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## EVALUATION OF SURFACTANT AND BIOSURFACTANT MIXTURE USEFULNESS IN OIL REMOVAL FROM SOIL, BASED ON PHYSICOCHEMICAL STUDIES AND FLUSHING EXPERIMENTS

Surface activity and wetting properties of nonionic surfactant Rokanol NL6, biosurfactant JBR 425 and their mixtures were investigated. On the basis of these investigations, the ability of both surfactants to remove the synthetic base oil (PAO 6) from sand was evaluated. Surfactants solutions were applied in soil flushing in column and in batch experiments. Column tests with the solutions of Rokanol NL6 and JBR 425 gave very poor results (25% oil removal), while washing in batch tests was much more efficient and the oil removal reached even 95%. The mixtures of both surfactants gave better results than those obtained for single compounds.

### 1. INTRODUCTION

Contamination of soil by petrochemical products and their derivatives is widespread and frequent due to their common use as, e.g., fuels, heating mediums, lubricants, drawing oils, etc. Examples of polluted sites are petrol stations, military basis, refineries, transport accidents sites, etc. Most of hydrophobic organic pollutants, called also non-aqueous phase liquids (NAPL), can be divided into two groups due to their density (LOWE et al. 1999). This division is important, as the consequences of oil spill onto soil surface and further migration into deeper layers, also into aquifers, are different.

Organic liquids, lighter than water (referred to as Light Nonaqueous Phase Liquids, LNAPLs), for example gasoline, jet fuel, heating oils, tend to accumulate above and slightly below the water-table. Organic liquids, heavier than water (Dense Nonaqueous Phase Liquids, DNAPLs), for example chlorinated solvents, PCB oils, creosote, coal tar, have the potential to migrate to great depths below the water-table (MULLIGAN et al. 2001).

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Remediation of polluted soil can be performed in *ex situ* as well, as *in situ* mode. In both systems the methods include physicochemical (e.g. thermal treatment, extraction, coal agglomeration, water flushing, soil venting) as well, as biological technologies (land-farming, composting, biodegradation, bio-extraction). Disadvantage of *ex situ* method is that the soil have to be excavated from site, thus, the *in-situ* methods are preferable. In Poland, biological remediation is practically the only method applied, while physicochemical remediation is popular in the USA (FIORENZA et al. 2000). The method of soil remediation by washing (pump-and-treat) is in the focus of many researchers. Efficient removal of NAPL's is difficult by traditional groundwater pumping, due to accumulation in soil pores, where they are hold by capillary forces arising from high NAPL/water interfacial tension (PENNELL et al. 1997). The use of surfactants increases the efficiency of the removal process.

Surfactants can enhance the removal of NAPLs from porous media by different mechanisms: mobilization and micellar solubilization of residual NAPLs trapped in porous media by capillary forces (LOWE et al. 1999, Mulligan et al. 2001). Surfactant accumulate at all interfaces existing in the system (e.g. NAPL/water, soil/NAPL, soil/water, air/water, air/NAPL). As a result, the interfacial tensions are decreased and also wetting of soil and NAPL are enhanced, which promotes mobilization of NAPL due to reduction of capillary forces. Physical mobilization may be desirable for the case of a LNAPL, where free product can be recovered in the vicinity of the water-table using skimmer wells, but may be undesirable in the case of a DNAPL, where a lowering of interfacial tension may result in vertical mobilization of DNAPL, deeper into the subsurface (MULLIGAN et al. 2001). A mobilized NAPL may also be trapped in surfactant solution in solubilized or emulsified form.

At sufficiently high concentration of surfactants, the micelles are formed. Micelles are aggregates of monomers of surfactant molecules which are capable to solubilize non-polar hydrophobic compounds, normally insoluble or only partly soluble in water. For most non-polar hydrophobic compounds, the locus of solubilization is the hydrocarbon core of the micelle (L et al., 1998). The increased solubility of organic materials in aqueous surfactant solutions is a phenomenon advantageous for NAPL's removal, because at higher surfactant concentration more organic contaminants can potentially be removed from soil in a flushing process (PENNELL et al. 1997, EDWARDS et al. 1991, DIALLO et al. 1994, JAFVERT et al. 1994, ABRIOLA et al. 2000).

In most cases of surfactant flushing, surfactant solution may form o/w emulsion with the NAPL. Surfactants can stabilize the emulsion by reducing the interfacial tension and decreasing the rate of coalescence (SCHRAMM 2005). Stability of emulsion depends on the type of surfactant. In general, macroemulsions are undesirable as they can reduce the permeability of a porous media through pore clogging. These emulsions can be detrimental to the remediation process because they are highly viscous and once formed can trap the contaminant in a less mobile phase.

