

Biotreatment Technique to Treat Oil Wells Drilling Wastes

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Abstract

The minimization, treatment and disposal of drilling wastes especially oily wastes are important environmental issues. In this research two fungal isolates named *Pleurotus ostreatus* and *Trichoderma harzianum* were chosen carefully for the purpose of biotreatment of oily drilled cuttings which resulting from drilling oil wells using oil based muds (OBMs).

A relationship of total petroleum hydrocarbon degradation in oily drilled cuttings with time has been obtained. The results showed that *Pleurotus ostreatus* and *Trichoderma harzianum* can be considered hydrocarbon degrading microorganisms and the used biotreatment is cost effective process since most of the materials used in the cultivation and growth of the present fungi were available and cheap agricultural wastes.

The best hydrocarbon degradation was observed in case of using both fungi together with 5 % by weight microorganisms concentration ratio (MCR) and with the same ratio of nutrients expressed as C/N/P equal to 100/50/10 nutrients components ratio which gave average total petroleum hydrocarbon degradation of about 205 ppm per day.

Keywords: oil wells, drilling wastes, biotreatment, fungal.

Introduction

Obviously, no oil or gas well can be drilled without creating waste. Drilling wastes include formation cuttings and drilling fluids with their chemical additives. The drilling waste solids from oil base mud (fluid) operations require specialized treatment prior to the appropriate "end-point" disposal. Sometimes, bioremediation is used as an interim treatment to reduce the overall level of hydrocarbon contamination prior to disposal step [1].

Biotreatment (also known as biological treatment or bioremediation) is a well-proven environmentally acceptable technology that uses microorganisms (fungi) to biologically degrade (break down) hydrocarbon waste into nontoxic residues and reduce contaminates concentrations to acceptable levels

Many microorganisms have been isolated from soil contaminated with oil, sedimentary lakes and petroleum tanks, which can utilize some petroleum components like

gasoline, kerosene, naphthalene, benzene, mineral oils and paraffin wax [2].

Also, many microorganisms involving bacteria, fungi and yeasts were isolated and studied for their ability of utilizing or producing hydrocarbons [3, 4, 5].

United States Environmental Protection Agency (USEPA) stated that there are many contaminants which can be treated through bioremediation like diesel fuel, oil and coal tar, lubricating oils, gasoline, kerosene, heavy and light oil, benzene, toluene, ethyl-benzene ...etc [6]. Table 1 gives the bio-degradability of different petroleum products from more degradable products to less degradable one.

The selected fungi, *Pleurotus ostreatus* (white type) and *Trichoderma harizanam* are screened for their ability in hydrocarbon degradation. These fungi can be utilized commercially for conversion of various agriculture products and wastes into fungal culture containing valuable protein. The agriculture byproducts like cereal,

straw, rice hulls, reed residues and cattail residues are available in Iraq with a dense association form occupy hundred square kilometers of land. *Pleurotus* mushroom can directly grow on these agriculture wastes involves preferential lignin and cellulose degradation due to its enzymatic activity [7]. Similarly *Trichoderma harizanum* is proved to have the ability of playing very important role in present biotreatment according to activity of producing extra cellular enzymes.

Table 1 Biodegradability of different petroleum products[6]

Biodegradability	Example constituents	Products in which constituent is typically found
Hydrocarbons and biodegradability		
More degradable ↓	n-butane, n-pentane, n-octane.	Gasoline
	Nonane	Diesel fuel
	Methylbutane, dimethylpenetes, Methyloctanes	Gasoline
	Benzene, toluene, ethyl benzene, xylenes	Gasoline
	Propoylbenzenes	Diesel, Kerosene
	Decanes	Diesel
	Dodecanes	Kerosene
	Tridecanes	Heating fuels
	Tetradecaes	Lubricating oils
	Naphthalenes	Diesel
	Fluoranthenes	Kerosene
	Pyrenes	Heating oil
	Less degradable	Acenaphthenes

Experimental Work

Experimental procedure

Many samples with different concentrations of hydrocarbon contamination were collected for this process. The sample with total petroleum hydrocarbon (TPH) concentration equal to 17600 ppm was selected to be the base of measuring the biodegradability by both types of microorganisms.

Biotreatments consisted of the following:

1. Un-amended soil (waste + soil),
2. Supplemented with fertilizers to provide a carbon: nitrogen: phosphorous ratio of 100/10/1, and
3. Supplemented with fertilizers to provide a carbon: nitrogen: phosphorus ratio of 100/50/10.

The two types of fertilizers were selected according to many studies which confirmed an optimum microorganism's growth with these types [8, 9].

