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Presence of Humic Acids in Landfill Leachate and Treatment by Flocculation at Low pH to Reduce High Pollution of This Liquid

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Abstract: Humic substances are abundant in landfill leachate, especially humic acids, which are insoluble at low pH in aqueous solutions. Focusing on the chemical properties of humic acids, we describe in this work a new method for a sustainable treatment of landfill leachate originated from solid wastes, which consists of the reduction of organic load (COD, chemical oxygen demand) and colour and is based in the gradual decrease in pH to the value in which HAs are insoluble in water solution. Zeta potential values mark the chemical stage of humic acids because of ionisation–protonation of the phenolic and carboxylic groups, and this parameter is monitored during flocculation, changing from −16.8 mV at pH 7.7 to 0.0068 mV at pH 2.0, when HAs precipitate. The final result is the reduction in the organic matter content (COD) and colour in the leachate, 86.1% and 84.7%, respectively. Solids produced by precipitation during the acidification treatment have been characterized by elemental chemical analysis and Fourier transform infrared spectrometry, concluding a high similarity in chemical composition with commercial and natural humic acids. Protonated humic acids at low pH can interact with other molecules by hydrogen bonds and form bigger molecular structures much more unstable in suspension, which conduct to precipitation. The mean diameter of the humic acids aggregates was measured, detecting the formation of big molecular structures at low pH. This process is analysed and compared economically with other processes proposed for landfill leachate treatment, resulting in a promising technique for the management of this residue.

Keywords: waste management; landfill leachate treatment; flocculation; humic acids; pH

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1. Introduction

Landfill leachate is a liquid produced by concentration and storage of the highly polluted liquid originated from solid wastes deposited in the landfill and is considered a complex liquid with high content of organic matter, ammonia, sulphate, chloride, and metals [1,2]. This liquid can be treated by biological treatment to reduce organic matter and toxicity [3,4] or by other treatment processes like flocculation, chemical oxidation, or reverse osmosis [5–7]. The nature and concentration of the organic matter in landfill leachate are the main factors affecting the successful treatment of this liquid.

Concentration of organic matter can be very different in landfill leachates, and normally, when the COD value is low, landfill leachate can be processed by biological treatment [1,2,8,9]. In high organic loaded leachates, the reduction of COD is normally not well performed [10–12]. Organic matter present in these high organic loaded leachates has the origin mostly in composting of organics from solid wastes (composting leachate) [13–15].

Biological treatment combined with flocculation or oxidation is accepted currently as the most effective treatment of landfill leachates [16–19]. Flocculation is economically sustainable, compared to other processes like ozonation or Fenton oxidation [20–22]. If biological treatment is planned to be applied, the biodegradability of the organic compounds present in the leachate has to be considered [23].

In landfill leachates, the presence of humic substances (HSs) has been described in the literature [24–26]. Especially in composting leachate, the odour which is proximate to wood soil and the dark yellow and black colours of most landfill leachates are produced by HSs [27–29]. HSs are known to be recalcitrant compounds [30,31] and conduct to low reduction of COD in the biological treatment. They have been cited to be abundant in landfill leachates, reaching sometimes 60% of the total organic matter [30,32].

HSs are divided into two fractions: humic and fulvic acids (HAs and FAs), with different solubility pertaining to pH [33]. HAs are insoluble at low pH and FAs are soluble at low, medium, and high pH [24,32,34,35]. The insolubility of HAs when the pH is low is due to the protonation under acidic conditions of the functional groups which are present in these substances: carboxylic acids and phenolic alcohols. The difference in the pH-dependent forms of the carboxylic acids and phenols produces a Zeta potential variation due to ionisation–protonation [36]. In addition, protonation of the functional groups of the HAs at low pH can facilitate the formation of H-bonds among different molecules and induce flocculation of the intermolecular structures formed. At a higher pH (slightly acid or neutral), carboxylic acids and phenolic alcohols are ionized, and the Zeta potential increases because of the formation of positive ions in the HA surface. This increase in the Zeta potential absolute value as a consequence of ionisation of the functional groups of HAs can maintain in suspension HAs because of electrostatic repulsion between different molecules. In the literature, ionisation of carboxylic acids at a pH over 3.5–4.0 and phenolic groups over 5.5–6.0 is reported [37]. In accordance with these considerations, flocculation of HAs from landfill leachate has to be performed at low pH, because at a slightly acidic, neutral, or high pH, HAs will be maintained in suspension [38].

In this article, we prove an important presence of HAs in landfill leachate, which proceed from composting leachate, a frequent situation in high-COD leachates. These recalcitrant organics are flocculated at low pH in accordance with their chemical properties and stability of aqueous suspensions. Flocculation at low pH is the main treatment for the reduction in recalcitrant compounds (HAs), and the explanation of this novel procedure is focused on the chemical properties of HAs at different pH values. Flocculation at low pH significantly reduces the COD value of landfill leachates, especially with high organic load, and is considered an effective and sustainable treatment of this polluted liquid. The presence of HAs in landfill leachate was proved via elemental chemical analysis (CHNS) and infrared spectrometry (FT-IR), and the evolution of the molecular size of the HAs and aggregates are monitored by the analysis of the mean diameter during the flocculation at low pH.

2. Materials and Methods

2.1. Characterisation of Landfill Leachate

Landfill leachate was characterized in a laboratory analysing the samples collected in the leachate deposit (March–June) of the Waste Treatment Centre (WTC) of Salamanca, Spain. In the characterisation of this highly polluted liquid, pH, organic load (chemical oxygen demand, COD), colour, solids (total solids, TS and volatile solids, VS), nitrogen compounds (organic nitrogen, ammonia, nitrates, and nitrites), phosphate, sulphate, chloride, and metals were measured by the standard methods described in the literature [39].

