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INFLUENCE OF THE pH INDICATOR ON DISSOLVED ORGANIC CARBON FOR DETERMINATION THE HAZARDOUSNESS OF INDUSTRIAL WASTE

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Abstract

The paper presents the influence of pH on the dissolved organic carbon in industrial waste samples as a decision indicator in determining the hazardousness of the waste at storage according to the environmental legislation. Waste storage is a common method of management and is realizing according to GO 95/2005, which requires limit concentrations of the indicators analyzed according to each type of deposit (inert, non-hazardous, and hazardous). For the analysis of the dissolved organic carbon, 6 samples of waste from different sectors of activity were subjected to the leaching test and the eluate was analyzed on a multi N/C 3100 equipment at both the pH of the waste, itself and between 7.5 and 8 pH units. From the results obtained it is found that the modification of the pH leads to significant variations in the concentration of the dissolved organic carbon, variations which can provide essential information for the subsequent management of the waste.

Keywords*: dissolved organic carbon, hazardous, industrial waste, inert, non-hazardous*

Introduction

Waste management has become a priority in the 21st century because of the increase in global population, high food consumption and industrialization. Until 2100, waste generation is expected to triple globally (Minelgaitė & Liobikienė 2019). The largest chemical industries such as refineries, pharmaceuticals, automobiles and textiles use water, solvents and polymers to reach hazardous waste. They can generate a large amount of hazardous organic waste with a high moisture fraction, that is, a low ratio between free and bound water (Worrall et al. 2019). Because of the large amounts of waste generated, it is becoming increasingly difficult to place new storage facilities. That is why an important issue is to develop new strategies for reducing the volume of waste (Li et al. 2018). Also, waste management is considered an activity of public interest carried out in accordance with the provisions of this law and the regulations adopted under this law. According to GO 95/2005, it helps those who own or manage the waste. A characterization is made to determine the hazardous / non-hazardous nature and to include them on the waste list, to observe transport forms and also to determine the type of deposit in which a waste can be accepted (Kim et al. 2018).

To be accurate and conclusive results, there must be a sampling process and all the preliminary operations of the real waste analysis (packaging, storage, preservation, transport, pretreatment, etc.) (Arama et al 2015). To be included on the list for a particular storage class, a waste is subject to testing, consisting of a general characterization performed with standardized methods of analysis for the determination of physical-chemical composition and for testing of leachate behavior and / or variation in characteristics in the short and long term. The indicators to be tested and the maximum admissible limits are set for each type of deposit. GO 95/2005 specifies the categories of solid, granular waste, chemical characteristics for admission to storage and methods of testing these specific properties. The main test is the leachability analysis, which simulates in the laboratory the washing of stored material by natural precipitation. The liquid resulted from washing is called "Leachate". The test is complex by the various conditions in which it is performed and the way the results are calculated. According to GO 95, if the waste exceeds minimum value for DOC at its own pH, it can alternatively be tested at L/S=10 l/kg and at pH between 7.5 and 8.0 pH units (GO 95/2005).

The paper presents the influence of pH on dissolved organic carbon in industrial waste samples for determination the hazardousness of the waste at storage according to the GO 95/2005.

Materials and methods

To achieve the main objective, 5 types of samples from different fields of activity from industrial waste were selected and listed below (Figure 1):

D1 - sludge from the sewage treatment plant - textile industry;
D2 - sludge resulted from industrial wastewater treatment plant;
D3 - sludge resulted from car wash;
D4 - sludge resulted from urban wastewater treatment;
D5 - waste from the ash hearth from the incineration plant;
D6 - waste from filter ash from the incineration plant.

