



BIOREMEDIATION IN EXPLOITATION OF OIL AND GREEN CHEMISTRY

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INTRODUCTION

Oil industry is the largest or potentially the largest source of pollutants for all ecosystems. This applies to all segments, from exploitation to processing, transportation, storage and use of fuel and raw materials for petrochemical industry.

Exploitation produces spent drilling fluid which is being collected and transported to landfills where it is treated. In the past it was deposited below the borehole, into mud pits, so there are many of them all over the world now as historical pollutants. In Serbia, too, at this moment there are about a hundred of them untreated, in oil fields.



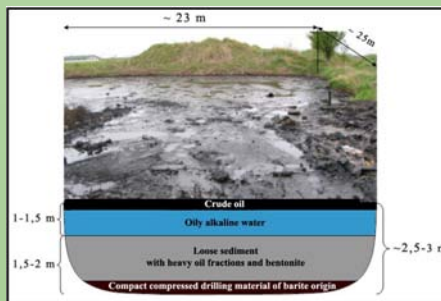
Spent drilling fluid is a very complex waste including oil (in average approx. 40 g/kg dry matter).

Consortia of zymogenous microorganisms isolated from mud pits have proven to be highly active in the degradation of crude oil, i.e. total petroleum hydrocarbons (TPH). The bioremediation procedure that we apply, that is explained in the presentation on one example, starts with the adjustment of pH, biostimulation (adjustment of the special ratio C_{org}:N:P), homogenisation and bioaugmentation by microbial consortia biomass. Aeration is achieved with mixing use of construction machinery. The process lasts up to 6 months during which TPH is reduced from the initial about 40 to approximately 1.5 g/kg DM, with the increase in the concentration of humic substances, which means that soilification (man-made-soil) is being created. Land obtained in such a way used for the cultivation of corn and soy as industrial crops.

The fundamental postulates of the green chemistry are the reduction of the: level of pollution, quantities of waste, total material, environmental risks, energy and costs, and all that is being observed in the biotechnology that we have developed and applied in tens of mud pits, having the volume of cc. 1000 m³ (1500 t), on average.

MATERIALS AND METHODS

The mud pit (20 m × 30 m × 2 m) consisted of several layers in the following order (starting from the top): (1) Crude oil, agricultural organic plant matter and, to a smaller degree, waste; (2) oily alkaline water; (3) loose sediment with heavy oil fractions and bentonite; and (4) compact compressed drilling material of barite origin, slightly contaminated with oil.



The treatment of the mud pit consisted of the following phases.
Phase 1 – Oil and water layers, after separation in place, were transported in tanker trucks to the nearest oil plant station for storage of these fluids for the next steps of utilization.
Phase 2 – Stabilization of the loose sediment using phosphate salts of alkaline and alkaline earth metals and mixing it with the soil dug out from the edge of the mud pit.
Phase 3 – Setting aside a layer of the stabilized soil from the edge of the mud pit, and enriching it with natural sources of organic carbon, nitrogen and phosphorus from poultry manure.
Phase 4 – In situ bioremediation of the stabilized sediment mixed with soil from the edge of the mud pit.

This procedure was based on an original laboratory-scale procedure, developed on the basis of the properties of contaminated area.

Composite samples for monitoring and analyses were taken at the beginning and every 60 d during the bioremediation process, which lasted for 180 days (0, 60, 120 and 180 d).

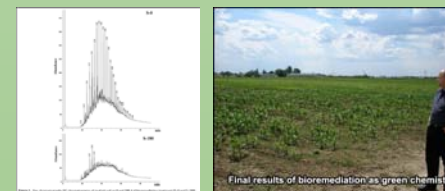
RESULTS AND DISCUSSION

Changes in numbers of TPH and HD microorganisms as indicators of degradation of HDs are crucial parameters for monitoring the effectiveness of bioremediation processes. The numbers of microorganisms and other parameters determined during the bioremediation process are shown in Table 1.

Table 1 Changes in mud pit soil parameters during the 180 d bioremediation process.

Parameters	S-0*	S-60	S-120	S-180
Time of bioremediation (days)	0	60	120	180
Moisture (%)	22.5 ± 1.2	23.9 ± 1.1	20.4 ± 1.2	19.4 ± 1.3
WHC (%)	74.0 ± 2.8	73.0 ± 3.1	75.0 ± 2.7	76.0 ± 2.8
Loss on ignition (%)	15.5 ± 0.7	15.2 ± 0.7	14.2 ± 0.8	13.5 ± 0.7
TPH (g kg ⁻¹)	32.2 ± 1.5	17.5 ± 0.9	8.3 ± 0.4	1.5 ± 0.1
TC (CFU g ⁻¹)	1.1 × 10 ⁸	7.5 × 10 ⁸	7.7 × 10 ⁸	3.4 × 10 ⁹
HD (CFU g ⁻¹)	8.8 × 10 ⁶	4.2 × 10 ⁶	4.7 × 10 ⁶	8.2 × 10 ⁶
HD (N ⁺)	8	56	61	23

WHC: water holding capacity; TPH: total petroleum hydrocarbon; TC: total chemoorganoheterotrophic HD hydrocarbon.
*After mixing, watering, biostimulation and recontamination.
*Values of HD within the TC.
In all standard results: a deviation for six measurements.



After bioremediation treatment, the TPH level (measured as mineral oil) was 1.24 ± 0.1 g kg⁻¹ in the mud pit soil. The maximum level of TPH stipulated after bioremediation is 5000 mg kg⁻¹, or 5.0 g kg⁻¹ of dry soil. This indicates that the process of bioremediation was successfully implemented in the current study. The bioremediated mud pit soil would also comply with the Canadian standard, which stipulates TPH of below 3280 mg kg⁻¹, or 3.28 g kg⁻¹ in farm soils.

The high degree of biodegradation of TPH in this study was likely a consequence of the activity of the zymogenous microbial consortia, which were derived from microorganisms that had naturally flourished in the contaminated soil at the site.

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