The pH was measured using a pHmeter with precision 0.1 pH units (CRISON MicropH 2000, Crison, Barcelona, Spain).

COD and colour were chosen for monitoring the effectivity in the treatment of landfill leachate by flocculation at low pH. COD was measured in triplicate by the colorimetric closed reflux method (5220D, [39]), using $HgSO_4$ to avoid the interference of Cl^- as described in the standard method (precipitation of $HgCl_2$). Because of the high concentration of organics in leachate (high COD value), samples were diluted 8 times, and a pattern calibration line was used for COD values in the range 2000–20,000 mg/L (potassium hydrogen phthalate). Because of the presence of HSs in the landfill leachate which can interfere in colour analysis, the spectrophotometric method was selected for measuring colour by detecting the maximum absorbance wavelength (chromatic method, method 2120C, [39]).

Solids were analysed by the standard methods described in the literature for total and volatile solids, based on thermal treatment at 105 °C and 550 °C (TS: 2540B, VS: 2540E [39]).

Organic nitrogen (N_{org}) and ammonia (NH_4^+) were analysed with the standard method (Kjeldahl, 4500-NH_3 B and E, [39]) after filtration by Millipore filters (0.45 µm). N_{org} analysis was performed performing a previous digestion in H_2SO_4 before Kjeldahl distillation (4500-N_{org} B, [39]).

Samples were also filtered using Millipore filters (0.45 µm) for NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, and Cl^- analysis and measured via ionic chromatography (ICS 2000 ISO 10304-1 [40], Dionex, Thermo Fisher Scientific, Madrid, Spain). ICS 2000 measurement conditions for 10 µL injection volume were as follows: cell temperature: 35 °C, column temperature: 30 °C, eluent flow rate: 1.00 mL/min (35 mM KOH), and applied current: 50 mA. The column used was 4 × 250 mm IonPac AS19, and the guard was 4 × 50 mm IonPac AG19 (Dionex, Thermo Fisher Scientific, Madrid, Spain). The software Chromeleon 6.5 SP2 of Dionex was employed for calibration and measurement of all these anions together in a unique chromatogram.

Metals present in leachate were analysed via ICP-MS (Agilent 7800, Agilent Technologies, Madrid, Spain, Chemical Analysis Service of the University of Salamanca). Because of the high organic content in landfill leachate, the samples were treated with concentrated nitric acid in a closed Teflon glass (50 mL final sample volume). The ICP-MS spectrometer was calibrated with two multi-element patterns prepared from certificated Panreac standard solutions (1000 mg/L). Measurement flux conditions of the ICP-MS were as follows: plasma gas: 15 L/min, auxiliary gas: 0.9 L/min, nebulisation gas: 0.99 L/min, and cell gas (Helio): 4.5 mL/min.

2.2. Analysis of Humic Acids

HAs analysis in the literature is based on a suggested method with two variants, depending in concentration (5510, [39]). In natural waters with a low HSs content, the method proposed is a concentration of HSs by using ionic exchange columns and the measurement of dissolved organic carbon (DOC) [41]. In liquids with high HSs content, HAs have to be precipitated at acid pH, attending the chemical properties of HAs by the method described by Christensen et al., 1998 [30,32,34]. Following the method of Christensen et al., 200 mL leachate samples were acidified with HCl concentrated to pH = 1.0 and placed for 24 h. The precipitate after this time was purified twice during 48 h in total with 100 mL acid solution (0.5% HF v/v and 0.5% HCl v/v). The resulting precipitate, filtered by Millipore filters (0.45 µm), was purified 3 times with HCl acid solution (pH 2.0), separated in small portions, and placed for a further analysis in an incubator (35 °C, 5 days).

HAs obtained by the procedure described before were characterized via CHNS analysis using a LECO CHNS-932 analyzer (Leco Instruments, Madrid, Spain, Elemental Microanalysis Service of the UCM, Madrid University) and infrared spectrometry (FT-IR,

Perkin Elmer SpectrumTwo, Perkin Elmer-Pharmatech, Madrid, Spain). Infrared spectra were obtained from samples prepared in pellets of the HAs from leachate and commercial AHA (Aldrich humic acid) in KBr, measuring the absorbance in the range of wavenumber 4000–400 cm^{-1}.

2.3. Reduction in pH

The reduction in pH in landfill leachate was performed using H_2SO_4 9 M for acidification. Samples were collected during pH reduction separated by 0.5 units of pH and COD, colour, and Z potential were quantified in triplicate to monitor leachate treatment related to the chemical properties of the HAs.

Zeta potential and mean diameter were analysed in samples using the same equipment (Malvern Zetasizer Nano ZS, Malvern Panalytical, Massy, France).

3. Results and Discussion

3.1. Composition of Landfill Leachate

Composition of landfill leachate is shown in Table 1 where most important parameters are recorded (pH, organic load, solids, colour, and nutrients). COD value is very high: 42,000 ± 2516 mg/L, in view of other data from the literature [1,2,4] but is coincident with values for leachates with a high content of organic matter [24,42]. The high value of the organic matter concentration is due to the characteristics of this liquid, produced from the solid wastes deposited in the landfill and the liquid originated from them, and mixed with the fluid residue proceed from composting of the organic fraction of these solids (composting leachate) [43]. As a consequence of aerobic oxidation of organic matter, composting process produces the formation of HSs, conducing to the formation of alcohols (phenols) and especially carboxylic acids [44].

Table 1. Characterisation of landfill leachate described by the most important parameter values: pH, organic load (COD), solids (total and volatile solids, TS and VS), colour, nutrients (nitrogen and phosphorous compounds), sulphate and chloride. In nutrient analysis (N-compounds, SO_4^{2-}, PO_4^{3-} and Cl^-) five independent samples of landfill leachate were obtained in spring (March–June) from the WTC. Samples of pH, COD, TS, VS, and colour were analysed in triplicate from one sample from the WTC.

