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Transport of Ions in Quartz Sand

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1. Introduction

Contamination of environment with heavy metals is widely increasing due to their industrial applications development. Cr is used as daily basis in i.e. the metallurgic, tanning, and plating industries [1]. Cr (III), which is more environmentally stable, is considered to be less mobile than more toxic Cr (VI) [2]. Decreased mobility of Cr (III) is contributed to strong adsorption onto negatively charged surfaces and the ability to form complex molecules with organics as well as formation of oxides and hydroxides and other insoluble minerals in soils [3]. Concentration of lead in environment has increased during last sixty years mainly because its use in antiknock additives in petroleum. In the environment the ionic forms of lead have been found to be most persistent [4]. Nickel is of concern in many parts of the world. The concentration of nickel in soils is very high, especially near metal refineries and in dry sludges [5]. Deposits naturally existing in environment are very complex. Therefore studies on simple systems are so important. Results presented below were received from one-dimensional studies. However concentration and pH changes were measured only along the main axis of the tested deposit and only overall metal concentrations were measured. This allowed for observing main differences in movement of metals under investigated conditions and their susceptibility to changes of these conditions.

2. Materials and methods

2.1. Equipment

All experiments were conducted in a horizontal PVC tube, ID = 103 [mm], filled up with quartz sand, with both sides closed and connected to the feed container (20 L) of deionized water. Deionized water flow was applied to the experiments in order to accelerate movement of ions through the investigated medium. Eight sampling apertures were bored, ID = 100 [mm] along the tube axis, and closed with rubber stoppers. The distances between apertures were 100 [mm], and distances between aperture and the tube ends were 150 [mm]. Additional two apertures were bored on tubes end caps, one on each. Tube was equipped with two nozzles placed on end caps, which enabled water flow through the sand during experiments. Water inlet was placed below the tube axis while water outlet was placed above. This enabled flow of solutions of metals to be kept along the tube axis, preventing its gravity flow, and accumulation in the bottom part of investigated media. The aperture on water in-let side was used for introduction of metals solutions.

2.2. Preparation of quartz sand deposit

Sieved quartz sand was used as an inert medium. Diameters of sand particles were not smaller than 250 [nm](size fraction of -600 +250mm) and sand bulk density (d) was equal to 1.63 [g/cm^3]. It was impossible to carry out experiments with sand deposit containing particles of diameters less than 250 [nm]. During experiments fine particles were carried with the water flowing through and accumulated at the end of the tube making sand deposit non-homogenous and rendering difficult to keep water flow constant during experiments. Before each experiment sand was washed with 0.1 M H_2SO_4 and then with water until its pH achieved 6.5÷7.5. Then sand was placed into the tube and washed overnight with deionized water. Additional preparations were required in experiments with modified sand deposits. Ion attachment efficiencies in quartz surface modified with cationic (Cetyltrimethylammonium bromide, CTAB) and anionic (Sodium dodecyl sulfate, SDS) surfactants were investigated and compared to these for non-modified deposits. Sand used for tests with cationic surfactant, after washing in 0.1 M H_2SO_4 and water, was washed several times in 10^{-4} M CTAB solution and then left in freshly prepared solution for several hours in order to saturate its surface with CTAB. Choice of concentration of surfactant was based on its Critical Micelle Concentration (CMC): 361 [mg/l] [6, 7]. Concentrations less than this enabled quartz surface to be modified with surfactants particles, not micelles. After washing sand was loaded to the tube and washed overnight with deionized water to remove an excess of surfactant. Due to negatively charged quartz surface under investigated conditions (pH = 6.5÷7.5) anionic surfactant could not have been adsorbed. Therefore, anionic surfactant was continuously introduced into the testing tube during experiments. Sand washed with 0.1 M H_2SO_4 and then with water until its pH = 6.5÷7.5 was placed into the tube and then washed with 10^{-4} M SDS solution. Choice of surfactants concentration was based on its Critical Micelle Concentration (CMC): 2100 [mg/l] [6, 7], and was kept on the same level as of CTAB solution concentration. SDS solution flow performed a double function: (i) modified conditions in sand deposit and (ii) accelerated movement of ions (function of deionized water in other experiments).

