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FLOTATION OF SERPENTINITE AND QUARTZ USING BIOSURFACTANTS

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Abstract. Biosurfactants produced by *Bacillus circulans* and *Streptomyces* sp. were used for biomodification of both serpentinite and quartz surfaces. The biosurfactants produced by bacteria possess the ability to decrease the surface tension of water from 72 to 28.6 mNm⁻¹ (*Bacillus circulans*) and to 29.3 mNm⁻¹ (*Streptomyces* sp.).

This paper demonstrated biomodification of quartz and serpentinite surfaces by the biosurfactants adsorption. The effect of biosurfactants adsorption onto mineral surface properties was investigated by microflotation. Additionally, IR-ATR spectroscopy was used for characterisation of the biomodified surfaces of quartz and serpentinite. Flotation experiments indicated that these biosurfactants effectively changed the properties of mineral surfaces and the separation of minerals can be realized.

keywords: biosurfactant; flotation; surface tension; quartz, serpentinite

1. Introduction

Biosurfactants are amphiphilic compounds produced by microorganisms that exhibit surface activity. These metabolite products can be categorized into four groups (i) lipopeptides, (ii) lipoproteins, (iii) glycolipids, (iv) phospholipids. In comparison to synthetic surfactants, biosurfactants possess several advantages such as a low irritancy, high biodegradability and low toxicity. For these reasons, they are ecologically acceptable.

Biosurfactants are applied in pharmaceutical, cosmetic, detergent and food industries (Banat et al., 2000). A spectacular application of biosurfactants is the microbial enhanced oil recovery (MEOR) and viscosity reduction of heavy crude oil for pipeline transport. Biosurfactants enhance emulsification of hydrocarbons and accelerate oil remediation.

Application of biosurfactants as bioreagents in mineral processing operations (bioflotation or bioflocculation) is a new way for upgrading minerals (Rao et al., 2010). In recent years, several studies have been carried out on the use of biosurfactants as flotation reagents. Knowledge of adsorption of biosurfactants at the solid-liquid interface is essential for understanding the basic mechanism of flotation and lubrication. Adsorption of biosurfactant on a substratum surface alters

hydrophobicity of the surface and causes a facilitation of microbial adhesion. For mineral processing, bioflotation is very important to understand the role of metabolic products in biomodification of the mineral surface.

Chemoautotrophic bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*, which usually live in aqueous acid solution in mines, are able to depress sulfide minerals. It is a result of surface oxidation. Selective flotation of complex sulfide ores, particularly chalcopyrite, sphalerite, and pyrrhotite using xanthate as collector, needs application of bioreagents (Pecina et al., 2009).

Bacteria attach to the surface by a complex of exopolysaccharides, called glycocalyx, forming a biofilm. The colonization of the surface by bacteria can lead to modification of the surface property (Das et al., 2009).

Magnesium silicate can be used for storage of CO₂ by mineral carbonation. Dissolution of natural serpentinite in acids and precipitation of magnesium carbonate require quartz to be removed. Carbonation of natural serpentinite seems to be an interesting alternative to geological reservoirs for storage of CO₂ (Teir et al., 2009).

Serpentinite can be used as a conventional raw material in the ceramic industry. Mechanical resistance of serpentinite depends on the quantity of quartz in the raw materials (Diaz, Torrecillas 2007).

The aim of this paper was to investigate flotation of quartz and serpentinite in the presence of biosurfactants and nickel ions as an activator.

2. Materials and methods

2.1. Microorganisms and biosurfactant production

Bacteria were isolated from soil samples. Soil samples were collected from a gas station soil. The samples were collected in sterilized glass bottles. The isolation procedure was carried out using the serial dilution-agar plating technique. Two pure cultures (*Bacillus circulans* and *Streptomyces* sp.) were selected. The strains were grown on a liquid mineral salt medium consisting of K₂HPO₄ (7 g/dm³), KH₂PO₄ (3 g/dm³), MgSO₄·7H₂O (0.1 g/dm³) (NH₄)₂SO₄ (1 g/dm³), Yeast extract (0.5 g/dm³), saccharose (10 g/dm³) and glycerin. Microorganisms were cultured in 500 cm³ shake flasks containing 250 dm³ of medium. The cultures were incubated in a rotary shaker at the temperature of 26 °C. The cell growth and surface tension were monitored with respect to time. The cultures from the end of exponential growth phase were centrifuged (3500 rpm for 25 min) and the cell-free culture broth was used as the broth for flotation experiments. The cell concentration was determined by the optical density measurements at wavelength 550 nm (OD₅₅₀) using a spectrophotometer.