Parameter	Mean ± SD
pH	7.7 ± 0.1
COD	42,000 ± 2516
TS	16,410 ± 486
VS	10,076 ± 620
Colour	0.537 ± 0.000
N_{org}	3795 ± 314
NH_4^+	2484 ± 340
NO_3^-	417 ± 115
NO_2^-	11 ± 1
SO_4^{2-}	223 ± 64
PO_4^{3-}	39 ± 18
Cl^-	11,710 ± 1978

Concentrations in mg/L, except pH (pH units) and colour (ABS_{474nm}).

The value of solids is high in leachate (total solids, TS: 16,410 ± 486 mg/L), with high proportion of organic solids: more than 60% of TS are vs. (VS = 10,076 ± 620 mg/L, Table 1).

Colour in landfill leachate has been analysed frequently in the literature by the method of the Pt-Co scale [45,46], which compare the tonality of the liquid with prepared standard solutions of K_2PtCl_6 with $CoCl_3$. This method does not reflect the real colour of this liquid because the maximum wavelength absorbed is not measured.

The analysis of colour in the leachate was performed by the chromatic method described in Section 2.1, which obtains the predominant wavelength absorbed by this liquid, shown in Figure 1. Although colour in the leachate can change after flocculation at low pH, by this method, the original colour of the liquid was measured. This predominant wavelength was 474 nm, which is assigned in the chromaticity diagram to dark blue tonalities. The quantitative value of colour obtained is high in Table 1 (ABS = 0.537), and the external appearance of this liquid is dense with a dark brown colour and a blue-yellowish iridescence.

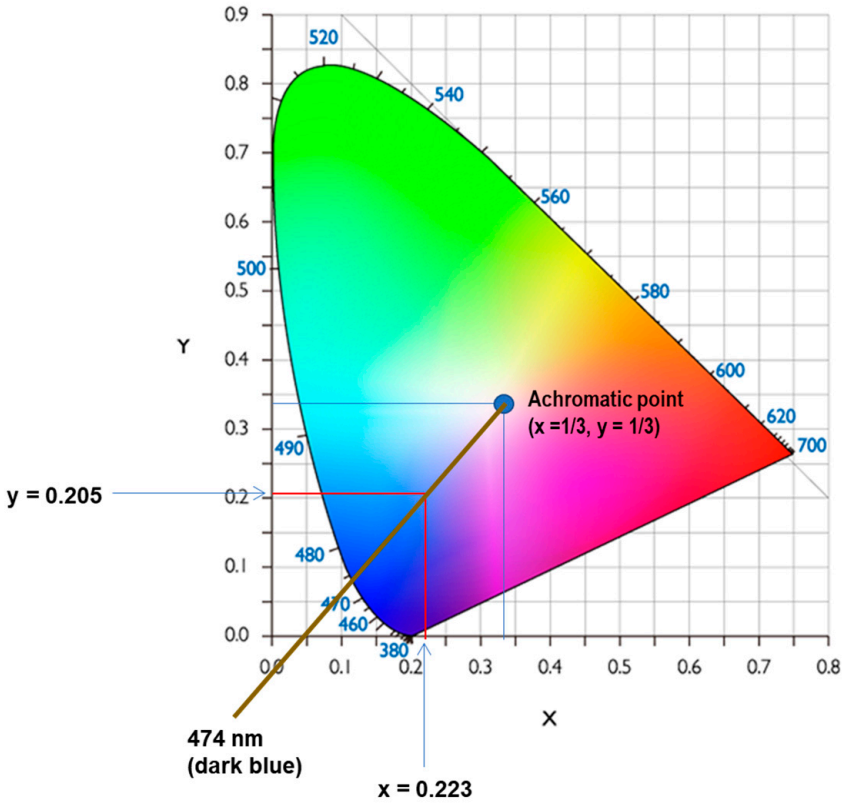


Figure 1. Chromaticity diagram for landfill leachate, where x = 0.223 and y = 0.205 are the trichromatic coefficients obtained by spectrophotometric method for colour analysis (2120C, [39]). Dominant wavelength, obtained by the union of the achromatic point and the trichromatic coefficients point, is 474 nm (dark blue colour).

The concentrations of nutrients reported in Table 1 show high content of Cl^-, NH_4^+, NO_3^-, and SO_4^{2-}, the most abundant negative ions in this liquid. Cl^- is extremely abundant, reaching a concentration close to 12 g/L; also, ammonia is highly abundant (2.5 g/L), and PO_4^{3-} and NO_2^- are present in low concentration [47]. These concentrations for nutrients are consistent with the values obtained by other authors [24,42,48,49].

Metal ions content in landfill leachate shows high concentrations of alkali metals Na^+ and K^+ (>2000 mg/L) and abundance of alkaline earth metals Ca^{2+} and Mg^{2+} (150–600 mg/L, Figure 2). P(V), Al^{3+}, and Fe^{3+} appear in this liquid with visible concentration (10–40 mg/L). Zn^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} contribute in very low concentrations (1.2–2.1 mg/L) and other cations (Ni^{2+}, As^{5+} and Pb^{2+}) below 1 mg/L. The content of metal ions in this landfill leachate can be considered normal in accordance with data from literature [42,49,50].

