

ENHANCEMENT OF DECONTAMINATION OF PETROLEUM HYDROCARBONS IN CRUDE OIL POLLUTED SOIL BY USING CYCLODEXTRINS

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Abstract

Soil contaminated by total petroleum hydrocarbons is a well-recognized worldwide problem because of its strong persistence in the environment and its potentially toxic effects on human beings, animals and microorganisms. During the past three decades, the research and development of remediation technology for petroleum hydrocarbons-contaminated soil have been systematically studied such as the physical, chemical and bioremediation technologies. To address the associated environmental concerns, innovative remediation technologies are urgently needed. Cyclodextrins are nonhazardous and environmentally acceptable organic substances that have been shown to be biodegradable in soil and water after their introduction into an environmental system. The decontamination technique based in cyclodextrin extraction has been developed to eliminate petroleum hydrocarbons. Cyclodextrins have successfully been used in soil cleaning technologies as solubiliser-carrier molecules. These molecules can transfer continuously the insoluble contaminants from the soil surface to the aqueous phase by complex formation. In the aqueous phase the microorganisms can degrade the contaminants much easier partly because these molecules become available for the microbial cells, partly because the entrapment of contaminants by cyclodextrins reduces their toxicity.

Key words: decontamination, petroleum hydrocarbons, polluted soils, cyclodextrins

INTRODUCTION

Cyclodextrin, an important class of polysaccharides with a cyclic oligosaccharide, is formed by the action of cyclodextrin glucosyl-transferase on starch and belongs to the cage-type molecule family (Kankan et al., 2020). Structurally, the molecule is a slightly conical ring, which is characterized by a dimensionally stable hydrophobic cavity and hydrophilic outer surface with primary hydroxyl groups lying on the above and the secondary hydroxyl groups below (Li et al., 2016). Its axial cavity structure can provide a hydrophobic microenvironment, which can accommodate the appropriate size of hydrophobic molecules, and form a unique and readily soluble host-guest inclusion complex in terms of geometric compatibility, thus increasing the solubility of hydrophobic molecules in the aqueous phase (Rekharsky and Inoue, 1998; Fernando et al., 2019).

MATERIALS AND METHODS

Cyclodextrins were the first compounds studied in terms of complexation behaviour and catalytic properties, the objective being to mimic enzymes. The first publication appeared in 1891, when Villiers reported the isolation of two different types of crystalline compounds from the degradation of starch treated with *Bacillus amylobacter* bacteria. Villiers characterized these compounds by their physical properties and named them "cellulosins". A few years later Schardinger published more physical data relative to these compounds. He continued with the isolation of the bacterium responsible for the formation of cyclodextrins (*Bacillus macerans*) which is today the most used source in the world for the production of cyclodextrins. Because of his pioneering work, cyclodextrins are often referred to as Schardinger dextrins (Fenyvesi, 1996).

RESULTS AND DISCUSSIONS

The determination of the total petroleum hydrocarbon parameter (THP) is carried out by gravimetric methods and instrumental analysis methods with modern equipment.

The gravimetric methods of analysis are not very precise, being vulnerable to many and varied sources of errors (such as non-selective extraction), while the instrumental methods (IR spectrometry, gas chromatography, mass spectrometry and combined methods) provide results, comparable very good, which is essential to arrive at a correct assessment, within admissible limits, of a possible pollution in such a complex matrix as the soil.

The samples are subjected to a solid-liquid extraction with a specific solvent in the Soxhlet apparatus, consisting of a flask, extractor and refrigerant. The extraction time is at least 4 hours, depending on the hydrocarbon content of the analysed sample (SR 13511:2007). The solvent used is not selective and there is a high probability of the risk that, in addition to petroleum hydrocarbons, it also extracts part of the organic matter of the soil (Toti et al., 1999).

The total hydrocarbon content in oil is expressed in mg/kg, relative to dry substance (105°C), and is calculated with the formula:

$$THP(mg/kg) = \frac{(m_2 - m_1) - (m_4 - m_3)}{m} 10^6$$

where:

m_1 - mass of the capsule without sample residue, in grams;

m_2 - the mass of the capsule with the sample residue, in grams;

m_3 - mass of the capsule without the control residue, in grams;

m_4 - the mass of the capsule with the control residue, in grams;

m - mass of the sample used, in grams.

Instrumental methods are modern analytical methods that, through the

precise results obtained, allow us to correctly evaluate the potential negative effect of hydrocarbons on the soil. The speed, precision, sensitivity, reproducibility of these methods and, above all, the expansion of their use on a wider scale and in all countries seriously engaged in the prevention and combating of soil pollution with oil, are just as many arguments that necessarily require their use (Saterbak and et al., 2000).

