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A FEASIBILITY STUDY FOR BIOREDUCTION OF PETROLEUM COMPOUNDS IN REFINERY SEWAGE SLUDGE USING COMPOSTING

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Abstract. *The scope of this work was to report about the potential recycling of by petroleum compounds high concentrated refinery sludge originating from the Joint Stock Company Slovnaft Bratislava and thus to replace currently still operating incineration. Composting of the sludge was choosen using two different amendment materials, i.e. wood chips and wheat straw. A plastic, closed system – reactor with mechanical aeration was examined during these experiments. The biological sludge contained for composting materials unusual high concentrations of petroleum hydrocarbons, ranging from 500 to 20 000 mg/kg. However, the other sludge parameters like high content of biogenic compounds, nutrients and proteins including appropriate microorganisms count for biodegradation and low toxic metal concentrations priorize composting before other disposal technologies. During the process studied, the temperature, microorganism count, C : N ratio, moisture and TPH concentrations in the composts BS/S and BS/C have been checked, regularly. A higher biodegradation efficiency and TPH removal in the compost BS/S has been confirmed by the analyses (52%) than in the compost BS/C (18%) after 4 months-composting.*

Key words: *composting, refinery sludge, petroleum compounds, biological waste disposal, biodegradation.*

Composting is an aerobic microbially driven process that converts solid organic wastes into a stable, sanitary, humus-like material. Composting process reduces the bulk considerably and return safely the final product back to environment (Alan El–Din, 1980).

A wide variety of materials are suitable for composting including sewage sludge, animal and agricultural wastes and household refuse. Almost all the widely used composting systems are aerobic, with the main products being water, carbon dioxide and heat (Poincelot, 1972).

Energy or heat production is essential to the success of the composting process. Two distinct temperature phases occur during composting. First, a mesophilic phase in which microbial action raises the temperature up to 40 – 45 °C, forcing the process into a thermophilic phase in which the mesophilic micro-organisms are inactivated and are replaced by thermophles (45 – 65 °C). At these higher temperatures, both animal and plant pathogenic microorganisms are inactivated, as well as insect pests, their eggs and weed seeds. To support air penetration into composted material, sawdust, wheat straw, peat, manure, refuse and garbage, lawn, tree trimmings, wood chips have all been successfully used (Epstein, 1997).

The most important operational factors are: aeration, temperature, moisture, C : N ratio and pH level. In the compost pile, the critical oxygen concentration is about 15 %, below which anaerobic microorganisms begin to exceed aerobic ones. Oxygen is not only required for aerobic metabolism and respiration, but also for oxidizing the various organic molecules that may be present (Spinosa, 1995).

There are two main methods of composting. Open systems do not require a reactor but employ piles and windrows, whereas closed systems take place within a specially constructed reactor and involve a high degree of mechanization (Bernal et al., 1998).

Some field-scale composting of petroleum-contaminated sludge originated from washing of forest machines was realized in 1990 by Joint Stock Company Lesy Krnov. The used sludge in which the petroleum compounds ranged between 15 000 to 20 000 mg/ kg of dry matter was mixed with wood chips. After 8 months, the bioreduction of petroleum compounds in the composted material reached 66% (Baèík, 1994).

In 1998 at the University of Saskatchewan, composting of highly contaminated refinery sludge (30% of crude oil per dry matter) was realized with two different bulking agents (peat and Solv II-agent). The total petroleum hydrocarbons (TPH) concentration in composted material decreased after 7 months in the peat compost to 30% and in the Solv II compost to 55%, respectively (Milne et al., 1998).

Composting of industrial sludges with less than 5% TPH of dry matter is now-a-day favoured before other disposal technologies especially incineration process. In Slovakia about 40 years ago, the Peat Factory started to compost industrial sludges and soils contaminated with petroleum compounds. Currently, VÚRUP-Slovnaft is only one company which employes bioremediation procedure for hazardous waste disposal of Slovnaft refinery, e.g. by EFPA (Environmental Fuel Project Apollo) about 110 000 t of solid waste was decontaminated using bioremediation incl. composting (Polakovièov á, 2002).

The scope of the submitted paper was to report about the potential recycling of by petroleum compounds high concentrated refinery sludge originating from the Joint Stock Company – Slovnaft Bratislava and thus to replace currently still operating old incineration technologies. As the potential recycling method, composting of the sludge was choosen using two different amendment materials, i.e. wood chips (further abbreviation with the symbol C) and wheat straw (abbreviation with the symbol S). A plastic, closed system – reactor with mechanical aeration was examined during these experiments.