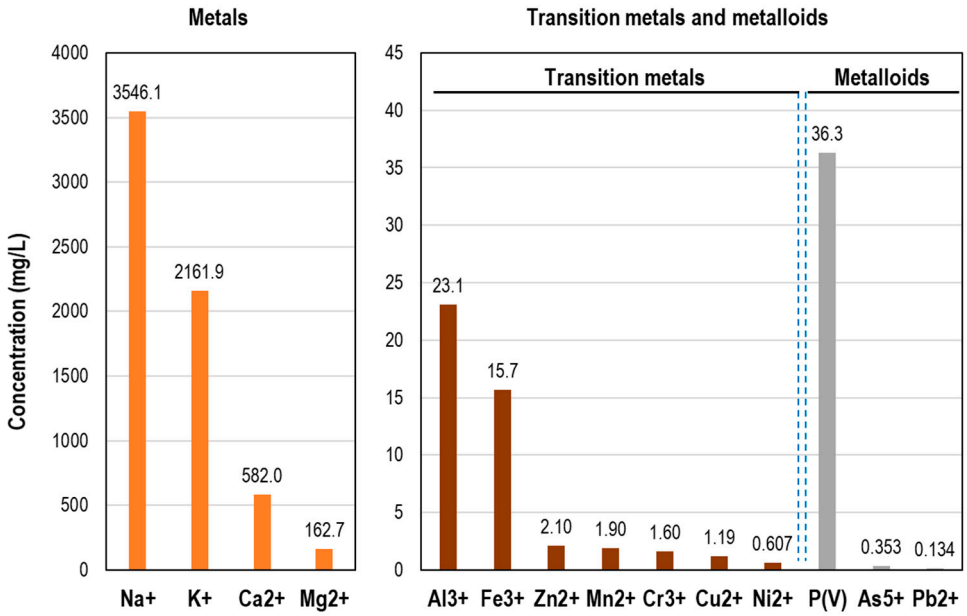


Figure 2. Concentration of metal ions in landfill leachate (metals, transition metals, and metalloids), obtained in one sample from the WTC (average relative SD 2%). Metals and metalloids are shown in the horizontal axe and concentration in leachate (mg/L) in the vertical axe, with the numerical value of concentration over the corresponding bar. Cd^{2+} and Hg^{2+} were detected in trace concentrations (<3 µg/L and <0.1 µg/L, respectively).

3.2. Flocculation of Landfill Leachate at Low pH

Flocculation of landfill leachate at low pH was performed by using H_2SO_4 9 M for a gradual acidification. This liquid flocculates at pH 5.0 (Figure 3a), and COD is reduced from an initial value of 42,000 ± 2516 mg/L to a final value of 5850 ± 923 mg/L at pH 2.0 (86.1% reduction, numerical values and analysis reproducibility in Supplementary Materials, Table S1).

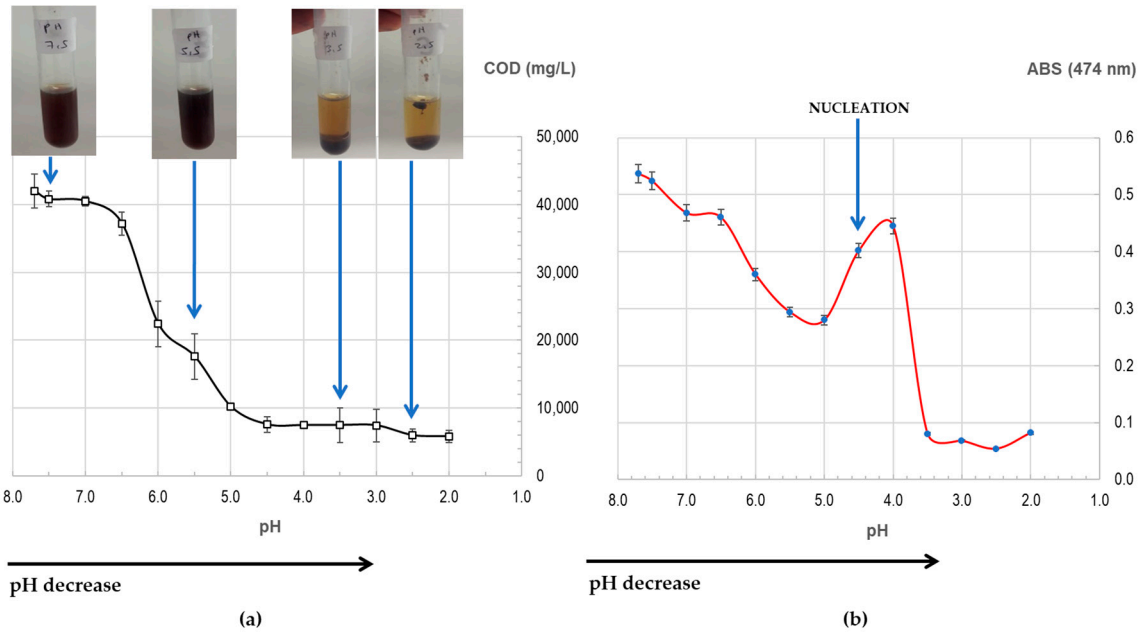


Figure 3. Results of flocculation of landfill leachate at low pH in COD (**a**) and colour reduction (**b**). Error bars represent SD of three independent measurements. Nucleation occurs in colour reduction graph (**b**) at pH 4.5. Numerical values of the graphs in Supplementary Materials, Table S1.

Colour reduction is observed during flocculation at low pH in Figure 3b from initial ABS_{474nm} = 0.537 ± 0.000 (pH 7.7) to 0.082 ± 0.000 (pH 2.0, 84.7% reduction, numerical values and analysis reproducibility in Supplementary Materials, Table S1). ABS increases at pH 4.5 and more visible at pH 4.0, and this is explained by nucleation, the beginning of flocculation, when the incipient formed flocs increase ABS and precipitation starts. This flocculation experiment was repeated three times, and the behaviour observed was the same, producing clearly flocculation and precipitation with formation of an important quantity of foam.

