



The application of biosurfactants into removal of selected micropollutants from soils and sediments

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ABSTRACT

The environment comprises soils and sediments in which micropollutants may accumulate and establish as a result of the secondary source of contamination. Micropollutants may migrate from soils into surface and grounds waters as well as cause an increase in bioavailability for organisms. Micropollutants contamination of sediments may result in the water pollution. As a result of chemical reactions taking place among the compounds present in the environment the derivatives, whose identification is fragmentary known at present, are formed. Remediation methods relying on the immobilization of contamination or its removal may be carried out in the place of its formation (*in situ*) or out of the place of its original location (*ex situ*). Bacteria being able to form biosurfactants are of an increasing interest as they have low toxicity as well as they can easily biodegrade. Therefore, *in situ* application of natural biosurfactants may be considered to be a good remediation alternative as they are not hazardous for water and soil organisms. On the one hand, high costs related to their production and application logy should be taken into account, however, their usage may be economically attractive. The aim of this study was to present the possibility of using biosurfactants as additives in removal processes of selected micropollutants from soil–water environment.

Keywords: Biosurfactants; Removal; Micropollutants; Heavy metals; PAH; TPH; PCB

1. Introduction

Surfactants are surface-active substances consisting of hydrophobic and hydrophilic portions. The surfactants are applied in the production of medicines, food and cosmetics due to their ability to lower interfacial tension as well as to ensure the stabilization of emulsion [1].

Biosurfactants are formed under environmental-friendly conditions and in their production some renewable sources of carbon e.g. industrial wastes are used [2]. Among low molecular weight biosurfactants are glycolipids, lipopeptides and fatty acids, whereas high molecular weight biosurfactants include proteins and lipids. The chemical composition and size particles of biosurfactants are included in Table 1 [3].

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Table 1

Classification of biosurfactants according to chemical composition and size particles [3]

Class	Particle size	Group	Name	Producer
Glycolipids	L	Rhamnolipids Trehalolipids		<i>Pseudomonas aeruginosa</i> <i>Rhodococcus erythropolis</i> <i>Arthrobacter</i> sp. <i>Mycobacterium</i> sp. <i>Corynebacterium</i> sp.
		Sophorolipids		<i>Torulopsis bombicola</i> <i>Torulopsis apicola</i> <i>Torulopsis petrophilum</i> <i>Ustilago maydys</i>
Lipopeptides and lipoproteins	LH	Cellobiolipids	Gramicidins Polymyxins Surfactin Subtilisin Serrawettin Lichenysin	<i>Bacillus brevis</i> <i>Bacillus polymyxa</i> <i>Bacillus subtilis</i> <i>Bacillus subtilis</i> <i>Serratia marcescenes</i> <i>Bacillus licheniformis</i> <i>Corynebacterium lepus</i>
Fatty acids	L	Fatty acids		
Lipids		Lipids		<i>Nocardia erythropolis</i>
Phospholipids		Phospholipids		<i>Acinetobacter</i> sp. <i>Penicillium spiculisporum</i> <i>Acinetobacter calcoaceticus</i>
(a) Glikolipids	H		BD4 emulsan Alasan Biodispersan Mannan-lipid-protein Liposan	BD 413 <i>Acinetobacter radioresistens</i> KA 53 <i>Acitenobacter calocoaceticus</i> sp. <i>Saccharomyces cerevisiae</i> <i>C. tropicalis</i> <i>Candida lipolitica</i>
(b) Others	H		Rag 1 emulsan Emulsan 378	<i>Acinetobacter calcoaceticus</i> <i>Pseudomonas aeruginosa</i> <i>Acinetobacter calcoaceticus</i> RAG
Special	H	Fimbrie Compounds of cell structures		<i>1Streptococcus</i> sp. <i>Staphylococcus aureus</i>

L—low molecular weight, H—high molecular weight.

