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Assessment of Humic and Fulvic Acid Sorbing Potential for Heavy Metals in Water

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Abstract: Pollution of water sources with heavy metals is a pressing environmental issue. To this end, various procedures are being used to remediate water, including sorption. The aim of this study was to investigate the effectiveness of humic acids (HAs) and fulvic acids (FAs) for the removal of metals from water. Specifically, HA and FA were examined for their potential to be used as sorbent materials for 26 heavy metals, alkali metals, and alkaline earth metals. HA and FA were isolated from lignite samples from two mines (Mavropigi mine and South Field mine, Kozani, West Macedonia, Greece). Experiments were carried out using natural mineral water without pH adjustment, so as to gain a better overview of the sorption efficiency in real-life samples. The results showed that FAs were able to sorb most of the examined metals compared to HAs. Several metals such as Ba (34.22–37.77%), Ca (99.12–99.58%), and Sr (97.89–98.12%) were efficiently sorbed when 900 ppm of FAs from both sources were used but were not sorbed by HAs from any source ($\leq$0.1%). Due to the functional groups on the surface of FA, it is plausible to conclude that it can remove more metals than HA. Meanwhile, lignite from the South Field mine was found to be more efficient for the sorption efficiency in lower concentrations (300–600 ppm), whereas lignite from the Mavropigi mine was more effective in higher concentrations (900 ppm). For instance, higher removal rates were observed in Mo (62.84%), Pb (56.81%), and U (49.22%) when 300 ppm of HAs of South Field mine were used, whilst the employment of 900 ppm of HAs from Mavropigi mine led to high removal rates of As (49.90%), Se (64.47%), and Tl (85.96%). The above results were also reflected in a principal component analysis, which showed the dispersion of the metal parameters near to or far from the HA and FA parameters depending on their sorption capacity. Overall, both HA and FA could be effectively utilized as sorbent materials for metal removal from water samples. The results of the research indicate a potential application to the remediation of water from metals under dynamic conditions in order to protect public health.

Keywords: heavy metals; alkali metals; alkaline earth metals; lignite; sorption; metal removal; water remediation

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1. Introduction

Heavy metals are persistent toxic pollutants that accumulate in the environment and pose serious risks to human and animal health [1]. They enter water sources due to various types of industrial, agricultural, and household activities and cause water pollution [2]. Heavy metals are toxic, even at low concentrations [3]. Cadmium, lead, mercury, arsenic, and chromium are among the most dangerous and most common contaminants in water sources [4], as they accumulate in the body over time and can lead to long-term health problems [5]. The heavy metals mentioned above [6] are just a few examples of metals whose consumption could cause serious health issues [7]. Consequently, heavy metals in water are a serious environmental issue that requires attention. In addition to heavy metals, alkali metals and alkaline earth metals are two other categories of metals that are less frequently studied. These metals are essential for many biological processes, making their presence in drinking water vital for human health [8]. However, high concentrations of these metals in water can have adverse effects on human health [9], such as hypertension, heart disease, and kidney damage [10]. Besides these side effects on human health, alkali and alkaline earth metals also contribute to the formation of scale deposits in industrial processes, which reduces equipment efficiency and increases maintenance costs. In addition, the presence of these metals in wastewater can also have adverse impacts on the environment [11], affecting aquatic life and decreasing the quality of water [12]. Therefore, it is easily conceived that the removal of all the above metals from water is important to ensure safety of drinking water, reduce the risk of adverse health effects, and minimize the negative impacts on the environment.

Various methods have been developed to date to address the issue, including chemical precipitation [13], ion exchange [14], and membrane filtration [15]. While these methods have shown efficacy in the removal of metals, they are frequently associated with high costs and have limited effectiveness, particularly when focusing on metals present at low concentrations. For instance, chemical precipitation requires adding chemical agents to water, which can cause additional waste and increase the overall costs [14]. Similarly, the process of ion exchange not only requires thorough control of pH and temperature to avoid unnecessary ion exchange, but also the expenses associated with ion exchange resins are considerable [16]. Membrane filtration is also considered as an expensive process, especially in large-scale applications [14]. It may also require pretreatment to remove organic matter that can damage the membrane [13]. Nevertheless, the efficacy of membrane filtration in removing metals at low concentrations may be questioned by the ability of certain small-sized metal ions to pass through membranes [17].

Sorption has attracted significant attention as an alternative method for the removal of metals from water due to its simplicity, efficacy, and affordability [18]. It is highly selective for certain metals and has high efficiency for low metal concentrations [19]. Given its scalability, sorption is a genuine option for treating water on a large scale [20]. Several types of sorbents have been developed and tested so far for the removal of metals from water including zeolites [21], clay [22], chitosan [23], biochar [24], and active carbon [25]. Humic acids (HAs) and fulvic acids (FAs) are naturally occurring sorbents that are abundant in soil and water [26]. HAs are high-molecular-weight, hydrophilic, and amorphous organic acids that can form strong complexes with metal ions due to their carboxylic, phenolic, and hydroxyl functional groups [27]. FAs, on the other hand, are low-molecular-weight, hydrophilic, and yellow-to-brown-colored compounds that can complex with metal ions through their carboxylic, phenolic, and amino functional groups. Therefore, they can be used to effectively remove metal ions from water samples [28].

The aim of this study was to examine removal of twenty-six metals (silver (Ag), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), thallium (Tl), uranium (U) vanadium (V), and zinc (Zn)) from natural mineral water with the use of 300, 600, and 900 ppm of HA and FA as sorbents. To the best of our knowledge, this is the first time that a sorption study of such metals with these sorbent materials is carried out. In regard to the water used in this study, experiments were carried out using natural mineral water, instead of distilled or deionized water which is commonly used in similar studies. This is because natural mineral water is a water that can be found in natural water sources and contains a range of dissolved salts, minerals, and other trace metals that can affect the sorption process. On the contrary, distilled or deionized water is free from the above-mentioned elements and ions, making the sorption process more efficient. However, this may not lead to accurate results [29]. As a result, we opted to use natural mineral water with no pH changes to better simulate real-life conditions. As such, we aimed to provide insights into the effectiveness of the two sorbents under conditions closer to real-life scenarios. The simultaneous sorption of 26 metals in environmental settings is more representative of the true challenges faced in water remediation. Introducing such complexity aligns with the overarching goal of addressing practical environmental concerns. The results of this study will provide a valuable contribution to the advancement of cost-effective methods for water remediation, specifically targeting the removal of diverse metallic contaminants. The sorption experiments were carried out under static conditions. By employing static conditions, this research sought to provide a baseline understanding of the capabilities of the sorbents in removing metals without introducing the complexities associated with dynamic flow systems. This approach aligns with the common practice of first assessing sorption efficiency before delving into more intricate dynamic studies.

2. Materials and Methods

2.1. Chemicals, Reagents, and Raw Materials

All the reagents used were at least of analytical grade. Sodium hydroxide was purchased from Carlo Erba (Emmendingen, Germany), and hydrochloric acid (37%) and nitric acid (65%) were purchased from Panreac (Barcelona, Spain). An ICP Multi-Element Calibration Standard (purchased from Reagecon, Lismacleane, Ireland) was used in all experiments.

Commercially available natural mineral water with a pH level of 8.5 (conductivity level of 182 µS/cm, $CaCO_3$ 98 mg/L, Ca^{2+} 2.4 mg/L, Mg^{2+} 22.3 mg/L, Na^+ 0.6 mg/L, K^+ 0.3 mg/L, $NH_4^+ < 0.1$ mg/L, HCO_3^- 106 mg/L, $Cl^- < 5$ mg/L, $SO_4^{2-} < 5$ mg/L, NO_3^- 1.9 mg/L, and $NO_2^- < 0.05$ mg/L), intended for human consumption, was used in all experiments. For the preparation of the HA and FA, lignite from two mines (Mavropigi mine and South Field mine) located in the broader area of the Kozani Region, West Macedonia, Greece, was used. The location of the two mines is illustrated in Figure 1.