2.2. Mineral samples

Mineral samples of quartz and serpentinite (Mg₃(Si₂O₅)OH₄) were obtained from Osiecznica mine and Grochow mine, respectively. Both mines are located in Lower Silesia (Poland).

The mineral samples were dry ground using a porcelain ball mill and then wet sieved. The +125 - 250 μm fraction was used for microflotation experiments. The particle size distribution of the sample was determined using Malvern Mastersizer 2000. The particle size analysis showed that the mean diameters for quartz and serpentinite were 231.1 μm and 227.5 μm , respectively. The specific surface area of the samples was measured using FlowSorb II 2300, according to the BET method. Helium and nitrogen was used as the gas mixture. The BET surface area was found to be 0.19 g m^{-2} for quartz and 7.62 g m^{-2} for serpentinite. The X-ray powder diffraction analysis indicated that the sample of quartz was of high purity.

2.3. Microflotation experiment

The flotation experiments have been conducted using a glass Hallimond tube (height of 43 cm, diameter of 3.8 cm, and total volume of column about 500 cm^3). Pure nitrogen at a flow rate of 50 cm^3/min for 20 min was used for flotation. For flotation tests, 1 g of mineral samples of size +125 - 250 μm was added to 0.12 dm^{-3} total volume suspensions. The suspension containing biosurfactants or anionic surfactant sodium dodecyl sulphate (SDS was purchased from POCh) was transferred to the microflotation tube and floated. Flotation recovery was calculated as the ratio of floated to unfloted material.

Before flotation, mineral samples were activated with a variable concentration of hexahydrate nickel chloride solution (5 \cdot 10⁻⁴ M, 10⁻³ M 3 \cdot 10⁻³ M, 5 \cdot 10⁻³ M, 10⁻² M, 5 \cdot 10⁻² M respectively) for 1 hour. The biosurfactants and SDS were conditioned with activated mineral for 2 hour.

2.4. Surface tension measurement

The surface tension of the culture broth was measured using a Krüss 12 T (Krüss Optische-Mechanische Werkstätten, Hamburg, Germany) ring tensiometer as a qualitative indicator of biosurfactant production. The surface tension measurements were carried out at temperature of 20 \pm 1⁰C. All of the measurements were repeated five times and their average values were plotted.

2.5. Zeta potential measurements

The zeta potential of mineral samples were measured using Malvern ZetaMaster. The mineral samples (< 40 μm) were dispersed in a 1 mM NaCl solution (indifferent electrolyte) and the pH was adjusted using diluted solutions of HCl and NaOH. All experiments were conducted with the pH progressively changed from pH 10 to 1.5, with a 15 min equilibration time at each new pH value. The zeta potential profiles for serpentinite and quartz were carried out in the absence and presence of biosurfactants (broth solution).

3. Experimental studies

Separation of pure bacterial surfactant from the broth is complicated. For this reason the whole fermented solution as a mixture of biosurfactants and metabolic products was used. In this study, the microorganism growth and surface tension changes during the incubation period are presented in Figs. 1 and 2 for the *Bacillus circulans* and *Streptomyces* sp. The reduced surface tension of broth was an indicator of biosurfactant production. The cultures growth was controlled by measuring the changes in culture medium turbidity as a function of the bacteria cell density. Figure 1 shows that the highest bacterial cell density appears at cultivation time of 20 h. In this period a sharp drop in surface tension value (from 49.0 to 30.48 mNm⁻¹) was observed. Under the studied conditions the stationary phase of growth was reached and microbial surfactants synthesis was noticed. The highest surface tension reduction of the broth was achieved after 24 h (28.4 mNm⁻¹). The surface tension value remains unchanged for further cultivation, which indicates that culture was stable.

