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OPTIMIZATION OF PHENANTHRENE REMOVAL IN BIO-SLURRY REACTOR:  
FOCUS ON MASS-TRANSFER PROCESSES

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# ABSTRACT

This thesis is the result of experiments carried out in Marne la Vallée university laboratories and deal with the optimization of Phenanthrene removal from the soil with a bio-reactor. It focuses on mass-transfer processes.

The polycyclic aromatic hydrocarbons are organic chemicals produced in incomplete combustions of organic matters, such as oil, coal, wood. The PAHs are produced by both natural and anthropogenic sources, even though the latter one represents the main form of pollution.

The PAHs are very toxic, cancerogenic and mutagenic and for their ubiquitous occurrence in the environment, represent a great concern.

The bio-remediation is an organic pollutant remediation method which uses the metabolism of microorganisms culture in order to degrade dangerous chemicals. The aim of this thesis, as above mentioned, is to optimize the working conditions of one of the system adopted to conduct a bio-remediation process called soil-slurry bioreactor.

The soil-slurry bioreactor foresees the PAHs removal from the soil in a bio-reactor and in controlled conditions, such as agitation, aeration, pH, temperature. These latter are set in order to enhance as much as possible the microorganisms growth and, therefore, the pollutant degradation.

The experiments have been carried out with a glass bioreactor (6 liters of working volume) of 30 cm of height and 17.5 cm of diameter with a curved bottom. This bioreactor has a connection with the air, which gets blown in by glass sparger from the bottom. A mechanical agitation is also contemplated and is produced by a propeller connected to a motor, able to reach up to 2000 rpm. The bioreactor is also provided with a thermal jacket formed by two glass walls connected to a cryostat working with water as heat-transfer fluid which permit to keep the desired temperature stable.

For the experiments the Phenanthrene, a PAH with three fused rings, has been used.

Preliminarily, several calibration tests have been carried out, in order to make the measurements procedures efficient and reproducible.

The high pressure liquid chromatographer (HPLC) have been used to identify and quantify the chemicals. the range from 0,0005 to 0,25 mg/l has been investigated. The fluorescence detector worked well with all the concentration range, even though, in order to reach higher precision, two calibration curve have been built, one for low and one for high concentrations.

The UV-VIS detector showed good results just for the high concentrations, probably due to its less sensitivity.

Preliminarily, spiking and extraction test have been carried out as well, in order to define a procedure to measure the phenanthrene concentrations in the soil. Soils at three different concentrations have been spiked, and the extraction with a mechanical agitator have been tested.

The extraction have never reached more than 70% efficiency . in order to improve the extraction percentage the combined use of the mechanical agitator and ultrasonic bath as well as sequential extraction from the water/acetone phase has been suggested.

Volatilization experiments have been also carried out in order to understand the effect of volatilization on the whole removal process. Two test in beaker have been carried out, focusing on the effect produced by the stirring and the bubbling. The results showed that the bubbling make the volatilization faster, reaching the 50% just after three hours. The acceleration induced by the aeration totally vanished after 24 hours.

With or without the aeration, at the beginning the volatilization grew steeply, trend particularly marked in presence of aeration, tending asymptotically to the zero with increasing the time.

Moreover a correlation has been proposed, in order to predict the volatilization rate. An exponential relationship between the Phenanthrene concentration in liquid phase and the constant of volatilization has been defined.

Finally oxygen mass-transfer tests in the bio-reactor has been carried out in order to investigate the effects of the operational variables on the oxygen absorption. The tests have been performed with a polarographic sensor able to determine the exact quantity of oxygen in solution and a data logger which allow to save and check the data from a display.

The results have showed that the mechanical agitation has a different effect at the low and the high speeds on the  $k_La$ . It has produced a surge of the  $k_La$  at the low speeds and a linear increasing at the high ones, while the bubbling basically has showed a quadratic trend. The results also have showed that the interaction among these operational variables produces a progressive reduction of their individual influence on the oxygen mass-transfer rate, of almost the 50%.

Different soil content has been also tested. The results have showed a general decreasing of  $k_La$  with the increasing of the soil content.

The effect of salinity on the oxygen absorption has been investigated similarly. The results showed that saltier solutions make higher  $k_La$  values. The above mentioned effect vanished with increasing of agitation.

In order to predict the oxygen absorption a correlation between the  $k_La$  and the operation variables has been investigated. The results have showed that the increasing of the soil content reduce the positive influence on the oxygen absorption of the stirring and the bubbling.

The tests have showed that the stirring and the bubbling have essentially the same influence on the oxygen mass-transfer. The more the soil content is and the more their effects become similar in term of efficacy and quality. In order to identify the perfect combination among the oxygenation techniques, a fully volumetric volatilization test and the definition of a global equation, which allow to obtain the minimization of volatilization and the maximum microorganisms growth rate, have been suggested.

