CHEMICAL CHARACTERISTICS OF HUMIC SUBSTANCES FROM A MSWIR LANDFILL LEACHATE

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1. Introduction

In municipal solid waste incineration residues (MSWIR) landfill sites, humic substances (HSs) are formed from the unburnt organic matter and it has been shown that some amount migrates with leachate. HSs in landfill sites have the ability to bind and transport heavy metals and hydrophobic organic pollutants to the environment [2), 7)]. Although the characteristics and properties of the HSs in leachate from municipal solid waste (MSW) landfills had been conducted, information concerning HSs in MSWIR landfill leachate is still scarce. The aim of this research is to make clear the characteristics of HSs in leachate from a determined MSWIR landfill site and to investigate its chemical properties by investigating its elemental composition, carbon functional groups distribution and thermal change.

2. Materials and Method

Leachate samples were taken from F landfill site located in F city. F landfill site is a semi aerobic type of landfill, which is in operation since 1988 and it's mainly disposed with MSWIR (54 %). Leachates samples were also taken from two different landfill sites (H and B) in F city. H and B are already closed landfill sites, and were mainly disposed with MSW. HSs were extracted following the International humic substances society (IHSS) procedure. Dissolved organic carbon (DOC) concentration was measured with a TOC-TN analyzer (TOC-V/CPN TNM-1, Shimadzu co.) in order to calculate the concentration of HSs in leachates. In order to investigate the chemical properties of the HSs isolated from F landfill site, elemental composition, CP-MAS ^{13}C-NMR and TG-DTA analysis were performed. Elemental composition of humic acid (HA) and fulvic acid (FA) isolated from the leachates was investigated with a CHN coder (YANAKO CHN coder MT-50). Because of the low content of HA in leachate, the distribution of carbon functional groups was analyzed only in the isolated FA with a CP-MAS ^{13}C-NMR spectrometer (JNM-CMX300, JEOL Co.). Finally, thermogravimetric (TG) analysis was also performed to the isolated FA by a TG-DTA 2000SA (Bruker, AXS) and differential thermogravimetric (DTG) curves were calculated from the results.

3. Results and Discussions

HSs concentrations in leachate samples from F landfill site ranged between 0.3-2.4 mg-C/l for FA and 0.01-0.6 mg-C/l for HA. Previous investigations[3)] had already showed that FA was mainly contained in leachate. Also, HSs concentration in F landfill leachate was compared with average HSs concentrations in other landfill leachate from F city and it was noticed that HSs' carbon from F landfill leachate represent 48 % of the DOC against 32 % in leachate H and 39 % in leachate B.

The results from elemental analysis (Table 1) were compared, and a lower carbon content was noticed in the composition of HSs from F leachate (49.1 % for FA and 47.2 % for HA) against H (55.3 % for FA and 55.6 % for HA) and B (55.1 % for FA and 52.1 % for HA). In contrast, a higher oxygen content was found in HSs from F leachate (66 % for FA and 41 % for HA), compared with H (37.1 % for FA and 33.8 % for HA) and B (37.4 % for FA and 38.2 % for HA). The elemental composition of HSs from others MSW landfill leachates taken from literature data [2), 6)] was also used and it was found that although carbon content in FA from F leachate was lower than H and B leachate, it was in the range presented in literature data. In the case of the carbon in HA and the oxygen in both FA and HA from F leachate, their contents exceed the range presented in literature data. The O/C ratios for HSs from F leachates (0.91 for FA and 0.98 for HA) also differed from the O/C ratios for HSs from H, B and literature data (0.47-0.68 for FA and 0.36-0.73 for HA). According to Christensen et al.[7)], a high O/C ratio may indicate a high content of carboxylic groups, phenolic groups or carbohydrates.