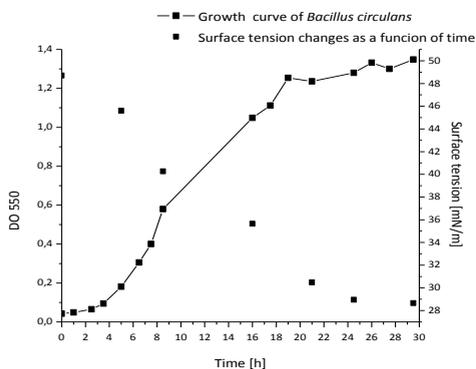


Fig. 1. Growth curve of *Bacillus circulans* and broth surface tension changes as a function of time

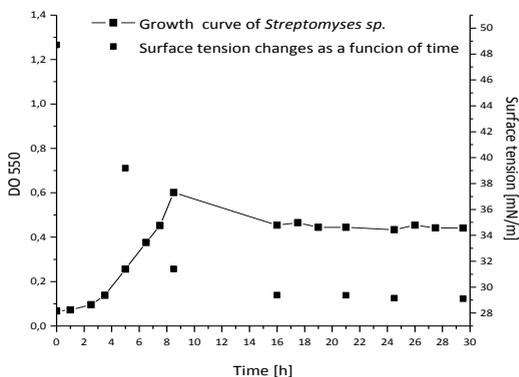


Fig. 2. Growth curve of *Streptomyces* sp. and broth surface changes as a function of time

Figure 2 illustrates that the highest turbidity of the culture medium correlated with cell density was noticed after about 8 hours from inoculation. In this period the culture moved from the logarithmic phase of growth to stationary phase and the strain of *Streptomyces* sp. started production of biosurfactants. Moreover, the surface tension value at the equilibrium phase reached 29.7 mNm⁻¹ and stayed strongly reduced to the end of the experiments.

Biosurfactants have amphiphilic nature. For this reason, the biosurfactant molecules adsorb readily at the solid-liquid interface and results in biomodification of the mineral surfaces. Physical adsorption is realized by electrostatic interactions between the biosurfactant head group and oppositely charged surface. Chemisorption demands chemical interaction between surfactant and mineral (Gallos et. al., 2007). In this paper microbial surfactants adsorption onto quartz and serpentine surfaces in the

presence of several of nickel ions concentrations as an activator was investigated. Also, a possible use of biosurfactants as a quartz and serpentinite collector or modifier was examined by microflotation tests. Results of quartz and serpentinite flotation using SDS, *Streptomyces sp.* broth and *Bacillus circulans* broth as the collector are presented in Figs 3-5, respectively. Nickel chloride at concentrations of $5 \cdot 10^{-4}$ M, 10^{-3} M, $3 \cdot 10^{-3}$ M, $5 \cdot 10^{-3}$ M, 10^{-2} M, and $5 \cdot 10^{-2}$ M was used as an activator of mineral surface. The pH value maintained during the flotation experiments was in the range of 5.9-7.6, which was constant for samples with *Streptomyces sp.* broth, *Bacillus circulans* broth and SDS, respectively. Figures 3-5 show a strong effect of the activator concentration on the rate of quartz and serpentinite flotation.

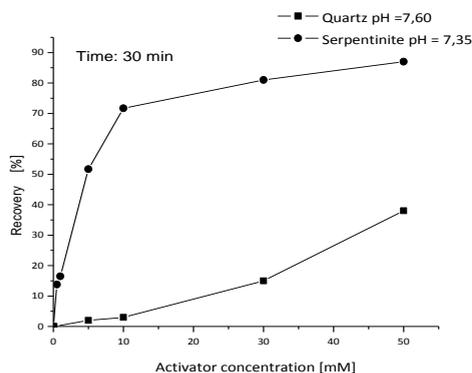


Fig. 3. Flotation recovery of quartz and serpentinite using SDS ($5 \cdot 10^{-3}$ M) as collector in a function of activator concentration (Ni^{2+} ions)

