# The Efficiency of Flocculants in Biological Treatment with Activated Sludge


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*Studies were made on the water from the oil sludge basin where petroleum residues were stored as well as sludge from the treatment plant of wastewater from refinery. The aim of the experiment program is biodegradation of petroleum waste deposit and removal of contaminants, turning it in a state that allows chemical, physical and biological treatment. Contaminants of these samples are damaging the environment and there is important to find solutions in order to eliminate these contaminants. Five samples were collected from different sampling points. Samples were homogenized, then mixed and an average sample of 1000 mL was studied. From this average sample there were prepared three solutions of different concentrations: 1 % (v/v), 3 % (v/v) and 6 % (v/v) diluted with waste water coming from the waste water treatment plant, whose composition meet the regulation for a wastewater treatment plant. On these samples it has been studied the decreasing of contaminants concentration after the treatment with chemical flocculants: $FeSO_4$ 3%, $Ca(OH)_2$ 20% and IP114 polyelectrolyte 0.2 ppm. After physical and chemical treatment the highest concentration sample was analyzed, focusing on contaminants biodegradability in contact with biological sludge by biological treatment using a pilot plant.*



*Keywords: oil sludge, biodegradation, contaminants, flocculants*


A pollutant is any natural or unnatural material that is present in the environment at unnaturally high levels. Concern about pollution is meaningful only in the context of a pollutant impact on the biosphere. How a pollutant affects the biosphere has been conventionally characterized in terms of easily quantifiable measures such as the chemical oxygen demand (COD), biochemical oxygen demand (BOD), *p*H and total suspended solids. These measures are important, but they are grossly insufficient for assessing the full impact of a discharge on the biosphere. Many pollutants directly affect the metabolic biochemistry of the diverse life forms that inhabit the various ecosystems. When the biochemical impact is adverse, the pollutant is toxic.

Flotation processes have been proven suitable to remove both suspended solids and oils at a time from a great variety of turbid waters, such as eutrophic natural water, pulp industry effluent, textile and dyeing industry, food industry, municipal wastewater, tannery process wastewater, petrochemical wastewater, oil production and refining and electroplating and battery industries In this work, the second order central composite design was used to investigate the effects of coagulant and flocculant doses and pH on turbidity, suspended solids and oil contents of a wastewater originating from the dewatering process of a refinery.s storage tank [1]. Sources of these sludges are storage tank bottoms, oil-water separators, flotation and biological wastewater treatment units, cleaning of processing equipment, and soil from occasional minor spills on refinery grounds. The composition of these sludges varies according to their origin, storage, and treatment history. In a typical case hydrocarbons, water, and mineral solids are present in roughly equal proportions. Oily sludges constitute a disposal problem and, among other options, biodegradation in soil or "landfarming" offers a cost-effective and environmentally acceptable alternative. In contrast to burial in anaerobic landfills, this mode of disposal leads to the relatively rapid biodegradation of the hydrocarbons by soil microorganisms, thus reducing the danger of groundwater contamination [2].

Soil pollution is the worst pollution because it is difficult to control and measure it and the soil cleaning is harder than water purification. The soil could be polluted: directly – by residues discharge on urban or country lands or fertilizers and pesticides throwing on farmlands; indirect – by pollutants disposal from atmosphere, by acid rains water, pollutants wind transportation, soil infiltration of contaminated waters. The most damaged soils are in the neighborhood of pollution sources [3-6].

Contamination level of the soil also depends on rainfall regime due to the atmosphere washing and contaminants transportation and disposal on the soil. Oil sludge basin also contributes to environment pollution due to acid tars and slurry from waste water purification plant [7-12].

The experiments are useful for waste water purification plants by optimum batching of the floculants in order to remove chemical contaminants to obtain a sort of waste water that allows the insertion in aerating basin with activated biologic sludge for biological purification whose aim is to discharge superior quality water in to the river [13-15].