The process of production of biosurfactants is related to the dynamic growth of population of bacteria. The biosurfactants are often produced when the population reaches the stationary state. Under such conditions, the growth of cells is limited by the low contents of nitrogen and iron [4]. It is confirmed in the literary sources that the production of biosurfactants by the non-growing cells which are immobilized in gel [5]. The mentioned way of production lowers the costs of the process as the carbon coming from the matrix is fully used [6].

The type of the carbon source in the matrix is regarded as the most important factor influencing on the production of biosurfactants [7]. Many biosurfactants are formed under utilization of hydrophobic nutrient substrates e.g. n-alkans. There are also bacteria able to produce biosurfactants on the inoculum including glucose or ethanol, glycerol (inoculum with hydrophilic energy source) [8]. The addition of non polar compound e.g. hexadecane causes isolation of biosurfactant from the cells surface [9]. The speed of the growth of the culture increases provided that the

limit to the access to the nitrogen occurs [10]. Some other factors such as: the presence of mineral salts, pH, temperature and the access to the oxygen all have some impact on the synthesis of biosurfactants mainly to the growth and the activity of the cells [11]. Biosurfactants have also been successfully applied in the medicine due to their antimicrobial, antifungal and antivirus properties [12]. It was found that glycolipids inhibit the progress of leukaemia as well as the cancer of the lungs and brain, whereas sphorolipids inhibit the progress of liver and pancreas cancer, respectively [13].

2. Remediation of soils and sediments contaminated with inorganic micropollutants using biosurfactants

Biosurfactants have been successfully applied in the remediation of soils polluted with heavy metals [6,14]. Low molecular mass biosurfactants are often considered since the method of their isolation and production is well known [15]. An increasing efficiency in the removal of heavy metals by anion biosurfactants is explained by the mechanisms of the processes of desorption and complexation. In Fig. 1 the desorption of heavy metals from the soil during flushing with biosurfactant is depicted [16]. The particles of surface-active agent cumulating in the border solid phase—soil solution lower of interfacial tension and capillary forces as well as the particles participate in the process of bonding metals. The afore mentioned processes are accelerated by the presence of heavy metals in the soil solution. The process of desorption is accelerated in the water phase by the complexation of

cations of heavy metals by particles and micelles of biosurfactant. The formed bindings between cations of the metal and negatively charged part of biosurfactant are strong enough to remove the complexes in the process of flushing completely [17].

The process of remediation of soil using biosurfactants can be carried out both under *ex situ* and *in situ* conditions. While carrying out the remediation under *ex situ* conditions, the portion of soil is placed in the container together with the solution of the surface active agent [1,6,17]. After flushing, the soil should be separated from the liquid phase that contains the complex: biosurfactant and heavy metals. Afterward, the process of precipitation of the surface active compound is required together with releasing the ions of the heavy metal into water.

Under *in situ* conditions when biosurfactant is added and recovered, the investigations are carried out using the system of drainages and ditches in the place of soil contamination.

The efficiency of conducted studies depends on many factors including: the type of pollutants, way of flushing and type of biosurfactant. In the studies carried out by Paraszkievicz, the onefold flushing the soil with the 0.1% solution of surfactin in 1% NaOH resulted in the removal of 25% Cu, 6% Zn and 5% Cd, respectively, whereas five-time flushing increased the removal of heavy metals up to: 70% Cu, 25% Zn and 15% Cd, respectively [16].