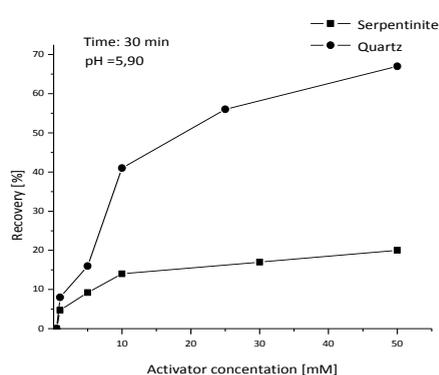


Fig. 4. Flotation recovery of quartz and serpentinite using *Bacillus circulans* broth as collector in a function of activator concentration

The microflotation tests in the presence of SDS clearly show that both minerals flotation recovery increases when the concentration of the activator ions increases. At pH close to 8 adsorption of $\text{Ni}(\text{OH})^+$ ions takes place on the silica and serpentinite surfaces and their amount increases with the concentration of NiCl_2 . The presence of these ions on the silica and serpentinite surfaces results in the appearance of local positive charges. That allows interacting with the anionic surfactant molecules and thereby increasing surface hydrophobicity. The stable surface structure of quartz favors physical adsorption of the collector. Anionic nature of SDS and positive charge of the activated quartz surface cause that the collector is electrostatically attracted to the surfaces. That allows to carry out silica flotation process with yield of 37% at the concentration of activator ions about $5 \cdot 10^{-2}$ M. One can see that at the same activator concentration the recovery of serpentine reaches a value of 87% (Fig. 3). It is related to a different mechanism of adsorption. In the case of serpentinite SDS interacts both with Ni^{2+} ions (physical adsorption) and the surface ions Mg^{2+} (chemical adsorption). Moreover, the observed differences between the recovery of quartz and serpentinite can be caused by different specific surface areas of used minerals.

An analysis of experimental results of activated silica and serpentinite (Fig. 4-5) flotation indicates that for both medium broths the flotation yield increases with increasing activation ions concentration. The flotation profile is similar to the flotation using anionic collector. It can be concluded, according to the previous assumptions, that the two cultivation media contain anionic biosurfactants in their composition. Biomolecules were able to adsorb onto mineral surfaces, causing their modification. In the case of culture medium derived from *Bacillus circulans*, the flotation recovery of silica reached a high value of 68%, while the yield of the silica flotation using the broth from *Streptomyces sp.* is more than twice lower (30%).

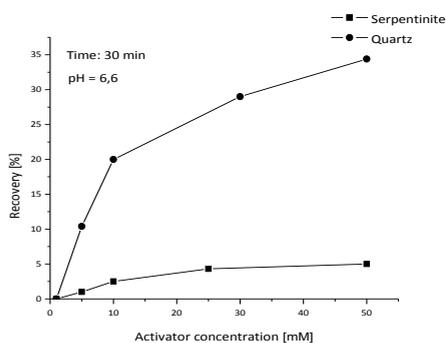


Fig. 5. Flotation recovery of quartz and serpentinite using *Streptomyces sp.* broth as collector as a function of activator concentration

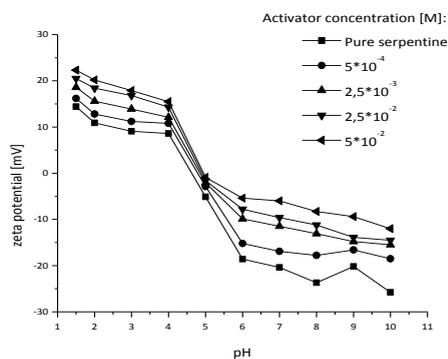


Fig. 6. Zeta potential of activated quartz and pure serpentinite as a function of pH (indifferent electrolyte 1 mM NaCl solution)

