NATURAL ATTENUATION IN A RESIDUAL SOIL FROM SOUTHERN BRAZIL CONTAMINATED WITH DIESEL AND BIODIESEL MIXTURES

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ABSTRACT
The intense and growing consumption of fossil fuels generates the need to seek more environmentally suitable alternative. To meet this need the biodiesel enter in the fuel market. In Brazil is now being mixed a ratio of 5% of biodiesel in diesel fuel. This mixture can be considered as a contaminant of soil if some accident occurs. There are many processes used for remediation contaminated soils. Among these processes, bioremediation is a good technique, because the microorganisms are considered efficient biodegraders due to its abundance, species diversity and its versatility and ability to adapt to adverse environmental conditions. The monitored natural attenuation stands out mainly due to low cost and low intervention in the natural area conditions. The aim of this study was to evaluate the degradation in a clayey soil contaminated with diesel and biodiesel mixtures. The soil was contaminated with 4% of fuel over the mass of dry soil. The soil moisture after contamination was 34%. It was used six different percentages of biodiesel with the diesel (0, 5, 12.5, 20, 50 and 100 percent). It was molded in 12 bioreactors being 2 bioreactors for each percentage of contamination. Samples were collected at 105 days after the contamination. These were analyzed quantitatively by Soxhlet method. The results show that mixtures with higher percentages of biodiesel showed higher degradation. This demonstrates that the biodiesel is more biodegradable than diesel.

Key words: Biodiesel, bioremediation, natural attenuation

RESUME
El consumo intenso y cada vez mayor de combustibles fósiles genera la necesidad de buscar alternativas ambientales adecuadas. Para cubrir esta necesidad es que el biodiesel fue incorporado en el Mercado de combustibles. En el Brasil ahora se está mezclando una proporción de 5% de biodiesel en el combustible diesel. Esta mezcla se puede considerar como contaminante del suelo y de los recursos hídricos si suceder um accidente. Hay muchos procesos de recuperación usados para los suelos contaminados. Entre estos procesos, el biotratamiento es una buena técnica, porque los microorganismos se consideran los eficientes biodegradadores debido a su abundancia, diversidad de la especie y su flexibilidad y capacidad de adaptarse a las condiciones ambientales adversas. La atenuación natural supervisada se destaca principalmente debido al bajo costo y a la intervención baja en las condiciones naturales del área. La meta de este estudio era evaluar la degradación en un suelo arcilloso contaminado con las mezclas del diesel y del biodiesel. El suelo fue contaminado con uma proporción de 4% de combustible sobre la masa del suelo seco. La humedad del suelo después de la contaminación era el 34%. Fueron utilizadas seis porcentajes del biodiesel con el diesel (el 0, 5, 12.5, 20, 50 y 100 por ciento). Fueron moldeadas en 12 biorreactores que eran 2 biorreactores para cada porcentaje de la contaminación. Las muestras fueron recogidas en 105 días después de la contaminación. Éstas eran analizadas por el método de Soxhlet cuantitativo. Los resultados demuestran que las mezclas con porcentajes más altos del biodiesel demostraron una degradación más alta. Esto demuestra que el biodiesel es más biodegradable que el diesel.

1 INTRODUCTION

The environment concern is increasing because the human activities generate large environmental changes. The increasing soil and groundwater contamination by petroleum fuels (diesel, gasoline and other products) has been highlighted in recent decades, mainly due to the frequency which these episodes are happened and the severity with which the environment is affected (SPINELLI, 2005). According to data from FEPAM (2010), from August 2006 until September 2010 were registered in Rio Grande do Sul State (located in southern Brazil) 26 environmental accidents involving oil fuels such as diesel, gasoline and biodiesel. These accidents have contaminated the soil and in some case the groundwater.

The biodiesel is being added in the Brazilian energy matrix as a component with the diesel. This alternative energy source was introduced by Law number 11,097 in 2005, which provides for the introduction of biodiesel in the Brazilian energy matrix and was fixed at 5% (five percent-B5) by volume. The addition of 20% of biodiesel in diesel oil (B20) will be required probably until 2018.

The production of biodiesel as an alternative fuel source can provide considerable gains and benefits to the

environment. According to Pinto et al. (2005) the use of biodiesel has lower emissions of carbon dioxide (CO_2), carbon monoxide (CO), sulfur oxides (SOx) and particulate matter.

A variety of physical-chemical and biological processes have been used to remediate contaminated soils. However, many of these have high technology cost and major intervention in the site. The biological process is an internationally known technology and widely used to removal oil contaminant. This happened mainly due to efficiency and the low cost when compared to physical-chemical alternatives (ABDUSALAM e OMALE, 2009; KARAMALIDIS et. al, 2010).