The method using foams of biosurfactant is also common in the process of heavy metals removal from the soils and sediments. As the foam has low density and high surface area, these features enable the deeper

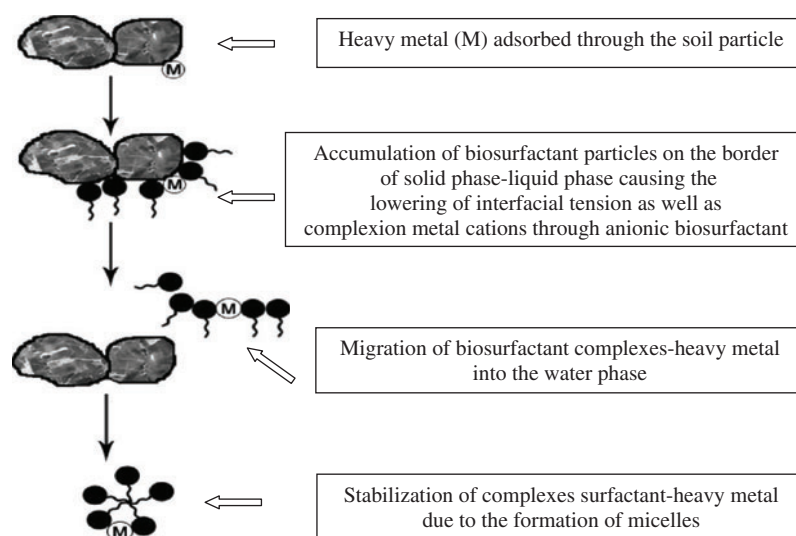


Fig. 1. Desorption of heavy metal from the soil during flushing with biosurfactant [16].

penetration through the porous ground and they increase the contact of biosurfactant with the pollution [18].

Mulligan i Dahrazma investigated the efficiency of rhamnolipid in the removal of heavy metals from sediments [19]. The sediments originated from Canal Lachine (Canada) surrounded by the steelworks and the sediment samples contained: 140 mg/kg of Cu, 572 mg/kg Pb, 4,854 mg/kg of Zn and 145 mg/kg of Cr and 76 mg/kg of Ni, respectively. The sediment samples were flushed with the solution of 0, 5, 1 and 2% rhamnolipid with 1% of NaOH and without NaOH in a continuous flow configuration. It was achieved up to 37% of Cu, 13 of Zn, and 27% of Ni by applying the rhamnolipid without additives. The addition of 1% of NaOH to 0.5% rhamnolipid removed Cu up to four times compared with 0.5% the sole rhamnolipid.

In the other studies, rhamnolipid and saponins as well as lipids of mannosylerythritol lipids were applied in order to remove heavy metals from the soils and sediments [20]. Soil samples coming from the Canada contained 260 mg/kg (dry matter - d.m.) of Cu, 170 mg/kg d.m. of Ni, 890 mg/kg d.m. of Zn and 230 mg/kg d.m. of petroleum hydrocarbons, respectively. Five-time flushing with the solution of saponin (30 g/L) made it possible to remove the 88% of Zn at pH 3 and 76% of Ni at pH 5. The highest percentage of removal of Cu (46%) was obtained with flushing soil with the solution of 2% of rhamnolipid at pH 6.5. The usage of mannosylerythritol lipids with the concentration of 4% at pH 5.6 resulted in the low percentage of the removal of Zn (17%) and Ni (36%) from the soil, respectively. In the same studies, sediment samples coming from a lake in Japan contaminated with heavy metals were also investigated. The highest efficiency in the removal of Zn (33%) and Pb (24%) was obtained using saponin (30 g/L) at pH 5. The application of 2% of rhamnolipid at pH 6.5 made it possible to remove Cu (84%) [20].

In other studies, Mulligan et al. evaluated the efficiency of surfactin, rhamnolipid and sophorolipid in the removal of Cu (110 mg/kg d.m.) and Zn (3,300 mg/kg d.m.) from sediments [18]. By the single washing 0.5% of rhamnolipid managed to remove 65% of Cu and 18% of Zn, whereas 4% sophorolipid removed 25% of Cu and 60% of Zn, respectively. It came out that surfactin was less effective achieving the removal of 15% of Cu and 6% of Zn, respectively. The sequential extraction was made for further description of metal bounds. It was proved that rhamnolipid and surfactin could remove the organically bound copper, whereas sophorolipid the carbonate and oxide-bound zinc.