Figures 4 and 5 show the results of flotation experiments using activated serpentinite. As for silica, we are dealing with biomodification of mineral surface. However, in this case, the flotation recovery is much lower. The analysis of the results indicates that serpentinite flotation using culture medium from *Bacillus circulans* gave flotation yield about 18%, while flotation testes carried out after the interaction with broth solution from *Streptomyces sp.* made it possible to obtain only 5% recovery. As one can see, there are large differences in the flotation recoveries of both minerals. Therefore, it seems possible to selectively float quartz from serpentinite. The obtained lower bioflotation results, when compared to the flotation test with SDS, can be attributed to the fact that broths containing polysaccharides, proteins and organic acids make the surface of serpentine and quartz more hydrophilic. Moreover, large yields differences between quartz and serpentinite flotation for the same medium broth result from differences in interacting of broth compounds with activated mineral surfaces (interaction and complex formation between Mg^{2+} and broth compounds could occur), and consequently from the different adsorption degrees of these elements on both mineral surfaces.

Differences in the flotation yields for serpentinite and quartz resulting from the application of different broths can be caused by different composition of the broth, as well as differences in pH values of the flotation feed solutions.

The flotation data are in accordance with the zeta potential evaluation. The zeta potential and isoelectric point of serpentine and quartz were measured for pure mineral samples and for samples in the presence of biosurfactant as a surface modifier.

Figures 6 and 7 show the changes of the zeta potential as a result of the activation of the mineral surface. In the presence of Ni^{2+} ions significant changes in the value of zeta potential is observed. Increasing amount of activator ions at the particle surface increased the zeta potential values. Moreover, the isoelectric point (IEP) of pure quartz is around 2.5, which is close to the IEP values reported in literature (Kosmulski, 2009). The IEP of serpentinite was above 4.3. The isoelectric point of serpentine is strongly dependent on the mineralogical composition of the mineral. The presence of activator ions (Ni^{2+}) caused the IEP of both minerals to increase. Figure 8 depicts the result of electrokinetic measurements for biomodified serpentinite and quartz.

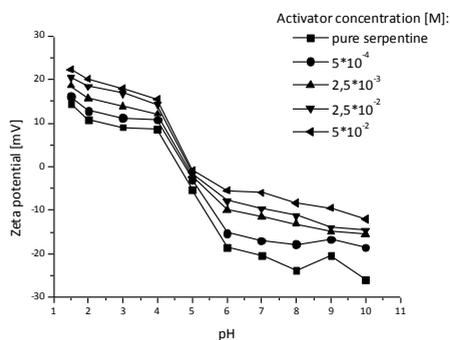


Fig. 7. Zeta potential changes of pure and activated serpentinite as a function of pH (indifferent electrolyte: 1 mM NaCl solution)

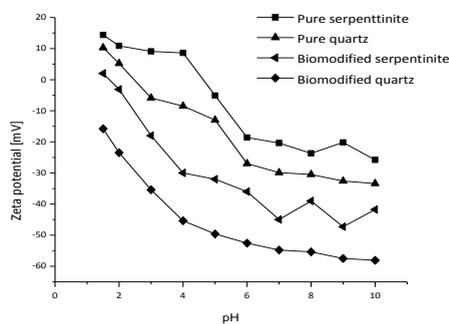


Fig. 8. Zeta potential changes of biomodified (broth of *Bacillus circulans*) minerals as a function of pH (indifferent electrolyte: 1 mM NaCl solution)

Surfactant molecules from the bulk can adsorb on the particle and control the surface charge as well as the hydrophobic character of the surface. The surface became more hydrophobic resulting in changing the surface properties of mineral and zeta potential values. It can be seen that the pH of IEP for both minerals has shifted towards lower pH. The zeta potential values of serpentinite and quartz were decreased when the broth from *Bacillus circulans* was added. Moreover, the zeta potential profiles for both minerals after interaction with the metabolite solution were similar.

Additionally, the IR-ATR spectroscopy and optical microscope were used for the characterization of surface properties of pure samples of quartz and serpentinite before and after interaction with biosurfactants.

