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EVALUATION OF TWO DIFFERENT METHODS FOR THE QUANTIFICATION OF HUMIC SUBSTANCES IN LANDFILLS IN SOUTHERN BRAZIL

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ABSTRACT

Although landfills are an alternative for the disposal of large quantities of solid urban waste generated due to urbanization, economic and population growth, the process ultimately produces complex leachates composed mainly of biologically refractory substances, such as humic and fulvic acids. In this context, the study aimed to quantify the humic substances of four different leachates using two different methods described previously by Sheng and the Ministry of Agriculture, Livestock, and Food Supply. From the results, it was observed that in both leachates, the concentration of fulvic acids was higher than that of humic acids, due to the high solubility of this compound. Furthermore, it is concluded that Sheng's method is not suitable for the quantification of humic substances in landfill leachates due to its colorimetric nature for determination in water. In addition, the MAPA method has shown to be an excellent alternative for the quantification of humic substances.

Keywords: Landfill. Leachate. Physicochemical characterization. Humic acid. Fulvic Acid.

1 INTRODUCTION

The increase in economic development has resulted in a rise in individuals' purchasing power. This, coupled with population growth, has resulted in a rise in statistics related to the generation of urban solid waste (USW).[1]. The solid waste panorama carried out by the Brazilian Association of Public Cleaning and Special Waste Companies – ABRELPE shows that the generation of USW in Brazil during the year 2022 reached approximately 81.8 million tons, of which, around 61% of Collected USW was sent to landfills.[2].

The degradation process of USW in landfills is mainly anaerobic and consists of several sequential reactions.[3]. The leachate resulting from the decomposition of MSW is a complex and polluting aqueous matrix composed of various substances, mainly biologically refractory ones, known as recalcitrant substances. These substances are characterized by their difficulty or impossibility of degradation and have high environmental persistence.[4]. The presence of these substances can originate from various sources, including environmental pollutants, pesticides, industrial waste, and complex organic compounds. This poses a challenge for environmental remediation due to the slow or practically non-existent natural decomposition.[5].

Therefore, it is essential to understand the characteristics of leachate from landfills to develop appropriate treatment strategies. However, the methods for quantifying these substances in leachate are still inconclusive, as quantification methods for soil and water are reported. This work aimed to quantify humic substances in landfill leachate. This will contribute to the advancement of knowledge on methods of quantifying leachate from landfills and aid in the development of efficient treatment technologies.

2 MATERIAL & METHODS

For the development of the present study, four leachate samples were collected from landfills located in different regions of the State of Rio Grande do Sul, Brazil: Leachate 1 — raw leachate collected directly from a landfill located in the northern region of the state; Leachate 2 — leachate collected from the same site as Leachate 1, after biological treatment; Leachate 3 and 4 — leachate collected from the same landfill, but from two different cells, A and B, respectively.

First, the leachate samples were subjected to physicochemical characterization regarding moisture and ash content according to the analytical methods described by the National Energy Laboratory.[6].

The total humic substances were quantified using two different methods as shown in Figure 1: (1) the spectrophotometric/colorimetric method previously described by Sheng et al.[7], and (2) the methodology developed by the Ministry of Agriculture, Livestock and Food Supply.[8], with adaptations. To apply the MAPA method, the leachates were dried in an oven at 65 °C ± 5 °C. Then, an alkaline extraction was performed to obtain the total humic extract. The humic acids were precipitated at pH 1, while the fulvic acids remained in solution. Finally, the total organic carbon content was then determined by chemical oxidation with dichromate for each of the fractions obtained. For comparison purposes, we selected and analyzed some leachate samples in an accredited laboratory (Pró Ambiente, Porto Alegre, Brazil) that also uses the methodology described by MAPA.

