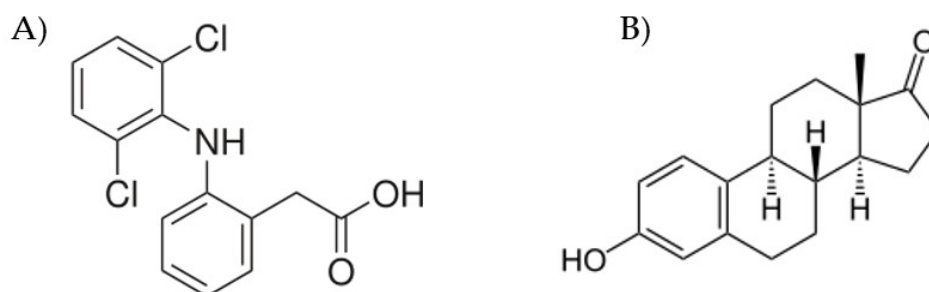
nf—not found, ¹ source: [29].

The affinity of humic substances to selected pharmaceuticals was determined by the sorption of the tested pharmaceuticals on FAs, which contained micropollutants in addition to the elementary elements of H, O, N, and C. The qualitative and quantitative characteristics of HS are shown in Table 4. The commercial product was highly contaminated with potassium (76,405 mg/kg) and sodium ions, probably due to the method used to obtain HS.

The spectrum of FA HumiAgra is shown in Figure 3. A band with a peak at 1600 cm⁻¹ is visible, which can be classified as a carboxyl band. In the 3300–2500 cm⁻¹ range, two peaks of 3300 and 2950 cm⁻¹ stand out, corresponding to the stretching vibrations of O-H in carboxylic acids. This is confirmed by the simultaneous occurrence of a band with a peak of 1600 cm⁻¹. Of particular interest is the 800–1300 cm⁻¹ band. An intense and extensive band occurred here, in which significant maxima of 1100 and 1050 cm⁻¹ can be distinguished. This band is related to the absorption of C-O groups of secondary and tertiary alcohols and carboxylic acids. The spectrum of FA HumiAgra is largely consistent with those obtained for FAs from anthropogenic and urban environments (Figure 2). The slight discrepancies may be due to their significant potassium content of 76,405 mg/kg on a dry weight basis (Table 4). The content of inorganic micropollutants in FAs HumiAgra, as measured by the amount of ash, was 38.13% (m/m). These elements include Al, B, Ba, Co, Ca, Cu, Fe, K, Mg, Na, Mn, Sr, and Zn (Table 4). These elements can influence the sorption process on FAs of the pharmaceuticals, Diclofenac and Estrone, the formulas shown in Figure 4.

Table 4. Micropollutants in HS HumiAgra.

Element	Result	Unit
C	34.24	% (m/m)
H	3.21	% (m/m)
N	0.83	% (m/m)
O	53.42	% (m/m)
Al	31	mg/kg
B	202	mg/kg
Ba	2	mg/kg
Co	101	mg/kg
Ca	992	mg/kg
Cu	776	mg/kg
Fe	47	mg/kg
K	76,405	mg/kg
Mg	150	mg/kg
Na	1636	mg/kg
Mn	165	mg/kg
Sr	6	mg/kg
Zn	157	mg/kg
Ash	38.13	% (m/m)

**Figure 3.** IR spectrum of FA HumiAgra.**Figure 4.** Formulas of the pharmaceuticals used in the study: (A) Diclofenac and (B) Estrone.

The graph below shows the results of analyte adsorption on fulvic acids.

The graph (Figure 5) shows the percentage of analyte loss after 4 h of shaking a 10 mg/L of fulvic acid solution with a single analyte of 1 µg/L. The results indicate high sorption of pharmaceuticals on FAs. Diclofenac removal amounted to 50% and

Estrone—90%. Hence, it can be concluded that FAs are excellent carriers of organic pollutants contained in municipal wastewater. Due to their high mobility and ability to form organic and inorganic complexes, they contribute to the pollution of surface waters with substances that should be removed in the wastewater treatment process. The pH of the solution in which the sorption was carried out was 7.33. At a given pH, carboxyls are dissociated. Hydroxyl groups can also dissociate. Therefore, sorption of pharmaceuticals can occur with aromatic and aliphatic groups through bridging, which may involve multivalent cations such as Al, Co, Ca, Cu, Fe, Mn, Sr, and Zn forming HS micropollutants.

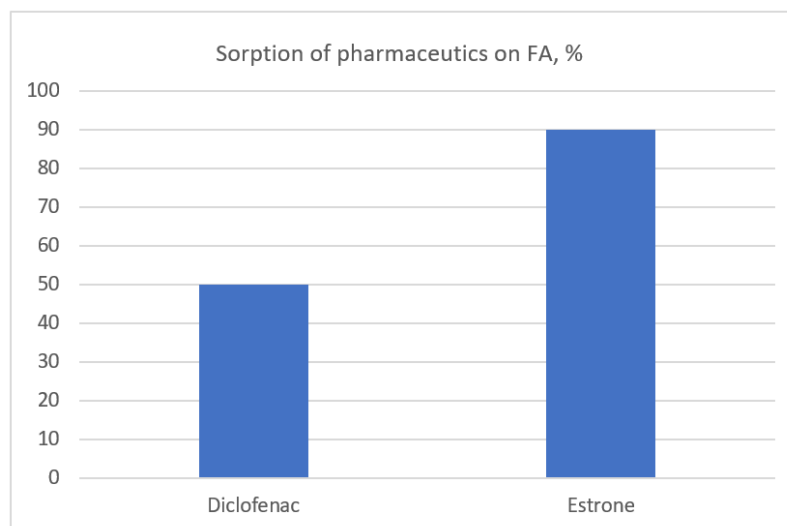


Figure 5. Sorption of selected pharmaceuitics on FA HumiAgra.

4. Summary

The following conclusions can be drawn based on the study. Humic substances are commonly found in municipal management and are discharged into surface waters together with treated wastewater. They have a structure composed of aromatic elements and aliphatic chains, including carboxyl and hydroxyl chains, which sorb metal cations, including heavy metals. The quantities of inorganic micropollutants discharged by FAs vary and depend on the composition of the raw sewage and the treatment technology used and can amount to more than 1100 tons/year in Poland. The adsorbed cations can, by bridging, sorb anionic inorganic micropollutants and organic substances. Studies have shown that FAs carry pharmaceuticals into surface waters through aliphatic-aromatic sorption. Such a relationship was obtained for the two pharmaceuticals tested, Diclofenac and Estrone, whose sorption to FAs from a solution of 10 mg/L FAs amounted to 50% for Diclofenac and 90% for Estrone, with a concentration of 1 µg/L. Based on the study data, surface water's primary source of micropollutants is treated municipal wastewater, and FAs are the transfer agent. Removing FAs from treated wastewater will reduce micropollutant migration in the aquatic environment.

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Conflicts of Interest: The authors declare no conflict of interest.

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