Materials and Methods

Dewatered biological sludge from the mechanical-chemical-biological waste water treatment plant at the refinery-petrochemical company Slovnaft Bratislava, impacted by high concentration of petroleum hydrocarbons, was used for composting. The physicochemical characterization of the applied sludge is present in Tables 1 and 2.

techniques to determine low metal concentration. The spectrometer was equipped with a Deuterium background correction system and a hydride system to detect easily ionized elements as well (Veeken, 1998; D I N 38 409; S T N 46 5735).

Total nitrogen was determined by Kjeldahl method, phosphorus photometrically and total carbon by Carlo Erba CHN – Analyser (Italy). Microorganism count was done according to classical plate count method (S T N 46 5735).

Preliminary composting began with measurements to determine the percent of moisture, pH, temperature, C, N, P elemental analyses, dry matter and microbial activity by CO_2 production. These measurements were taken on a weekly basis and are a part of the operation records. Sampling of the material was based on a stratified random sampling plan homogenously from the whole reactor volume according to S T N 46 5735. Sampling of the material to determine the concentrations of contaminants took place on a monthly schedule after initial sampling.

Table 1. Some physicochemical parameters of refinery sludge, wheat straw and wood chips (downward) as starting materials for the composting performed

Total Carbon % wt	Total Nitrogen % wt	Total Phosphorus % wt	Total Potassium % wt	TPH by IR mg/kg	Dry Matter %	Combustion Solids %
39.8	6.9	2.1	0.3	15 478.6	9.4	79.6
47.8	0.5	0.1	0.5	433.6	87.8	95.6
49.8	<0.1	-	-	105.3	81.7	99.7

Table 2. Review of heavy metals content in mg/kg of dry matter in the used refinery sewage sludge (1) and accepted level i.e. tolerated maximum for agricultural compost according to STN 46 5735 (2)

Element	(1)	(2)
Cu	59.2	1200
Ni	38.7	200
Cd	3.7	13
Cr	22.8	1000
Pb	61.5	500
Zn	4267^{X}	3000
Hg	3.4	10
Mo	20.5	25
As	<0.3	50

A 50 kg of biological sludge with a 20 kg of cut wheat straw (wood chips were used for the second experimental, parallel reactor) together with a 2.7 kg (4 kg) KNO_3 - purum, Mikrochem Bratislava, were mixed by means of Kneading machine, type 7183 (Přerov, Made in Czech Republic) and composted in a plastic – 290 L closed system reactor during a time period from the October 30th till the March 2nd 1999.

Content of petroleum hydrocarbons in composted materials was analysed according to DIN 38 409 on a FTIR Nicolet Impact 410 Spectrometer (USA) and of potassium and heavy metals by AAS spectrometry on a Varian SpectrAA-40 (Australia) equipped with both a flame device and graphite furnace

On the day basis, a strict regime was followed to ensure the optimal conditions for sludge composting:

1) manual digging of compost to aerate or to dry if required,
2) monitoring of moisture conditions and irrigation if required,
3) monitoring of pH conditions and adjusting with 0.1 mol/L H_3PO_4 if required,
4) monitoring of temperature inside and outside of compost and move the experimental reactors indoor if necessary.

In conclusion, the compost maturity by germination index G.I. test using garden cress *Lepidum sativum, L.* was verified.

Results and Discussion

The concentrated activated sludge from the biological stage of waste water treatment facility in Slovnaft is dewatered on belt presses to a dry matter content of approx. 10% wt. and incinerated. The oil drawn-off from the surface level in the mechanical stage is after dewatering pumped into the sludge incinerator, there to be used as fuel, respectively. The sludge incinerator is equipped with multiple-hearth furnace, whereas the flue gas is fed into the deodorization unit and purified in the wet cyclone separators before entering into the stack. The construction of the plants is based on the technology of the Japanese firm Kurita, finalized for Slovnaft in the year 1985. The principle diagram for current waste water and sewage sludge disposal at the plant describes the scheme bellow (Figure 1).