2.3. Preparation of feed solutions

Concentrations and volumes of ion's solutions concentrations introduced to the investigated sand deposit were established based on results of additional tests carried out before main experiments (determination of isotherms of adsorption for each metal tested). The main criteria were: quartz sand sorption capacity for each metal in constant temperature, volume of samples possible to be achieved during tests, minimum sample volume (20 [ml]) and minimum ion's concentration levels required for ICP analysis (0.01 [mg/l] for Cr^{3+} and Ni^{2+}, and 0.03 [mg/l] for Pb^{2+}) [8]. Solutions were prepared with salts: Cr^{3+}: Chromium (III) potassium sulfate 12–hydrate (BDH Laboratory Supplies, Poole, BH 15 1TD, England, Lot K 19803554 417, Prod 2775845), Pb^{2+}: Lead (II) acetate 3-hydrate (BDH Laboratory Supplies, Poole, BH 15 1TD, England, R: 47-33-48/22, S: 53-44) and Ni^{2+}: Nickel chloride 6-hydrate, extra pure (Riedel de Haen, Sigma – Aldrich Laborchemikalien GmBH, EG nr.: 237-743-0, CAS nr.: 7791-20-0). 15 [ml] of each metal solution was introduced to the tube during the experiment. Concentrations tested: Cr^{3+} and Ni^{2+} solutions: 10000 [mg/l], Pb^{2+} solution: 100000 [mg/l].

2.4. Sample analysis

Samples were drawn from the central part of investigated deposit using 10 [ml] syringes and needles (Length: 51 [mm], ID: 0.51 [mm]). pH of the samples was measured directly after sampling. Ion's concentrations were measured after dilution (5 [ml] of sample from the deposit was diluted to 50 [ml] with deionized water), digestion (30 [ml] of solution was digested with 3 [ml] HCl and 1 [ml] HNO_3) and 12 – hour heating in 70 ˚C [3]. pH of samples were measured with Jenway 3320 apparatus, equipped with double junction pH / reference electrode (VWR pH Electrode, Art No./VWRI: 662 – 1761, Batch No.: 46 – 04) calibrated daily with $pH = 4$ and $pH = 7$ buffers. Concentrations of ions in prepared samples dilutions were measured using ICP spectroscopy, apparatus Varian Vista.

2.5. Experiments

All experiments were carried out under following assumptions: quartz sand deposition tested contains particles of diameter exceeding 250 [μm], which is homogenous in each point, testing tube is fully packed with deposition inside, pH of the deposit is neutral ($pH = 6.5 \div 7.5$), residue of metals in washed sand does not exceed the limit of detection of analytical method used, water / anionic surfactant flow is constant and is carried through the whole deposit's cross section area, solutions of metals are moving along testing tube's axis while the time of solutions introduction into the sand deposit is very short.

First two series of experiments were carried out with non-modified sand deposit, at different water flow rates: 0.5÷0.6 [ml/s] and 1.0÷1.1 [ml/s]. This enabled to determine the influence of water flow rate on ion's movement. Following experiments were carried out with modified quartz sand surface and water flow rate 0.5÷0.6 [ml/s]. In this part influence of presence of surfactants on ion's movement was investigated. During each experiment two main parameters were measured: pH and concentration of metals. pH was measured along testing tube, in each sampling point. Samples were drawn 20, 30, 40, 60 and 80 [min] after introduction of ion's solution into the sand deposit. Information about pH distribution along the deposit and its changes in time gave a picture of solution behavior under investigated conditions and was helpful in a final interpretation of the ion's concentrations analysis results. Ion's concentrations changes were measured in separate experiments, in two sampling points: 30 and 40 [cm] from solutions injection point, 15, 35, 45 and 70 [min] after ion's solution introduction. These experiments enabled to establish the rate of movement of metals in quartz sand deposit under investigated conditions.