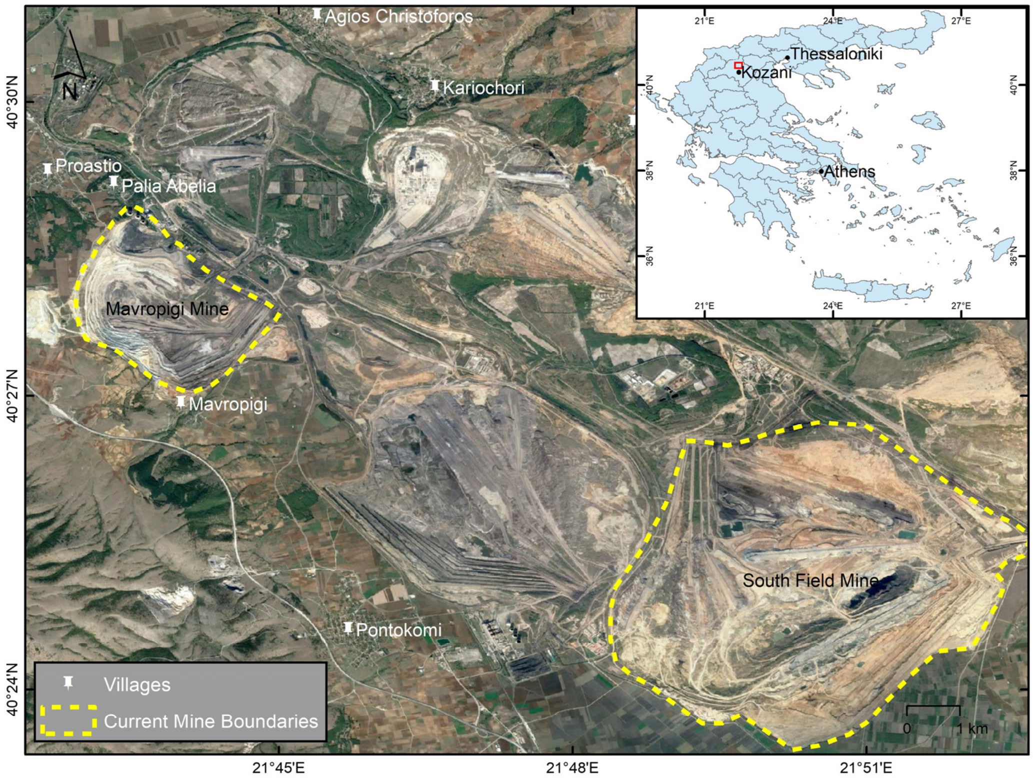

Figure 1. Location of the mines where the lignite was sourced.

2.2. HA and FA Preparation

Lignite from Mavropigi mine contained 35.3% water and yielded 2.36% HA and 4.67% FA. Likewise, lignite from South Field mine contained 55.8% water and yielded 1.45% HA and 5.19% FA. HA and FA were prepared according to a previous procedure [30]. In brief, 150 g of lignite powder (the water content of the lignite was determined gravimetrically, after drying at 105 °C for 24 h according to the ASTM method D4959-07 [31]) was mixed with 850 g of double distilled water and the mixture was stirred for 1 h. The pH of the mixture was then adjusted to 9 using NaOH and then left to stand for 24 h. The supernatant containing HA and FA was isolated by separating them from the precipitate by filtering through the paper filter and centrifuging for 5 min at 4000 rpm, using a NEYA 16R centrifuge (Remi Elektrotechnik, Ltd., Palghar, India). For HA and FA separation, the pH of the supernatant solution was first adjusted to 1 using HCl, and then centrifuged for 5 min at 4000 rpm. The precipitate (HA) was isolated, and the pH of the supernatant was adjusted to 5, using NaOH. The water was removed from the supernatant by evaporation. Finally, both HA and FA were dried for 24 h at 105 °C.

2.3. Fourier Transform Infrared (FT-IR) Analysis

A Shimadzu FT-IR Prestige21 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) with a bright ceramic light source, a potassium bromide (KBr) beam splitter, a high-sensitivity DLATGS (Deuterated Triglycine Sulphate Doped with *L*-Alanine) detector, and high-energy throughput optical elements was used to obtain the FT-IR spectra. For each sample, a total of 64 scans were captured at a resolution of 4 cm^{-1}, ranging from 4000 to 400 cm^{-1}. To produce KBr pellets, 400 mg of KBr and 1 mg of HA/FA sample powder were carefully combined using a hydraulic press.

2.4. Sorption Process

Bottled natural mineral water was spiked with the metals at concentrations of 10 ppb. Then, an amount of HA or FA was added. The mixtures were placed in an ultrasonic bath for 5 min (so as to finely disperse the sorbent and maximize the area available for sorption) and then stirred for 30 min at 900 rpm to ensure to achieve maximum mass transfer. Then, the solutions were centrifuged for 10 min at 4500 rpm and the % removal of metals in the supernatant was determined by Agilent 7700 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Agilent Technologies, Santa Clara, CA, USA). Along with the samples, a blank sample (non-spiked bottled water containing 600 ppm HA or FA) was also analyzed.

2.5. Distribution Coefficient (K_d) Calculation

An essential parameter for determining the sorption of a metal from the water (liquid phase) to the sorbent (solid phase) is the distribution coefficient (K_d). The calculation of K_d was performed according to the equation of Sedeño-Díaz et al. [32] with some modifications. Equation (1) determines the K_d, which is the ratio of sorbed metal concentrations to dissolved metal concentration in water:

$$K_\text{d} = \frac{[M_\text{sorbed}]}{[M_\text{dissolved}]}, \tag{1}$$

where K_d denotes the distribution coefficient in L/Kg, $[M_\text{sorbed}]$ represents the concentration of sorbed metal in mg/Kg of sorbent, and $[M_\text{dissolved}]$ indicates the dissolved metal concentration in water in mg/L.

LogK_d offers valuable information into the process of metal sorption. Metals with a logK_d > 4 are indicative of high affinity to bind in the sorbent, whereas values of 2 < logK_d < 4 show a medium affinity of metals to the sorbent. Metals with a logK_d < 2 are predominantly dissolved in the liquid phase [33].

2.6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Before analysis with the ICP-MS, 2% v/v HNO_3 was added to the samples. The Agilent 7700 ICP-MS (Agilent Technologies, Santa Clara, CA, USA) instrument was operated for the determination of metals. Calibration curves were prepared for the quantification of each metal using 5 points and including a blank solution. To ensure accuracy, the calibration standard solution was analyzed after every 10 samples. Also, a blank solution was analyzed to ensure no carryover effects. Data were analyzed using ICP-MS MassHunter Workstation Software (version A.01.02).

2.7. Spectroscopic Measurement and Analysis

Using an ultra-pure water solution as a reference, the UV-Vis absorption spectra of the samples were measured using a spectrophotometer (Shimadzu UV-1700 PharmaSpec Spectrophotometer, Kyoto, Japan) with a quartz cuvette (path length of 1 cm). After filtration, all of the samples were measured. Bottled natural mineral water that had been contaminated with the metals at 10 ppb quantities served as the control sample. A blank sample (non-spiked bottled water with 600 ppm HA or FA) was also examined along with the samples. Additionally, theoretical spectra were calculated as the sum of the control and blank samples.