## Experimental part

Materials, reagents and equipment used: WTW pH meter, magnetic stirrer AREC VELP, graduated flasks 100ml, 500mL, 1000mL, automatical pipette Rota Filler 3000, Imhoff cone, pilot plant treatment (aeration tank, decantation apparatus and pump gas-lift recirculation), air compressor, $FeSO_4$, $Ca(OH)_2$, polyelectrolit IP114, $NH_4NO_3$, $FeSO_4$ and NPK complex (nitrogen : phosphorus : kalium).


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For the biodegradation of contaminants, sample 6% was tested in the pilot plant (fig. 1) in order to study the behaviour in contact with microorganisms from biological sludge.

The experimental plant used in the laboratory (fig. 1) is composed of:

- 5 liters capacity feeding vessel mounted on a height that is fed with the sample to be tested (1 liter dilution sample of 6 % after removing the flocculants sediment);
- air spray system for maintaining the viability of activated sludge;
- aeration tank – 700 ml capacity, size: diameter 7 cm, length 50 cm, provided with connector to the bottom through which air is introduced into the system to provide the necessary oxygen for microorganisms in biological sludge and to maintain the bacterial suspension in contact with the sample inserted into the feeding vessel.

A glass frit with fine pores is mounted above the connector through which oxygen diffuses in aeration tank, maintaining the sludge in suspension. Above the glass frit is an inlet connector that insert into the system the dose of wastewater flow by adjusting the drop of 0.5 mL / min. At the top is provided a pipe for discharge, where the suspension of biological sludge mixed with water discharged into the system settling, consists of:

- decanter –800 mL capacity, size: diameter 7 cm, length 50 cm, provided with connector to the bottom for biological sludge disposal and at the top with connector to discharge.
- purified water collecting vessel.

The connections between vessels are done with silicone rubber tube and bottlenecks are made with screw terminals. The plant sits on a metal base. Aeration tank filled with biological sludge (190 ml/L sediment volume measured at 30 min in Imhoff cone) and aeration started keeping dissolved oxygen conditions of 3 - 5 mg / mL and dispensing nutrients: 20% $NH_4NO_3$ solution, dose of 5 mL / h, $FeSO_4$ of 2% concentration in dose of 1 mL/h and complex NPK (nitrogen : phosphorus : kalium) 5 % concentration in dose of 1 mL/h.

**Results and discussions**

The five sampling from industrial waste storage tank were about 1 liter each; samples were homogenized for 1 hour on an AREC VELP magnetic stirrer. Chemical and physical appearance of the mixture: gray black color, pungent odor, dense oily sample, and after filtering there were not distinguished two phases. Because of the consistency, analysis as such could not be realized and it was necessary to dilute it with waste water from Parshall flume of the wastewater treatment plant. Chemical analysis of the mixture is presented in table 1.

Dilution water used for sample dillution was input water from water treatment plant (Parshall flume). Chemical and physical properties of dillution water are presented in table 2.

Samples analyzed were collected from oil residue basin (by mixing five samples taken from different points) and then diluted to concentrations of 1, 3 and 6% with waste water coming from the Parshall flume of wastewater treatment plants coming from refinery. The experimental plant used in the laboratory are presented in figure 1.

**Table 1**
CHEMICAL ANALYSIS OF SAMPLE MIXTURE

| Nr. Crt. | Analysis | Amount |
|---|---|---|
| 1. | Dry substance | 1,970 g/L |
| 2. | Ash | 886 mg/L |
| 3. | Inorganic substance | 44.97 % |
| 4. | Organic substance | 55.03 % |

**Tabel 2**
CHEMICAL AND PHYSICAL PROPERTIES OF DILUTION WATER

| Nr. Crt. | Analysis | Amount |
|---|---|---|
| 1. | pH | 8.2 |
| 2. | Extractable in petroleum ether | 195 mg/L |
| 3. | Sulphonic acids | 7 mg/L |
| 4. | Naphthenic acids | 12 mg/L |
| 5. | Suspensions | 172 mg/L |
| 6. | CCO-Cr | 896 mg/L |
| 7. | Sulphides | 0 mg/L |
| 8. | Fix residue | 435 mg/L |
| 9. | Phenol | 0.85 mg/mL |
| 10. | Furfural | 0 mg/L |