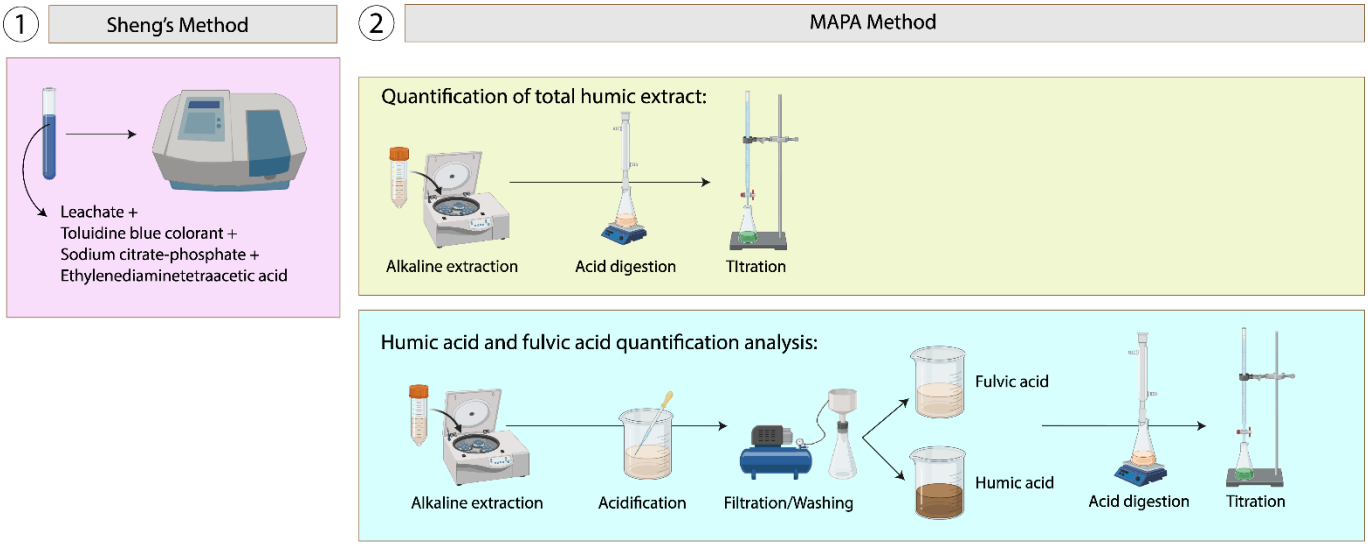

Figure 1 Schematic flow chart of the methodologies carried out according to the method described by Shen and by MAPA.

3 RESULTS & DISCUSSION

Table 1 summarizes the results relating to physical-chemical characterization, the quantification of humic substances using the method described by Sheng.[7], and the quantification of total humic extract, humic acid, and fulvic acid using the method described by MAPA.[8].

Table 1 Physicochemical characterization and evaluation of humic substances (SH), total humic extract (THE), humic acid (HA), and fulvic acid (FA) by two different methods in leachate samples.

Assay	Moisture (%)	Ash (%)	Sheng's method1.[7]	MAPA method.[8]		
			HS (mg/L)	THE (mg/L)	HA (mg/L)	FA (mg/L)
Leachate 1	98.94	27.95 ± 0.80	83.70 ± 11.70	2,603 ± 95.9	870.7 ± 120.9	1,857 ± 110.8
Leachate 2	98.75	67.46 ± 0.42	39.10 ± 7.20	2,113 ± 52.8	309.6 ± 73.3	1,446 ± 185.6
Leachate 3	98.61	32.98 ± 0.36	164.20 ± 7.50	4,506 ± 67.5	1,811 ± 115.3	2,459 ± 302.8
Leachate 4	99.43	20.73 ± 2.35	81.40 ± 2.80	1,171 ± 33.3	267.4 ± 48.14	593.3 ± 84.9

The measured values for humic substances found using the Sheng method were lower than expected. However, the method described by Sheng[7] was originally developed to measure the number of humic substances in water, i.e. it attempts to detect concentrations significantly lower than those found in leachate, in addition to the fact that the method considers humic substances as humic acid only, whereas leachate has humic acids and fulvic acids in its composition. It is important to note that the dark color of the leachate can interfere with the read absorbance of the sample, providing misleading values due to the colorimetric nature of the method. Furthermore, the sample dilution process can increase statistical errors, compromising the representativeness of the result.

Method 2, carried out using the MAPA methodology, resulted in a significant reduction in the concentration of total humic extract, humic acid, and fulvic acid from leachate 1 to 2 due to the biological treatment applied to leachate 2. Additionally, a smaller percentage reduction in fulvic acids was observed, which can be attributed to their better solubility and lower molar mass, making their removal more complex. There is a significant difference between leachate 3 and 4, despite both being raw leachates removed from the same landfill but from different cells. The reason for the difference between the two leachates is due to the type of waste deposited in each cell. The composition of the waste has a significant impact on the generation of leachate, along with other factors such as the altitude and rainfall of each cell, as well as the age and degradation time of the leachate. Upon evaluating the leachate sample for the presence of fulvic and humic acids, it was observed that fulvic acid was predominant in all analyzed samples in terms of percentage due to the compound's high complexity in removal and solubility in any pH range, as noted by Stevenson.[9].