Table 1. Elemental composition of HSs from three leachates (F, H and B) in F city

HSs	Name	Mainly disposed	H	C	N	O	Total
			(%)				
FA	F	**MSWIR**	4.9	**49.1**	1.2	**44.8**	100
	H	MSW	6.2	55.3	1.4	37.1	100
	B	MSW	5.8	55.1	1.7	37.4	100
	Literature data [2), 6)]	MSW	6.4-9.6	45.6-50.9	2.4-12.0	32.8-35.2	-
HA	F	**MSWIR**	5.2	**47.2**	1.2	**46.4**	100
	H	MSW	5.8	55.6	4.8	33.8	100
	B	MSW	5.2	52.1	4.5	38.2	100
	Literature data [2), 6)]	MSW	2.0-8.8	56.1-57.1	2.0-8.3	26.7-30.2	-

Table 2. Relative composition of carbon functional groups and aromaticity of FA from leachates

Name	Source	Composition (%)				Aromaticity (%)
		Aliphatic	Methoxyl	Aromatic	Carboxyl	
F	MSWIR leachate	43	4	**36**	17	**43.4**
H	MSW leachate	36	15	32	17	38.6
B	MSW leachate	42	6	30	22	38.5

The CP-MAS ^{13}C-NMR spectra (Figure 1), showed a strong presence of aromatic carbon functional groups (110-160 ppm) in FA from F leachate (36 %) compared with FA from leachates (28-32 %). After calculating the aromaticities, it was confirmed the high aromaticity (43.4 %) of FA from F leachate compared with aromaticities (38.5 and 38.6 % for HSs in H and B leachate respectively).

Finally, the TG and DTG thermograms of FA from F leachate are shown in Figure 2. First it was noticed a weight loss between 70 to 110 ºC due to dehydration reactions[5]. From DTG thermogram, two peaks are evident. The main peak shows the degradation of functional groups and is represented by the thermogram between 160-340 ºC [4), 6)]. Moreover, from the thermogram above 340 ºC a secondary peak can be noticed at 400 ºC. Stevenson[4] suggested that weight loss above 400 ºC represents the degradation of aromatic structures. Therefore, apparent aromaticity was also calculated by integrating DTG curves of FA. The result agrees with the CP-MAS ^{13}C-NMR spectra results, showing an aromaticity for FA from F leachate of 39.6 %.

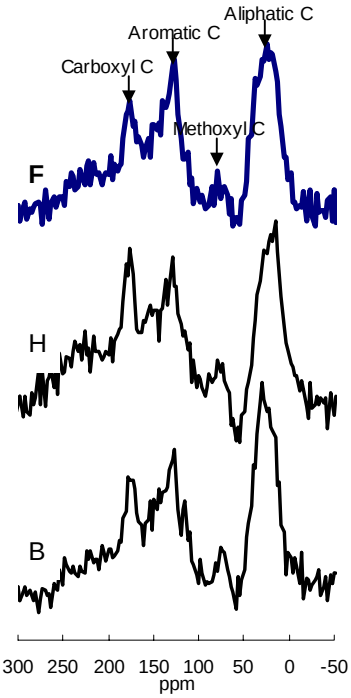

Figure 1. CP-MAS ^{13}C-NMR spectra of FA isolated from three landfill leachates (F, H and B)

4. Conclusions

HSs extracted from a MSWIR landfill leachate (F) showed a different elemental composition with low carbon content (49.1 % for FA and 47.2 % for HA) and high oxygen content (44.8 % for FA and 46.4 % for HA) compared with other MSW landfill leachate. The high O/C ratios for HSs from the MSWIR landfill leachate suggested a high content of carbohydrates, carboxyl or phenolic groups. In agreement with the elemental composition, CP-MAS ^{13}C-NMR and TG analysis showed that FA from a MSWIR leachate had high aromaticity compared with other FA from MSW leachates. Further studies should investigate more the aromaticity of HSs from MSWIR leachates, considering that aromatic carbons functional groups are known to be the main way of binding between HSs and hydrophobic organic pollutants [2), 5)].

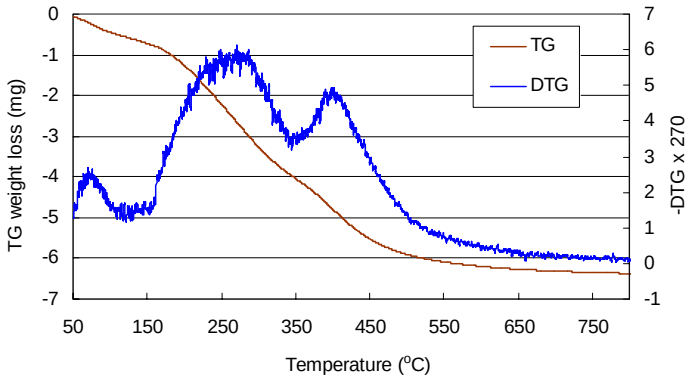

Figure 2. TG and DTG thermograms of isolated FA from F landfill leachate

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