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Investigation of Analysis Methods For Detection of Humic Substances Within Leonardite

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Abstract: Leonardite is a lignite form, which has undergone oxidation at high rate during the carbonization process. It has economic value because it contains humic substances at high rate. While it is used in organic agriculture, as soil conditioner, it is also used in other industrial fields such as cosmetics and medicine. Physical properties such as color, as well as chemical properties such as solubility in alkaline media and humic content are examined for the definition and characterization of leonardite. In particular, the detection of humic substance content is the most important feature used in the industrial usage of leonardites. Various instrumental analysis techniques and wet chemical analysis techniques are utilized for this purpose. However, it is a matter of debate whether these methods are applicable for the industry. In this study, instrumental and chemical methods used in the analysis of humic substance were examined. Along with these, industrial, reliable and fast methods have been determined as well.

Keywords: Leonardite, humic substance, chemical analysis, instrumental analysis.

Introduction

Leonardite is a natural organic material which is formed in the soil after millions of years of decomposition (Zoraida et al., 2007). Leonardite has economic value because it contains humic substances such as humic acid and fulvic acid (Tan, 2003). Humic substances are obtained from cheap sources such as leonardite. It is mainly used in many sectors such as agriculture, cosmetics, pharmaceutical industry and animal feed (Dizman and Tutar, 2016; Alak and Müftüoğlu, 2014; Dizman, 2012). For many years, fertilizers obtained from mineral sources such as nitrogen, phosphorus and potassium have been used for the purpose of increasing fertility in agriculture, but later it turned out that such fertilizers cause serious ecological and sociological problems (Özkan, 2008). For this reason, producers have begun to use organic materials that will increase the amount of organic matter in the soil. In Turkey, the usage of imported and domestic humic substances has become widespread in recent years. The determination of solid humic substances in the material such as leonardite is made according to Turkish standards (TSE 5869 ISO 5073) in Turkey (Canıeren, 2015). The reliability of this method is a matter of debate and has two main problems. Since the method is based on total carbon detection, the other organics cannot be separated from each other in the determination of humic substance. The second problem is that the equations which are used in the calculation of humic content in two different samples with different carbon contents contain fixed values. In this case the humic content is determined as an approximate value. On the other hand, in addition to the TSE method, instrumental and wet chemical analysis techniques are also used in the determination of humic content. However, the selectivity and sensitivity of these methods are controversial.

Some studies conducted in recent years upon analyzing humic substances are reviewed in below;

(Tarhan, 2011) has designed a highly efficient leaching method for the recovery of humic substance from some biochemical sources. The author tried to identify the humic content of these sources and conducted a study to develop a new flow injection method (FIA) which is expected to be an alternative to standard methods for analyzing humic content. He has developed a new, fast, precise and selective flow injection method with chemometric approximations by modifying the HPLC system for the quantification of humic substances. (Tarhan, 2011) claimed that the proposed FIA method suggested that it requires less dilution with a wide calibration range (0-2000 mg), he also put forward the system that was able to identify humic acid samples with different concentrations and proved that 60 analyses could be done per hour.

(Saito and Seckler, 2014) have benefited from the low carbon content of the inorganic groups found within the humic materials and have utilized from the potential of the electrical conductivity of the salts. Thus, they tried to analyze the humic substances by measuring the difference of electrical conductivity of the humate salts formed in the humic material.

(Giannouli et al, 2009) examined the humic and fulvic acid contents of 26 different low grade lignites in their study. In order to characterize the lignites, they have detected pH, electrical conductivity and performed maceral analysis. Finally, they detected carboxylic and phenolic functional groups by using FTIR device to determine the humic content.

Peleato, (2013) and Persson and Wedborg, (2001) have conducted humic substance analysis using the liquid chromatograph and fluorescence spectrum. Firstly they

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passed samples through a UVA detector by an organic carbon detector. Then they detected the organic and inorganic groups. Finally, they have claimed that these organic values allow for the simultaneous quantification of humic substance.

In this study, controversial methods which are used to determine the content of humic substance have been examined, and industrial and reliable methods have been reviewed.

Analysis Methods of Humic Substances

Conventional alkali leaching is used to separate humic substances such as humic acid and fulvic acid from the inorganic part of leonardite. In this method, the humic substance is dissolved by an alkaline such as NaOH, KOH, $Na_4P_2O_7.10H_2O$ and the organic part is taken into the solution. Then the content of humic substances is calculated by various analytical chemical and instrumental methods. In this study, the methods used in the analysis of humic substances have been examined under two headings; chemical methods and instrumental analysis methods, and explanatory information has been given about these methods.