2.8. Statistical Analysis

The mean of three assays was employed to illustrate the results, and the standard deviation is provided in the tables. Using IBM SPSS Statistics (Version 29.0) statistical software (SPSS Inc., Chicago, IL, USA), a one-way analysis of variance (ANOVA) test was conducted to determine whether there were statistically significant differences between samples. Principal component analysis (PCA) was also performed in this study to determine the extent to which of the measured parameters were correlated. Principal component analysis (PCA) was conducted through the JMP® Pro 16 software (SAS, Cary, NC, USA).

3. Results and Discussion

3.1. Characterization of the Sorbents

The morphology of a solid can be characterized with remarkable efficacy using established methodologies like scanning electron microscopy (SEM), X-ray diffraction (XRD), and FT-IR. Nevertheless, there are specific challenges associated with their application in the examination of HA and FA surfaces. Despite employing various physicochemical methodologies alongside extensive research, the chemical structure of HA and FA remains inadequately understood, according to Schnitzer and Monreal [34]. The amorphous and heterogeneous nature of HA and FA represents a significant obstacle [35]. HA and FA lack long-range order and show structural heterogeneity, as opposed to crystalline substances which possess well-defined structures amenable to X-ray crystallography. In certain metal sorption studies [36–38], the application of SEM and XRD was regarded redundant, as well. The rationale for employing FT-IR spectroscopy to characterize sorbents stems from its ability to differentiate functional groups present on the surfaces of the sorbents. By analyzing the fingerprint spectrum generated by the absorption of infrared radiation by particular chemical bonds, FT-IR spectroscopy can ascertain the chemical composition of the sorbent. The HA and FA compounds were analyzed using FT-IR spectroscopy based on our previous study [30]. Figure 2 provides spectra of HA and FA together with their model structures suggested by Wang et al. [39]. Large absorption peaks were observed in the spectra about 3410 cm^{-1}, which may be linked to the stretching vibrations of the carboxyl or phenolic $-OH$. The specific peak was found greater in FA rather than HA. These peaks could denote impurities associated with the lignite source. In addition, the acidity of both HA and FA increases as the peak width increases because this indicates stronger intramolecular connections [40]. The aromaticity of the two acids was denoted with C=C stretching vibrations in the benzene ring, which are responsible for the prominent peaks at 1610 cm^{-1} [41]. Carboxyl and ketonic carbonyl (C=O) stretching account for the 1710 cm^{-1}

peak [42], whereas the 1130–1190 cm^{-1} and 1150 cm^{-1} peaks are attributable to the C–O stretching of polysaccharide-like molecules and C–O stretching of different alcoholic and ether groups, respectively [43]. Both HA and FA were found to have considerable peaks in that area. The absence of peaks in ~1400 cm^{-1} denotes the absence of N-H and C=N stretches in FA. However, a small but considerable peak was observed in HA, indicating the nitrogen presence in HA [40]. The assumption that the investigated substances were HA and FA was further reinforced by the similarity of the acquired spectra with those of earlier research.

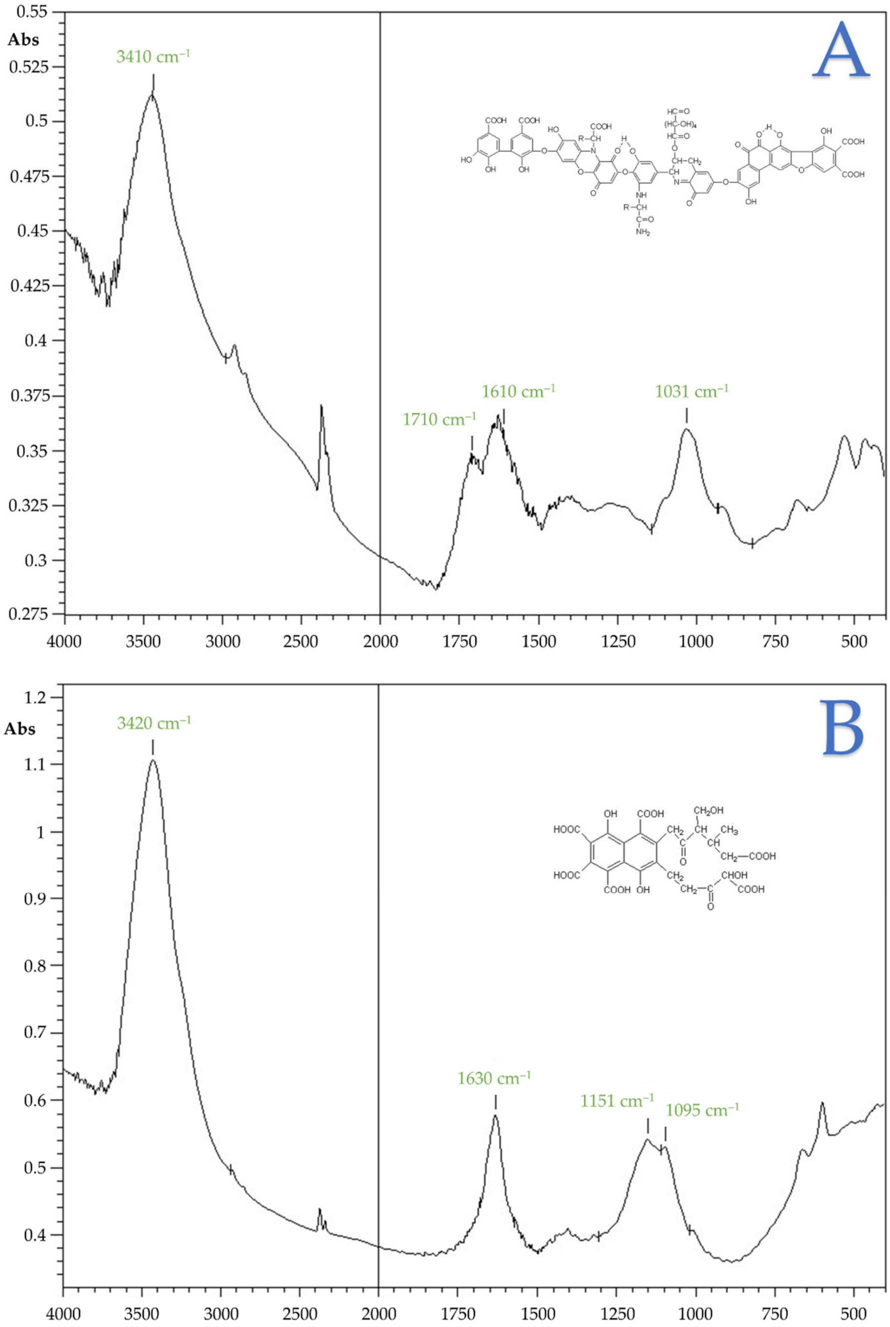

Figure 2. FT-IR spectra of HA (plot (**A**)) and FA (plot (**B**)) along with the structures.

3.2. *Removal of Metals by HA*

The origin of lignite can have an impact on the yield of HA extracted, as well as on their sorption properties [44,45]. Therefore, lignite samples from two mines were examined.