Palashpriya et al. investigated the impact of biosurfactant isolated from a marine bacterium on the removal of heavy metals from solutions containing heavy metals [21]. The studies were carried out by applying biosurfactant mediated into removal of heavy metals. It was found that at the concentration of $5\times$ of 100 ppm of lead and cadmium was removed.

In another studies, Hong et al. investigated the efficiency of saponin on the removal of heavy metals from polluted soils [22]. They carried out the process of washing achieving the removal of 90–100% of Cd and 85–98% of Zn. The sequential extraction was made for further description of metal-bounds. It was concluded that saponin was successfully applied in removing the exchangeable and carbonated fractions of heavy metals from soils.

In the study conducted by Juwarkar et al., rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* strain BS2 was applied in order to remove Cd and Pb from the artificially polluted soil [23]. It was found that di-rhamnolipid was capable of removing leachable or an available fraction of Cd and Pb as well as the bounded metals. 92% of Cd and 88% of Pb after 36 h of leaching were removed using rhamnolipid. In the experiments, with the usage of tap water $\approx 2.7\%$ of Cd and 9.8% of Pb were removed from the contaminated soil. It was proved that only freely available or weakly bound forms of Cd and Pb were removed. It was also observed that biosurfactant was more effective in leaching of metals as pH of the leachates coming from the soil sample polluted with heavy metals was low (pH 6.60–6.78) in comparison with the soil sample treated with tap water (pH 6.90–7.25). That was explained by the high dissolution of metal species from the contaminated soil. Furthermore, a decrease in toxicity of metals to soil microflora took place since the microbial population of the polluted soil increased after removal of metals by biosurfactant. It confirmed the possibility of applying biosurfactants in the bioremediation of the soil polluted with Cd and Pb.

Hernández-Soriano et al. investigated the potential of the anionic surfactant Aerosol 22 (A22) for the release of Cd, Cu, Pb and Zn from a metal-amended soil in the area of Mediterranean by carrying out the batch experiments to assess the release kinetics [24]. The highest release of metals occurred at an increase in solution/soil ratio to 100 (mL/g). When pH was lower than 7 the minor amounts of metals were leached, an increase in pH above 7 resulted in desorption rates of 50–55% for Cd, Cu and Zn but only 35% for Pb. It was found that higher extractive capacity, especially of Cd and Cu took place due to complexed metal-carboxylic groups from Aerosol 22.

3. Remediation of soils contaminated with organic micropollutants using biosurfactants and surfactants

In the studies carried out by Farias et al. on the stabilization of silver nanoparticles in the liquid phase, the authors used a biosurfactant produced by *P. aeruginosa* cultivated in a low-cost medium formulated with 2.5% vegetable oil refinery residue and 2.5% corn steep liquor and distilled water [25]. The investigations proved that the low-cost biosurfactant could be used for nanoparticle synthesis as a non-toxic and biodegradable stabilizing agent.

In the recent work, conducted by Waghmode et al., the biosurfactant produced by *Bacillus subtilis* strain isolated from the soil samples and produced with the usage of four different substrates and its emulsification activity was compared against sodium dodecyl sulphate [26]. The results showed that coconut and soyabean waste are the best substrates for biosurfactant biosynthesis, which may have some potential industrial applications as a cheaper carbon source. Additionally, its antimicrobial activity was also found against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas* and *Salmonella typhimurium*.

Rahman et al. investigated the biodegradation of hydrocarbons in the soil polluted with gasoline using *ex situ* bioremediation [27]. The authors investigated the behaviour of the soil treated with gasoline-spilled soil originating from a gasoline station using various amendments including, among others, mixed bacterial consortium and rhamnolipid biosurfactant produced by *Pseudomonas* sp. DS10-129. It turned out that all tested additives together with rhamnolipid had significant positive effects on the bioremediation of the investigated soil; approximately 67 and 78% of the hydrocarbons were effectively degraded within 60 d.