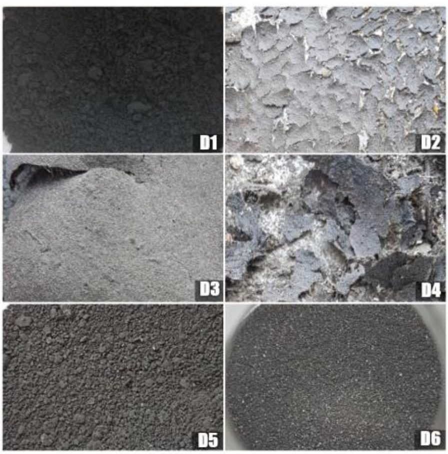

Figure 1. Study types of waste

For analysis of dissolved organic carbon, a Multi N/C 3100 analyzer was used. This is a compact and very efficient device for determining the total carbon content and/or the total nitrogen content of aqueous samples. Decomposition takes place in the multi N/C 3100 by thermocatalytic high temperature oxidation in the presence of special catalysts. This enables quantitative decomposition even for stable, complex carbon and nitrogen compounds. The modular versatility of the multi N/C 3100 (Figure 2) permits individual adaptation. Analytically, dissolved organic carbon (DOC) is characterized as organic molecules capable of passing through a 0.45μm filter (Regan et al 2017).

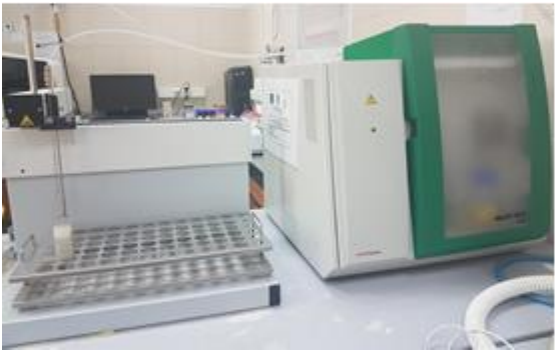

Figure 2. Analyzer with sample dispenser

For DOC analysis the samples most of the time need filtration. The most commonly often used filter is 0.45 μm, but sometimes when the sample is too dense, the filter pump can be used. If small amounts of water are being filtered (30 or 40 mL), more practical is to use syringe filters. Most important is that the filters do not release any DOC during filtration.

pH Correction

For pH correction, 40 mL of each sample was introduced in a vial and corrected with a HCl 0.1 N or NaOH 0.1 N solution and bring between 7.5 – 8 pH units (Table 1).

Table 1. pH correction, pH units

Samples	Initial - pH	Final – pH
D1	4.1	8.0
D2	6.1	7.5
D3	6.6	7.5
D4	8.7	7.5
D5	9.1	7.7
D6	9.6	7.6

Preparation of waste samples

The preparation of the waste samples for the readability of the dissolved organic carbon was carried out in several steps according to the scheme in Figure 3.

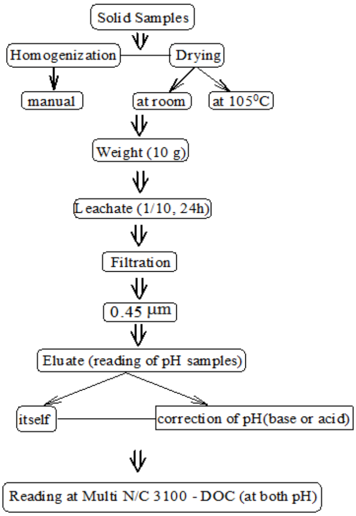

Figure 3. Sample preparation scheme

Results and Discussion

In Table 2 are presented the results obtained for all types of waste samples analysed.

Table 2. Results

Samples	pH – initial (pH units)	DOC – initial (mg/kg s.u.)	pH – final (pH units)	DOC – final (mg/kg s.u.)
D1	4.1	634	8.0	401
D2	6.1	980	7.5	787
D3	6.6	869	7.5	692
D4	8.7	938	7.5	785
D5	9.1	878	7.7	996
D6	9.6	543	7.6	611

From the results obtained it is found that the DOC shows different concentrations by pH variation, even if this variation is not significant. Thus, pH correction in the basic range (9.1 - 9.6 pH units) leads to an increase in DOC concentration. The pH correction between 4.1 – 8.7 pH units range decrease the DOC concentration (Figure 4 and Figure 5). These variations depend on how organic matter is bound in each type of waste.