The microorganisms are considered efficient biodegrades due to its abundance, species diversity, catabolic and anabolic versatility and ability to adapt to adverse environmental conditions (MORAES e TORNISIELO, 2009). Still, according to Benedict et al. (2004), the processes are simple and applicable to large areas. Among the various bioremediation techniques, the most frequently used are the natural attenuation, the biostimulation and the bioaugmentation (MARTINS et al., 2003; BENTO et al., 2004; LIN et. al, 2010).

The natural attenuation is the answer of hydrogeological systems to contamination involving chemical, physical and biological processes that, under favourable conditions, act without human intervention, reducing mass, toxicity, mobility, volume or concentration of soil contaminants over time (BOSCOV and GIMENEZ, 2008). According to Jacques et al (2007), the natural attenuation is the technique that uses natural processes to degrade and reduce contaminant concentrations to acceptable levels. The assessment of biodegradation by this method are needed several studies that will be capable of evaluating the rate of degradation or reduction of the contaminant (MENEGHETI, 2007).

In contaminated soils the efficiency of natural attenuation or bioremediation process depends largely on the capacity of biodegradation of indigenous microorganisms (PENET et al., 2006).

Although biodiesel is a biodegradable fuel more than fossil fuel, its biodegradability is still unknown in many types of soil. Also do not know the influence of different amount of biodiesel added to diesel oil, such as the degradation rate by the action of indigenous microorganisms in clayey soils.

The aim of this research was to found the influence of different amount of biodiesel in diesel oil in biodegrading capacity in a residual soil from southern Brazil.

2 MATERIALS AND METHODS

The study was conducted in the laboratory of environmental geotechnics, at the University of Passo Fundo, Rio Grande do Sul State, Brazil.

2.1 Soil

In this study was used a B-horizon basalt residual soil, commonly found in southern Brazil which belongs to the geological province of Rio Grande do Sul highlands, according to the geology of Rio Grande do Sul and Parana basin according to the Brazil geology (BERTORELLI; HARALYI, 1998).

The samples were collected to 1.2m depth. The Figure 1 presents the soil horizon with its brown color characteristic. The Table1 shows some geotechnical and physical-chemical soil properties.

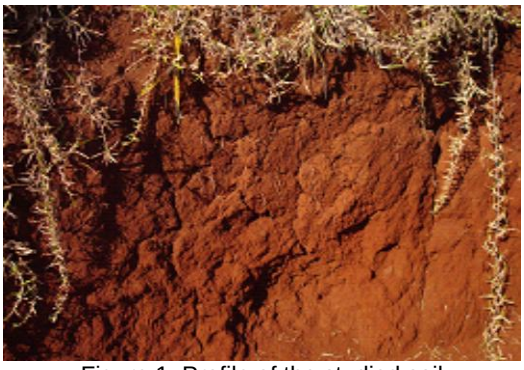

Figure 1: Profile of the studied soil

Table 1: Geotechnical and physico-chemical soil

Parameter	Value
Clay (%)	68
Silt (%)	5
Sand (%)	27
Liquid Limit (%)	53
Plasticity limit (%)	42
G	2.67
Natural moisture (%)	34
Specific weight natural (kN/m³)	16.3
Void Index	1.19
Degree of Saturation (%)	75.7
Porosity (%)	54
pH	5.4
Organic Matter (%)	< 0,8
Cation Exchange Capacity (cmolc/dm³)	8.6
Hydraulic conductivity (m/s)	$1.39x10^{-6}$

Source: Prietto et al.(2010)

The pedological classification, according to Streck et al. (2008), is a red dystrophic oxisol humic (Passo Fundo unit). From the geotechnical point of view the soil is classified as CH (clay with high plasticity). The soil has a low pH, high clay content, low organic matter content and low cation exchange capacity (CEC), typical of soils with a predominance of clay mineral kaolinite.

2.2 Bioreactors

In the tests were used cylinders with bioreactors function. These cylindrical had 24cm in diameter and 24cm high, with a volume of 0.010852 m^3 (figure 2).

2.3 Soil contamination and bioreactors setting up

The soil was contaminated with different mixtures of diesel and biodiesel, which are called B0, B12.5, B20, B50 and B100 (the number together with B shows the percentages

of biodiesel used in the mixture). The contamination was made with 4% of contaminant related to soil dry weight. The soil moisture used was 34% and specific weight was 16 kN/m^3. These values represent the soil field characteristics, i.e. void index of 1.19 and porosity of 54%.