In the studies carried out by the biosurfactant produced by *Candida sphaerica* in a digester containing 5% of vegetal oil refinery waste and 2.5% was applied in order to remove motor oil from among other soils [28]. It came out that in dynamic tests the isolated biosurfactant removed more than 86% of the motor oil adsorbed to clay, silty and sandy soils. Under static conditions the crude biosurfactant removed from 75 to 92% of the oil contained in clay and silty soil, respectively, whereas the isolated biosurfactant removed 50% of the oil from sandy soil. The possibility of applying the biosurfactant in biotechnological processes for environmental decontamination was proved.

Lai et al. investigated the method of evaluating the oil removal capability of biosurfactants for oil-contaminated soils coming from a heavy oil-polluted site [29]. Two biosurfactants were identified and compared

with that of synthetic surfactants in order to remove the total petroleum hydrocarbon (TPH) from the soil. It was found that biosurfactants exhibited much higher TPH removal efficiency than the synthetic ones examined. The petroleum hydrocarbon removal for the soil contaminated with ca. 3,000 mg TPH/kg dry soil was: 23, 14, 6 and 4%, respectively, using 0.2 mass % of rhamnolipids, surfactin, Tween 80 and Triton X-100. In the case of the soil contaminated with ca. 9,000 mg TPH/kg dry soil, the removal efficiency increased to 63, 62, 40 and 35%, respectively. The TPH removal efficiency also increased with an increase in biosurfactant concentration from 0 to 0.2 mass %.

Song et al. studied simultaneous removal of phenanthrene and cadmium from the polluted soils using saponin [30]. The desorption of phenanthrene from polluted soil took place due to the partition of phenanthrene into surfactant micelle. The removal of cadmium occurred as a result of complexation of cadmium with the external carboxyl groups of saponin micelle. Saponin was able to remove 87.7 and 76.2% of cadmium and phenanthrene at the concentration of 3,750 mg/L. Thus, saponin has shown the potential for the removal of both heavy metals and polycyclic aromatic hydrocarbons.

Chi used flushing solutions with different nonionic surfactants, in order to successfully apply them in the remediation of selected polycyclic hydrocarbon (PAH)-contaminated soils with different organic carbon contents [31]. The author confirmed that nonionic surfactants can be effectively used in the remediation of hydrophobic organic compound-contaminated soils. Naphthalene and anthracene were investigated in the study. Enhanced solubility reached as high as 30 times that of water solubility occurred in the soil with 500 ppm PAH. Desorption efficiencies of Tween 80 (T80) and Triton X-100 (TX-100) solutions in the naphthalene-contaminated soil were 2.4- and 2.0-fold higher in comparison with the efficiency of sodium nitrate solution, respectively. In the case of various anthracene-contaminated soil, enhanced desorption efficiencies were 11 and 24 times greater than that of sodium nitrate solution when using T80 in soils, and 14 and 27 times higher when using TX-100, respectively. It was also pointed out that the surfactant may cause colloid mobilization and then clog soil pores. It was concluded that the concentration of 0.1% of T80 and TX-100 is optimal for the soil remediation in the field.

Tsai efficiently applied two-stage remediation scheme using surfactant washing and Fenton-like oxidation in the remediation of fuel-oil polluted soil [32]. In the first step, he applied biodegradable Simple Green (SG) (50 g/L) surfactant to flush fuel-oil

polluted soils with initial TPHs concentration of 50,000 mg/kg. He observed that approximately 90% of TPH could be removed after washing with 45 pore volumes (PVs) of SG followed by 25 PVs of deionized water, while the soil TPH concentration dropped from 50,000 to 4,950 mg/kg. In the further step, he applied Fenton-like oxidation stage with the initial soil TPH concentration was approximately 4,950 mg/kg founding that TPH removal efficiency increased with increased H₂O₂ concentrations.