Figure 9 and 10 illustrate IR-ATR spectroscopy spectra of activated surfaces of silica and serpentine. Silica is the final products of silicates decomposition caused by water and carbon dioxide. A general formula of silica (SiO_2) does not fully reflect the interactions between atoms. The structure of quartz surface shows a large amount of OH groups. It can be noticed that the most important role in the adsorption process on the mineral surface is played by siloxane bonds ($\equiv \text{Si-O-Si} \equiv$) and silanol groups (Si-OH) (Mesquita, 2003). In the spectrum of Ni^{2+} ions activating silica, six characteristic vibrations were observed (Fig. 9). The absorption peak at 650 cm^{-1} corresponds to the stretching vibrations of diatomic O-H units. The absorption bands at $777.62 - 794.40 \text{ cm}^{-1}$ are characteristic for the symmetric stretching vibration of the $\equiv \text{Si-O-Si} \equiv$ bond. The peak at 1062.93 cm^{-1} represents vibrations of the $\equiv \text{Si-O-Ni}$ bond and peak at 1082.51 cm^{-1} is due to asymmetric stretching vibration of the Si-O-Si bond. Finally, the absorption pick at 1163.63 cm^{-1} is from vibrations of the valence Si-O bond.

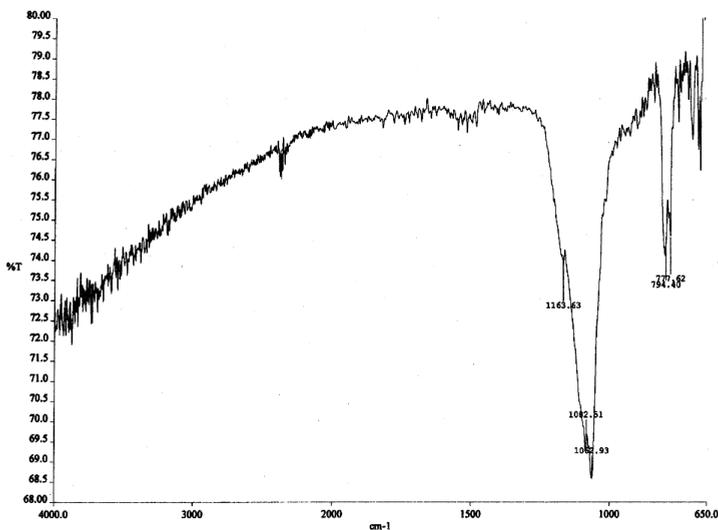


Fig. 9. ATR-IR spectrum of quartz surface activated by Ni^{2+} ions

Serpentinite ($\text{Mg}_3(\text{Si}_2\text{O}_5)\text{OH}_4$) is a layered silicate, which belongs to the group of clay materials. The spectrum of activated serpentinite (activation using nickel ions) contains four characteristic bands (Fig. 10). Adsorption band at 672.35 cm^{-1} corresponds to the vibrations of O-H bonds. Peak at 885.11 cm^{-1} represents deforming vibrations of Si-OH groups. The IR band at about 963.48 cm^{-1} is attributed to the stretching vibrations of $\equiv \text{Si-OH}$ bonds, and the band at 1011.88 cm^{-1} is characteristic for the vibrations of $\equiv \text{Si-O-Ni}$ bond.

In this paper the changes in the IR spectra of activated minerals, as a result of biomodification, were examined. Figures 11 and 12 illustrate the IR-ATR spectra of silica and serpentine after the biomodification process. The broth from *Bacillus*

circulans was used for biomodification. The spectrum of biomodified silica shows some significant differences compared to the spectra of silica activated by Ni^{+2} ions.