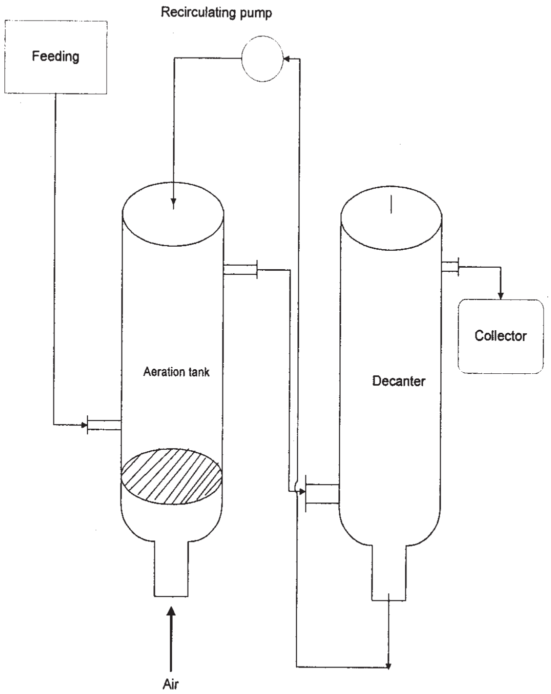


Fig. 1. Laboratory experimental plant

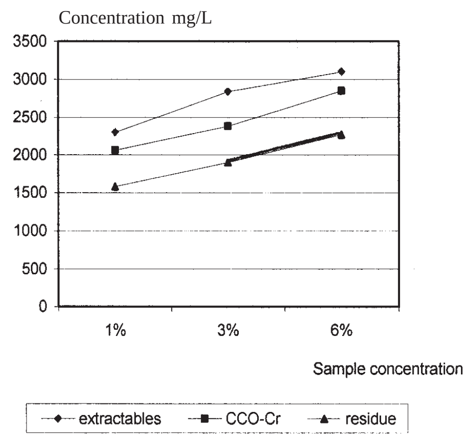


Fig. 2. Chemical quality of dilutions before treatment with flocculants

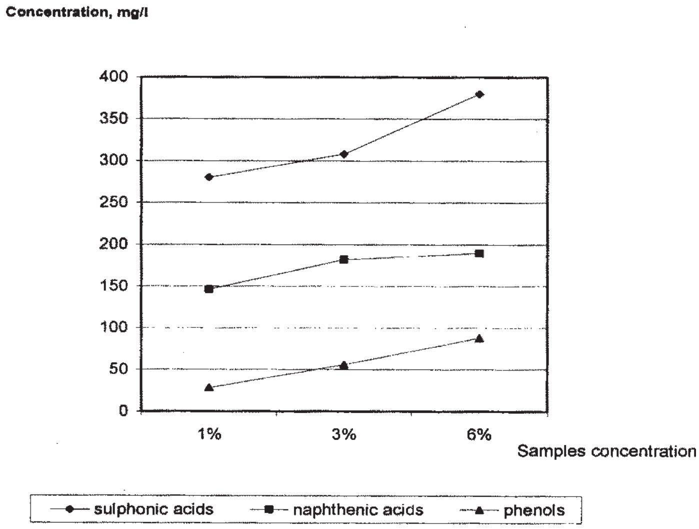


Fig. 3. Chemical quality of dilutions before treatment with flocculants

Analysis of diluted water samples were made on 1 liter from the total amount of 2.5 L prepared from each one. Experimental results are presented in figures 2 and 3 where is plotted the analysed contaminants concentration before treatment with flocculants.

The remaining 1.5 liters of each sample was subject to treatment with the flocculants in the following dosage: $FeSO_4$ 3%, $Ca(OH)_2$ in 20% and IP114 polyelectrolyte 0.2 ppm, the dose per 100 mL sample analysed. The purpose of chemical treatment was to remove a part of pollutants by crowding them in colloidal suspension after reagents flocculation.