The adaptation of surfactant flooding to soil washing has recently become an accepted practice in many countries (FIORENZA et al. 2000, LOWE et al. 1999). However, successful surfactant usage to enhance remediation is strongly dependent on the proper surfactant (or surfactant system) selection that will efficiently mobilize or solubilize NAPLs. Various types of surfactants are used in the surfactant flushing experiments (LOWE et al. 1999, FOUNTAIN et al. 1996, HARWELL et al. 1999). In the majority of research investigations nonionic surfactants are used (BUTLER, HAYES 1998, GUHA et al. 1998, EDWARDS et al. 1991, PENNELL et al. 1997, FOUNTAIN et al. 1996). Their solubilizing capacity were widely investigated. Anionic surfactants application is limited due to possibility of their reaction with the cations in the soil, however, they are readily investigated too (CHU, KWAN 2003, CHUN et al. 2002, MULLIGAN et al. 2001). Some of the synthetic surfactants used in soil remediation are hardly biodegradable and have a negative influence to the environment. For these reasons, in many areas of industrial applications including soil remediation, there is a tendency to substitute synthetic surfactants by more environmentally friendly natural surfactants, mostly produced by microorganisms. Biosurfactants have a considerable potential for soil remediation because of the following reasons: they reveal very useful properties, such as low critical micelle concentration, or good thermal stability; they are naturally occurring; they are biodegradable and generally nontoxic to microorganisms. Thus, if they remain in the soil after washing processes, the environment will not be damaged (BOGNOLO 1999). In some laboratory experiments it was found that comparing to SDS and Tween 80 (BAI et al. 1997) or to Tween 60 (KUYUKINA et al. 2005, SCHEIBENBOGEN et al. 1994) they are also more efficient in residual oils or hydrocarbons removal.

On the basis of the above considerations, it was decided that the objective of this research will be the investigation of the possibility of soil remediation improvement by using the mixture of non-ionic surfactant and biosurfactant, instead of single non-ionic surfactant solutions. It was expected that usefulness of these surfactants and their mixtures will be evaluated basing on physicochemical investigations, and further it will be verified in flushing of polluted soil experiments.

The scope of physicochemical investigations of surfactants solutions include interfacial tension reduction, wetting and solubilizing ability. The experiments on oil removal from the soil (oiled sand) were performed with using solutions of surfactants, selected on the basis of physicochemical measurements. The oil washing from the sand was carried out in column and batch experiments, simulating *in situ* and *ex situ* procedures, respectively.

## 2. MATERIALS AND METHODS

In the present work synthetic surfactants, polyethoxylated alcohol, Rokanol NL6 (PCC Rokita S.A., Poland) and biosurfactant (rhamnolipid JBR 425, Jeneil Biosur-

factant Company, USA) were used. Rhamnolipids are the most common group of biosurfactants, produced by *Pseudomonas aeruginosa* and *Pseudomonas fluorescens*. Synthetic base oil, PAO 6 (polyalphaolefine, Lotos S.A., Poland) was selected as hydrophobic pollutant. Synthetic oils application have increased recently, however, these oils were never used in earlier carried investigations on remediation.

As a model soil the sand was selected due to its uniform mineral composition, low particle porosity, and for its extremely low amount of fractional organic carbon. The sand was taken from the area localized in Gdansk near LOTOS Refinery pipeline. Prior to use, the sand was washed five times to remove colloidal material, and oven dried for 24 hours at 105 °C prior to packing. Sieve analysis shows that 90% of particles have a diameter between 0.1 mm to 0.5 mm.

## 2.1. PHYSICOCHEMICAL INVESTIGATIONS PROCEDURES

### Surface tension measurements

The surface tension (at the air/water interface) and interfacial tension (at the water/oil interface) measurements were performed with using Krüss DSA 10 apparatus, Drop Shape Analysis System. The time necessary for a drop to reach adsorption equilibrium varied between 10 and 30 min. The concentration of surfactants solutions were changed from 0.0001 to 1 g/dm<sup>3</sup>. The critical micelle concentration (CMC) of the surfactants was determined from the dependence of the surface tension on the logarithm of the surfactant concentration. The CMC values were obtained as intersection of linear extrapolated values of the surface tension, below and above the CMC.