When comparing our results with those sent by the laboratory (Table 2), similarities are observed. Small differences may be attributed to the date of analysis and the brand of reagents used. As this is a volumetric method that is susceptible to variations, small differences are considered acceptable. Additionally, the accredited laboratory did not provide information on the variability of the analysis, which is a crucial measure for the report. It should be noted that in the laboratory analysis, the concentration of humic acid was found to be higher than that of fulvic acid in leachate 4. However, both concentrations were below the laboratory's detection limit, which compromises the representativeness of the results.

Table 2 Evaluation of total humic extract (THE), humic acid (HA), and fulvic acid (FA) according to the accredited laboratory.

Assay	THE (mg/L)	HA (mg/L)	FA (mg/L)
Leachate 1	-	-	-
Leachate 2	1,900	-	-
Leachate 3	-	1,300	1,700
Leachate 4	-	600	400

The results show significant discrepancies between the two methodologies. However, it should be noted that the Sheng methodology was developed for quantifying humic substances in water, while the method developed by the Ministry of Agriculture, Livestock and Food Supply is intended for fertilizer analysis (see Table 3). Therefore, comparing the methodologies is challenging due to the significant disparity between their principles. Additionally, it is essential to note that neither methodology was originally developed to quantify humic substances in leachate, but rather in other sources. However, despite the discrepant results, there is a notable similarity between them. Both analyses show a reduction in the amount of humic substances after the leachate undergoes biological treatment, as seen in the comparison between leachate 1 and leachate 2. Additionally, a significant difference was observed between leachate 3 and leachate 4 in both methodologies. This highlights that leachate 3 contained a considerably higher amount of humic substances compared to leachate 2.

Table 3 Comparison between Sheng's and MAPA methodology.

Method	**Sheng's method**	**MAPA method**
Quantification Source	Water	Fertilizers and correctives
Application principle	Binding of Toluidine Blue dye to humic acid molecules	Determination of Total Organic Carbon content
Similarities	1. Biological treatment reduces the number of humic substances, evidenced in the comparison between leachate 1 and leachate; 2. Additionally, leachate 3 and leachate 4 exhibit a notable difference in the two methodologies.	

4 CONCLUSION

The recalcitrance of humic substances makes their removal challenging, which in turn makes the efficient treatment of leachate from landfills difficult. In this context, the quantification stage is crucial for understanding the effluent and finding more effective treatment alternatives. A comparative analysis of two methodologies showed notable differences in the results obtained for the same leachates. However, the method described by MAPA was the most effective, producing values closer to those reported in the literature and showing promise for this type of analysis.

REFERENCES

[1] KUMSCHLIES, M. C. G., SCHALCH, V. 2023. Rev. AIDIS. 16 (1). 82-110.
[2] ABRELPE. (2022). Panorama de resíduos sólidos no Brasil. https://abrelpe.org.br/panorama/.
[3] POHLAND, F. G. GOULD, J. P. 1986. Water Sci. Technol. 12. 177-192.
[4] CHRISTENSEN, T., KJELDSEN, P., BJERG, P. L., JENSEN, D. L., CHRISTENSEN, J. B., BAUN, A., ALBRECHTSEN, H., HERON, G. 2001. Appl. Geochem. (16). 659-718.
[5] SILVA, A. C. 2002. Tratamento do percolado de aterro sanitário e avaliação da toxicidade do efluente bruto e tratado. 126 f.
[6] NREL. 2012. Determination of structural carbohydrates and lignin in biomass (Protocol NREL/TP-510-42618).
[7] SHENG, G.-P., ZHANG, M.-L., YU, H-Q. (2007). Analy. Chimi. Acta. 162-167.
[8] MAPA (2017). Manual de métodos analíticos oficiais para fertilizantes e corretivos. 240 p. ISBN 978-85-7991-109-5.
[9] STEVENSON, F. J. 1994. Humus Chemistry: genesis, composition, reactions. 2nd ed., New York: John Wiley. 496 p.

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