3. Results and discussion

3.1. Cr^{3+} migration

During the migration of Cr^{3+} ion's solution influence of both: water flow rate and surface modification on movement of ions were investigated. The most significant differences in transport of metal were noticed in deposit modified with CTAB. For the same water flow rate, in the presence of cationic surfactant adsorption of ions was greater than in presence of anionic surfactant and in not modified deposit. The lowest chromium residues in sand were found in the deposit modified with SDS. Molecules of anionic surfactant, that were not adsorbed on deposits surface under investigated conditions (quartz sand surface is negatively charged in $pH > 3$), were probably binding with metal ions and moved together. These complexes have different affinity to the quartz sand surface than chromium ions. Therefore, in the presence of SDS, solution of Cr^{3+} was washed out from the testing tube in the shortest time. Changes in water flow rate did not influence chromium adsorption on sand surface significantly. Front of the solution was moving faster through the deposit and within 45 minutes was found 70÷80 [cm] from the solution introduction point while for the water flow rate 0,54 [cm], after the same time period, front was found

50 [cm] from the samples introduction point. These values base on pH distribution measurements. Initial pH of the chromium solution injected into the testing tube was pH = 3.2. The lowest pH was found in the solutions with the highest metal ions concentrations.

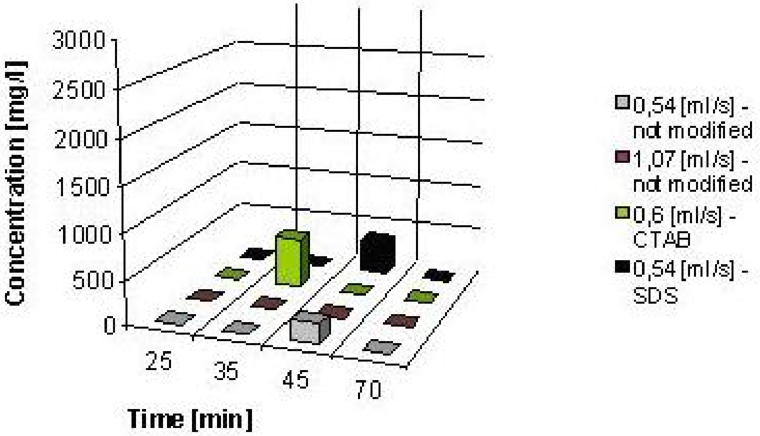

Fig. 1. Changes of Cr^{3+} concentrations in deposit solution 40 [cm] from solution introducing point

Rys. 1. Zmiany stężenia Cr^{3+} w roztworze w złożu 40 cm od punktu w wprowadzenia

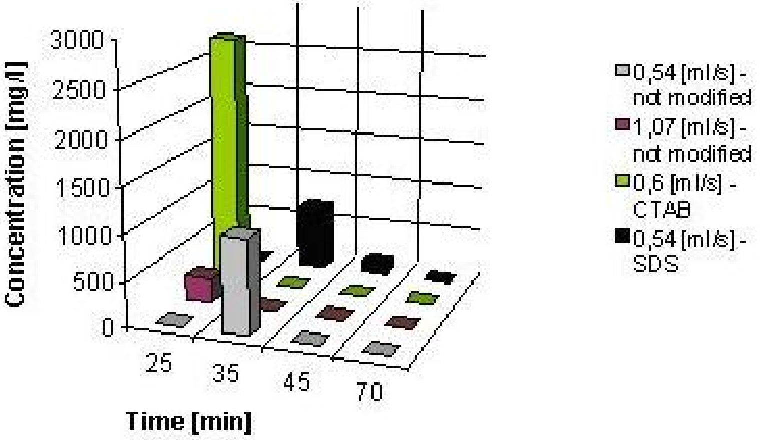

Fig. 2. Changes of Cr^{3+} concentrations in deposit solution 30 [cm] from solution introducing point

Rys. 2. Zmiany stężenia Cr^{3+} w roztworze w złożu 30 cm od punktu w wprowadzenia

3.2. Ni^{2+} migration

During the migration of Ni^{2+} ion's solution influence of both: water flow rate and surface modification on movement of ions were investigated. The most significant differences in transport of metals were noticed in deposit modified with CTAB. Similarly to the chromium solution migration, for the same water flow rate, in the presence of cationic surfactant adsorption of ions was greater than in presence of anionic surfactant and in not modified deposit. The lowest nickel residues in sand were found in the deposit modified with SDS. In the presence of SDS solution of Ni^{2+} ions was washed out from the testing tube in the shortest time (60 [min]). In comparison to the chromium solution migration through the deposit modified with CTAB nickel solution front was more width, but was moving slower. Main part of Ni^{2+} solution was still present in the deposit after 70 [min] while after that time chromium solution was nearly completely washed out (constant, neutral pH values along the testing tube). Changes in water flow rate did not influence nickel adsorption on sand surface significantly. Front of the solution was moving faster through the deposit for the flow rate 1.03 [ml/s] and after 30 [min] was found 60 [cm] from the solution introduction point while for the flow rate two times lower, after the same time period, front was found 30 [cm] from the samples introduction point. These values base on pH distribution measurements. Initial pH of the nickel solution injected into the testing tube was pH = 4.3. The lowest pH was found in the solutions with the highest metal ions concentrations.

