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Application of biosurfactants and non-ionic surfactants for removal of organic matter from metallurgical lead-bearing slime

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ABSTRACT

The paper presents evaluation of different extracting solutions used for removal of organic matter, especially polycyclic aromatic hydrocarbons (PAHs), from slime produced in copper smelting. A series of extraction experiments was conducted using biosurfactants and non-ionic surfactant solutions of various concentrations. The results showed that the efficiencies of organic matter removal by biosurfactants were at the level of 20–30% and depended on the type of the used biosurfactant. Biolen Biogrease L, and mixture of alkylobenzenesulfonic acid and oxyethylene fatty alcohol were effective for removal of polycyclic aromatic hydrocarbons (above 50%), whereas Zymbiose-enz. was ineffective. Non-ionic surfactants were found to be more effective in removing organic matter than biosurfactants. In the case of non-ionic surfactants the removal efficiencies depended on the concentration. Increase of Tween 80 concentration caused decrease in the efficiency of organic matter removal. The similar results were obtained for Nonoxynol 14. By contrast, the increase of Nonoxynol 10 concentration resulted in increase of organic matter removal efficiency.

1. Introduction

Cationic, anionic and non-ionic surfactants are used mainly for washing or flushing. They contain both hydrophobic and hydrophilic portions making them ideal for solubilization of hydrophobic compounds. Anionic and non-ionic surfactants are less likely to be absorbed by soil. Cationic surfactants were used to lower aquifer permeabilities by sorption on the aquifer materials. Numerous studies indicated that pre-treatment of soil by washing it with surfactant to solubilize hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs) enhanced biodegradation of those contaminants [1–6]. Khodadoust et al. [7] used non-ionic surfactants, e.g. Igepal CA-720, Tween 80, to remove phenanthrene from a field soil. Kim et al. [8] examined desorption rate of naphthalene and phenanthrene from soil slurry with Triton X-100, Tween 80 and Brij 30.

Some surfactants, so-called biosurfactants, are biologically produced from yeast or bacteria of various substrates such as sugars, oils, alkanes and waste. In most cases they are synthesized as metabolic by-products. Biosurfactants are grouped into glycolipids, lipopeptides, phospholipids, fatty acids and neutral lipids. Their critical micelle concentration (CMC) generally ranges from 1 to 200 mg/l. Three natural roles for biosurfactants have been proposed: (i) increasing surface area of hydrophobic water-insoluble growth substrates; (ii) increasing bioavailability of hydrophobic substrates by increasing their apparent solubility or desorbing them from surfaces; (iii) regulating attachment and detachment of microorganisms to and from surfaces. Biosurfactants enhance emulsification of hydrocarbons, have the potential to solubilise hydrocarbon contaminants and increase their availability for microbial degradation. At present, biosurfactants are mainly used in studies of enhanced oil recovery and hydrocarbon bioremediation. Solubilization and emulsification of toxic chemicals by biosurfactants have also been reported. Inakollu et al. [9] studied the microbial biodegradation rate of hexadecane, dodecane, benzene, toluene, *iso*-octane, pristane (2,6,10,14-tetramethyl pentadecane), naphthalene, and phenanthrene in the presence and absence of a mixture of rhamnolipid biosurfactant. They showed that the biodegradation rate of PAHs, naphthalene and phenanthrene, decreased by 25 and 27%, respectively, when the surfactant was used.

Deschenes et al. [10] showed that the rhamnolipids from the same strain in bioslurry can enhance the solubilization of four-ring PAHs more significantly than three-ring PAHs. It is well-known fact that pH, particle size, permeabilities, contaminants of the waste and CMC of the surfactants strongly influence the removal efficiencies.

Lead-bearing slime is a waste which is produced in wet dedusting of gases coming from shaft furnaces during production of

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Table 1
Characteristics of organic matter separated from slime

Parameters	Average (g/kg)
Total organic matter	87
Aromatic fraction	72.9
Aliphatic fraction	7.7
Acidic fraction	6.4

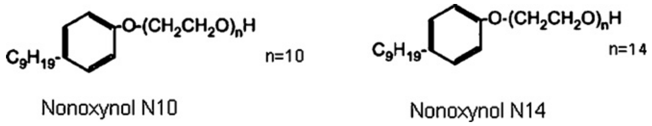

Fig. 1. Structure of Nonoxynols.

copper matte from Cu concentrates in Poland. The slime contains about 35–45% of lead and 5–15% of organic carbon. The organic matter in the slime is mostly composed of mixture of aromatic compounds, including polycyclic aromatic hydrocarbons. Application of slime as Pb source in metallurgical process of lead smelting is limited because of organic compounds content. The high content of organic matter in the slime leads in the first stage of the process to high concentration of organic compounds in the furnace off-gases, which in extreme conditions can result in uncontrolled explosions inside the furnace. In consequence there is a need to conduct highly expensive operation of furnace gases afterburning and their cleaning.