### Wetting properties

Wetting properties were investigated by the drop-collapse method (JAIN et al. 1991, BODOUR, MILLER-MAIER 1998). This method is based on the behavior of droplets of aqueous solutions on a solid substrate. The investigations were performed in the polystyrene lid of a 96-microwell (12.7×8.5 cm) plate (Brand GmbH, Germany). Each well was coated with 3.5 µl of oil PAO 6 and equilibrated for 1–2 hours. Then a 2 µl drop of surfactant solution was sited with a syringe in the center of the well. On the basis of photos, the diameter of each drop at the contact surface with the solid was measured. For every concentration, at least 10 droplets were measured, and mean diameter was calculated. The surfactant concentrations used in this research were both, below and above the CMC (0.0002–0.7 g/dm<sup>3</sup>).

### Solubilization

Solubilization experiments were carried out in glass beakers containing 100 cm<sup>3</sup> of aqueous solution of nonionic surfactant. PAO 6 oil drops were added using the microtitrator; the drop mass was 0.0035–0.0045 g. After each drop the mixture was stirred to obtain clear solution for about 15–30 minutes at 2000 rpm using a Heidolph

RZR1 stirrer and the light absorption was measured at 520 nm by a Varian Cary 50 UV/VIS spectrophotometer. Significant increase of light absorption, assigned to dispersion, but not solubilization of the added oil, was taken as the end-point. All runs were carried out at constant temperature, 25 °C. Triplicate experiments were made and the averaged results are presented.

## 2.2. OIL REMOVAL PROCEDURES

### **Washing in column experiments (simulation of in-situ method)**

The flushing experiments were performed in a glass column (52 cm long and 4 cm in diameter) equipped with Schott filter at the bottom. The contaminated sand was prepared using a spiking method: 600 g of dried sand was mixed with 100 cm<sup>3</sup> of the spiking solution (18g of PAO 6 oil dissolved in petroleum ether), so the initial oil content in the soil was about 30 g/kg. The contaminated sand was placed on the tray for 1 day to evaporate the ether and then was placed into the column. The uniform packing was warrant. All flushing experiments were carried out in down-flow mode to make the conditions similar to the field process and the flow rate was 20 ml/min. 20 pore volumes (2 dm<sup>3</sup>) of surfactant solutions were used in column flushing and the experiment have lasted for about 100 min. The concentration of used surfactants solutions varied from 0.5 to 5 g/dm<sup>3</sup>. The contaminated sand and the sand after washing were extracted with petroleum ether to determine the content of the oil. The solvent was rotary-evaporated and the amount of extracted oil was determined gravimetrically. Every column experiment was repeated at least twice and the mean values are presented in the paper.

### **Washing in batch experiments (simulation of *ex situ* method)**

The 250 g of contaminated sand (prepared as above) was mixed with 300 ml of surfactant solution and shaken in IKA HS 260 shaker for 30 min. After that time the mixture was allowed to stand and after separation of the fluid from above the sand, the remained oil in the sand was determined as above. The concentration of used surfactant solutions was in the range from 0.33 to 5 g/dm<sup>3</sup>. Every batch experiment was repeated at least twice and the mean values are presented in the paper.

## 3. RESULTS AND DISCUSSION

### 3.1. PHYSICOCHEMICAL INVESTIGATIONS

During washing of oiled soil with surfactant solutions, a three-phase system is formed. In such system, the tensions at the air/water and oil/water interfaces determine the conditions of oil mobilization and they are crucial for remediation of contaminated soil.

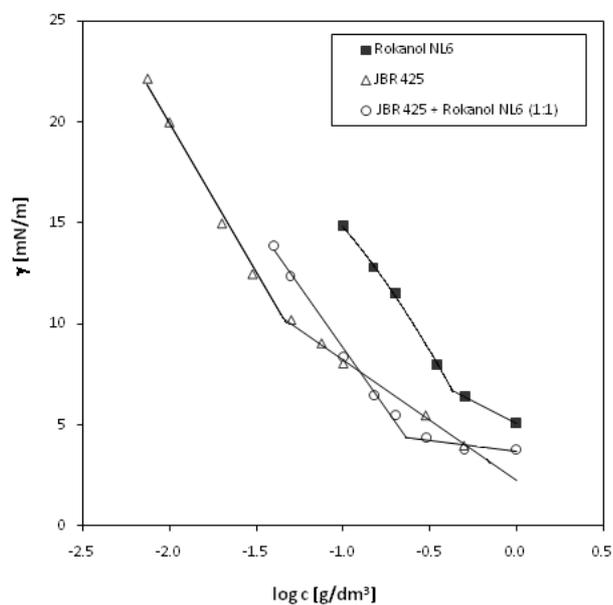


Fig. 1. Interfacial tension isotherms of aqueous solutions of Rokanol NL6, biosurfactant JBR 425 and their mixtures (1:1) at the PAO 6 oil/water interface