The results from the removal experiments for HA can be seen in Table 1. According to the results, both isolated HAs were able to sorb and remove most of the examined metals. In all cases, as the concentration of HA increased, the removal efficiency statistically significantly increased ($p < 0.05$). The results showed that the HAs from both mines were able to sorb various metals, with different efficiencies. For instance, when 300 ppm HA was used, a high removal capacity for some metals, such as Cu (67.48%), Mo (62.84%), Pb (56.81%), U (49.22%), and Ag (46.95%), was achieved. On the contrary, HAs were not found (≤0.1%) to be able to sorb and remove Al, Ba, Ca, Cr, Fe, Mg, Mn, Na, and Sr, which indicates some selectivity of HAs toward certain metals. It was observed that the removal of most divalent metals, such as alkaline earth metals, was low in both HA sources. The polyelectrolyte and polydisperse nature of humic acids make their interactions with metal ions particularly complicated. From a merely electrostatic, nonspecific connection of metal cations with the net negative charge on the surface of a humic particle to specialized interactions in the creation of complexes and chelates with functional groups, metal ions may form bonds with humic acids in a number of ways [46]. Interfering with ion inhibition is also influenced by the ionic radius, electronegativity, and other parameters [47]. In addition, divalent cations (such as Ca^{2+} and Mg^{2+}) were found to have a more potent competitive impact and steric hindrances than monovalent cations (such as K^+ and Na^+) in a study by Wang et al. [48]. The removal of the other examined metals (As, B, Be, Cd, Co, K, Li, Ni, Se, Tl, V, and Zn) was found to be moderate compared to the above. Irrespective of the lignite source, it is important to highlight that as the concentration of HA increased, a statistically significant difference ($p < 0.05$) in the % removal of most metals from the water sample was observed. This pattern was not consistent in the metals that had 0.1% removal and some individual metals such as Cu and Mo. Regarding the lignite samples from the two mines, it appeared that the lignite from the Mavropigi mine was more effective when 900 ppm of the lignite was used in the metals. By employing 900 ppm of HA sorbent, the removal of As (49.90%), Co (29.90%), Se (64.47%), and Tl (85.96%) was higher in the lignite from Mavropigi mine, whereas lignite from South Field mine was found to be more effective in the removal of Cd (41.08%), K (26.52%), and Zn (49.17%). However, HA from the South Field mine was found to be more efficient at a lower concentration (300 ppm) in certain metals, such as Mo (62.84%), Pb (56.81%), and U (49.22%). It should be noted that regardless of the lignite mine source, the efficiency of humic acids was not adequate in the case of removing alkaline earth metals.

Table 1. % Removal of metals (and their mean logK_d) with 300, 600, and 900 ppm of HA isolated from lignite from two mines.

Metals	**HA from South Field Mine (ppm)**			**HA from Mavropigi Mine (ppm)**		
	300	**600**	**900**	**300**	**600**	**900**
Ag	$46.95 \pm 1.46^{C,c}$ (3.47)	$89.39 \pm 2.88^{B,b}$ (4.15)	$99.35 \pm 3.46^{A,a}$ (5.23)	$40.86 \pm 1.26^{C,c}$ (3.36)	$88.27 \pm 2.68^{B,b}$ (4.10)	$99.78 \pm 3.67^{A,a}$ (5.70)
Al	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
As	$14.47 \pm 0.44^{E,c}$ (2.75)	$24.29 \pm 0.79^{C,b}$ (2.73)	$34.11 \pm 1.16^{B,a}$ (2.76)	$17.69 \pm 0.54^{D,c}$ (2.86)	$33.8 \pm 1.14^{B,b}$ (2.93)	$49.90 \pm 1.56^{A,a}$ (3.04)
B	$14.02 \pm 0.44^{C,c}$ (2.74)	$31.79 \pm 0.99^{B,b}$ (2.89)	$49.56 \pm 1.53^{A,a}$ (3.04)	$14.54 \pm 0.48^{C,c}$ (2.75)	$32.01 \pm 1.03^{B,b}$ (2.89)	$49.47 \pm 1.52^{A,a}$ (3.04)
Ba	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Be	$8.71 \pm 0.27^{C,c}$ (2.5)	$18.07 \pm 0.53^{B,b}$ (02.57)	$27.44 \pm 0.81^{A,a}$ (2.62)	$8.15 \pm 0.25^{C,c}$ (2.47)	$17.61 \pm 0.50^{B,b}$ (2.55)	$27.06 \pm 0.79^{A,a}$ (2.62)
Ca	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)

Table 1. *Cont.*

Metals	**HA from South Field Mine (ppm)**			**HA from Mavropigi Mine (ppm)**		
	300	**600**	**900**	**300**	**600**	**900**
Cd	14.21 ± 0.66 ^{E,c} (2.74)	27.64 ± 1.29 ^{C,b} (2.80)	41.08 ± 1.97 ^{A,a} (2.89)	11.97 ± 0.66 ^{E,c} (2.66)	22.5 ± 1.32 ^{D,b} (2.68)	33.02 ± 1.97 ^{B,a} (2.74)
Co	6.54 ± 0.24 ^{E,c} (2.37)	14.46 ± 0.46 ^{D,b} (2.45)	22.39 ± 0.71 ^{B,a} (2.51)	3.59 ± 0.14 ^{F,c} (2.09)	16.75 ± 0.56 ^{C,b} (2.53)	29.90 ± 0.91 ^{A,a} (2.68)
Cr	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	3.53 ± 0.12 ^{C,c} (2.09)	6.21 ± 0.21 ^{B,b} (2.04)	8.22 ± 0.27 ^{A,a} (2.00)
Cu	67.48 ± 2.12 ^{B,b} (3.84)	98.95 ± 3.55 ^{A,a} (5.20)	99.23 ± 3.71 ^{A,a} (5.16)	48.08 ± 3.17 ^{C,b} (3.49)	98.24 ± 3.45 ^{A,a} (4.97)	99.15 ± 3.66 ^{A,a} (5.11)
Fe	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
K	9.81 ± 0.31 ^{D,c} (2.56)	18.16 ± 0.54 ^{B,b} (2.57)	26.52 ± 0.79 ^{A,a} (2.60)	1.27 ± 0.05 ^{F,c} (1.63)	6.42 ± 0.21 ^{E,b} (2.06)	12.84 ± 0.41 ^{C,a} (2.21)
Li	9.18 ± 0.28 ^{C,c} (2.53)	18.45 ± 0.57 ^{B,b} (2.58)	27.72 ± 0.84 ^{A,a} (2.63)	7.78 ± 0.23 ^{C,c} (2.45)	17.05 ± 0.51 ^{B,b} (2.53)	26.31 ± 0.77 ^{A,a} (2.60)
Mg	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Mn	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Mo	62.84 ± 1.91 ^{C,b} (3.75)	94.05 ± 2.98 ^{A,a} (4.42)	99. 27 ± 4.02 ^{A,a} (5.18)	42.38 ± 1.48 ^{D,c} (3.39)	85.18 ± 2.98 ^{B,b} (3.98)	98.13 ± 3.98 ^{A,a} (4.77)
Na	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Ni	4.18 ± 0.15 ^{C,c} (2.16)	9.24 ± 0.36 ^{B,b} (2.23)	14.30 ± 0.57 ^{A,a} (2.27)	2.28 ± 0.09 ^{D,c} (1.89)	4.24 ± 0.16 ^{C,b} (1.87)	8.48 ± 0.32 ^{B,a} (2.01)
Pb	56.81 ± 2.23 ^{C,c} (3.64)	91.25 ± 3.92 ^{A,B,b} (4.24)	99.86 ± 3.77 ^{A,a} (5.90)	46.31 ± 1.52 ^{D,c} (3.46)	90.31 ± 3.42 ^{B,b} (4.19)	98.67 ± 3.87 ^{A,a} (4.92)
Se	21.74 ± 0.85 ^{E,c} (2.97)	34.21 ± 1.32 ^{D,b} (2.94)	46.69 ± 1.82 ^{B,a} (2.99)	20.14 ± 0.85 ^{E,c} (2.92)	42.31 ± 1.62 ^{C,b} (3.09)	64.47 ± 2.32 ^{A,a} (3.30)
Sr	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Tl	17.20 ± 0.63 ^{E,c} (2.84)	31.85 ± 1.23 ^{D,b} (2.89)	46.51 ± 1.78 ^{C,a} (2.99)	29.86 ± 1.13 ^{D,c} (3.15)	57.93 ± 2.11 ^{B,b} (3.36)	85.96 ± 3.27 ^{A,a} (3.83)
U	49.22 ± 1.86 ^{C,c} (3.51)	88.06 ± 3.44 ^{B,b} (4.09)	99.69 ± 3.95 ^{A,a} (5.55)	37.53 ± 1.42 ^{D,c} (3.30)	81.44 ± 3.16 ^{B,b} (3.86)	98.69 ± 4.01 ^{A,a} (4.92)
V	28.70 ± 1.09 ^{C,c} (3.13)	61.67 ± 2.32 ^{B,b} (3.43)	94.64 ± 3.64 ^{A,a} (4.29)	33.77 ± 1.25 ^{C,c} (3.23)	64.51 ± 2.42 ^{B,b} (3.48)	95.24 ± 3.67 ^{A,a} (4.35)
Zn	11.42 ± 0.43 ^{E,c} (3.63)	30.29 ± 1.16 ^{C,b} (2.86)	49.17 ± 1.87 ^{A,a} (3.03)	14.28 ± 0.44 ^{E,c} (2.74)	26.71 ± 1.06 ^{D,b} (2.78)	39.13 ± 1.53 ^{B,a} (2.85)