The objectives of the present study were (i) evaluation of organic matter desorption efficiency, especially PAHs, from the slime by non-ionic surfactants and (ii) application of commercial biosurfactants for organic matter removal. The following surfactants were selected: Nonoxynol N10, Nonoxynol N14 and Tween 800. For studies of biosurfactants commercial enzymatic mixture Zymbiose-enz. and Biogrease L were used.

In this study, the use of various surfactants was examined with respect to the solubilization/desorption of organic matter, especially polycyclic aromatic hydrocarbons, from slime. A series of extraction experiments was performed to determine the ability of each selected non-ionic surfactant and biosurfactant for the organic matter removal.

2. Materials and methods

2.1. Slime

The used in investigation sample of lead slime was taken from material deposited in a copper smelter. Its organic matter content is presented in Table 1. Concentration of heavy metals in the slime is listed in Table 2.

2.2. Extractants

Biosurfactants Zymbiose Enzymatic Liquid (Zymbiose-enz.), Biolen Biogrease L, mixture of enzymes, 15% alkylobenzenesulfonic acid and 5% oxyethylene fatty alcohol (enzymatic washing powder) water solution were used. The non-ionic surfactants, such as Nonoxynol 10 (N10), Nonoxynol 14 (N14), and polyoxyethylene sorbitan monooleate (Tween 80), were selected on the basis of the results presented in various papers [7,8,11–13]. Fig. 1 presents structures of Nonoxynols. Experiments were performed with biosurfactants Zymbiose-enz. and Biogrease L. For enzymatic washing powder (EPW), the 5% solution was used. In the case of non-ionic surfactants, experiments were performed at three different surfactant concentrations (3%, 5% and 7%). The extractions were performed using slime to water mass ratio of 1:5. When biosurfactants, e.g. Zymbiose-enz., Biolen Biogrease L and EPW, were used vials were mechanically shaken for 5 h. After that, the mixtures were filtrated with cellulose filter. For non-ionic surfactants the vials were shaken on a rotary shaker table at 250 r min^{-1} for 24 h. After shaking, the slime–solution mixture was centrifuged at 4000 r min^{-1} for 25 min.

Table 2
Concentration of heavy metals in slime

Element	Concentration (%)
Lead, Pb	32.5
Copper, Cu	0.42
Zinc, Zn	5.13
Arsenic, As	4.24
Iron, Fe	0.14
Sb	0.10

2.3. Analytical method

The samples of slimes before and after organic matter removal were extracted with methylene chloride in ultrasonic field. The obtained solution was dried with anhydrous sodium sulphate (Na_2SO_4) and the solvent was evaporated. The aliphatic and aromatic fractions were separated from organic matter by column liquid chromatography according to the methods described by Czaplicka et al. [14].

The solid samples after treatment with surfactants were extracted by liquid–liquid method using methylene chloride. For separation of surfactant from the samples Florosil columns were used.

Qualitative analysis of aromatic compounds was performed by means of GC/MS, using PerkinElmer model Clarus 500 chromatograph. It was equipped with a mass detector, DB-5 capillary column of 30 m length and inner diameter of 0.25 mm, and a split-splitless injector.

Metals in slime and extracts from experiments were analyzed by atomic absorption spectrophotometer (AAS).

3. Results and discussion

3.1. Characteristics of organic matter desorbed from the slime

In lead-bearing slime heavy metals and organic compounds coexist. The investigated sample of slimes included 87 g/kg of organic matter. The organic matter mainly consists of aromatic compounds (72.9 g/kg): up to 84% of organic matter can be separated from the slime. The qualitative analysis showed that the desorbed organic matter contained also aliphatic and acidic compounds. The contents of aliphatic and acidic compounds were 8 g/kg and 6.5 g/kg, respectively (Table 1).