IR spectrometry is a method that measures the absorbance of a sample depending on the type and abundance of chemical bonds existing in the structure of the hydrocarbon components in the soil sample (Kasper et al., 1991). This method involves 3 stages: Extraction using a specially selected solvent, which does not contain C-H bonds; In the case of this research, the solvent is 1,1,2-trichloro-1,2,2-trifluoroethane or carbon tetrachloride. Interferences with soil compounds (organic matter and humus) that do not enter the structure of oil are eliminated by adsorption on activated silica gel of hydrocarbons, followed by their elution with an appropriate solvent. Measurement of absorbance at 3000 cm^{-1} and calculation of hydrocarbon concentration using a calibration curve made up of standard hydrocarbons (Bishop, 1997). The analysis of the total hydrocarbon parameter (THP) is based on measuring the absorbance at 3000 cm^{-1} and calculating the data using the following formula (Bishop, 1997):

$$THP = \frac{mg/l * vf}{g(v)}$$

where: mg/l – hydrocarbons (mg/l) (from the calibration curve)

vf – final extract volume (l)

$g(v)$ – weight (g) or volume (l) of the sample

It should be noted that this method is not recommended for the determination

necessary to identify the presence of hydrocarbons and to assess the possibility of contamination risk. Instead, this method is used, however, to establish the types of connections in the case of soil remediation, already assessed as being contaminated with oil (Bishop, 1997).

A method approved by the Environmental Protection Agency (EPA) and recommended for determining the presence of hydrocarbons and evaluating the possibility of contamination risk is Method 418.1. This consists in determining the THP by extraction in a solvent (freon) from a mixture and reading the results with the help of an IR spectrometer. The results of this method depend on the selectivity of the solvent used to extract as much as possible only the hydrocarbons contained in the oil (Reid et al., 1998; Sadler and Connel, 2003).

As part of the physical and chemical analysis laboratory for soil science, agrochemistry and environmental protection within the National Research and Development Institute for Pedology, Agrochemistry and Environmental Protection, Bucharest, the method based on liquid-solid extraction of petroleum products together with other organic substances is also used from soil and/or waste in organic solvent (carbon tetrachloride, tetrachlorethylene). After retaining the polar substances on the fluorisil, the petroleum products are dosed from the purified extract of the organic solvent used by infrared spectrophotometry, measuring the absorbance at 2930 cm^{-1} corresponding to the bond - CH_2 (SR 7877-2:1995).

The content of petroleum products in the soil is expressed in mg/kg dry matter and calculate:

a) Automatically, with the help of the software after entering the identification data of the sample, the name of the method; the result is related to the concentration factor (extract volume/soil mass).

b) Manual, with the formula:

$$c = c_c * \frac{V_{ex}}{m_p} * SF * \frac{100}{su}$$

in which:

c - the content of the petroleum product relative to the dry mass, in mg/kg;

c_c – the concentration of petroleum products extrapolated on the calibration curve for the sample extract to analyze;

V_{ex} - volume of extract, ml;

m_p mass of soil pretreated for analysis, g;

SF the overload factor resulting from the pretreatment;

su dry substance content, %.

For air-dried soil, the formula applies:

$$c = c_c * \frac{V_{ex}}{m}$$

in which:

c – the content of the petroleum product relative to the dry mass, in mg/kg;

c_c – the concentration of petroleum products extrapolated on the calibration curve for the extract of the sample to be analyzed;

V_{ex} - volume of extract, ml;

m – mass of air-dried soil, g;

Gas chromatography is a technique used for the separation and detection of components in a mixture. With the help of gas chromatograms, results are obtained in a wide range from butane (n-C₄-C₁₀) to dotricontan (n-C₃₂-C₆₆) (Bishop, 1997).

In the case of contaminated soils, since most hydrocarbons cannot be extracted from samples with the same efficiency, this type of analysis (gas chromatography) is possible, especially in the case of volatile substances, by applying special

procedures to obtain a satisfactory recovery from the matrix (Xie, 1999), as follows from the following.

Some specific analytical aspects related to the determination of volatile hydrocarbons As mentioned before, the hydrocarbon components of gasoline have low molecular masses and are volatile, the major components of gasoline being benzene and its alkyl substituents (Banerjee and Gray, 1997).

Very few regulations include a definition of the boiling point for volatile compounds, taking into account that some volatile substances (eg naphthalene) sublime without boiling, while others evaporate in significant quantities before reaching their boiling point. Australian Standards (1999) define the boiling point or sublimation temperature of a volatile compound as the passage of that compound from a solid state to a gaseous state under normal conditions (Sadler and Connel, 2003). Regarding the preparation of soil samples containing volatile substances for analysis, there are two procedures: the "headspace" method and the solid-liquid extraction method with different solvents, although the two procedures used do not necessarily lead to the same result.