Capital letters (i.e., A–F) denote statistically significant differences ($p < 0.05$) among the same metal of the various concentrations and mines. Small letters (i.e., a–c) denote statistically significant differences ($p < 0.05$) for the various concentrations of the same mine. Data are presented as mean ± standard deviation of triplicate determinations.

In a previous study [49], HAs were examined for their ability to be used as sorbents for Cu, Fe, Pb, Ni, Co, Ca, Cd, Zn, Mn, and Mg. According to the results, HA could effectively sorb the abovementioned metals, when the pH of the water was adjusted to 3.5. Under these conditions, it was found that 1 mol of HA can bind 1 mol of Cu or Fe, while it can bind 2 mols of Ni, Co, Cd, Zn, Mn, and Mg. The above percentages were attributed to the mechanism of interaction for the removal process. In general, HAs were found to sorb the metal ions via their acidic carboxyls and their phenolic carboxyls [49]. Compared to our case, a different removal behavior was observed. HAs were not found able to sorb Fe, while the removal efficiency for each metal was found to be different (Cu > Mo > Pb > U > Ag > V>S > Tl > As > Cd > B>Zn > K>Li > Be > Co > Ni > Na, Mg, Al, Ca, Cr, Mn, Fe, Sr, Ba) compared to the above study (Cu > Fe > Pb > Ni > Co > Ca > Cd > Zn > Mn > Mg). This can be partially justified by the fact that in the study of Padney et al. [49], the removal efficiency was examined by using a single metal in each batch experiment, and not altogether. When more than one metal is present in the sample solution, binding sites can be occupied by other metals and decrease the removal efficiency for one specific metal. This was the case in the study of Klucakova et al. [46]. In this study, it was showcased that HA exhibited 100% removal efficiency for Cu when it was the only metal in the solution, while the removal efficiency decreased by almost 10% when Cd, Pb, and Zn were also present in the solution. Therefore, it is easily conceived that when more metals are present in the water sample, interactions are more complex and the overall removal efficiency can vary. In addition, another important parameter that can affect the overall removal process is the pH of the solution, since it can affect the dissociation of the functional groups on the surface of HA. Moreover, at a pH below five, hydrogen ions can compete with the metals for the binding sites on HA functional groups, resulting in lower extraction efficiencies. As such, examining the removal behavior at pH values above five can be considered an asset, since it both resembles more realistic conditions, and interactions with hydrogen ions are avoided [49]. Another reason for the overall lower removal efficiency recorded in our case is the concentration of the HA that was used. In a previous study, it was found that HAs exhibit 100% removal efficiency for Fe (6.68 ppm) and Pb (8.52 ppm) [50]. However, in order to achieve such efficiency, 5 g/L of HA was used. This is nearly five times more HA compared to our highest tested concentration. Combined with the fact that only two metals were examined, the removal efficiency was found to be increased.

Another benefit of using HA for the removal of metals is that they can increase the pH value of the treated water or maintain it at a constant value, due to the absorbance of hydrogen ions [50]. This can help to increase the quality of water for marine organisms. In our case, no changes in the pH value of the water were recorded prior to and after the removal process. This is probably due to the fact that the pH value was 8.5, so the concentration of hydrogen ions was infinitesimal and their removal by HA did not significantly affect the overall pH value. As a result, it is important to emphasize that pH adjustment is not required to ensure efficient extraction.

3.3. Removal of Metals by FA

The results of the removal of various metals using FA isolated from lignite from two mines are presented in Table 2. According to the results, for all the metals tested, an increase in the concentration of FA from 300 to 900 ppm resulted in higher metal removal percentages (statistically significant at $p < 0.05$), while minor variations, depending on the mine from which the lignite was sourced, were recorded. It can be seen that almost 100% of the metals, Ag, Ca, Cu, Na, Pb, Sr, and V, were sorbed and removed from FA in both mines, indicating their high affinity for FA. Likewise, Mg, Al, Cr, and Fe were not sorbed ($\leq$0.1%) in any tested concentration of FA. Statistically ($p < 0.05$) higher removal was observed in the Mavropigi mine compared to the South Field mine in the metals Cd, Co, Mo, Tl, and Zn when 900 ppm of FA was employed. On the contrary, FA from South Field sorbed the metals B, Li, and U with significantly higher removal percentage in the same concentration. What is most interesting is the greater affinity of FA with more metals than HA, irrespective of the lignite source. Metals such as Ba, Ca, Na, and Sr were removed at a considerable rate. Specifically, the latter three metals were almost removed (~100%) from the water sample when 900 ppm FA was used, whereas metals such as K and Ni also had a significantly higher removal rate (>40%). It could be concluded that more metals were removed using FA due to functional groups on the surface of the specific sorbent that can result in up to 20 times higher capacity for metal ions compared to HA [51].

Table 2. % Removal of metals (and their mean logK_d) with 300, 600, and 900 ppm of FA isolated from lignite from two mines.