During flocculation at low pH, Z potential value was analysed (Figure 4). The initial value of Z potential in landfill leachate is −16.8 ± 1.4 mV at pH 7.7 and when the pH value decreases below 5.0, Z potential diminish quickly to zero (Figure 4 and numerical values and analysis reproducibility in Supplementary Materials, Table S1). The decay in absolute value in Z potential is highly evident at pH below 3.5. This initial value of Z potential in leachate (−16.8 ± 1.4 mV), in the range −15 to −25 mV, is in accordance with the value obtained recently by other authors [46,51]. Decay of Z potential to zero is the clear evidence of protonation of all the functional groups of HAs in landfill leachate, because is the demonstration of the neutral surface of the molecules without ionic charges.

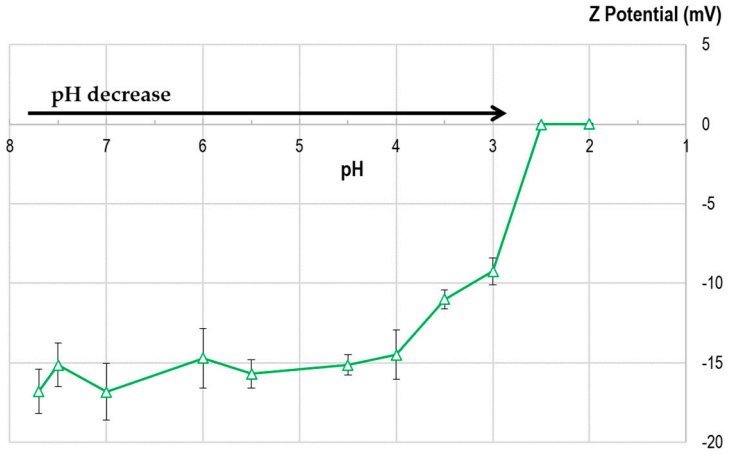


Figure 4. Results of the analysis of Z potential during the flocculation of landfill leachate at low pH, from the initial value of pH 7.7 in the leachate, to the final value of pH 2.0, in the graph from the left to the right. Horizontal axis represents pH, and vertical axis on the right refers to Z potential value in mV. Error bars represent SD of three independent measurements. Numerical values of Z potential in Supplementary Materials, Table S1.

Mean diameter was measured during flocculation at low pH to follow particle size evolution in landfill leachate. The initial distribution of particles in this liquid is not very diverse attending mean ± SD values in leachate in Figure 5 (83.03 ± 53.52 nm), because the standard deviation is lower than expected. During flocculation at low pH procedure, particle size increases at pH = 5.0 (from 83.03 ± 53.52 nm to 162.70 ± 62.35 nm) and big particles are formed at pH 3.0 and 2.0 in Figure 5 (921.5 ± 411.1 nm, 6.6% and 1780.0 ± 608.5 nm, 5.0%, respectively). The explanation of the formation of these big aggregates is assumed to be the intermolecular interaction of different molecules of HAs by formation of H-bonds. Mean diameter was measured in the precipitate, resulting in a solid composed by much bigger particles: 5590 ± 579.8 nm (100%). This value in the size of the particles (5.6 μm) is coincident with the observed value in the literature for the aggregates of natural HAs, several micrometres [52].

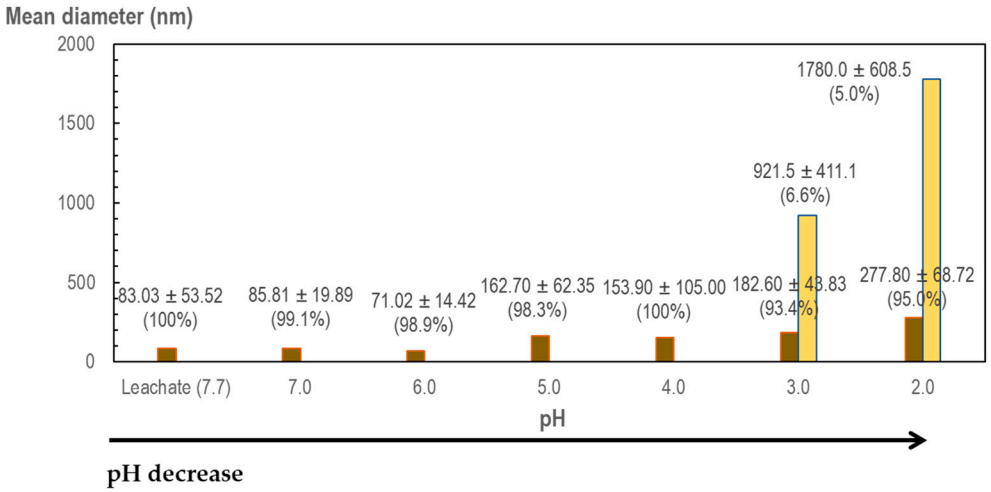


Figure 5. Particle size (mean diameter, nm) during flocculation at low pH of landfill leachate, mean ± SD (triplicate). Formation of big aggregates by intermolecular H-bonds is confirmed at pH 3.0 and 2.0 (yellow bars).

Flocculation of landfill leachate with the decrease in pH is explained because of the presence of HAs in this residue, with an important fraction of the liquid produced in composting of organic matter from solid wastes. The typical molecular structure of a HA is a long aromatic chain with some ramifications in which the functional groups are located. These functional groups are carboxylic acids normally situated at the end of the aromatic chain, phenolic groups distributed in the molecule, and also few sugar and peptides located in the central part of the molecule (Figure 6, HA).