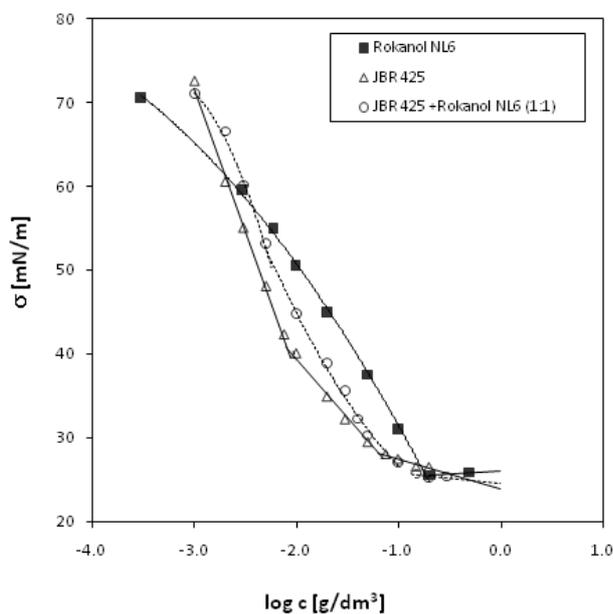


Fig. 2. Surface tension isotherms of aqueous solutions of Rokanol NL6, biosurfactant JBR 425 and their mixtures (1:1) at the air/water interface

In figures 1 and 2 the surface and interfacial tension isotherms are presented. The results relate to Rokanol NL6, biosurfactant JBR 425 and their mixtures 1:1 w/w.

The degree of lowering of NAPL-water interfacial tension that will occur upon exposure to surfactants is deciding about NAPLs' mobilization in the soil when surfactants flooding is applied. Reduction of interfacial tension to the very low level, below 1 mN/m, enables great vertical mobilization of NAPL (FIECHTER 1992). As it can be seen from figures 1 and 2 the investigated surfactants are capable of lowering surface and interfacial tension to the values facilitating the mobilization of residual NAPL. The minimum interfacial tension for investigated surfactants and mixtures were as follows: 2.8 mN/m for biosurfactant, 5.1 mN/m for Rokanol NL6 and 3.8 mN/m for the 1:1 mixture of both surfactants (figure 1).

The CMC value is especially significant for the solubilization process, as it shows the quantity of surfactant needed for efficient solubilization of contaminant. The CMC values obtained from isotherms presented in figure 2 were as follows: 0.07 g/dm<sup>3</sup> for biosurfactant JBR 425, 0.19 g/dm<sup>3</sup> for Rokanol NL6 and 0.12 g/dm<sup>3</sup> for the mixture of both surfactants.

Surface activity of surfactants may be evaluated basing on e.g. effectiveness in surface tension ( $\sigma$ ) or interfacial tension ( $\gamma$ ) reduction at concentration equal to CMC,  $\Pi_{\text{CMC}}$  (surface pressure). For oil/water interface the surface pressure  $\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$ , (where  $\gamma_0$  is the interfacial tension between water and oil while  $\gamma_{\text{CMC}}$  is the interfacial tension between oil and surfactant solution of concentration equal to CMC). In these investigations the obtained  $\Pi_{\text{CMC}}$  values were 52.1 mN/m for JBR 425, 56.1 mN/m for Rokanol NL6 and the highest value, 58.3 mN/m was obtained for mixture of both surfactants. Thus, one can state that the mixture of JBR 425 and Rokanol NL6 reveal synergistic effects in effectiveness of interfacial tension reduction, which is advantageous, as smaller amount of surfactants can be used when mixtures is applied for soil remediation.

The results of wetting properties of surfactants solutions are presented in figure 3. The mean diameter of 10 droplets for each concentration and the standard error (bars) are presented.

It can be seen from figure 3 that there is a strong correlation between droplets diameter and surfactant concentration. There are three regions of linear correlation between drop diameter and surfactant concentration, the first at the low content of surfactant (below the first break point), the second, intermediate region and the third one at the high concentrations (above the CMC, the second break point). The intermediate region is occurring between 0.005÷0.02 g/dm<sup>3</sup> for biosurfactant or 0.005÷0.1 g/dm<sup>3</sup> for Rokanol NL6 and the 1:1 mixture of both surfactants. The reason for the presence of intermediate region may indicate the pre-micellization of investigated surfactants at the oil/water interface (admicelle or hemimicelle formation) at surfactants concentration lower than CMC.