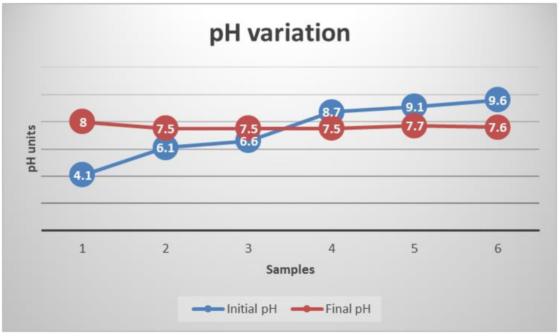

Figure 4. Experimental results of pH

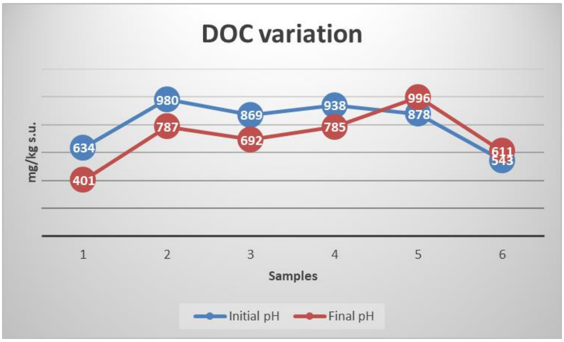

Figure 5. Experimental results of DOC

Through the GO 95/2005, the maximum admissible values for leachate-specific indicators are established, based on which the class of landfill (inert, non-hazardous, hazardous) in which the analyzed waste can be accepted as well as the limit values for certain waste indicators used as additional criteria for establishing the deposit class.

The evaluation of leachate quality resulting from leaching tests is done by comparing the values of the quality indicators determined for leachate with the limit values stipulated in the GO 95/2005.

In Table 3, the maximum admissible limits for the leachate-specific indicators (for L/S of 10: 1 between the levigator and the sample weight) are presented in order to accept a waste in one of the mentioned storage classes, according to the GO 95/2005, as well as the values of the indicators determined for leaching corresponding to the analyzed waste.

Table 3. Results for the DOC indicator analysis reported to GO 95/2005

Samples	UM	Determined Values - DOC		The maximum permissible value (mg/kg s.u) L/S =10 l/kg		
		Initial	**Final**	**inert**	**non-hazardous**	**hazardous**
D1	mg/kg s.u	634	401	500	800	1000
D2	mg/kg s.u	980	787	500	800	1000
D3	mg/kg s.u	869	692	500	800	1000
D4	mg/kg s.u	938	785	500	800	1000
D5	mg/kg s.u	878	996	500	800	1000
D6	mg/kg s.u	543	611	500	800	1000

The leachate quality analysis, resulting from the leaching test, at the L/S ratio of 10 l/kg, and the comparison of the values of the quality indicators determined with the values stipulated in the GO 95/2005, highlighted the following:

Before correction (initial values):

The values of the samples: D1, D6 are within the appropriate limit values required for acceptance of the waste at storage on non-hazardous waste landfills.

The values of the samples: D2, D3, D4, D5 are within the appropriate limit values required for acceptance of the waste at storage on hazardous waste landfills.

After correction (final values):

The value of the sample: D1 is within the appropriate limit values required for acceptance of the waste at storage on inert waste landfills.

The values of the samples: D2, D3, D4, D6 are within the appropriate limit values required for acceptance of the waste at storage on non-hazardous waste landfills.

The value of the sample: D5 is the within the appropriate limit values required for acceptance of the waste at storage on hazardous waste landfills.

Conclusions

The influence of pH depends of type of waste and also to be more neutral. A value appropriate of 7.5 pH units is more stable than a higher one. The industrial waste depends on what they are made. For final values of DOC, the conclusions are next: D1 could be storage on inert waste landfills, D2, D3, D4 and D6 could be storage on non-hazardous waste landfills and D5 could be storage on hazardous waste landfills.

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