Maturi proposed the combination of applying surfactants and electrokinetic remediation in order to remove heavy metals and PAHs from clayey soils [33]. He pointed out that sequential use of 5% Igepal CA-720 followed by 1 M citric acid may be a successful remedial option to remove mixed contaminants containing heavy metals and PAHs from the soils.

Martel investigated the behaviour of surfactants on the PCBs mobilization from the polluted soil [34]. He applied two anionic biosurfactants (Nansa HS 85 S, a dodecylbenzene sulfonate) and alcohol (*n*-butanol) in sand columns with the contaminated soil originating from the site. It was found that 99% of PCBs was removed after the injection of 10 PVs of flushing and no more than 25% was removed in the field. The former presence of spill of a surfactant resulted in the formation of gel and as a consequence blocked the pores. Thus, ethanol was chosen in order to solubilize the surfactant and to modify the alcohol ratio. It was concluded that although the application of surfactant can remove PCBs, the presence of other chemical should also be taken into consideration.

4. Conclusions

Biosurfactants are very promising products in remediation technologies as they are less toxic, highly biodegradable, stable at extremes of pH, temperature and salinity. The main advantage of biosurfactants is the diversity of physical and chemical properties allowing for their application in the remediation of both inorganic (heavy metals) and organic micropollutants (PAHs, petroleum hydrocarbons and PCBs) from the soils and the sediments, e.g. rhamnolipid. Additionally, the environmentally friendly way of their production, applying industrial wastes and renewable carbon energy increase the potential application of biosurfactants in environmental protection. The usage of biosurfactants regarding nanoparticles as well as the stabilization of nanoparticles before applying during remediation needs to be of high concern.

Mulligan indicates the problem of investigations into the solubilization and bioconversion mechanisms

of both organic and inorganic compounds by biosurfactants in order to predict the fate and transport of contaminants [1]. She also pointed out that saving energy and meeting the water requirements as well as keeping environmental safe soil with its physical, chemical and biotic properties in the context of sustainable techniques of remediation is needed.

The main disadvantage of biosurfactants is the high cost of isolation of the afore mentioned compounds and high costs of inoculum. According to Makkar [6], the biosurfactant surfactin (98% purity) originated from Sigma Chemical Company costs approximately \$153 for a 10 mg vial. Rosenberg and Ron gave the example of the cost of the RAG-1 emulsan containing broth and it was 50 \$/kg [35]. They estimated that the cost would increase due to the necessity of extraction, concentration or purification of the product. Makkar also pointed out that the cost of chemical surfactants is relatively low around one dollar but taking into consideration the possible environmental damage possibly caused by biosurfactants the total cost increases. The author predicts that the ideal price of biosurfactant would be in the range 3–5 \$/Lb. The factors responsible for a decrease in costs are the following: cheap or waste substrate to lower the initial raw costs, the use of novel multistep downstream processing methods, recombinant and mutant hyperproducer microbial strains. The usage of low-cost agro-based raw material as non-expensive carbon sources as well as enhanced biodegradation *in situ* makes biosurfactants more economically attractive than synthetic surfactants.

References

- [1] C.N. Mulligan, S.K. Sharma, A. Mudhoo, *Biosurfactants: Research Trends and Applications*, Taylor & Francis Group, CRC Press, Boca Raton, FL, 2014.
- [2] A. Shafiei, A. Hamid, T. Fooladi, W.M.W. Yusoff, Surface active components: Review, *Curr. Res. J. Biol. Sci.* 6(2) (2014) 89–95.
- [3] K. Paraszkiwicz, J. Długoński, *Microbial biosurfactants—Synthesis and application*, *Biotechnology* 4 (2003) 82–91 (in Polish).
- [4] K. Konichi, U. Mitsuyoshi, Molecular design of the microbiological cell surface toward the recovery of metal ions, *Curr. Opin. Biotechnol.* 22 (2011) 427–433.
- [5] J.D. Desai, I.M. Banat, Microbial production of surfactants and their commercial potential *Microbiol. Mol. Biol. Rev.* 61 (1997) 47–64.
- [6] R.S. Makkar, S.S. Cameotra, I.M. Banat, Advances in utilization of renewable substrates for biosurfactant production, *AMB. Exp.* 1(5) (2011) 1–19.
- [7] M.J. Rosen, J.T. Kunjappu, *Surfactants and Interfacial Phenomena*, fourth ed., Wiley, Hoboken, NJ, 2012 ISBN 1-118-22902-9.