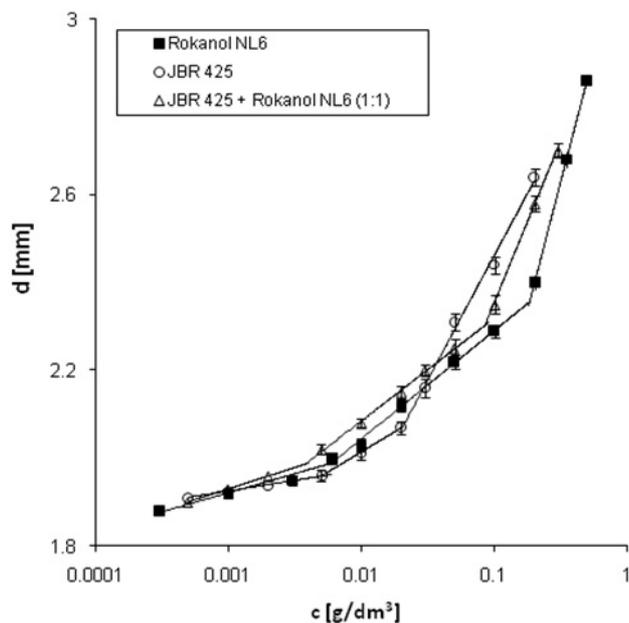


Fig. 3. The dependence between surfactant concentration and the diameter of a droplet on a surface coated with PAO 6 synthetic oil

Analyzing the results one can say that at low concentrations Rokanol NL6 had slightly better wetting properties than that of biosurfactant, for example for the 0.01 g/dm<sup>3</sup> solutions the mean diameters of a drops were as follows: 2.01 mm for biosurfactant, 2.03 mm for Rokanol NL6 and 2.08 mm for the 1:1 mixture. However, at higher surfactant concentrations 0.1 g/dm<sup>3</sup>, JBR 425 solutions have wetted the oil surface more efficiently (the drop diameter was 2.44 mm) than Rokanol NL6 solution (2.29 mm). Similar dependences on surfactant concentration were earlier observed in case of wetting of the surfaces coated with PCE or DCB with Rokanol L10 and JBR 425 solutions (PASTEWSKI et al. 2006).

In the current research however, there was stated a very positive effect of blending of biosurfactant with Rokanol NL6. As it can be seen in figure 3, the wetting of PAO 6 oil with the solutions of both compounds mixtures was more efficient than that in case of single components solutions. This was especially visible in the intermediate range of surfactant concentration (below 0.05 g/dm<sup>3</sup>), which is advantageous from economic point of view.

Summarizing, one can state, that the mixtures of Rokanol NL6 and biosurfactant JBR 425 reveal synergistic effects in interfacial tension reduction and in wetting properties in the systems, where NAPL is represented by synthetic base oil PAO 6.

Thus, the use of such mixtures in oiled soil flushing should improve mobilization of the oil comparing with results obtained when single components solutions are applied.

Solubilization mechanism contributes to oil removal during surfactant flushing. In figure 4 the solubility of PAO 6 oil in Rokanol NL6 solutions is presented.