Metals	**FA from South Field Mine (ppm)**			**FA from Mavropigi Mine (ppm)**		
	300	**600**	**900**	**300**	**600**	**900**
Ag	48.24 ± 1.64 ^{C,c} (3.49)	89.33 ± 2.92 ^{B,b} (4.14)	99.19 ± 3.78 ^{A,a} (5.13)	42.72 ± 1.67 ^{C,c} (3.40)	85.96 ± 3.03 ^{B,b} (4.01)	98.45 ± 3.92 ^{A,a} (2.05)
Al	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
As	14.12 ± 0.55 ^{D,c} (2.74)	24.34 ± 1.11 ^{C,b} (2.73)	34.57 ± 1.31 ^{B,a} (2.77)	14.24 ± 0.52 ^{D,c} (2.74)	26.37 ± 0.99 ^{C,b} (2.78)	38.51 ± 1.50 ^{A,a} (2.84)
B	16.26 ± 0.65 ^{E,c} (2.81)	30.68 ± 1.19 ^{D,b} (2.87)	45.10 ± 1.54 ^{B,a} (2.96)	15.87 ± 0.61 ^{E,c} (2.80)	34.51 ± 1.35 ^{C,b} (2.94)	53.15 ± 2.03 ^{A,a} (3.10)
Ba	10.51 ± 0.46 ^{E,c} (2.59)	22.36 ± 0.72 ^{C,b} (2.68)	34.22 ± 1.26 ^{B,a} (2.76)	14.22 ± 0.55 ^{D,c} (2.74)	24.72 ± 1.14 ^{C,b} (2.74)	37.77 ± 1.53 ^{A,a} (2.83)
Be	9.94 ± 0.43 ^{C,c} (2.57)	17.75 ± 0.74 ^{B,b} (2.56)	25.56 ± 1.2 ^{A,a} (2.58)	8.57 ± 0.35 ^{C,c} (2.49)	17.14 ± 0.69 ^{B,b} (2.54)	25.72 ± 0.99 ^{A,a} (2.59)
Ca	51.85 ± 1.93 ^{B,b} (3.56)	98.76 ± 3.4 ^{A,a} (5.12)	99.58 ± 5.21 ^{A,a} (5.42)	52.01 ± 1.99 ^{B,b} (3.56)	98.34 ± 2.7 ^{A,a} (4.99)	99.12± 3.71 ^{A,a} (5.10)
Cd	15.80 ± 0.51 ^{C,c} (2.80)	27.73 ± 1.12 ^{B,b} (2.81)	39.65 ± 1.45 ^{A,a} (2.86)	7.86 ± 0.29 ^{D,c} (2.45)	17.09 ± 0.69 ^{C,b} (2.54)	26.32 ± 0.91 ^{B,a} (2.60)
Co	8.23 ± 0.32 ^{D,c} (2.48)	14.70 ± 0.61 ^{B,b} (2.46)	21.16 ± 0.81 ^{A,a} (2.47)	5.97 ± 0.26 ^{E,c} (2.33)	10.48 ± 0.44 ^{C,b} (2.29)	14.99 ± 0.56 ^{B,a} (2.29)
Cr	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Cu	52.57 ± 1.96 ^{C,b} (3.57)	98.12 ± 3.5 ^{A,a} (4.94)	99.89 ± 3.84 ^{A,a} (6.00)	46.26 ± 1.79 ^{C,c} (3.46)	90.12 ± 3.22 ^{B,b} (4.18)	99.95 ± 3.36 ^{A,a} (6.35)
Fe	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
K	23.75 ± 0.88 ^{C,c} (3.02)	47.50 ± 1.92 ^{B,b} (3.18)	71.25 ± 2.72 ^{A,a} (3.44)	21.55 ± 0.78 ^{C,c} (2.96)	47.50 ± 2.02 ^{B,b} (3.18)	68.45 ± 2.63 ^{A,a} (3.38)
Li	10.98 ± 0.41 ^{D,c} (2.61)	19.27 ± 0.71 ^{C,b} (2.60)	27.56 ± 0.98 ^{B,a} (2.63)	12.8 ± 0.45 ^{D,c} (2.69)	26.19 ± 1.02 ^{B,b} (2.77)	39.54 ± 1.52 ^{A,a} (2.86)
Mg	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Mn	3.34 ± 0.15 ^{C,c} (2.06)	5.97 ± 0.23 ^{B,b} (2.02)	8.60 ± 0.32 ^{A,a} (2.02)	≤0.1 (≤0.52)	≤0.1 (≤0.22)	≤0.1 (≤0.05)
Mo	43.78 ± 1.61 ^{C,c} (3.41)	79.60 ± 2.81 ^{B,b} (3.81)	97.67 ± 4.61 ^{A,a} (4.67)	23.57 ± 0.82 ^{D,c} (3.01)	49.12 ± 1.75 ^{C,b} (3.21)	74.66 ± 2.91 ^{B,a} (3.52)
Na	56.1 ± 2.19 ^{B,b} (3.63)	98.76 ± 3.82 ^{A,a} (5.12)	99.59 ± 4.75 ^{A,a} (5.43)	41.1 ± 1.54 ^{C,b} (3.37)	98.12 ± 4.13 ^{A,a} (4.94)	99.28 ± 4.52 ^{A,a} (5.19)
Ni	17.99 ± 0.68 ^{D,c} (2.86)	31.02 ± 1.19 ^{B,b} (2.87)	44.05 ± 1.71 ^{A,a} (2.94)	19.17 ± 0.81 ^{D,c} (2.90)	26.67 ± 1.08 ^{C,b} (2.78)	44.17 ± 1.72 ^{A,a} (2.94)
Pb	48.37 ± 1.72 ^{C,b} (3.49)	91.26 ± 3.38 ^{A,B,a} (4.24)	99.36 ± 4.90 ^{A,a} (5.24)	50.96 ± 1.88 ^{C,c} (3.54)	87.86 ± 3.54 ^{B,b} (4.08)	98.13 ± 5.73 ^{A,a} (4.77)
Se	19.51 ± 0.64 ^{C,c} (2.91)	34.84 ± 1.33 ^{B,b} (2.95)	50.18 ± 2.05 ^{A,a} (3.05)	20.68 ± 0.70 ^{C,c} (2.94)	36.93 ± 1.55 ^{B,b} (2.99)	53.17 ± 2.04 ^{A,a} (3.10)
Sr	39.33 ± 1.66 ^{C,c} (3.33)	85.50 ± 3.32 ^{B,b} (3.99)	97.89 ± 3.81 ^{A,a} (4.71)	37.48 ± 1.46 ^{C,c} (3.30)	87.15 ± 2.89 ^{B,b} (4.05)	98.12 ± 3.19 ^{A,a} (4.76)
Tl	17.46 ± 0.52 ^{C,c} (2.85)	31.75 ± 0.98 ^{B,b} (2.89)	46.04 ± 1.93 ^{A,a} (2.98)	10.73 ± 0.43 ^{D,c} (2.60)	20.24 ± 0.79 ^{C,b} (2.63)	29.76 ± 1.07 ^{B,a} (2.67)
U	8.49 ± 0.38 ^{D,c} (2.49)	16.65 ± 0.54 ^{C,b} (2.52)	24.81 ± 0.81 ^{B,a} (2.56)	14.87 ± 0.51 ^{C,c} (2.77)	27.06 ± 0.94 ^{B,b} (2.79)	39.24 ± 1.49 ^{A,a} (2.86)
V	54.42 ± 2.15 ^{B,b} (3.60)	96.12± 3.83 ^{A,a} (4.62)	98.45 ± 5.42 ^{A,a} (4.85)	53.73 ± 2.04 ^{B,b} (3.59)	95.65 ± 3.76 ^{A,a} (4.56)	98. 21 ± 5.53 ^{A,a} (4.79)
Zn	14.64 ± 0.58 ^{D,c} (2.76)	30.50 ± 1.17 ^{B,b} (2.86)	46.36 ± 1.84 ^{A,a} (2.98)	11.01 ± 0.46 ^{E,c} (2.62)	20.03 ± 0.74 ^{C,b} (2.62)	29.04 ± 1.19 ^{B,a} (2.66)

Capital letters (i.e., A–E) denote statistically significant differences ($p < 0.05$) among the same metals of the various concentrations and mines. Small letters (i.e., a–c) denote statistically significant differences ($p < 0.05$) for the various concentrations of the same mine. Data are presented as mean ± standard deviation of triplicate determinations.