The contaminated cuttings were crushed and mixed with soil at a ratio of 1:1 (weight to weight). Plastic

containers with a capacity of 500 g (0.5 kg) with a seven repeated samples (containers) for each case are prepared to make the various biotreatments. Different concentrations of microorganisms were used containing 1, 2, 3, 4 and 5% by dry weight of container total mixture. Two ratios of nutrients 3 % and 5 % (weighted ratio by dry weight of total mixture) were considered in cases of nutrients addition.

Each type of fungi was processed with the above treatments besides a combination of both types together. Temperatures and moisture were maintained at approximately 20 to 40° C and 15 to 35 % respectively. Also, there was some tillage to support aeration of the soil. 50-ml grab samples were taken at time zero and then at approximately two weeks intervals to measure progress in biodegradation process. Samples were taken at 0, 2, 4, 6, 8, 10 and 12 weeks and transported to the analytical laboratory and analyzed for their TPH concentrations. Periodic measurements of TPH contents (concentrations) were done by high pressure liquid chromatography (HPLC) device.

The special parameters concerning the biotreatment technology are selected and optimized with respect to world experiments in this option.

In general, biotreatment is optimum at soil water saturation of 20 % to 80 %, temperature between 20° C and 40° C, pH range from 5 to 9, moisture value less than 40 % and oxygen levels must be as high as possible [10,11].

Culture preparation

The microorganisms were grown on potato dextrose agar (PDA) composed essentially of 200 g potato, 20 g dextrose and 20 g agar dissolved in one liter distilled water [12]. The organisms were maintained in slants at 4°C.

Preparation of inoculums

The inoculums were prepared in one liter bottles. Two hundred grams of boiled wheat corn seeds or straw mixed with 6 % CaCO₃ and 2% CaSO₄ were added and sterilized at 121° C for one hour in two successive days. Grains were inoculated with mycelium, developed separately in Petri dishes and incubated at 25° C until the mycelium covered all the wheat seeds which took around 10 to 14 days [7].

Preparation of substrates

Parallel to the elaboration of the inoculums, the substrate was prepared for the development of the fungus. Substrates (agricultural wastes) should be first chopped to a length of 4 to 6 cm then soaked overnight in tap water, drained in the following day, dried to some extent and steamed at 80° C for 12 hours then they cooled and

packed in polyethylene bags (size $30 \times 60 \text{ cm}^2$) after mixing the spawn at a rate of 5% by wet weight of substrate and incubated at 25°C for 2 to 3 weeks in growing rooms have 30 % light intensity [7].

Results and Discussion

Fig. 1 illustrates the result of biotreatment technology which applied to oily drilled cuttings without nutrient addition. This Figure shows that total petroleum hydrocarbon concentration decreased when microorganisms' concentration ratio (MCR) increased. Also, this decreasing is more significant in the case of using both types of microorganisms together. The results of biotreatment by *Trichoderma harzianum* are relatively close to those of *Pleurotus ostreatus*.

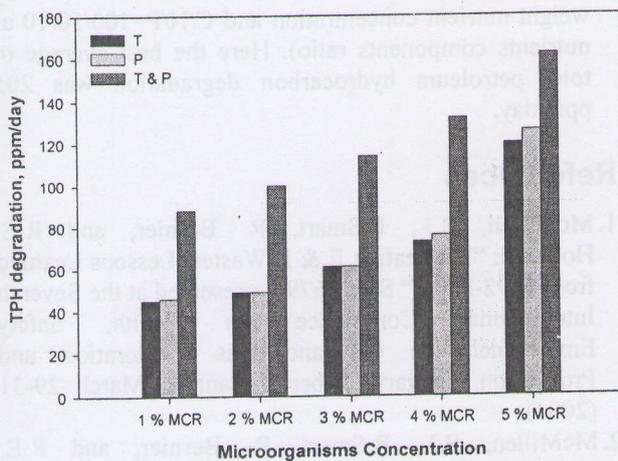


Fig. 1 Effect of microorganisms concentration ration on total petroleum hydrocarbons degradation at different microorganism types without nutrients

Fig. 2 and 3 show the effect of nutrients addition on biotreatment process with two ratios of nutrients components ($C/N/P=100/10/1$ and $C/N/P=100/50/10$). These treatments have been done with 3% nutrient ratio by weight. The results demonstrated the necessity of nutrients for the bioprocess which significantly reduced cuttings TPH concentration.

Fig. 4 and 5 show the effect of nutrients but with a 5 % nutrient ratio by weight. Here, the effect of increasing in nutrients ratio is shown in significant form especially with 5% MCR and with the action of both microorganisms together.

No significant differences were noticed with biotreatment by *Trichoderma harzianum* with that by *Pleurotus ostreatus*. In general, the addition of nutrients with the mentioned ratios ($C/N/P=100/50/10$) allow an optimal microbial growth and the biodegradation of hydrocarbons [9, 13, 14].