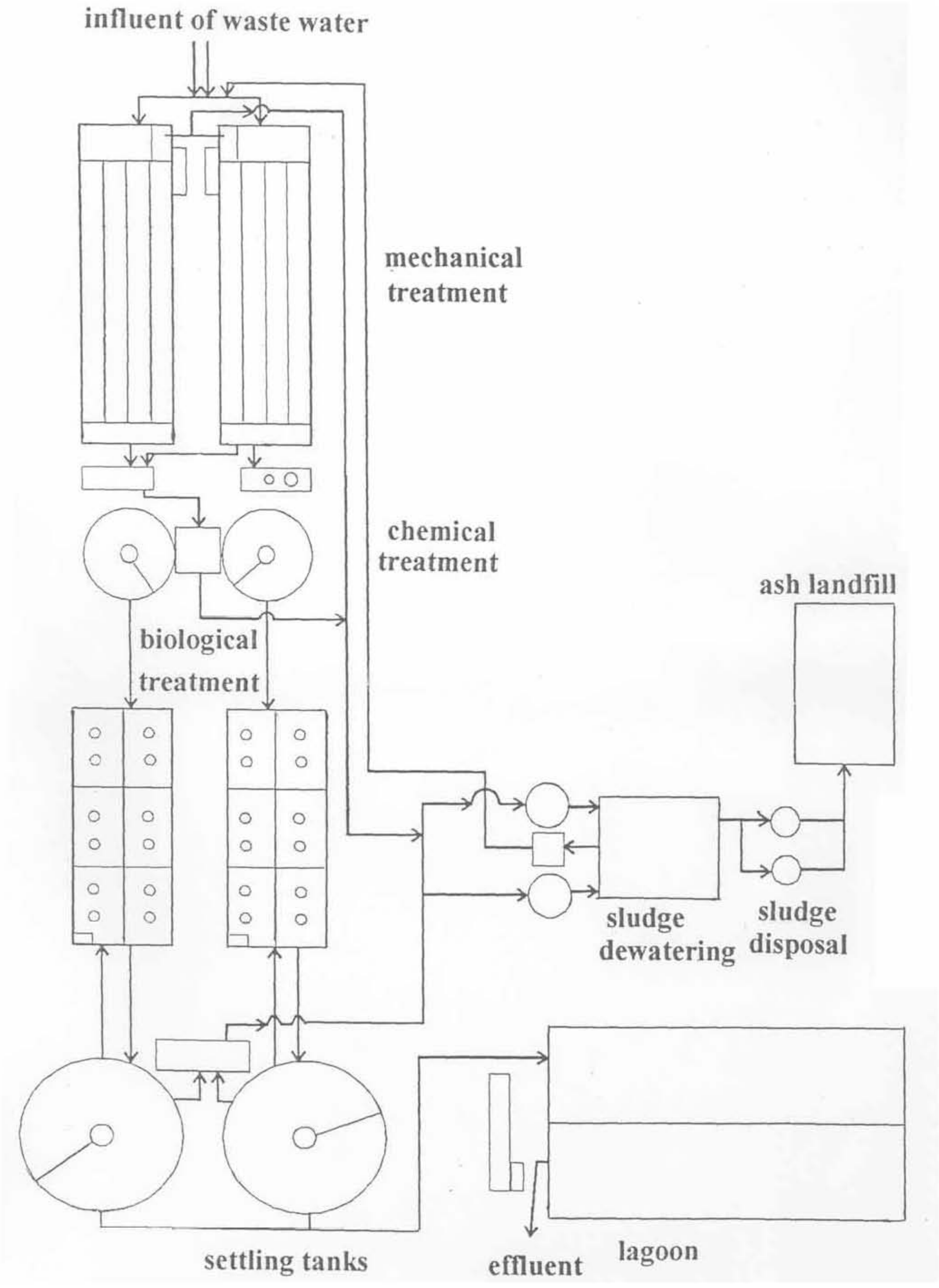

Figure 1. The scheme of the waste water treatment facility in Slovnaft

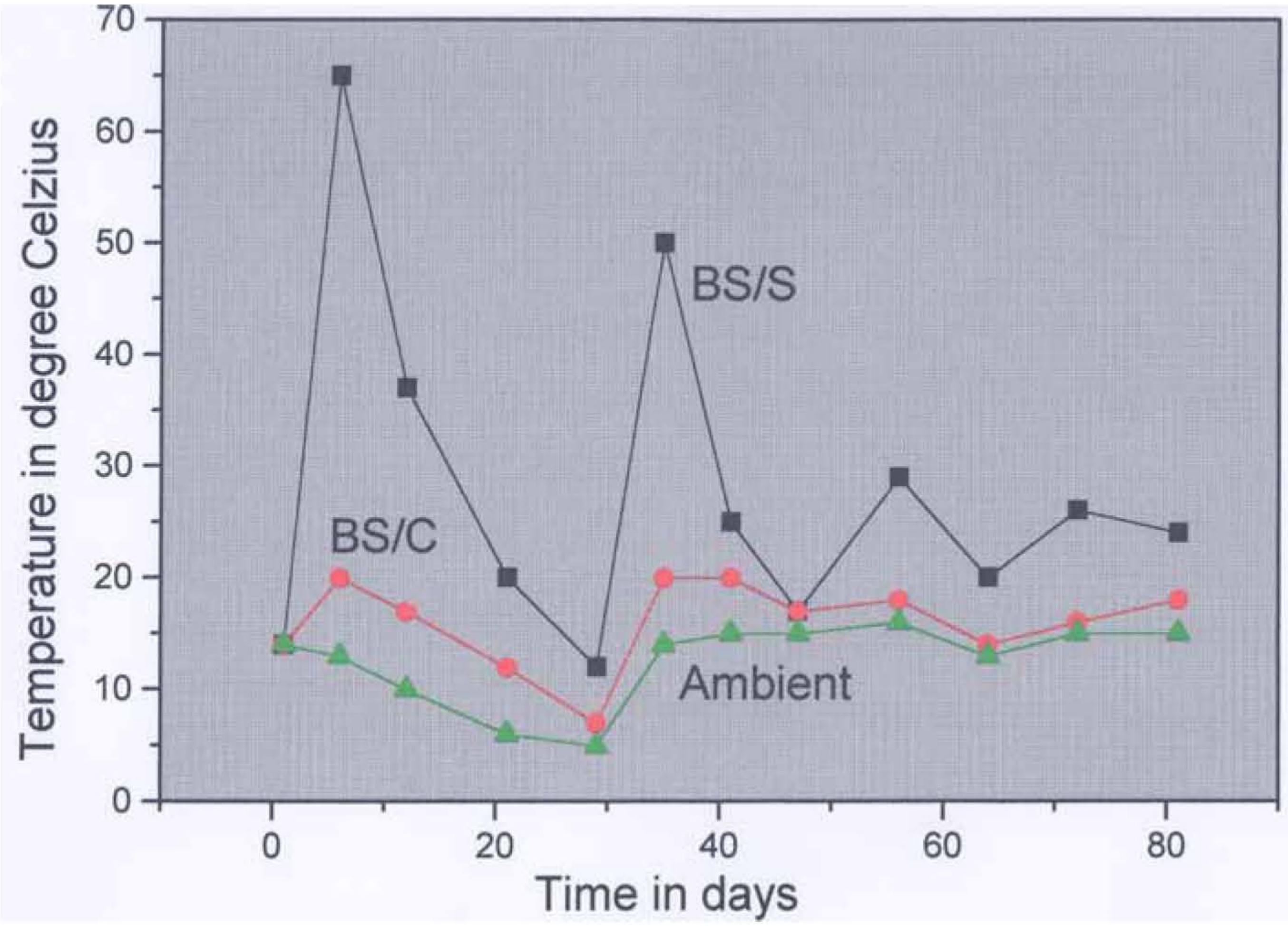

Figure 2. Temperature development in the composts studied and the ambient temperature measured

The biological sludge contains for composting materials unusual high concentrations of petroleum hydrocarbons, ranging from 500 to 20 000 mg/kg. However, the other sludge parameters like high content of biogenic compounds, nutrients and proteins including appropriate microorganisms count for biodegradation and low toxic metal concentrations priorize the sludge liquidation by composting for the near future (Table 1). Currently, the dewatered biological sludge is according to the Slovak Environmental Policy classified as hazardous waste (Waste Law 238/1991).

During the aerobic bioreduction process studied following conditions, i.e. temperature, microorganism count, C: N ratio, moisture and TPH concentrations in the composts BS/S and BS/C have been checked regularly. According to the Figure 2 a remarkable temperature drop after 30 days process in the compost BS/S, signalizing the thermic phase interruption, was registered. This phenomenon may have been caused by several factors due to the enhanced moisture conditions and thus due to the defficiency of air penetration through the composted material and secondly due to the lowering of ambient temperature up to 45 °C. The replacement of the experimental reactor into the other storage hall corresponded with the improved temperature development in the compost, afterwards. The temperature increased to 52 °C from the previous one, i.e.12°C.

The thermic phase development in the compost BS/C has not exhibited such expressive behaviour as in the compost BS/S, probably due to the slow biodegradation process ongoing in the wood chips. After two weeks of the ongoing composting process, some temperature increase in BS/C compost may characterize the sludge biodegradation finished, however contributing only by about 23% w/w. The biodegradation of other components, i.e. wood chips 77% w/w, proceeded very slowly, accompanying by milde temperature drop. Furthermore, this fact correlated with the results of microorganism count of both composts very well, whereas in the compost BS/C was this count and microbial activity lower than in the compost BS/S. In conclusion, in the compost BS/C some dramatic pH drop and some loss of the original acid-bitter smell appeared, simultaneously.