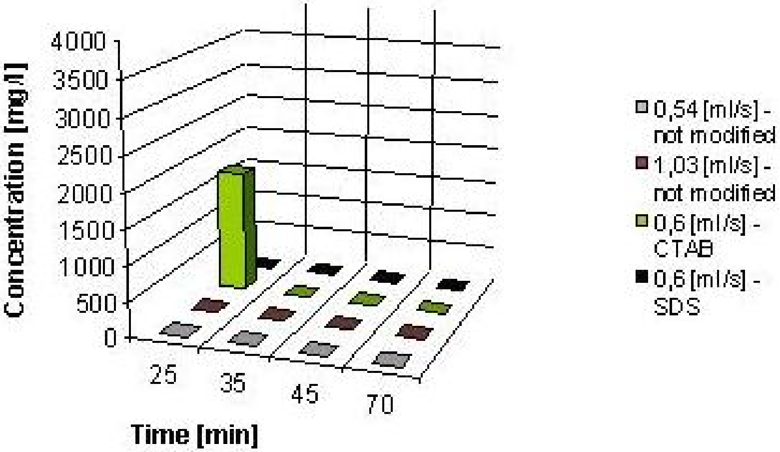

Fig. 3. Changes of Ni^{2+} concentrations in deposit solution 30 [cm] from solution introducing point

Rys. 3. Zmiany stężenia Ni^{2+} w roztworze w złożu 30 cm od punktu w wprowadzenia

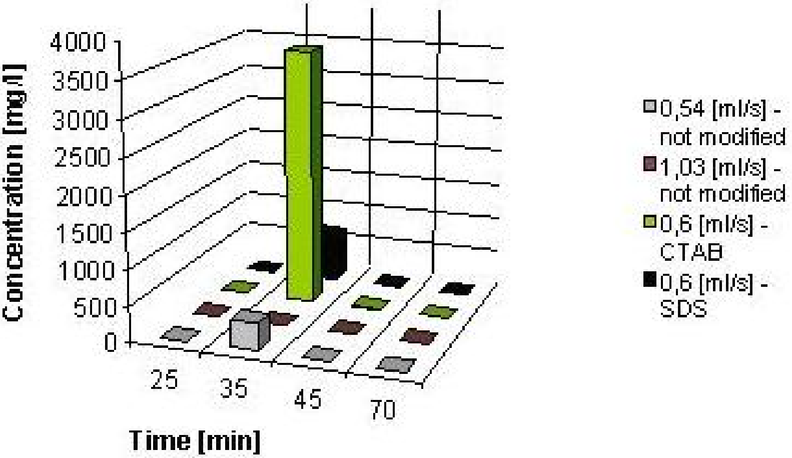

Fig. 4. Changes of Ni^{2+} concentrations in deposit solution 40 [cm] from solution introducing point

Rys. 4. Zmiany stężenia Ni^{2+} w roztworze w złożu 40 cm od punktu w wprowadzenia

3.3. Pb^{2+} migration

During the migration of Pb^{2+} ion's solution influence of both: water flow rate and surface modification on movement of ions were investigated. The most significant differences in transport of metals were noticed in deposit modified with CTAB. For the same water flow rate, in the presence of cationic surfactant adsorption of ions was greater than in presence of anionic surfactant and in not modified deposit. The lowest lead residues in sand were found in the deposit modified with SDS. Solution of lead ions was washed out from the deposit modified with SDS in the shortest time (60 [min]). Similar time period was needed to washed out solution during tests with not modified deposit and water flow rate 1,08 [ml/s]. Front of the solution moved through deposit modified with CTAB was compact and, alike chromium and nickel, metal adsorption on sand surface was the highest under this conditions. Changes in water flow rate did not significantly influence lead adsorption on sand surface but had an influence on shape of front solution: under higher flow rate conditions front was width. The same influence had the presence of anionic surfactant. Shapes of the solution fronts and times of solutions flows through the testing tube were establish using pH distributions in sand deposit under investigated conditions.