The "headspace" method involves collecting soil samples with immediate introduction and hermetic closure in a special container. Volatile hydrocarbons are found in the pores of the soil and will soon flood the free space left in the collection vessel. The volume of the collected sample depends on the concentration of volatile substances in the soil. The sample is transported to the laboratory at a temperature of 4°C, where it can be analysed directly from the air above the soil collected by gas chromatography with its variants (US EPA 5035, 1996; US EPA 5032, 1996 or US EPA 5021, 1996) (Sadler and Connel, 2003).

The solid-liquid extraction method with different solvents consists in collecting the sample with a special device that introduces the sample into a laboratory bottle with a known content of ultrapure methanol. After that, the methanolic fraction is analysed by gas chromatography.

A new extraction method, accelerated solvent extraction (ASE), provides much better results compared to the Soxhlet method. The extraction time is much shorter and the amounts of solvent used are much smaller, for example 10 g of soil can be subjected to extraction with maximum yield in less than 15 minutes, using only 10 ml of the solvent known as Dionex ASE 200. The detectors used in gas chromatography for the determination of volatile organic compounds in the soil are:

- ✓ flame ionization detector (FID) and
- ✓ plasma ionization detector (PID) or mass spectrometer (MS).

FID detectors are sensitive to all carbon compounds, while PID detectors are only sensitive to the energy of the lamp used. The columns used in the determination of volatile hydrocarbons are varied and, in general, boron capillary columns with a length of 105 m are used. The thermal regime used in gas chromatography is in the range of 40°-240°C with the detector maintained at 250°C and the injector at 200°C. Some specific analytical aspects related to the determination of semi-volatile and non-volatile hydrocarbons. In most cases of soil contamination with hydrocarbons, special attention must be paid to the presence of semi-volatile and non-volatile compounds, the analysis of these hydrocarbons also involves a chromatogram. The collection, handling of samples and the method of sample preparation is completely different from the steps taken in the case of volatile hydrocarbons. In this case, no procedures are necessary to prevent the loss of the analyte (the substance that is the object of the determination) during the collection of the respective sample.

Before performing the analysis of these components, it is necessary for the hydrocarbons to be brought into solution. The probability of adsorption of hydrocarbons on the soil increases with the increasing hydrophobicity of the molecules. The most common method for determining total petroleum hydrocarbons is gas chromatography. Depending on the degree of resolution and level of information, a number of measuring equipment may be involved. The most common requirement related to hydrocarbons is the determination of THP, which is the main characteristic of crude oil (Sadler and Connel, 2003).

One of the most important problems related to hydrocarbons as pollutants is the phenomenon known as the effect of atmospheric agents. This term refers to the change in the composition of hydrocarbons over time, under the action of various phenomena such as evaporation, solubilization, chemical reaction or biotransformation. In the case of volatile organic compounds, the significant process is evaporation, which causes a decrease in the concentration of hydrocarbons with time. Long-chain hydrocarbons are more exposed to various changes through other processes and, implicitly, it becomes absolutely necessary to identify the different products resulting from such reactions, which can be more dangerous than the initial ones (Ekechukwu and Young, 2004).

CONCLUSIONS

The analysis methods that can be used to determine the total hydrocarbon parameter in oil can be gravimetric, infrared spectrometry and gas chromatography. The gravimetric method has the following advantages: it does not require expensive equipment, and the necessary equipment can be found in any laboratory (laboratory glassware, water bath, analytical balance, glass chromatographic column, 50 ml glass capsules, oven, distillation installation).

Among the disadvantages of this method are low sensitivity, high interferences, high consumption of reagents, and the method is recommended for soils with total oil hydrocarbons over 1000 mg/kg.

IR spectrometry has the advantage of greater sensitivity compared to the gravimetric method, it being recommended for soils with total oil hydrocarbons of over 100 mg/kg, but compared to the gravimetric method, it requires higher costs for laboratory equipment. The gas chromatographic method has the advantage of greater sensitivity compared to the gravimetric method, it has a very good selectivity, being able to determine quantitatively including volatile compounds. Another advantage would be the lower costs required for the purchase of reagents. Compared to the gravimetric and IR methods, it requires higher costs for laboratory equipment.

Cyclodextrins are also non-toxic and easily degradable products in the soil, they do not pose any risks to life in the soil. The application of cyclodextrins has the role of improving the biological method of remediation of soils polluted with oil hydrocarbons by increasing the efficiency of the biodegradation process. They have the ability to favour the development of existing bacteria in the polluted soil and to increase the rate of biodegradability of petroleum hydrocarbons.

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