GC/MS analysis of aromatic fraction showed that PAHs, e.g. naphthalene, acenaphthalene, fluorene, biphenyl, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz(*a*)anthracene, benzo(*a*)pyrene, as well as methyl- and ethyl derivatives of naphthalene, methyl phenanthrene are present in the organic matter desorbed from slime. The concentration of selected PAHs in the slime is presented in Table 3. Heterocyclic sulphur compounds (benzothiophene, dibenzothiophene and their methyl derivatives) and phenols have also been identified. Fig. 2 shows a chromatogram of aromatic fraction separated from the slime. Contents of phenol and cresols were 39 mg/kg and 83 mg/kg, respectively.

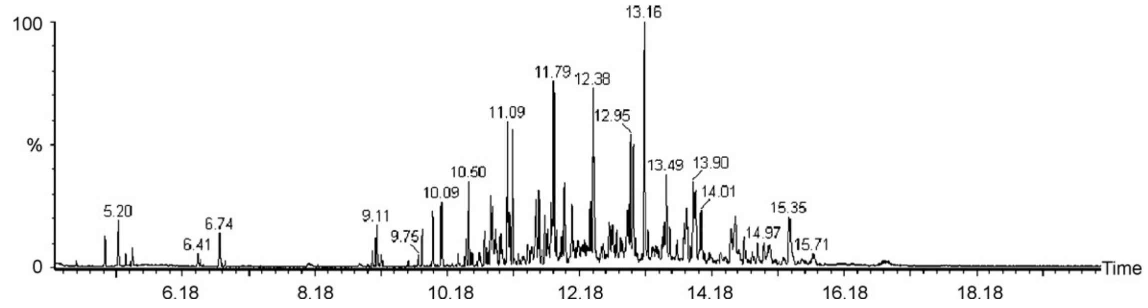

Fig. 2. Chromatogram of aromatic fraction separated from slime.

Table 3
Concentration of selected PAHs in slime

Compound	Concentration (mg/kg)
Naphthalene	77
Biphenyl	150
Acenaphthalene	254
Fluorene	153
Phenanthrene	505
Anthracene	55
Fluoranthene	63
Pyrene	37
Chrysene	20
Benz(*a*)anthracene	17
Benzo(*a*)pyrene	2
Total PAHs	1333

3.2. Removal of the organic matter by biosurfactants

When considering lead slime metallurgical processing, it is very important to remove organic matter. The biosurfactants used in these experiments: Zymbiose-enz. and Biogrease L removed 20%, and 30% of organic matter, respectively (Fig. 3). Application of 5% EPW was the most effective—53% of the compounds were removed from slime.

To determine removal efficiency of PAHs methylene chloride extracts were analyzed. The obtained results for Zymbiose-enz. showed that the removal efficiencies of selected PAHs (fluorene, phenantherene, fluoranthene, pyrene, and chrysene) were in the range from 13 to 29%. For Biogrease, from 20 to 50% of PAHs were desorbed from slime. In the case of EPW over 50% of PAHs were present in eluate. In Fig. 4 the removal efficiencies of PAHs from slime by using biosurfactants are presented. In all the cases, higher efficiency of fluorene removal was observed in comparison with other PAHs. The removal efficiency of phenanthrene was higher than pyrene or fluoranthene, but in all examined samples it was lower than for fluorene. It seems that the removal efficiency of PAHs depends on molecular mass, as the increasing molecular mass of compounds caused decrease of the removal efficiency.

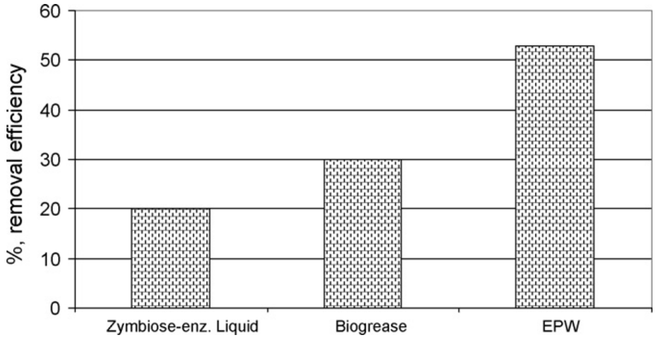

Fig. 3. The removal efficiencies of organic matter by biosurfactants.