Despite the many functional groups (such as carboxyl, phenolic hydroxyl, alcoholic hydroxyl, amino, etc.) on the surface of FAs (more functional groups contained compared to HA [51]) that make them suitable for heavy metal removal, the reports discussing their use as sorbing materials are scanty and sparse. In a previous study, it was showcased that FAs can effectively remove Cu from water [52]. Moreover, the affinity toward various metals is different. This is due to the functional groups on the surface of FA, since nitrogen-containing functional groups tend to bind stronger with metals, forming more stable complexes compared to oxygen-containing groups. However, the affinity for metals is also affected by the ionic and hydration radii of metal ions [51]. Finally, the region where the raw materials were sourced can have an impact on the removal performance, since it can affect the structure and functional group content of FA [53]. This is also showcased from our results, since it can be seen that FA from lignite from the two mines results in different removal percentages. Finally, in the study of Lalas et al. [54], it was suggested that FA can effectively remove Cd, Cr, Cu, Ni, and Pb from water. Moreover, it was suggested that FAs are more effective for the removal of Cr > Pb > Ni > Cu > Cd. However, the efficiency differs when the removal is examined from samples containing two metals simultaneously compared to a single metal study. This can justify the results obtained in our case, where it was found that Cr was not sorbed, while higher removal efficiency was recorded for Cu. By studying the removal performance in the presence of many metals simultaneously, a better overview of their efficiency is achieved. Finally, by comparing the removal efficiency between HA and FA, it occurs that FAs are more efficient in most cases to sorb the tested metals.

3.4. Spectroscopic Measurement of Sorption

Modeling the sorption process is a challenging task considering the numerous physical and chemical processes that take place. Conducting kinetic experiments and isotherm studies for a single metal involves meticulous control over experimental conditions, ensuring precise measurements over time. Although experimental data for single-metal sorption can be easily gathered, practical situations frequently necessitate the simultaneous sorption of multiple components onto a heterogeneous sorbent surface. Dynamic interactions between metal ions and functional groups are complex, which further complicates the kinetic modeling of such systems [55]. Numerous metals (transition metals, alkali metals, and alkaline earth metals) are frequently present in effluents from natural waters or wastewater. Recent studies [56,57] have provided evidence that adsorption isotherms actually aid in the development of a broader understanding of the adsorption mechanism. However, the majority of research studies concentrate on the adsorption of one [56–58], two [59–61], or even three metals [62]. In our case, the simultaneous sorption of 26 metals introduces a level of complexity that exponentially increases the number of variables and experimental permutations. This complexity extends to factors such as metal interactions (additive, synergistic, and antagonistic), competition for sorption sites, and dynamic changes in solution composition. Furthermore, several prominent isotherms, including Langmuir, Freundlich, and Dubinin–Radushkevich, rely on a number of assumptions which deserve considerable attention. The mentioned isotherms require monolayer sorption on a surface free of steric hindrances [63], and reliance on a single parameter [64], or the utilization of uniform microporous materials [65], respectively. As a result, no such study (kinetics and sorption isotherms) was carried out. The verification of the sorption process was conducted multiple times using a photometric approach in a test–retest stability study. Figure 3 illustrates the sorption outcomes of both HA and FA obtained from the respective mines. The absorbance of each solution was measured, beginning with water samples contaminated with 10 ppb of metals (control). It was evident that the absorbance in this case was exceptionally minimal (~0.02). A quantity of 600 ppm of each sorbent was introduced in another cuvette (blank), resulting in a notable increase in absorbance (>0.10 in most cases). Nevertheless, when the sorbent and the metals were mixed (sample), the absorbance was found lower compared to the cumulated value (theoretical sum of control and blank), strengthening the evidence of the sorption process. Absorbance of the South Field mine FA sorbent (sample) was still lower than theoretical (~0.15), but greater than the blank solution, which is especially intriguing. A possible reason could be the cumulated adsorption of this particular sorbent. Both HA and FA exhibited UV absorbance peaks. Specifically, the absorbance peak of both acids had a wavelength level of ~300 nm. The wavelength level could be attributed to the presence of an alkyl-substituted benzene ring structure and several π-bonds within both acids [66].

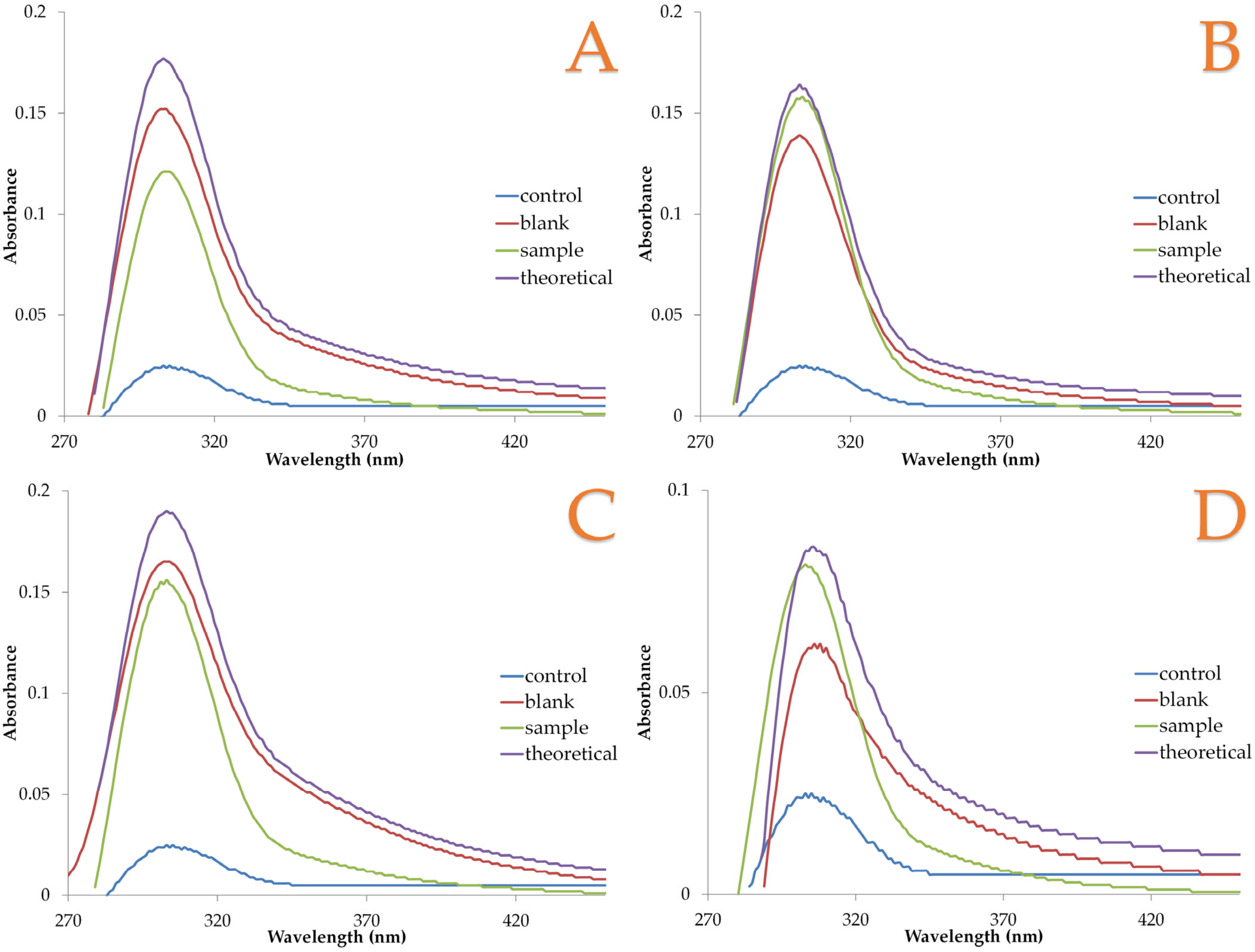

Figure 3. UV-Vis absorption spectra of control, blank, their mixture (sample), and the sum of the first two spectra (theoretical). Plots (**A**,**B**) showed HA and FA from the South Field mine, while plots (**C**,**D**) showed HA and FA from the Mavropigi mine.