Initial pH of the lead solution injected into the testing tube was pH = 5.7. The lowest pH was found in the solutions with the highest metal ions concentrations but differences between samples pH were smaller than for samples containing ions Cr^{3+} and Ni^{2+}, due to higher initial pH.

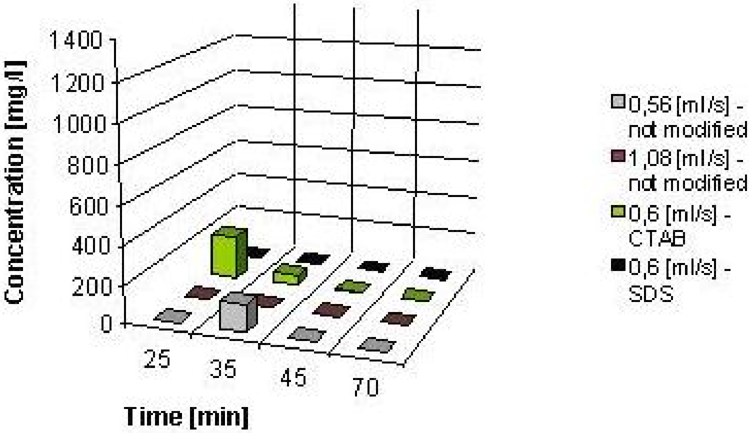

Fig. 5. Changes of Pb^{2+} concentrations in deposit solution 30 [cm] from solution introducing point
Rys. 5. Zmiany stężenia Pb^{2+} w roztworze w złożu 30 cm od punktu w wprowadzenia

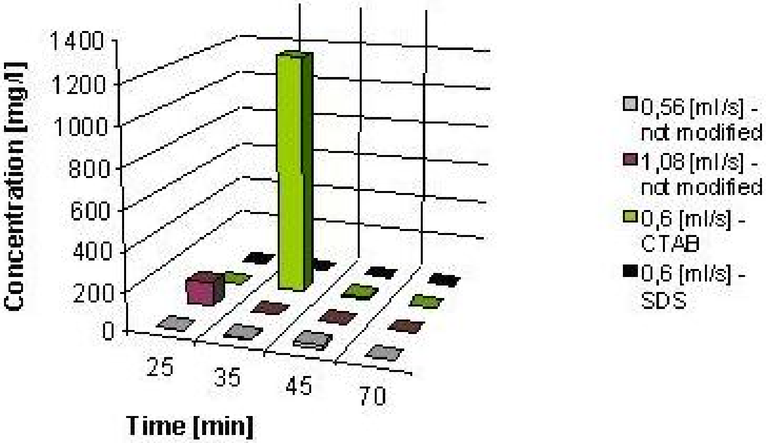

Fig. 6. Changes of Pb^{2+} concentrations in deposit solution 40 [cm] from solution introducing point
Rys. 6. Zmiany stężenia Pb^{2+} w roztworze w złożu 40 cm od punktu w wprowadzenia

The shape and the width of the front of the solution in investigated deposit provide useful information about the affinity of metals to the surface. Width front suggest that the rate of adsorption – desorption reactions is lower than the rate of solution movement and therefore, that the affinity of metal to the deposit surface is high. It should be noticed that desorption reactions are usually slower than adsorption reactions probably because of sorbat transformations (i.e. conversion from an adsorbed species to a surface precipitates), and due to large activation energies of desorption reactions [9]. According to the results received, in non-modified deposit, breadth of the front of chromium solution was the greatest. These results are compliant with results described by Bartlett and Kimble, who suggested that at low pH Cr(III) is well adsorbed on the negatively charged surfaces, despite that higher pH values usually promote adsorption, while at high values (pH greater than 5.5) chromium precipitate as base or oxide [10]. During these experiments susceptibility of chromium to changes of the conditions in sand deposit was found to be the greatest and susceptibility of lead - the lowest.