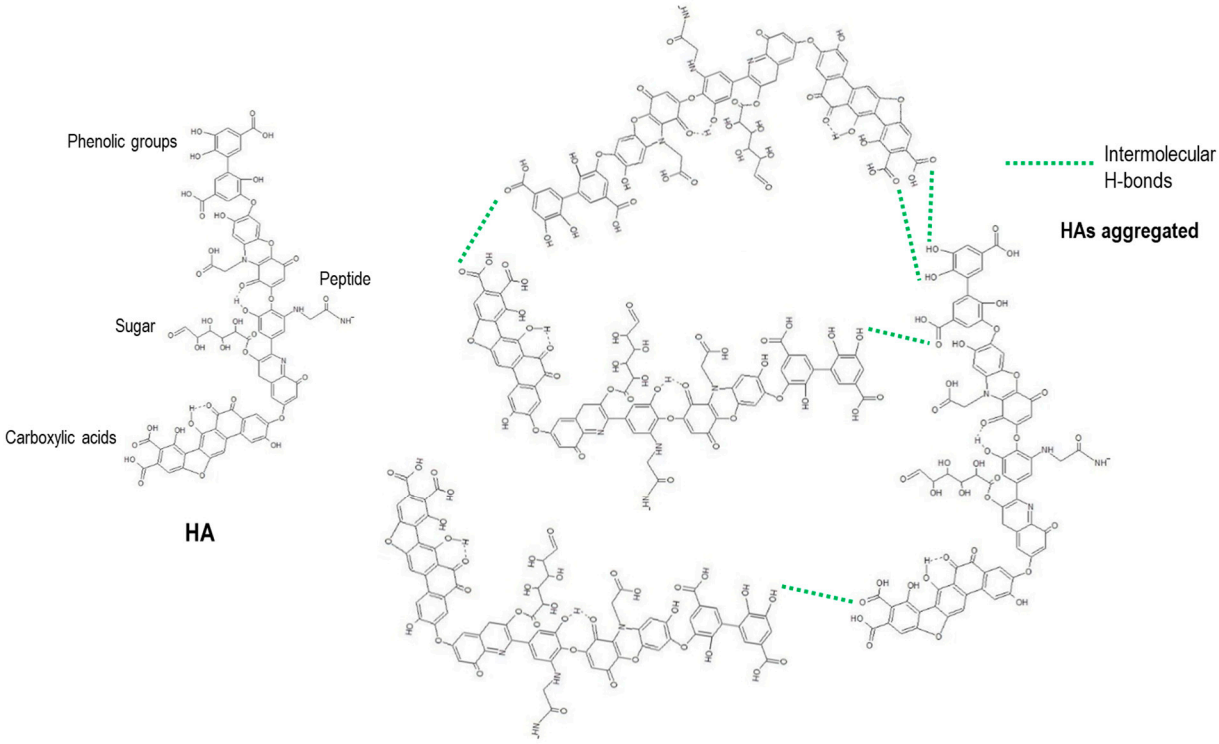


Figure 6. Proposal of the aggregation of humic acid molecules (HA) from landfill leachate protonated at low pH by intermolecular interaction and the formation of H-bonds (interrupted green lines).

In accordance with the chemical properties of HAs, in the gradual decrease in pH, phenolic alcohols are firstly protonated at pH below 5.5 and carboxylic acids lately at pH below 3.5 [37]. When the pH reaches 2.0 and the functional groups of the HAs are

protonated, the abundance of protons in the surface of the HA molecules favours the aggregation by interaction of intermolecular H-bonds [37,53]. In Figure 6, this aggregation has been visualized, showing the interaction of four molecules of HAs by intermolecular H-bonds for the formation of a round structure with much higher molecular weight. This structure formed by the union of HAs, with the functional groups protonated, will be maintained hardly in suspension and will precipitate.

While the precipitation process of HAs is producing, other organic molecules are dragged, and the reduction in the global COD value can be highly increased (86.1%). This high reduction in the COD value is much more than the expected in accordance with the percentage of HAs in the total organic matter [30].

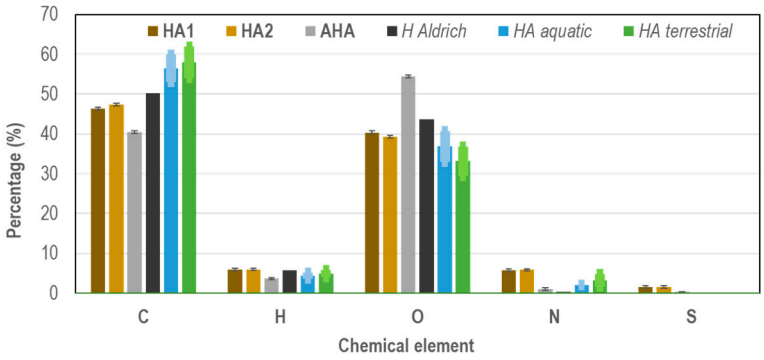
The visual appearance of landfill leachate changes significantly after flocculation at low pH. Clarification is produced from a dark brown, the initial colour observed in leachate, to a light yellowish-brown colour of a cleaner liquid (Figure 3a). During precipitation, the formation of foam is observed and is attributed to the formation of HA aggregates.

3.3. Humic Acids Characterisation

Samples collected from the precipitate and washed in HF-HCl acid medium (Section 2.2) were analysed after flocculation at low pH, in which HCl was used to avoid the interference of H_2SO_4 in CHNS chemical analysis. These samples were analysed via the CHNS analysis and FT-IR.