3.5. Principal Component Analysis (PCA)

PCA was employed to shed light on the correlation in several variables and to perform a more thorough examination of the data. It was intended to examine whether any correlation between the 26 analyzed metals and the two sorbents (HA and FA in concentrations of 300, 600, and 900 ppm) was observed. Figure 4 shows the identification of two principal components that together accounted for 97.44% of the variance based on their eigenvalues > 1. PC1 accounted for 72.6% of the variance, whereas PC2 accounted for 24.9% of the variance, respectively. The results showed that there was either a positive or negative correlation between the parameters. Parameters such as Ca, Na, Sr, V, Ag, Pb, Cu, Mo, U, Se, and U had positive correlation with PC1, whereas parameters such as Fe, Mn, Cr, Co, Be, Li, As, Zn, B, Tl, U, Se, Ag, Pb, and Cu had positive correlation with PC2. The parameters of sorbents were separated and grouped appropriately, as shown in Figure 3. However, the position and distribution of the metals in the four quartiles are of high interest. For instance, Cu, Ag, Pb, Se, and Tl had high percentage of removal (>60%) and were positioned in the first quartile and close to both sorbents. In addition, some metals had a higher removal percentage on a particular sorbent and were positioned closer to this sorbent and further away from the other, respectively. For example, Mo and U were positioned closer to HA in the first quartile, whereas V, Na, Ca, and Sr, which were positioned to the fourth quartile, had higher proximity to FA. Specifically, the three latter metals showed the lowest removal rate with HA ($\leq$0.1%), but the highest with FA, reaching almost 100%. Finally, metals that exhibited moderate removal rate (<60%), such as As, B, Be, Cd, Co, and Li, were found in the second quartile, whereas metals that showed the lowest removal rate in both sorbents such as Fe, Mn, and Cr were found in the same quartile but far from both sorbents.

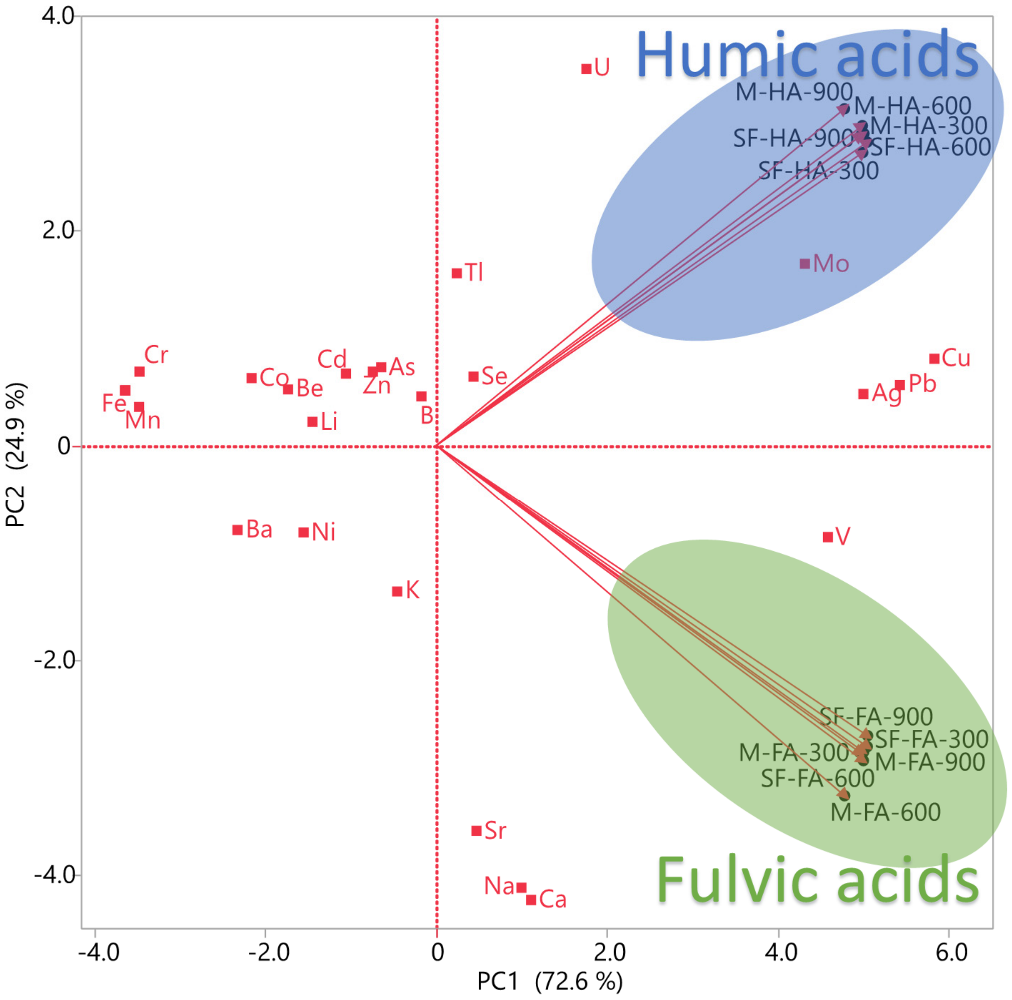

Figure 4. Principal component analysis (PCA) for the examination of the correlation between the metal and sorbent parameters. The sorbents humic acids (HAs) and fulvic acids (FAs) in concentrations of 300, 600, and 900 ppm from two different mine sources (Mavropigi—M; and South Field—SF).

4. Conclusions

The potential of HA and FA to be used as sorbing agents for 26 heavy metals, alkali metals, and alkaline earth metals was examined. Sorbents HA and FA were collected from two different mine sources (Mavropigi and South Field). According to the results, both HA and FA can be used for the removal of most of the examined metals, with varying efficiencies. Regarding the source of the lignite, it was observed that lignite from Mavropigi mine successfully removed metals As, B, Se, and Tl at high concentrations (900 ppm), whereas lignite from South Field mine was found to be more efficient at lower concentrations (300–600 ppm) for metals Cd, Mo, Pb, and U. In addition, the efficacy of humic acids in the removal of alkaline earth metals (Be, Mg, Ca, Sr, and Ba) was found to be inadequate, which might be due to the highly competitive effect from divalent cations. The removal capacity was quite low for Be, reaching only around ~27%. Likewise, the removal capacity for Ba, Ca, Mg, and Sr was practically insufficient ($\leq$0.1%). However, the results revealed that FA, irrespective of the mine source, was more effective in removing most metals that HA did not even sorb, such as Ba, Ca, Na, and Sr, with a rate close to 100%. This finding highlights the superiority of FA in metal removal as compared to HA. The fact that real water samples were used without any pH adjustment gives a better overview of the resulting removal in systems that better resemble real-life conditions. Additionally, the application of the PCA plot enhanced comprehension regarding the sorption and distribution of metals in HA and FA, since the metals were placed near the sorbents with the highest removal rate. An illustration of this can be seen in the proximity of Mo and U to HA, and V, Na, Ca, and Sr to FA. Overall, HA and FA are highly promising materials with potential applications in remediation of water sources, while their applicability can be further extended for the remediation of soils. The fact that HA and FA are abundant in nature, and can easily and cost-effectively be extracted, can be an asset for the development of a removal process. Moreover, HA and FA can further be used in conjunction with other sorbent materials in an effort to further enhance their removal properties and render existing sorbents more efficient. The use of static conditions in this study provides a foundation for future studies that may explore sorption under dynamic conditions in more detail. The outcomes of the static experiments can guide the design and parameters of subsequent dynamic studies, ensuring a more informed and targeted approach to understanding sorption behavior in flowing water systems.

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