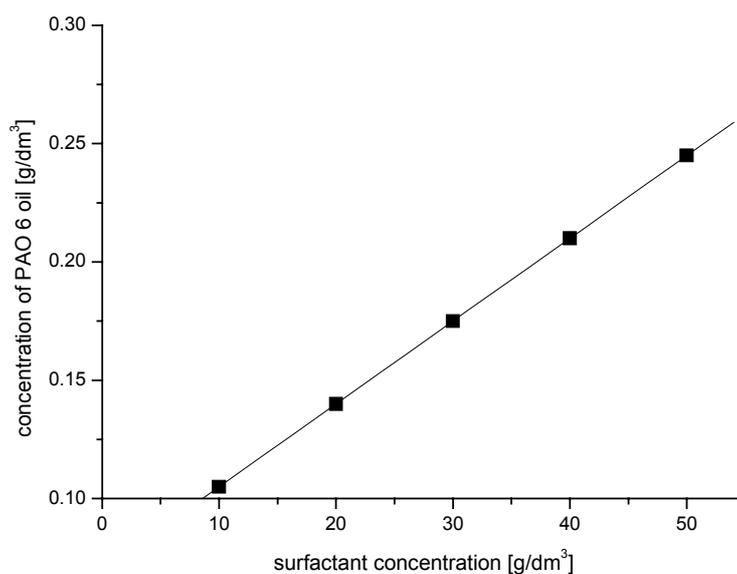


Fig. 4. The efficiency of PAO 6 oil solubilization in Rokanol NL6 solutions

The solubilization efficiency is rising with the increase of surfactant concentration, which is obvious. However, solubilization of this oil was poor, when compare with solubilization of other organic liquids, e.q. o-dichlorobenzene and tetrachloroethylene (PASTEWSKI et. al., 2006). At surfactant concentration of 30 g/dm<sup>3</sup> only 0.18 g of PAO 6 oil was solubilized in 1 dm<sup>3</sup> of Rokanol NL6 solution (figure 4), while in case of dichlorobenzene and tetrachloroethylene it was 6 g and 24.5 g in Rokanol L10 solutions (PASTEWSKI et. al. 2006). Moreover, solubilization of both chloroorganic compounds was more effective in solutions of biosurfactant JBR 425 than in solutions of non-ionic surfactants, 26 and 41 g/dm<sup>3</sup>, respectively (PASTEWSKI et al. 2006). Solubility of dodecane was 4 g/dm<sup>3</sup> in Rokanol L10 and 10 g/dm<sup>3</sup> in JBR 425 solutions (PASTEWSKI et al. 2007).

Such poor solubilization of PAO 6 oil, comparing to solubilization of above mentioned NAPL's may suggest that this mechanism will contribute to small extent in PAO 6 oil removal from soil.

## 3.2. OIL REMOVAL

In figure 5 the results of oil removal in the processes performed in column experiments are presented. In all cases the concentration of surfactants was above their CMC value and it varied from 0.33 to 5 g/dm<sup>3</sup>.

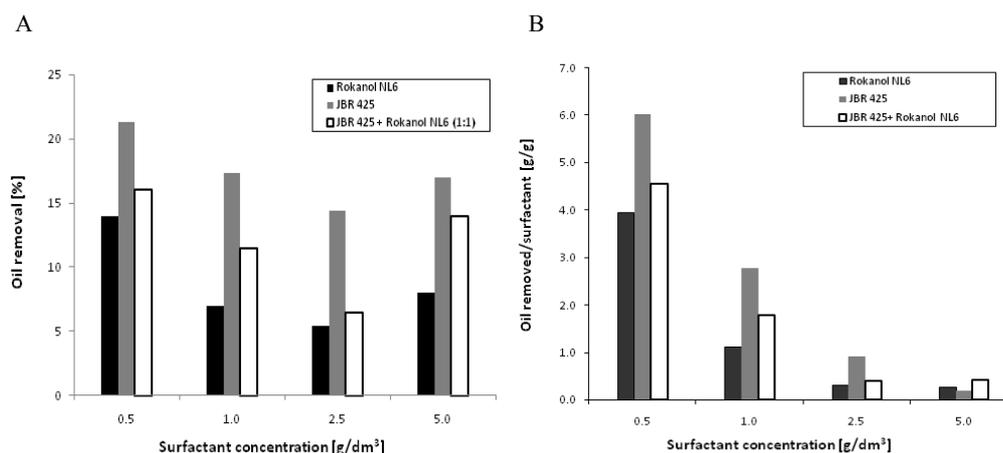


Fig. 5. Results of oil removal in column tests with aqueous solutions of Rokanol NL6, biosurfactant JBR 425 and their mixtures (1:1)

As it can be seen from figure 5, the oil removal from sand is very much dependent on surfactant concentration and surprisingly, with the increase of concentration, the removal efficiency decreases (figure 5A), except the highest surfactants concentration (5 g/dm<sup>3</sup>), when the oil removal increases. This was not expected, as the increase of surfactant concentration (above CMC) should result in the rise of micelles number, so the solubilization efficiency should also increase. Such observation suggests that solubilization is not a dominating mechanisms in oil removal. Only at highest surfactant concentration (5 g/dm<sup>3</sup>), a certain increase of oil removal was observed, which probably is a result of better solubilization of the oil or even emulsification. A very important observation is that the best results were obtained when biosurfactant solutions were used and that the addition of this compound to Rokanols' solutions enhances oil removal in comparison with the results obtained for single Rokanols' solutions. However, the best results of oil removal have not exceeded 25%, which is absolutely not satisfactory result.

In order to evaluate the effectiveness of surfactants usage in oil removal from sand, the results are presented in figure 5B. It is clearly visible that the higher the concentration of surfactant, the smaller amount of oil removed by one mass unit of surfactant. For example at the JBR 425 concentration of 0.5 g/dm<sup>3</sup>, the mass of removed oil in relation to the mass of used surfactant was 6 g/g, and it was only 0.19 g/g at concentration of

5 g/dm<sup>3</sup>. The reasons of poor results of oil removal in column flushing experiments can be different. Probably strong surfactants sorption onto soil grains, may result in decreasing of their concentration in solution. As it results from Park and Bielefeldt paper the sorption is higher at higher surfactant concentration (PARK, BIELEFELDT 2005). Only if sorption capacity of the soil is exhausted, the remaining concentration is not decreasing. This can also be the explanation of the oil removal increase at the highest surfactant concentration (figure 5A). It is also possible that macroemulsions which are readily formed in these systems are responsible for pores clogging and accumulation of the oil in the lower part of the column instead of removal it with the washing fluid. The same conclusions were drawn by DUFFIELD et al. (2003) from their research and the authors suggest that the viscous emulsions formation is the reason of poor remediation effect.