Saccharose was added to the compost BS/S one time during the process to enhance the microbial activity and thus to support petroleum hydrocarbons biodegradation, on the base of the C : N ratio falldown in above compost to 10 : 1 indicating the bioprocess finished. In another compost BS/C any saccharose was added, because the available C : N ratio was kept sufficiently high.

The moisture conditions in both experimental reactors have been maintained slightly higher than according to STN 46 5735 recommended value. In average, the BS/S humidity varied around the value 70% and BS/C around the 67%. However, any anaerobic conditions have arised during the process studied.

The TPH content in the composted substrate was expressed in relation to the whole volume of composted material, in efforts to present thoroughly the true pollution concentration. A higher biodegradation efficiency and TPH removal in the compost BS/S has been confirmed by the analyses, i.e. from the original value 80 659 mg total up to 38 340 mg TPH final, a 52% efficiency, than in the compost BS/C from 74 445 mg total up to 61 139 mg TPH final, where the drop represented only the 18% efficiency.

Although, the used analytical method for TPH determination in the composts studied may have been considered as unsufficiently selective, no differing the bio- and petrogenic parts of hydrocarbons, the attained TPH drop using composting was satisfactory. Some of the most significant indexes of bioprocess studied present Tables 3-5.

In conclusion, the product quality by the germination test was verified. As indicated, in the BS/S compost a 58% mature quality and in the BS/C compost a 75% one have been established. According to the STN 46 5735 the 80% mature value represents the bioprocess finished, confirming any organic substrate for prosecution of the bioprocess, respectively. Consequently to that results, in the compost BS/S may the fermentation continue, whereas in the compost BS/C no more. Later one was considered for sufficiently ripe.

Table 3. A comparison of some parameters in both composts biological sludge/ wheat straw (BS/S) and biological sludge/ wood chips (BS/C) at the begin and the end of the composting

	BS/S begin	BS/S end	Effic.%	BS/C begin	BS/C end	Effic.%
Weight (kg)	72.7	29.1	60	74	53.2	28.1
Weight of dry matter (kg)	23	8.4	63.5	22	19.7	10.7
Total Carbon (g)	10 263	3280	68	10 020	8470	15.5
Total Nitrogen (g)	513	260	49	501	360	28.1
C : N ratio	20 : 1	12.6 : 1	-	20 : 1	23.5 : 1	-
TPH (mg)	80 659	38 340	52.5	74 445	61 139	17.9

Table 4. Quality indexes of mature compost according to STN 46 5735 and indexes of composts BS/S and BS/C at the end of experimental process

Product Quality	STN 46 5735	BS/S	BS/C
Water %	40-65	66	64
Combustion Solids %	min. 25	78.4	86.1
Total Nitrogen vs. dry matter %	min. 0.6	3.1	1.8
C : N ratio	max. 30 : 1	12.6 : 1	23.8 : 1
pH	6-8.5	7.2	6.5

Table 5. Microorganism count per g of dry matter (1) and microbial activity by CO_2 production in mg /100 g of dry matter / d (2)

Data	October 13	October 17	December 10	December 14	January 25
Process Duration/d	16	20	43	47	89
(1) - BS/S	$8.6.10^7$	-	-	$1.1.10^6$	$9.7.10^7$
(1) – BS/C	$2.1.10^7$	-	-	$1.0.10^6$	$3.3.10^3$
(2) – BS/S	-	2037.4	1676.4	-	1132.4
(2) – BS/C	-	1034.0	967.0	-	658.3

Conclusions

On the basis of our feasibility study, composting of refinery sewage sludge performed during 4 months in two experimental 290 L plastic closed system reactors using two different amendment materials, i.e. wheat straw and wood chips decreased the high concentration of petroleum compounds in the sludge more efficiently (52.5%) in the compost with the wheat straw (BS/S) than in the compost (BS/C) with the wood chips (18%).

Above composted sludge closely resembled peat, being dark brown in color with a crumbly texture and having a pleasant earthy smell, finally. Straw produced a coarser compost than wood chips amendment and bulking agent. Generally, the used refinery sludge with high concentration of petroleum hydrocarbons has been managed to compost especially with the wheat straw as bulking agent, successfuly. The attained results will be used for the next phase research of refinery sludge composting.

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List of Abbreviations and Symbols

TPH	-	Total Petroleum Hydrocarbons
Effic.	-	Efficiency
DIN	-	Deutsche Industrie Normen
AAS	-	Atomic Absorption Spectrometry
BS/S	-	compost I of biological sludge and wheat straw
BS/C	-	compost II of biological sludge and wood chips