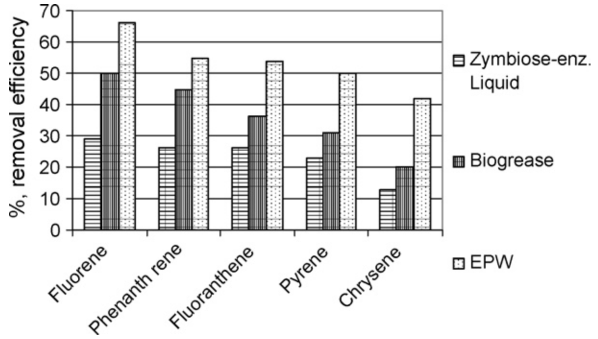

Fig. 4. The removal efficiencies of PAHs for biosurfactants.

3.3. Removal of organic matter by non-ionic surfactants

Three of non-ionic surfactants were selected to desorb organic matter: Nonoxynol 10, Nonoxynol 14 and Tween 80. The molecular weight of surfactants was 660, 735, and 1310, respectively. Their performance in removal of organic compounds was investigated at three different concentrations (3%, 5% and 7%) for each surfactant.

It was observed that the organic matter removal efficiency for 3% surfactant concentration decreases in the following order: Nonoxynol 14, Nonoxynol 10 and Tween 80 (Fig. 5). Analysis of the treated slime showed that in the case of Nonoxynol 14 examination, 63% of organic matter was adsorbed on slime after experiments. On the other hand, the results indicated that the removal efficiency was 77% for fluorene, 75% for phenanthrene, and 61% for pyrene, fluoranthene and chrysene. In the case of Nonoxynol 10 examination, 65% of organic matter remained on slime after experiments.

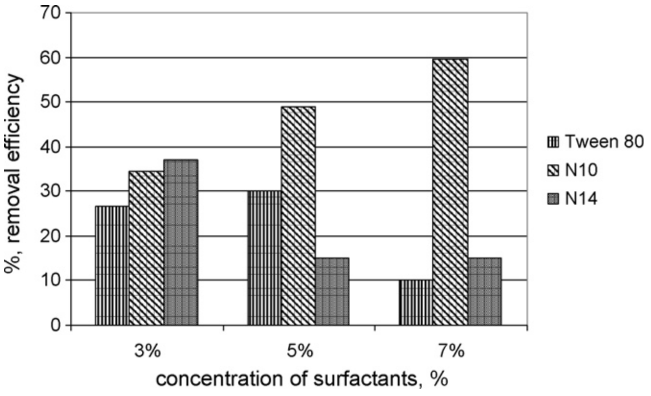

Fig. 5. The removal efficiency of organic matter using non-ionic surfactants.

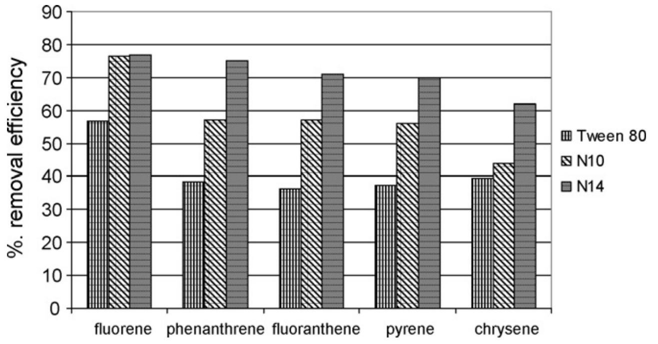

Fig. 6. The removal efficiency of PAHs by non-ionic surfactants at 3% concentration.

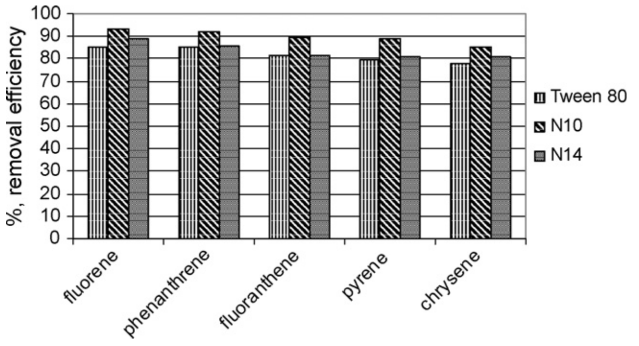

Fig. 8. Removal of PAHs by non-ionic surfactants at 7% concentration.