Chemical Methods

TSE 5869 ISO 5073 method

TSE 5869 ISO 5073 is used for the determination of the humic content of brown coal and lignite, which is registered by the Turkish Standards Institute. In this method, the content of humic substances is determined by the colorimetric method (Canieren, 2015). The method is based on the oxidation of the organic part with chromate and the remaining part chromate titration.

The method is given briefly as follows; 0.2 g of the sample is weighed and it is poured in a 250 ml flask. 150 ml of sodium pyrophosphate solution is added. It is heated for two hours in a water bath. Samples taken from the water bath are cooled till room temperature. Then purified water is added till the 200 ml line and filtration is carried out. The filtered extract is taken up and the potassium dichromate solution and sulfuric acid is added. After that, the preparated solution is heated in a water bath for 30 minutes. It is dilute with pure water when it comes to room temperature (Özkan, 2008). Three drops of indicator (phenanthroline) are dropped and titrated with ammonium iron (II) sulphate $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$) solution until the color turns to tile red. Finally the humic substance value is calculated. The steps of the TS 5869 ISO 5073 (TSE) method are schematically shown in Figure 1.

This method is a sensitive method depending on the experience of the analyst. During the sampling periode, analysts should be careful. In the case of working with liquid samples, it is difficult to take a representative sample so the error margin of the method also increases. This is one disadvantage of the method.

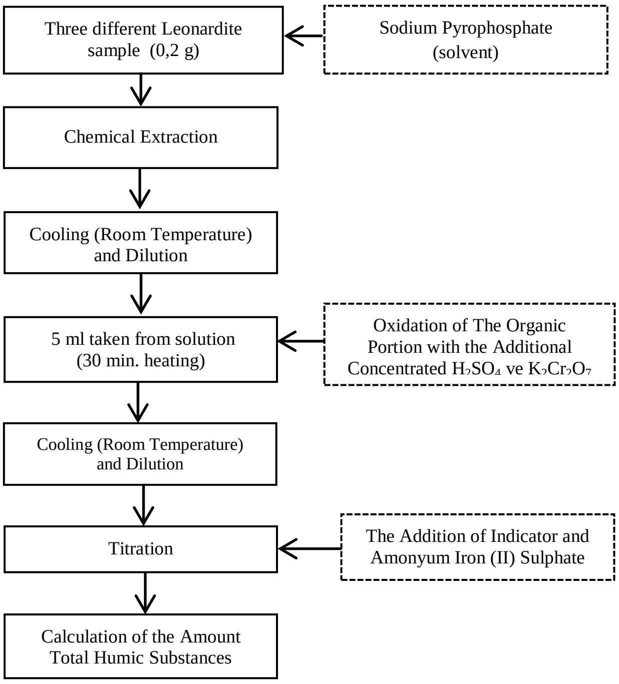

Fig. 1 The flow sheet of humic substance analysing method (TSE 5869 ISO 5073) for brown coals and lignite (Canıeren, 2015).

Chemical precipitation method

Chemical precipitation is a method which is used for the recovery of humic acid. The method is given briefly as follows; 2 g of humic acid sample is extracted with 0.5 M NaOH solution for 1.5 hours and centrifuged. After centrifugation the liquid is adjusted to pH <1. Then, the sample is centrifuged again. The gained solid is weighed which is humic acid (Aşık, 2008). The weight of the precipitated solid is divided into initial samples. The result gives the percentage of humic acid. In this method, unlike TSE method, humic acid and fulvic acids which constitute humic substances can be analyzed separately.

Schnitzer method

The Schnitzer method is given briefly as follows; first, 10 g of sample is weighed. Then it is placed in a 250 ml centrifuge tube. After then, 0.5 M NaOH solution is added to centrifuge tube and left to shake. The shaken samples are centrifuged twice. The humic material precipitates to the bottom of the tube after centrifugation. The amount of precipitated humic acid is proportional to the initial sample. Finally, the percentage of humic acid is calculated (Aşık, 2008). This method allows us to analyze humic acid and fulvic acid separately. Also, the method is suitable for studies that require more humic acid as a material and can be used for obtaining humic acid. Since it is a method with high chemical consumption and long extraction time, the practicality of the method reduces.