- [8] M. Banat, A. Franzetti, I. Gandolfi, G. Bestetti, M.G. Martinotti, L. Fracchia, et al. Microbial biosurfactants production, applications and future potential, *Appl. Microbiol. Biotechnol.* 87 (2010) 427–444. <http://dx.doi.org/10.1007/s00253-010-2589-0>.
- [9] R. Marchant, I.M. Banat, Biosurfactants: a sustainable replacement for chemical surfactants? *Biotechnol. Lett.* 34 (2012) 1597–1605, doi: 10.1007/s10529-012-0956-x.
- [10] M. Abouseoud, R. Maachi, A.A. Boudergua, A. Nabi, Evaluation of different carbon and nitrogen sources in production of biosurfactant by *Pseudomonas fluorescens*, *Desalination* 223 (2008) 143–151.
- [11] B.S. Saharan, R.K. Sahu, D. Sharma, A review on biosurfactants: Fermentation, current developments and perspectives, *Genet. Eng. Biotechnol. J.* (2011) GEBJ-29 1–14.
- [12] A. Krasowska, Biomedical Activity of Biosurfactants, Department of Biotechnology, Wrocław University, Institute of Biotransformation, Wrocław, 2010 (in Polish).
- [13] C.P. Kurtzman, N.P. Price, K.J. Ray, T.M. Kuo, Production of sophorolipid biosurfactants by multiple strains of the *Starmerella* (*Candida*) *bombicola* yeast clade, *FEMS Microbiol. Lett.* 311 (2) (2010) 140–146.
- [14] C.N. Mulligan, Recent advances in the environmental applications of biosurfactants, *Cur. Opin. Coll. Interface Sci.* 14 (2009) 372–378.
- [15] T.J.P. Smyth, A. Perfumo, S. McClean, R. Marchant, I.M. Banat, Isolation and analysis of low molecular weight microbial glycolipids, in: K.N. Timmis (Ed.), *Handbook of Hydrocarbon and Lipid Microbiology*, Springer, Berlin, 2010.
- [16] K. Paraszkiwicz, J. Długoński, Remediation of heavy metal-contaminated soil by microbial surfactants, *Biotechnology* 2(77) (2007) 81–94 (in Polish).
- [17] D.C.W. Tsang, I.M.C. Lo, R.Y. Surampalli, Chelating agents for land decontamination technologies, ASCE, Environment & Water Resources Institute, Technology & Engineering US, Reston, VA, 2012, 141–171.
- [18] C.N. Mulligan, R.N. Young, B.F. Gibbs, Heavy metal removal from sediments by biosurfactants, *J. Hazard. Mat.* 85 (2001) 111–125.
- [19] B. Daharazma, C.N. Mulligan, Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration, *Chemosphere* 69 (2007) 705–711.
- [20] C.N. Mulligan, C. Oghenekevwe, Y. Shimizu, Biosurfactant enhanced remediation of mixed contaminated soil and metal contaminated sediment, *Geoenviron. Eng. Semin.* 7 (2007) 19–24.
- [21] D. Palashpriya, M. Soumen, S. Ramkrishna, Biosurfactant of marine origin exhibiting heavy metal remediation properties, *Bioresour. Technol.* 100 (2009) 4887–4890.
- [22] K.J. Hong, S. Tokunaga, T. Kajiuchi, Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils, *Chemosphere* 49 (2002) 379–387.
- [23] A. Juwarkar, N. Anupa, V. Kirti, K. Dubey, S. Singh, D. Sukumar, Biosurfactant technology for remediation of cadmium and lead contaminated soils, *Chemosphere* 68 (2007) 1996–2002.