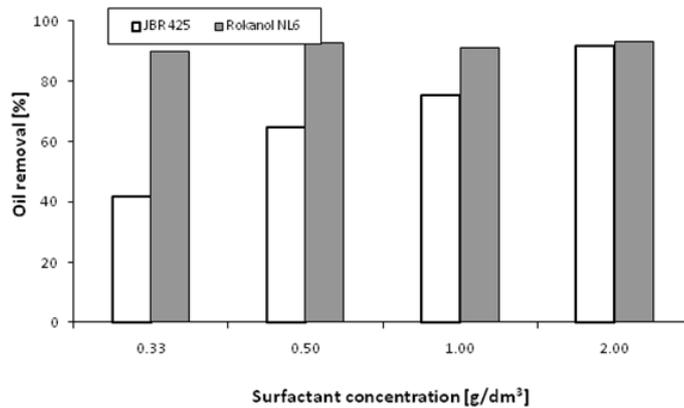


Fig. 6. Results of oil removal in batch tests at different surfactants concentrations in single component solutions

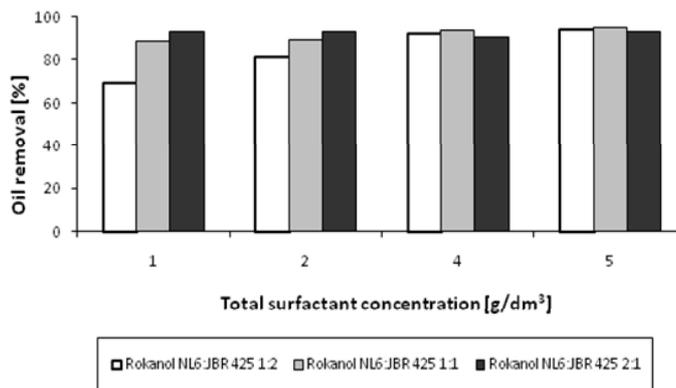


Fig. 7. Results of oil removal in batch tests at different composition of surfactants mixture solutions

Much better results were achieved when soil washing process was carried out in batch experiments (figures 6 and 7).

As it results from figure 6 the rise of biosurfactant concentration increases the oil removal, while in case of Rokanol NL6, the removal is high already at the lowest concentration ( $0.33 \text{ g/dm}^3$ ) and does not change with the increase of its concentration.

It is worth to mention that at the same surfactant concentration the number of micelles is different in cases of JBR 425 and Rokanol NL6 as the CMC values are different ( $0.07 \text{ g/dm}^3$  and  $0.196 \text{ g/dm}^3$ , respectively). And more, in order to remove e.g. 92% of oil PAO 6 from sand it is necessary to use Rokanol NL6 solution of concentration  $0.33 \text{ g/dm}^3$  (equivalent to  $2 \times \text{CMC}$ ) or biosurfactant solution of concentration  $2 \text{ g/dm}^3$  (equivalent to  $25 \times \text{CMC}$ ).

The content of oil in the fluid after sand washing in batch experiments was about  $16\text{--}18 \text{ g/dm}^3$ , thus it was much higher than expected, basing on solubilization experiments. These considerations confirm that solubilization mechanisms is not important in PAO 6 oil removal from the soil. Thus, mobilization is a dominating over solubilization mechanisms in this base oil removal.

In figure 7 the results obtained for nonionic surfactant and biosurfactant mixtures of different compositions are presented. It can be seen that mixtures are very effective in oil removal from sand. Only in cases where JBR 425 dominates (ratio Rokanol NL6:JBR 425 = 1:2) the results are lower than 90%. This suggests that biosurfactant is responsible for worsening of the oil removal. It is clearly visible in figure 8, where the effect of biosurfactant on effectiveness of oil removal by Rokanol NL6 is presented.