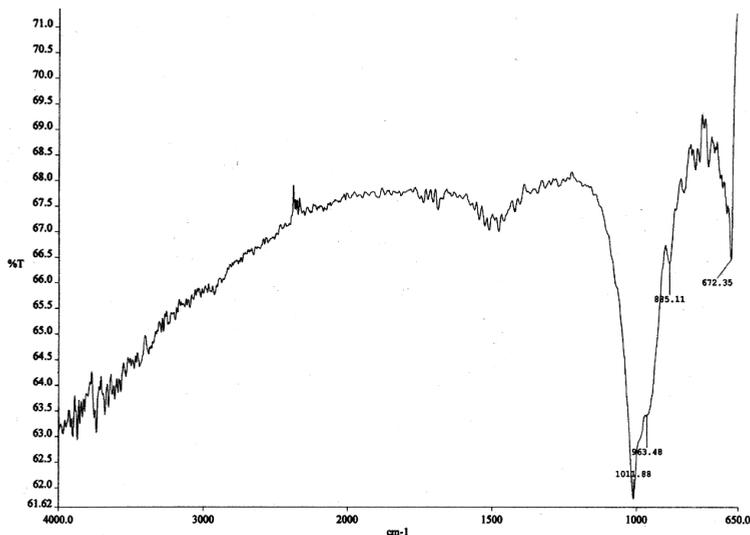


Fig. 10. ATR-IR spectra of serpentinite surface activated by Ni^{2+} ions

The adsorption band at 1170.78 cm^{-1} corresponds to vibrations of valence Si-O bond. The peak at 700.38 cm^{-1} represents the vibrations of O-H bonds. It is less intense compared to the band observed for the activated silica. A weaker band was observed at 1053.11 cm^{-1} . It is characteristic for the vibrations of $\equiv\text{Si-O-Ni-}$ bond. Additionally, the IR spectrum of biomodified silica has showed two new bands. These bands did not exist in the case of activated mineral. The first band at 797.64 cm^{-1} represents the symmetric stretching vibrations of the $\equiv\text{Si-OH}$ bonds. The second adsorption peak at 700.38 cm^{-1} is attributed to rocking vibrations of $-(\text{CH}_2)_n-$ ($n \geq 4$) bonds. Moreover, the IR spectra of silica which was biomodified by broth from *Streptomyces sp.* show similar changes when compared to the spectrum of silica biomodified by *Bacillus circulans*.

The IR spectrum of biomodified serpentinite is presented at Fig. 12. The distinct changes in the absorption frequency profile can be observed for the spectra of the activated mineral. The adsorption peak at 683.98 cm^{-1} is due to vibrations of O-H bond. However, it is less intense than the frequency corresponding to the activated serpentinite.

A weaker band, apparent at 1015.48 cm^{-1} . It corresponds to the vibrations of $\equiv\text{Si-O-Ni-}$ bonds. Additionally, we can see the band, which does not occur in the spectrum of the activated serpentinite. The adsorption peak at 746.06 cm^{-1} represents the rocking vibration of the $-(\text{CH}_2)_n-$ ($n \geq 4$) bond. Finally, the IR band at 834.55 cm^{-1} is attributed to the vibration of $\text{C}(\text{CH}_3)_3$ bonds. Furthermore, the IR-ATR spectrum was collected for biomodified serpentinite by the contact with the broth received from

Streptomyces sp. The observed changes in the IR spectrum of minerals were exactly the same as for the biomodification using *Bacillus circulans*.

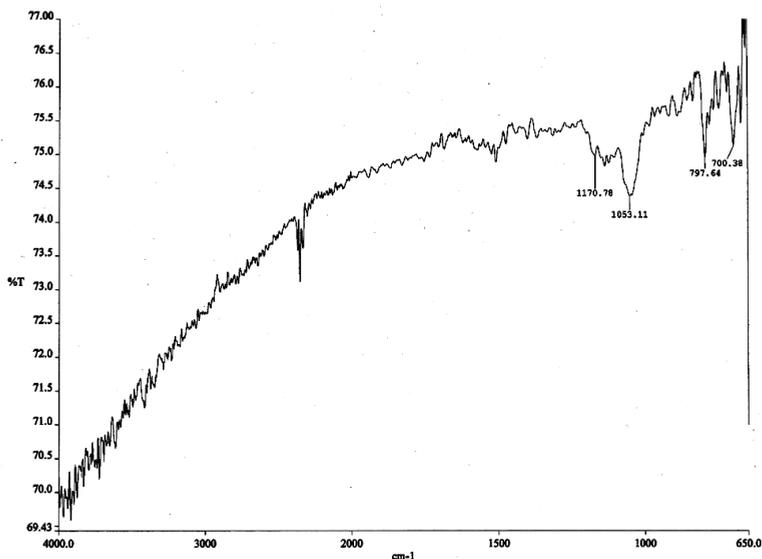


Fig. 11. ATR-IR spectrum of quartz surface biomodified by adsorption of *Bacillus circulans*