Figure 7 records CHNS elemental chemical analysis, where two independent samples of the precipitate (HA1 and HA2) were measured to assure reproducibility of the results obtained and HA from Aldrich (AHA), for comparison, was analysed and also compared with data of commercial (H Aldrich) and natural (HA aquatic and HA terrestrial) humic acids from literature. The results were normalized to 100% of total percentage of organic components, and oxygen (O) was obtained by the difference to 100% of the sum of the other four elements in percentage (C, H, N, and S). The ratios of hydrogen, oxygen, and nitrogen to carbon (H/C, O/C, and N/C) were obtained from the results of element analysis values. The carbon percentage in HAs from landfill leachate is in between the percentage of aquatic and terrestrial HAs and AHA (commercial) and close to those values and the value of H Aldrich from the literature [24]. The percentage of nitrogen in HAs is higher than the other references (natural and commercial HAs), due to amines and amides present in HA molecules and the important concentration of N-ammonia in the samples of landfill leachate (Table 1), which are coincident with the literature [24,54]. Oxygen, present in the main functional groups of the HAs (carboxylic acids and phenols), is very similar in percentage in HAs from landfill leachate and natural HAs, aquatic and terrestrial, especially aquatic. The sulphur percentage reference value has not been found in data from the literature, and the result measured from commercial HA (AHA) is below detection limit in Figure 7 (numerical values in Supplementary Materials, Table S2). The presence of S in the samples of HAs from landfill leachate ($1.60 \pm 0.35\%$, Supplementary Materials, Table S2) can be attributed to sulphate, which is abundant in leachate (Table 1).

With regard to element ratios in Figure 7, H/C ratio value close to 1.0 is indicative of a chemical structure with abundance of aromatic rings (AHA and natural HAs). When the value of H/C is over 1.0 (HA1 and HA2, landfill leachate), this is indicative of the abundance of aliphatic groups. O/C ratios in HAs from landfill leachate are higher related to natural humic acids (abundance of carboxylic acids and phenolic groups) but coincident with H Aldrich value from the literature and lower compared to analysed AHA value. N/C ratios are higher in HAs from leachate compared to the other values from natural and commercial humic acids, as commented before (ammonia in leachate, Table 1).



Ratio	HA1	HA2	AHA	*H Aldrich*	*HA aquatic*	*HA terrestrial*
H/C	1.53	1.52	1.08	1.35	0.74–1.15	0.56–1.29
O/C	0.65	0.62	1.01	0.65	0.42–0.58	0.36–0.51
N/C	0.11	0.11	0.02	0.01	0.029–0.034	0.022–0.076

Figure 7. Elemental chemical analysis (carbon, hydrogen, nitrogen, and sulphur: CHNS) of the precipitate of the landfill leachate after treatment at low pH (humic acids). The vertical axis represents percentage of the element included in the horizontal axis. HA1 and HA2 are two independent samples collected from the leachate precipitate. Aldrich humic acid (AHA) and humic acids from the literature are included for comparison (H Aldrich, HA aquatic, and HA terrestrial, [24]). Analysis of HAs (HA1 and HA2) and AHA were performed in triplicate and error bars record SD. For the external data (*HA aquatic* and *terrestrial*, from the literature), error bars represent the range in which the value is recorded.

The result of FT-IR spectrometric characterisation of HAs in the precipitate of landfill leachate after pH reduction treatment is shown in Figure 8, where FT-IR spectra of HAs (red line) and Aldrich humic acid (black line) are recorded.

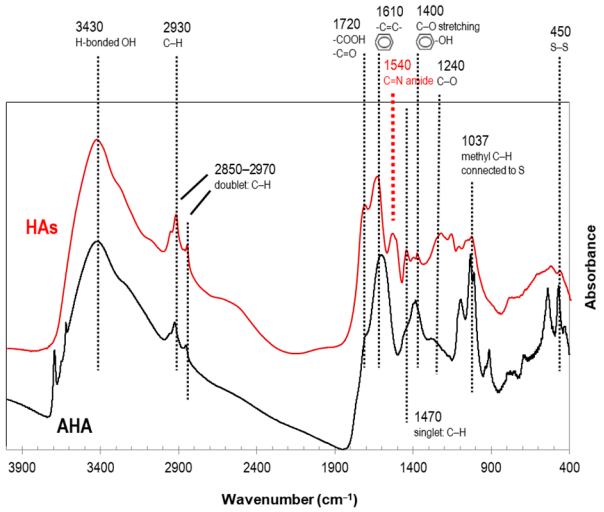


Figure 8. FT-IR spectra of humic acids proceed from the precipitate of landfill leachate (HAs, red line) and Aldrich humic acid (AHA, black line). Characteristic signals of humic acids are highlighted, red dashed line only for HAs in landfill leachate.

The most representative signals of HAs are assigned and explained in detail in accordance with the literature data [24,30,55]. There is a wide band (3400–3000 cm^{-1}) with the maximum at 3430 cm^{-1}, which is assigned to H-bonds formed between different molecules (aggregation of HAs) [30], and also, this signal is indicative of phenol, hydroxyl, and carboxyl functional groups (O-H stretching). There are two other significative signals appearing in HAs and AHA spectra and assigned to aliphatic groups (C-H) of organic structures: the singlet at 1470 cm^{-1} and especially the doublet at 2970–2850 cm^{-1}. In the FT-IR spectra of HAs in leachate and AHA, the characteristic peaks of C=O bonds

(1720 cm^{-1}) in ketonic and protonated carboxylic acid groups are visible, and the signals of stretching of double carbon bonds (C=C) are also highly visible (1610 cm^{-1}), typical of aromatic rings. There is a signal at 1540 cm^{-1} only visible in HAs and not AHA attributed to amide groups (C=N stretching), which is not visible in AHA due to a lower content of N (Figure 7). The peak at 1400 cm^{-1} is assigned to phenolic OH (C-O stretching and deformation of O-H). The slight signal located at 1240 cm^{-1} is attributed to the C-O bond (stretching). The peak at 1037 cm^{-1}, present specially in AHA and also visible in HAs, is assigned to rocking vibrations of aliphatic groups (C-H) connected to S. The S content observed in CHNS analysis in AHA was below the detection limit and was detected in HAs (Figure 7). Finally, the peak at 450 cm^{-1} has been assigned to S-S bonds [30], slightly visible in HAs from leachate and much more visible in AHA, with much lower S content.