The total mass of soil contained in the bioreactor was divided into 5 equal parts and each part was submitted to contamination and to static compaction within the bioreactor until found the field characteristic. It was initially added water until it reached 30% of moisture and, after well homogenized; it was added 4% of contaminant, leaving the soil again with the value of field moisture of 34%. The bioreactors were maintained in laboratory conditions with controlled temperature of 24ºC(±1ºC). The Figures 2 and 3 show the mix of the soil and the bioreactor after they were concluded, respectively.

Figure 2: Soil mix and the bioreactor setting up

Figure 3: Bioreactors conclude in the laboratory

2.4 Soil sampling and analysis

The contaminant degradation analysis in the soil mixtures was performed 105 days after the contamination.

Soil samples were collected randomly in the bioreactors through a metal sampler (Figure 4). For each bioreactor was collected around 15g of soil.

To evaluate the contaminant degradation in the soil was used the method based on Soxhlet gravimetric quantification of material extracted by solvent, adapted from Standard Methods for the Examination of Water and Wastewater (APHA,2000).

Figure 4: Soil sampling in bioreactors

3 RESULTS AND DISCUSSION

The Figure 5 shows the average percentage of residual contaminants still present in the soil at the end of the experiment.

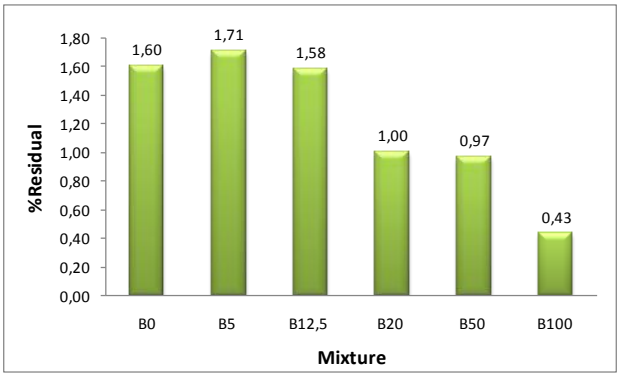

Figure 5: average residual contaminants at 105 days

All Mixtures have shown a reduction in residual contaminants at the end of the test when compared the percentage of initial contamination of 4%. The B100 was the mixture that presented the lower residual fraction with 0.43% of contaminant, followed by B50 and B20, with 0.97% and 1.0% respectively. These values indicate that the lower the residual percentage the higher is the degradation of these contaminants.

The degradation percentage in 105 days is shown in Figure 6.

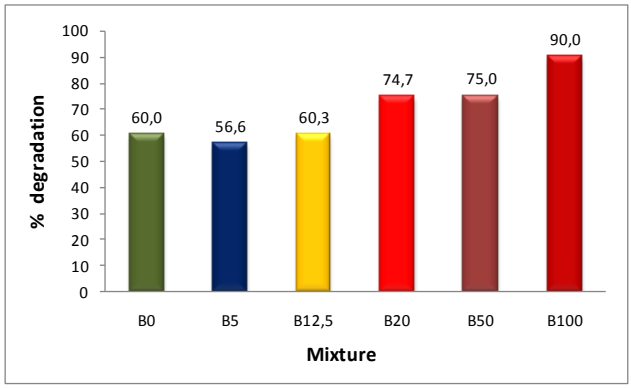

Figure 6: Degradation of mixtures after 105 days of testing

By the process of natural attenuation (indigenous microorganisms) after 105 days was observed that the contaminant degradation has occurred in all mixtures studied. As expected, the largest degradation occurs in the mixture B100 due to the higher biodiesel biodegradability.

It can also be observed in Figure 6 that the amount of degradation percentage of the contaminants increases with the biodiesel content in each mixture, i.e. the higher the amount of biodiesel in the mixture increased the biodegradation of contaminants by microorganisms.

The data obtained in this study corroborate the studies performed by Owsianiak et al (2009) and Pasqualino et. al (2006) that shown the biodiesel degradation was higher than the diesel. However, mixtures contained up to 12.5% of biodiesel did not show difference in biodegradation ratio when compared with diesel oil biodegradation. This shows that biodiesel is important from environmental point of view when added to mixtures in amounts above than 12.5% for improve the biodegradation in residual soil from southern Brazil.

4 CONCLUSIONS

From the results presented in this work it is possible to get the following conclusions:

- the use of natural attenuation technique is a good alternative for decontamination of clayey soils from southern Brazil contaminated with diesel and biodiesel mixture;
- up to 12.5% of biodiesel added to the mixture was not possible to find difference in degradation capacity;
- amount of biodiesel in the mixture above 20% increased the contaminant biodegradation by microorganisms;
- native microorganism has higher capacity to degrade the biodiesel contaminant (B100) then diesel contaminant (B0).

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