It was shown that biomodification of both minerals causes significant changes of the spectra. The intensity reduction of adsorption bands corresponding to vibrations of $\equiv\text{Si-O-Ni-}$ bonds was noted. It indicates that the biosurfactants adsorption on the minerals surface occurs through the $\equiv\text{Si-O-Ni-}$ center. Similarly, the intensity decrease of the band, characteristic to the vibration of O-H group, is probably due to the adsorption of biological surfactants onto the mineral surfaces.

Moreover, the appearance of new adsorption bands for biomodified silica and serpentine surfaces correspond to the hydrophobic tails of adsorbed biosurfactants.

By comparing the spectra of the biomodified silica and serpentine surface it can be concluded that many new groups appear onto the modified surface of serpentinite. Generally, the profile changes in the surface structure of both minerals, caused by biomodification using culture media, are similar. However, full explanation of biosurfactants adsorption mechanism onto the silica and serpentinite surfaces requires further detailed studies.

4. Conclusions

In this paper biomodification of quartz and serpentinite by biosurfactants adsorption was investigated. Biosurfactants from *Bacillus circulans* and *Streptomyces sp.* served as modifying agents for serpentinite and quartz flotation. The application of these modifying agents makes the separation process possible.

1. Biosurfactants adsorption is a result of interactions of hydrophilic parts of biomolecules with nickel center on the surfaces of minerals or with magnesium center on the serpentinite surface.
2. Flotation recovery of modified quartz and serpentine increases with increasing activating ion concentration. The maximum flotation yield (68%) corresponds with the maximum Ni^{2+} ion concentrations. This correlation was obtained for the activation process using silica and the culture medium of *Bacillus circulans*.
3. Adsorption of nickel ions on the mineral surfaces changes the value of zeta potential and isoelectric point. An increase of the activator concentration caused an increase in zeta potential values.
4. Biomodification of both investigated mineral surfaces caused a decrease of zeta potential values.
5. Biomodification of quartz and serpentinite caused important changes in the ATR-FTIR spectra of their surfaces. The appearance of new bands in the adsorption spectra of modified serpentinite correspond to the presence of hydrocarbon groups on the mineral surface.
6. Most changes in the silica and serpentine surfaces as a result of biomodification have a similar nature.

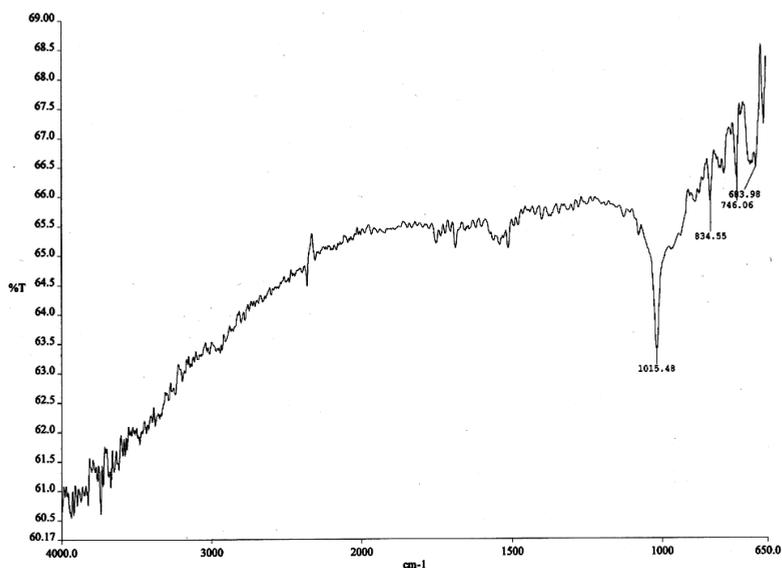


Fig. 12. ATR-IR spectrum of serpentinite surface biomodified by adsorption of *Bacillus circulans*

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