It was found that numerous types of fertilizers can be used in bioremediation, for example ammonium nitrate,

ammonium sulfate, super phosphates, urea and sulfur coated urea [8].

According to biotreatment results, one can conclude that the purified form *Pleurotus ostreatus* may play a very important role in treatments of infested soil added alone and/or together with *Trichoderma harzianum* where the compilation on soil nutrient is increased.

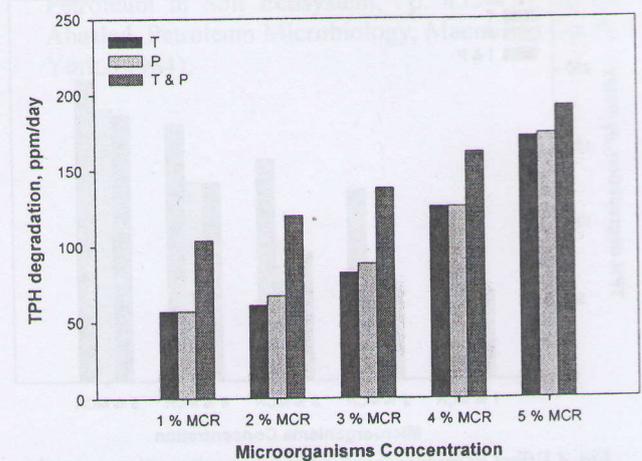


Fig. 2 Effect of microorganisms concentration ration on total petroleum hydrocarbons degradation at different microorganism types with 3% nutrients ratio and $C/N/P=100/10/1$

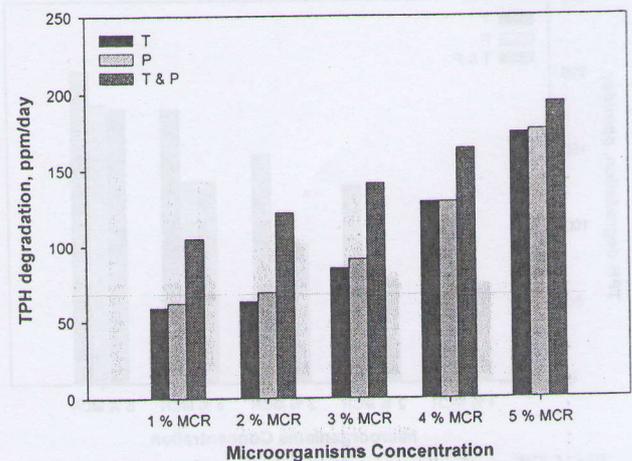


Fig. 3 Effect of microorganisms concentration ration on total petroleum hydrocarbons degradation at different microorganism types with 3% nutrients ratio and $C/N/P=100/50/10$

Finally, the following are noticed from these Figures:

- The results of *Trichoderma harzianum* are relatively close to those of *Pleurotus ostreatus*.
- Highest hydrocarbon degradations values can be noticed within the result of using *Trichoderma harzianum* and *Pleurotus ostreatus* in the same biotreatment.
- TPH concentration decrease with an increase in MCR.

- TPH concentration decrease with nutrients addition.
- TPH concentration decrease with an increase in nutrients ratio by weight.

With the same nutrients ratio, no significant difference in hydrocarbon degradation can be observed with the change in nutrients components ratio.

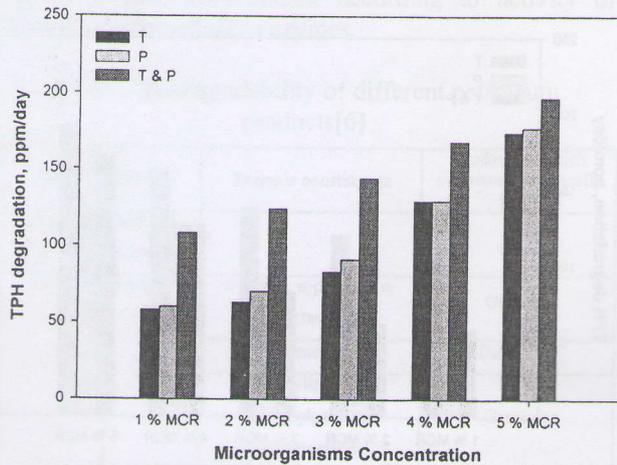


Fig. 4 Effect of microorganisms concentration ration on total petroleum hydrocarbons degradation at different microorganism types with 5% nutrients ratio and C/N/P= 100/10/1