Instrumental analysis methods

As in Leonardite, there are also humic substances in the earth and underground water. Lots of organic substances such as carbohydrates, carboxylic acids, phenols, amino acids and proteins are present in underground water (Her vd., 2003). Because of the complicated structure of organic materials, analysis can be done by representative standards (Peleato, 2013). When representative standards are used for humic substance analysis, the total organic carbon and dissolved organic carbon are calculated. Thus, humic analysis can be done (Gone, 2009). While organic materials in the source waters adsorb the high wavelength light, it is known that inorganic components do not adsorb light above 230 nm (Korshin, 1996). By using this property difference, it is possible to perform analysis of humic substances. This section will provide representative information on the application of two different methods, including liquid carbon chromatography and fluorescence excitation-emission matrices used in the analysis of humic substances.

Liquid chromatography – organic carbon detection

Chromatography in general is based on the principle that various substances move at a different speed between a fixed phase with the help of moving phase. The liquid chromatograph is used in the analysis of many organic substances. In this method, prior to chromatographic separation, the dissolved organics in the hydrofluoric and hydrophilic groups are detected by a UV detector. Hydrophilic organic materials are divided into five groups. These include biopolymers, humic substances, building blocks of humic substances, low molecular weight acids and low molecular weight neutrals (Peleato, 2013).

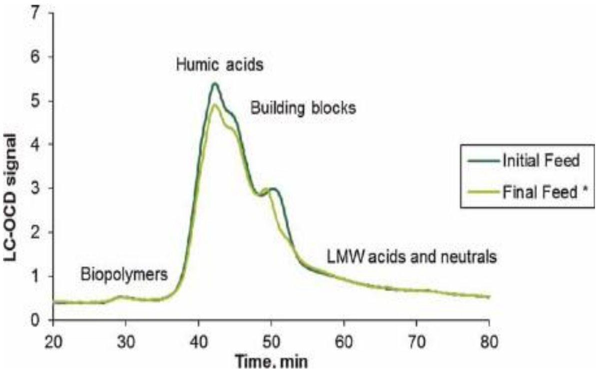

Fig. 2 A view of the wavelengths of functional groups which is obtained by a liquid chromatograph (Kazner, 2014).

Fluorescence excitation-emission matrices method

Analysis of fluorescence spectra is completed through collection of fluorescence excitation-emission matrices. These matrices represent the fluorescence intensity in the various excitation-emission pairs. Fluorescence spectrum analysis allows different components of the natural organic matter fractions to be distinguished from each other in a fluorescence spectrum. By means of the spectrum, humic acid, fulvic acid and aromatic proteins (tryptophan or tyrosine) can generally be identified (Figure 1).

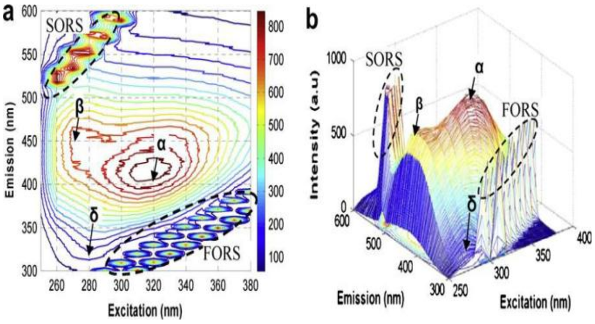

Fig. 3 Example freshwater FEEM with humic acid (α), fulvic acid (β), and protein-like (δ) peaks. (a) top-down view, (b) 3D view (Peiris et al., 2010), (Peiris et al., 2010).

This method gives fast and high precision results compared to other humic substance measurement techniques. In addition, the method can provide more selective results than UV detector measurements. It is also less affected by ambient motion (Persson and Wedborg, 2001).

Conclusion

In this study, chemical and instrumental methods were investigated for their use in analysis of humic substances. The aim of this study is to see the differences between the methods and to reveal problems present in them. The analysis times of the chemical methods are longer than the instrumental methods and it has also been determined that sensitive sampling is required during the analysis phase. When the chemical methods are compared among themselves, in the TSE method, the carbon content is added to calculation for each sample and this makes the method more reliable. However, in the TSE method, humic acid and fulvic acid cannot be analyzed separately and there are certain problems in the analysis of liquid samples as well. The reference institution conducts studies to solve the problems related to TSE 5869 ISO 5073 method. On the other hand the fluorescence excitation-emission matrices method gives rapid and high efficiency results compared to other humic substance measurement techniques. In addition, it can give more selective results than other instrumented methods and it is less affected by ambient motion. As a result, TSE 5869 ISO 5073 and fluorescence excitation-emission matrix methods are thought to be suitable for the needs of the industry as they can provide fast and reliable results.

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