- [24] C. Hernández-Soriano Mdel, A. Peña, M. Dolores Mingorance, Release of metals from metal-amended soil treated with a sulfosuccinamate surfactant: Effects of surfactant concentration, soil/solution ratio, and pH, *J. Environ. Qual.* 39(4) (2010) 1298–1305, doi: 10.2134/jeq2009.0242.PMID.20830918.
- [25] B.B. Charles, Farias, A. Ferreira Silva, R.D. Rufino, J.M. Luna, J.E. Gomes Souza, L. Asfora Sarubbo, Synthesis of silver nanoparticles using a biosurfactant produced in low-cost medium as stabilizing agent—Electron, *J. Biotechnol.* 17 (2014) 122–125, doi: 10.1016/j.ejbt.2014.04.003.
- [26] B. Waghmode, Ch. Kulkarni, S. Shukla, P. Sursawant, Ch. Velha, Low cost production of biosurfactant from different substrates and their comparative study with commercially available chemical surfactant, *Int. J. Sci. Technol. Res.* 3(3) (2014) 146–149, ISSN 2277-8616.
- [27] K.S. Rahman, M. Banat, I.M. Thahira-Rahman, J. Thayumanavan, T. Lakshmanaperumalsamy, Bioremediation of gasoline contaminated soil by a bacterial consortium amended with poultry litter, coir pith and rhamnolipid biosurfactant, *Bioresour. Technol.* 81 (2002) 25–32, doi:10.1016/S0960-8524(01)00105-5.
- [28] B. de Souza Sobrinho, H. Bezerra de Souza Sobrinho, J. Moura de Luna1, R.Dinz Rufino, A.L. Figueiredo, P. L Asfora Sarubbo, Application of biosurfactant from *Candida sphaerica* UCP 0995 in removal of petroleum derivative from soil and sea water, *J. Life Sci.* 7(6) (2013) 559–569, ISSN 1934-7391, USA.
- [29] C.C. Lai, Y.C. Huang, Y.H. Wei, Biosurfactant-enhanced removal of total petroleum hydrocarbons from contaminated soil, *J. Hazard. Mat.* 167 (2009) 609–614.
- [30] S. Song, S.L. Zhu, W. Zhou, Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponina a plant-derived biosurfactant, *Environ. Pollut.* 156 (2008) 1368–1370.
- [31] F.H. Chi, Remediation of polycyclic aromatic hydrocarbon-contaminated soils by nonionic surfactants: Column experiments, *Environ. Eng. Sci.* 28(2) (2010) 139–145, doi: 10.1089/ees.2010.0223.
- [32] T. Tsai, T. Kao, C.M. Surampalli, S.H. Liang, Treatment of fuel-oil contaminated soil by biodegradable surfactant washing followed by Fenton-like oxidation, *J. Environ. Eng. ASCE* 135 (10) (2009) 1015–1024.
- [33] K. Maturi, R. Camselle, Surfactant-enhanced electrokinetic remediation of mixed contamination in low permeability soil, *Sep. Sci. Technol.* 44 (2009) 2385–2409.
- [34] R. Martel, S. Foy, L. Saumure, A. Roy, R. Lefebvre, R. Therrien, U. Gabriel, P.J. Glina, Polychlorinated biphenyl (PCB) recovery under a building with an *in situ* technology using micellar solutions, *Can. Geotech. J.* 42(3) (2005) 932–948, doi: 10.1139/t05-027.
- [35] E. Rosenberg, E.Z. Ron, Bioemulsans: Microbial polymeric emulsifiers, *Curr. Opin. Biotechnol.* 8 (1997) 313–316.