However, 77% of fluorene, 57% of phenanthrene, pyrene and fluoranthene and 43% of chrysene were desorbed from slime (Fig. 5). There are two simultaneous processes taking place: (1) part of organic matter is desorbed from the slime and (2) we also observe sorption of surfactants on the slime surface. For Tween 80, about 75% of organic matter is adsorbed on slime after experiments, while 62% of PAHs was removed from slime under the same conditions, except for fluorene. The removal efficiency for fluorene amounts to 56%.

The use of 5% solutions of surfactants gave possibility for removal of organic matter from the slime in the range from 15 to 50%, depending on the type of surfactant. The removal efficiencies decrease in the following order: N10 > Tween 80 > N14 (Fig. 6). It was observed that the use of 5% concentration of N10 resulted in 50% removal of organic matter. When comparing it to results for 3% N10 concentration, we observed that the increasing concentration of N10 leads to increase in the organic matter removal. For N10, the removal efficiencies of PAHs were on the level of 66%, except from fluorene (Fig. 7). It was observed that 83% of fluorene was in eluate. In the case of Tween 80, similarly to results obtained for 3% concentration of this surfactant, about 70% of organic matter remained on slime after experiments. However, the removal efficiencies of fluorene and phenanthrene reached the level of 80%, while for pyrene, fluoranthene and chrysene the obtained level was 66%. The results indicated that increase of this surfactant concentration up to 5% caused increase of the removal efficiencies of PAHs.

The removal efficiencies of organic matter for 7% concentrations of surfactants ranged from 10% to 60%. The results showed that for N10 the efficiency reached the value of 60%. On the other hand, for N14 the removal of organic matter is on the same level as for 5% concentration of this surfactant—15%. In the case of Tween 80, the removal of organic matter decreased with increase of surfactant concentrations, and only 10% of organic matter was removed. As it can be seen in Fig. 8 the removal efficiencies of PAHs by Tween 80 ranged from 78% to 85% depending on the compound used. The higher removal was observed for fluorene and phenanthrene when compared to fluoranthene, pyrene or chrysene. Similar results were obtained for 7% concentrations of N14. In the case of N10, about 81–88% of PAHs were present in eluate. The highest removal of PAHs was observed for 7% concentration of N10. For fluorene and phenanthrene over 90% of these compounds was present in eluate, and 89% of fluoranthene and pyrene was removed from slime.

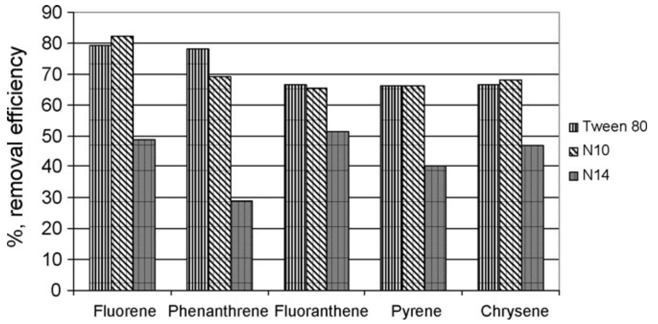

Fig. 7. Removal of PAHs by non-ionic surfactants at 5% concentration.

The obtained results demonstrated that for surfactant N10, increase of surfactants concentration leads to increase of organic matter removal efficiencies. This can be explained as a result of availability of more micelles for solubilization of organic matter. Formation of the non-ionic surfactants micelle allows the organic compounds to divide within the hydrophobic core of the micelle, which leads to the increase of apparent solubility of these compounds in the liquid phase. By contrast, for Tween 80 the decrease of the removal efficiency with increase of surfactant content was observed. The higher organic matter removal, as observed for Nonoxynols in comparison with Tween 80, may result from adsorption of the latte on the slime. Due to lower critical micelle concentration and higher hydrophile–lipophile balance number value for Tween 80 than for Nonoxynols, the micelle formation for Tween 80 should begin at lower surfactants concentration. The Tween 80 had better removal efficiency at concentration of 3% in comparison to 5% and 7% concentration. In the case of N14, the 5% concentration increase resulted in the decrease of organic matter removal. However, the removal of PAHs by 5% and 7% solutions is at the level similar to N10. This phenomenon may be explained by sorption of surfactants, characterized by higher molecular mass, on the slime.

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