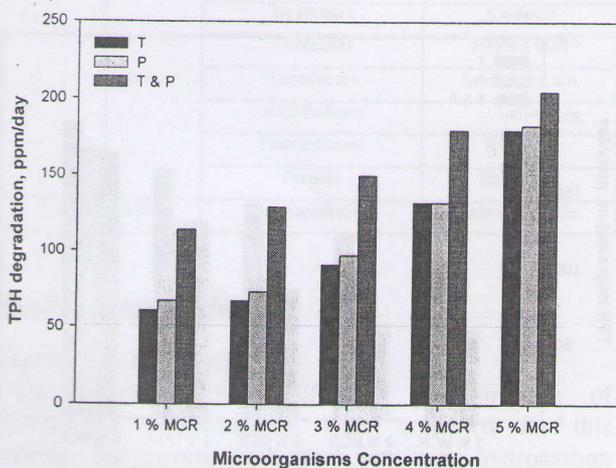


Fig. 5 Effect of microorganisms concentration ration on total petroleum hydrocarbons degradation at different microorganism types with 5% nutrients ratio and C/N/P= 100/50/10

Conclusions

1. For the first time, *Trichoderma harizanum* and *Pleurotus ostreatus* were proven through this study to be considered hydrocarbon degrading microorganisms.
2. *Trichoderma harizanum* which is known as biological control and fertilizer called "Al-Tahadi" is proved to have an important role in this biotreatment according to the activity of producing extra cellular enzymes.

3. The suitability of using different cheap and available agricultural wastes substrate in the cultivation of *Pleurotus ostreatus* will lead to the use of this fungus in wide range of biological treatment or control.
4. The used biotreatment can be considered as an effective treatment option since most of used materials at incubation and growth of microorganisms were available and cheap.
5. Specific local conditions can affect the biological activity. For example, certain levels of temperature degrees can limit all microbial activity and reduce the rate of hydrocarbon biodegradation. The study showed that the optimum humidity and temperature were 15 to 35 % and 20 to 40 °C respectively.
6. The best hydrocarbon degradation occurred by using the two microorganisms together with 5% by weight concentration ratio and with nutrient addition (5% by weight nutrient concentration and C/N/P=100/50/10 as nutrients components ratio). Here the best average of total petroleum hydrocarbon degradation was 205 ppm/day.

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Abstract

In this study the isomerization of desulfurized light Iraqi petroleum naphtha (Al-Dara Refinery) with boiling point range of 37 – 124 °C, 80.5 API specific gravity and 68.2 octane number, has been investigated. Two types of catalyst were prepared (PVHX and PVSrX), by impregnation of 0.8 wt% Pt on 13X zeolite. The catalyst activity and selectivity toward isomerization, and catalyst deactivation were investigated.

The isomerization unit consisted of a vertical tubular stainless steel reactor of 2 cm internal diameter, 3 cm external diameter and 58 cm height. The operating pressure was atmospheric for all experimental runs. The liquid flow of light naphtha was 0.4 L/h, and the catalyst weight was 50 gm. H₂/HC ratio used was 1 for all experimental runs. The isomerization process was studied at different temperatures of 210, 220, 225, 300, 325, and 350 °C. It was found that the optimum isomerization temperature is 270 °C.

The isomerization activities and selectivities as a function of time showed high activity at the beginning of the reaction and were deactivated rapidly. This indicates that the deactivation of PVHX and PVSrX results from pore blocking of pore mouth by the deposited carbon. The following deactivation decreasing order, PVHX > PVSrX was found. On the other hand, PVHX catalyst shows higher activity and selectivity than that of PVSrX.

It was concluded that, only an average of 90 wt% of the carbon atoms feed into the reactor (light naphtha) is detected in the product stream due to formation of coke deposits, which leads to catalyst deactivation. The results clearly showed that hydrogen is necessary for the hydrogenation of olefins in order to prevent oligomerization reaction that leads to coke formation and catalyst deactivation.

Keywords: catalytic isomerization, light naphtha, PVHX and PVSrX catalysts, deactivation

Introduction

Due to a heightened awareness of the environmental problem worldwide, expectations of clean and unleaded gasoline and world demand for gasoline have been increasing. Catalytic isomerization is regarded one of the most important processes in oil refineries which produce clean and high octane gasoline. Isomerization converts n-heptane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number. The common feedstocks for isomerization process is the light straight run naphtha, which consists of the lighter fraction C₃-C₆ [1, 2].

In general, a catalyst may lose its activity or its selectivity due to poisoning, fouling, sintering and loss of active species [1]. One of the most challenging tasks in the design and operation of industrial catalytic processes is the prevention, or at least the control, of catalyst deactivation. Loss of catalyst activity is often accompanied by a loss in selectivity. This leads to greater formation of undesired by-products such as carbon oxides, poor utilization of raw materials, waste of energy, and increased pollution [3,4]. Thus, solving deactivation problems is of paramount importance for the economic and ecologic performance of the process industry. Understanding deactivation mechanisms could