4. Conclusions

Cationic surfactants as CTAB are strongly adsorbed to soil minerals (quartz), which are generally negatively charged, and therefore are unsuitable for most remediation systems based on subsurface flushing through contaminated zones [7]. Presence of CTAB in investigated quartz sand deposit resulted in increase of adsorption of metal ions on the deposit surface. Presence of SDS increased mobility of metals more than increase of water flow rate, and significantly decreased adsorption of ions on sand surface. Anionic surfactants are widely used in oil recovery applications, especially due to their low tendency to adsorb, stability at high temperature and pressure and low costs [11]. This study suggests that these surfactants can be also useful in removal of metal contamination. We have determined that mobility of investigated ions in quartz sand increase in order: Ni (II) > Cr (III) > Pb (II) and is enhanced by the presence of anionic surfactant and increasing water flow rate

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References

1. **Nriagu, J. O., Nieboer E.:** *Chromium in natural and in human environments*. John Wiley and Sons, New York 1988.
2. **Patterson, R. R., Fendorf S., Fendorf M.:** *Reduction of hexavalent chromium by amorphous iron sulfide*. Environ. Sci. Technol. 31: 2039÷2044. 1997.

3. **Fendorf, S. E., Zasoski R.J.:** Chromium *(III) oxidation by δ-MnO_2: I. Characterization,* Environ. Sci. Technol., 26: 79÷85. 1992
4. **Hill J.S.:** *Speciation of trace metals in the environment.* Chemical Society Reviews, Vol. 26, 439÷457. 1997.
5. **Stawn G.D., Sparks L.D.:** *Effect of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and deposition in soil,* Soil Sci. Soc. Am. J., 64, 144÷156. 2000.
6. **Becher, P.:** in *Nonionic Surfactants.* M. J. Schick (Editor) Surfactant Science Series Vol.1, Marcel Dekker, New York, NY 1967.
7. **Pannell D.K, Abriola M.L.:** *Surfactant – Enhanced Aquifer Remediation: Fundamental processes and Practical Applications,* Elsevier, NY 1998.
8. Alcontrol Laboratories: *Analytical procedures Manual: Controlled* Copy No.: 2; Environmental Instruments; High-level Metal Routine.
9. **McBride M.M.:** *Environmental chemistry of soils.* New York: Oxford University Press. NY 1994.
10. **Bartlett, R.J. Kimble M.J.:** *Behavior of chromium in soils: I. Trivalent forms.* J. Environ. 5: 379÷383. 1976.
11. **Lake, L.:** *Enhanced Oil Recovery.* Prentice-Hall, Englewood Cliffs, NJ 1989.

Transport jonów metali przez piasek kwarcowy

Streszczenie

Migracja jonów metali przez porowatym ośrodku, utworzony z ziaren mineralnych, ma istotne znaczenie w takich procesach jak ługowanie i bioługowanie oraz w szeregu procesach biogeochemicznych. Transport toksycznych metali w stanowi poważny problem w ochronie środowiska naturalnego i powinien być dokładnie zbadany. W pracy przedstawiono wyniki badań migracji jonów Ni(II), Cr(III) i Pb(II) przez porowaty ośrodek utworzony przez piasek kwarcowy. Doświadczenia zostały przeprowadzone z wykorzystaniem poziomo usytuowanej rury, wypełnionej piskiem kwarcowym. Powierzchnia ziaren kwarcu była modyfikowana przez działanie kationowego (CTAB) i anionowego surfaktantu. Efektywność migracji jonów przez porowaty ośrodek mineralny była kontrolowana przez analizę profilu stężeń kationu w złożu. Adsorpcja kationowego surfaktantu sprzyja adsorpcji jonów do ziaren kwarcu. Odwrotnie, obecność anionowego surfaktantu sprzyja migracji jonów.

Obecność CTAB w badanym złożu kwarcowym powodowała wzrost adsorpcji adsorpcji jonów metali na powierzchni złoża. Obecność SDS spowodowała wzrost mobilności metali bardziej niż wzrost prędkości przepływu wody i znacząco zmniejszyła adsorpcję jonów na powierzchni piasku. Anionowe surfaktanty są szeroko stosowane do odzysku oleju, przede wszystkim dzięki ich małej tendencji do adsorbowania, stabilności w wysokiej temperaturze i ciśnieniu i niskich kosztach [11]. Badania sugerują, że te surfaktanty mogą być użyteczne w usuwaniu metali. Mobilność badanych metali w piasku kwarcowym wzrasta w kolejności: Ni (II) > Cr (III) > Pb (II) i wpływa na nią obecność anionowych surfaktantów i wzrost przepływu wody.