After flocculants adding, the samples were homogenized (on line) on AREC VELP magnetic stirrer for 1 h and then left resting for 2 h. After the rest time has elapsed the supernatant was discharged in another vessel. From these samples they have been repeated the analysis in the laboratory to study the effect of chemical treatment. Following laboratory analysis of the dilutions treated with flocculants, the results showed a decrease of contaminants concentration (presented in table 3).

Pilot plant supply was made in drop by adjusting the flow to a volume of 0.5 mL / min to 1000 mL sample dilution 6% (v / v) supernatant sample that resulted after treatment

**Table 3**

EXPERIMENTAL RESULTS FOR THREE SAMPLES WITH CONCENTRATIONS OF 1%, 3% AND 6% AFTER TREATMENT

| Nr. Crt. | Analysis | Sample 1% | Sample 3% | Sample 6% |
|---|---|---|---|---|
| 1. | Extractables in petroleum ther | 1070 mg/L | 1290 mg/L | 1420 mg/L |
| 2. | Fix residue | 900 mg/L | 1200 mg/L | 1400 mg/L |
| 3. | CCO-Cr | 880 mg/L | 1008 mg/L | 1180mg/L |
| 4. | Naphthenic acids | 50mg/L | 95mg/l | 120mg/L |
| 5. | pH | 8.5 | 8.8 | 8.5 |
| 6. | Sulphonic acids | 120 mg/L | 140 mg/L | 180 mg/L |
| 7. | Phenols | 8 mg/L | 28 mg/L | 40 mg/L |

with flocculants. It was analyzed the behavior of microorganisms in biological sludge and its biodegradation capacity following the dosage of sample 6% (v / v) which had the following chemical characteristics: *p*H 8.5; ether extractable 1420 mg /L; fixed residue 1400 mg / L; COD Cr 1180 mg /L; naphthenic acids 120 mg/L; sulphonic acids 180 mg/L; phenols 40 mg/L.

Chemical and microscopic analysis of the biological sludge used to fill the aeration tank pilot indicated a sample having: *p*H 8.3; volume of organic sludge 190 ml/L (sedimentation measured at 30 min); $NH_4^+$ 2.7 mg/L; $PO_4^{3-}$ 1.5 mg/L; dry matter 2090 mg/L; ash 40 mg/L; inorganic material 0.013 %.

Protozoa that have dominated the microbiological population from the sludge used were represented in high density by *Paramecium caudatum, Aspidisca polistila, Vorticella microstoma, Litonotus setigerum* and *Rotiferi*. Microscopic analysis of microbial population indicated lower abundance of fixed ciliates and growth of mass which promoted bacteria development in the tested biocenosis. Bacteria flakes from sludge showed a significant increase in *Nostoc* and *Anabena* filamentous bacteria and the occurrence of *Diatomeea* in large number.

After the exhaustion of feeding vessel, the purified sample from receiving vessel was analyzed. The efficiency of biological purification is indicated by the quality of the water collected from sample 6 % purification: extractables 80 mg/L; residue 250 mg/ L; COD-Cr 400 mg/ L; naphthenic acids 58 mg/ L; sulphonic acids 36 mg/L; phenols 8 mg/L; sludge from aeration tank after tested sample exhausing 48 ml/L.

## Conclusions

The analysed sample can be purified and contaminants reduction is significant by treatment in contact with biological sludge. In contact with analysed contaminators, the volume of the biological sludge from the instalation was decreased but the the micriobiological activity was increased. Hence, with the help of the microorganisms population from the biological sludge were removed 86% extractable substances in petroleum solvent, 90% naphtenic, the whole amount of phenols was removed and COD Cr decreased with 63%.

Through laboratory studies were found techniques for biodegradation of oil sludge, pollutants analysed from the discharging media and chemical waste storage.

Experiments carried out on samples taken from the chemical waste storage, have shown that after using flocculants in doses determined by laboratory testing, a part of the petroleum pollutants are eliminated through chemical treatment. The petroleum pollutants are removed with the help of microorganisms from the biological sludge through the biological treatment.

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Manuscript received: 22.10.2010