3.4. Application, Scalability, and Sustainability

Flocculation at low pH of landfill leachate is a sustainable process for the treatment of this highly polluted liquid, with content in composting leachate rich in humic acids, which actually is processed by ozonation or Fenton oxidation, as described in the introduction [56,57] or these processes combined with coagulation [58,59]. Reverse osmosis has also recently been described to reduce pollution and toxicity of this liquid [60] and the use of natural resources, like extracts of plants, were also applied as tentative processes, for example, in coagulation of high charged compost leachate (63,500 mg/L COD), reaching 39.8% in COD removal [61]. Most effective treatments for landfill leachate are currently proposed as combined or hybrid processes which enclose various operations: flocculation–ultrafiltration with 400 mg/L $FeCl_3$ and ultrafiltration membranes for industrial landfill leachate [62], Fenton oxidation–adsorption using biochar as adsorbent, with 82.6% of COD removal for an initial value of 3155 mg/L [63], advance electrolysis after nanofiltration (1281 mg/L COD, with removal of 87%) [64], and, more recently, the combination of physicochemical and biological treatments [65–67]. These treatments are less sustainable, produce more residues and with higher economical costs, and normally have been proven for leachates with lower organic charge and content in HAs.

In the process described in this article, the concentration of H_2SO_4 required for pH 2.0 is 0.01 M, and assuming a price of 10 euros/L of this chemical compound (36 M, 0.28 euros/mol), the price for the treatment of the landfill leachate is 2.8 euros/m^3. This cost is much lower compared to the processes proposed for COD reduction in landfill leachate, for example, electrocoagulation–oxidation [65] with 19 euros/m^3 in energy (32 kWh/kg COD) for a liquid with COD = 6 197.5 $\pm$ 539.9 mg/L or advance electrolysis with 7.2 euros/m^3 (91.9 kWh/kg COD for 1281 mg/L COD) [64]. In the coagulation–ozonation process [59], using polymeric ferric sulphate (250 mg/L) at pH 4.0 and ozone, the reduction in COD obtained was 88.3%, and the cost of ozone generation could be estimated from data for wastewater treatment in 100 kWh/(kg ozone) for 20 mg/L of ozone concentration, as described in the article: 0.2 euros/m^3 (COD = 3855 mg/L). The total cost of adding the flocculant (20 euros/kg, 5 euros/m^3) would be 5.2 euros/m^3.

Comparing flocculation at low pH with other flocculation processes adding chemicals like 700 mg/L alum to reach 54% of COD removal for a very low concentrated landfill leachate (1 020 mg/L COD [68]), the reduction in pH by the addition of H_2SO_4 0.01 M (980 mg/L) with 86.1% of COD removal for a high concentrated landfill leachate proposed in this work appears much more competitive and does not increase the metal concentration in the liquid favouring downstream processes.

During flocculation at low pH, the estimated volume of HAs produced is about 1/30 the volume of leachate treated (30 L for 1 m^3 of landfill leachate), and this precipitate is proposed to be applied in the amendment of agricultural lands, like is actually conducted

with solid sludges from wastewater treatment plants, although HAs are considered valuable products and could be used in a circular/sustainable process for the removal of heavy metals in wastewater [34,69].

Landfill leachate after flocculation at low pH could be biologically treated in a combined binary process flocculation–biological treatment for a further COD reduction [18], and in this case, pH has to be readjusted to a neutral value. No toxic/corrosive effects are expected because of sulfuric acid addition in low concentration (pH 2.0, H_2SO_4 0.01 M), only the increase in sulphate concentration in the liquid.

4. Conclusions

In this article, we present a new method for the treatment of highly polluted landfill leachate for a sustainable use and treatment of this residue, consisting in the flocculation at low pH. Highly polluted landfill leachate has a high proportion of composting leachate (composting of solid wastes), which means the abundance of humic acids in this liquid. In view of the chemical properties in aqueous solutions of these HAs, which are protonated at low pH and are ionized at medium–high pH, landfill leachate is effectively flocculated at pH 2.0.

Under acidic conditions, phenolic alcohols present in HAs are protonated at pH levels below 5.5 and carboxylic acids at pH levels below 3.5. The protonation of the functional groups of the HA molecules reduces the high Zeta potential absolute value to zero and conducts to the formation of intermolecular H-bonds, resulting in big aggregates which are unstable in solution and precipitate. During the precipitation process of HAs, other organic molecules are dragged, and COD and colour are reduced in high extent (84–86%).

The mean diameter of the molecules has been measured during flocculation at low pH, and the formation of big aggregates has been detected at pH 3.0 and 2.0 and also in the precipitate. This precipitate was analysed via the CHNS chemical analysis and infrared spectrometry (FT-IR), resulting very closed in chemical composition to commercial and natural HAs and showing in the FT-IR spectrum significative signals coincident with commercial HA, especially with carboxylic acids and phenolic alcohols, which are characteristic of the chemical structure of a humic acid. The formation of intermolecular H-bonds between HAs also has been detected by FT-IR spectrometry.

The economic analysis of flocculation at low pH applied to composting landfill leachate seems to describe a promising and sustainable technique compared with the actual methods used (flocculation, adsorption, oxidation, electrolysis, reverse osmosis) for COD and colour/turbidity removal.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su17020481/s1, Table S1: Numerical values for COD, colour (474 nm) and redox potential obtained in triplicate during flocculation of landfill leachate at low pH; Table S2: Numerical values of elemental analysis of HAs from landfill leachate (HA1 and HA2) and Aldrich HA (AHA) and data from literature. Analysed data (HA1, HA2 and AHA) are expressed as mean ± SD of three independent measurements.

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