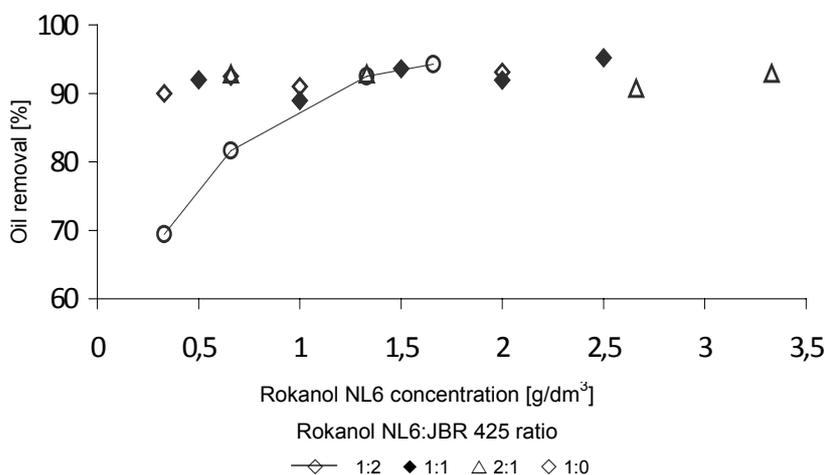


Fig. 8. Oil removal efficiency versus Rokanol NL6 concentration in single component solution and in the mixtures with biosurfactant JBR 425 of different compositions; (batch tests)

As it can be seen from figure 8, at particular concentrations of Rokanol NL6 the effect of oil removal was different, depending on the surfactant solution composition. In case of single component solutions of Rokanol NL6 the removal was always high (above 90%), while at the same concentration but in the mixture with JBR 425, the removal depends on composition of the mixed solution. In case of mixtures of 1:1, 2:1 Rokanol NL6:JBR 425 ratios there is not observed worsening of oil removal in comparison with its removal by Rokanol NL6 single solutions. In case of mixtures in which biosurfactant dominates (1:2 Rokanol NL6:JBR 425) the removal is evidently worse than that, for single Rokanol NL6 solution, especially at lower concentration.

Having in mind that the use of biosurfactants in soil remediation *in-situ* methods is definitely more advantageous than the use of synthetic nonionic surfactants, one can carefully select the best conditions, e.g. composition and concentration of surfactant flooding solutions, basing on the physicochemical investigations as well, as on the remediation experiments.

#### 4. CONCLUSIONS

The implementation of a surfactant flood is a very effective method of recovering contaminants from the subsurface. The advantage of this technology compared to certain other remediation technologies is the potential to remove large amounts of NAPL in a relatively short time.

Basing on the results (also from our previous researches) obtained in evaluating a particular surfactant's usefulness in hydrophobic pollutants removal from the soil one can state that biosurfactants are very promising comparing to tested nonionic surfactants. In the current research however, there was stated a very positive effect of blending of biosurfactant with Rokanol NL6, as their mixtures reveal synergistic effects in interfacial tension reduction and in wetting properties in the systems, where NAPL is represented by synthetic base oil PAO 6. Thus, it was expected that the use of such mixtures in oiled soil flushing should result in better remediation results than those, obtained with single components solutions. However, this was not the case.

In soil remediation by column experiments the best results were obtained when biosurfactant solutions were used and the addition of this compound to Rokanols' solutions enhanced oil removal in comparison with the results obtained for single Rokanols' solutions, but not exceeded the results observed for single biosurfactant solutions.

Comparing these effects with physicochemical results one can conclude that mobilization is a dominating mechanisms in oil removal, but not solubilization. The investigated surfactants are capable of lowering interfacial tension by the amount necessary to mobilize significant quantities of residual PAO 6 oil. Unfortunately, the oil removal in column experiments was not satisfactory (<40%).

The remediation in batch experiments was much more effective (>90%), however, the best results were obtained thanks to using Rokanol NL6, but not biosurfactant. The addition of biosurfactant to Rokanol solution decreases the oil removal from the sand, especially at the lowest concentrations of surfactants and in cases where JBR 425 dominates (ratio Rokanol NL6:JBR 425 = 1:2). Analysing these results and considering the mechanisms participating in oil removal one can conclude, that in dynamic soil washing the mobilization and emulsification are the dominating processes.

Summarizing one can state that in soil remediation, where mobilization and micellar solubilization is dominant, the use of biosurfactant JBR 425 solutions could be advantageous. This takes place in surfactants solutions flushing *in situ* procedures. Unfortunately, in order to achieve sufficient removal efficiency a high concentration of biosurfactant in solution would be necessary. Hence, its use in mixtures with synthetic nonionic surfactants, especially ethoxylated alcohols like Rokanols, might provide an interesting alternative for improving the remediation efficiency. At the currently high costs of biosurfactants production, their use in bioremediation will be profitable only under special circumstances. For example, when other technologies are either not applicable or inefficient. Moreover, use of biosurfactant in mixtures with nonionic surfactants also may decrease the cost and simultaneously increase the remediation efficiency.

In case of *ex situ* remediation (simulated by batch tests) the use of biosurfactant is disadvantageous, as it decreases oil removal comparing to that, when Rokanol was used.

#### ACKNOWLEDGEMENT

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