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## **THE EFFECT OF SURFACTANTS ADSORPTION ON THE HINDERED SETTLING OF MAGNESITE SOLID WASTE**

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Settling process is used to separate solid particles from water suspension. Many factors, like the presence of chemical compounds, affect this process. In this paper, the effect of surfactants addition on the settling velocity of magnesite solid waste was investigated. The studies were conducted in the presence of a natural surfactant (rhamnolipid from Jeneil Biosurfactant Co), cell culture filtrate of *Pseudomonas aeruginosa*, and a chemical surfactant (sodium dodecyl sulphate (SDS)). The addition of these compounds caused destabilization of the investigated suspension. A particle size increase and rapid sedimentation were observed. It was noted that the addition of biosurfactant caused a faster settling velocity in comparison to the SDS addition.

*Key words: biosurfactant, rhamnolipid, hindered settling, capillary suction time (CST)*

### INTRODUCTION

Sedimentation is the deposition by settling of a suspended material under the gravitation force action. Required condition of sedimentation is a difference of density of solid and water. This process depends on many factors like concentration of suspension, presence of chemical compound (polymer, surfactant and biosurfactant), and physical as well as chemical properties of liquid and solid.

Hindered settling of a suspension occurs in concentrated suspension. There is so much interaction between the particles that all settle at the same velocity and there is an evident suspension/supernatant interface. The segregation of particles is observed at a low solid concentration. The distinct sedimentation zones are formed due to settling of different size particles. There is no visible interface between suspension and supernatant.

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Biosurfactant are chemicals, which are produced by microorganism and they have both hydrophilic and hydrophobic moieties. They have a wide range of applications in many branches of industry because of advantages of biodegradability, low toxicity, biocompatibility and ability to be produced from renewable and cheaper substrates (Davis, 1999; Healy, 1996; Makkar, 2002; Singh, 1979). Major classes of biosurfactants include: glikolipids, phospholipids and fatty acid, lipopeptide/lipoproteins, polymeric surfactant, and particulate surfactants.

Rhamnolipid is a glikolipid, which is produced by *Pseudomonas aeruginosa*. These bacteria produce a mixture of four rhamnolipids, consisting of different association of rhamnose and hydroxy fatty acid (Arino, 1996).

The presence of biosurfactant in suspension can cause stabilization or destabilization of suspension. Destabilization of a suspension of fine particles is caused by formation of aggregates, which settle with high velocity. The molecules of surfactant interact with particle surface. In this case, the hydrophobic property of the mineral surface is usually produced. When the hydrophobic particles collide, the strong hydrophobic interaction causes an aggregation of particles (Murphy, 1995). Stabilization of suspension appears when the concentration of surfactant is too large. Then, the molecules adsorb onto surface forming aggregates of surfactant, called micelles.

The method of capillary suction time (CST) is one of the methods, which determines the filtration properties of a suspension and is used to quantify the dewatering characteristic of sludge. The lower the CST the better is the filterability of the sludge. The CST is affected by temperature, surface tension, the properties of filtrate paper, and concentration of suspension. CST is defined as the period of time required for filtrate to pass between two concentric circles as it flows radially outward from a sludge sample contained in an open-ended cylinder resting on a sheet or filter paper (Karr and Keinath, 1978).

## MATERIALS

The bacteria of *Pseudomonas aeruginosa* were used in this investigation. The microorganism was grown in liquid medium, which consisted of 2,0 % mannitol, 0,4 %  $\text{NH}_4\text{NO}_3$ , 0,4 %  $\text{KH}_2\text{PO}_4$ , 1,43 %  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , 0,0096 %  $\text{MgSO}_4$ , 0,0010 %  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , a pinch of  $\text{CaCl}_2$  and EDTA. The strain was cultured at room temperature for 72 h. After this time culture was centrifuged and the supernatant was used in this work. The amount of biosurfactant was estimated by measuring surface tension.

The experiment was carried out with magnesite solid waste. This mineral mixture was purchased from "Sobótka-Wiry" mine (Lower Silesia, Poland). The product was ground to the size below 45  $\mu\text{m}$ . The density of this mineral was 2.60  $\text{g/cm}^3$ .

Rhamnolipid purchased from Jeneil Biosurfactant Company JBR599 was used in these investigations. It was a semi-solid form of rhamnolipids at 99 % concentration.

The biosurfactants mixture was produced from sterilized and centrifuged fermentation broth. The literature data (Arino, 1996) suggest that two major rhamnolipids, RLL and RRL were present in this solution. Both biosurfactants were anionic.

Sodium dodecyl sulphate (SDS) was used as an anionic chemical surfactant.

### PROCEDURE

The hindered settling process was investigated in glass cylinders. In each experiment 50 ml of mineral suspension was used. During the investigation a time of the liquid/suspensions interface moving was noted. These data was used to calculate settling velocity ( $Q[\text{cm/s}]$ ). A plot of  $\log Q$  against the solid concentration was made, and then these plots were used to calculate a particle diameter. The value of settling velocity of diluted suspension was estimated by extrapolating the results to the zero solid concentration. The particle diameter was calculated using the Stokes equation. The height of sediment was measured after two days.

The capillary suction time apparatus is shown in Fig. 1. During the investigation the times ( $T_1$  and  $T_2$ ) of reaching radius  $R_1$  and  $R_2$  were observed. The value of CST was estimated as the difference of  $T_2$  and  $T_1$ .

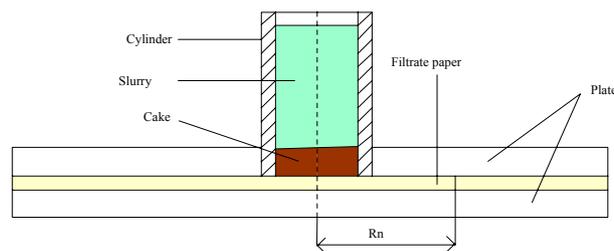


Fig. 1. Schematic diagram of capillary suction apparatus

### RESULTS AND DISCUSSION

The addition of surfactants changed the diameter of mineral particles and the sedimentation rate in the wide range of the surfactants concentration. The selected data of settling velocity were shown in Fig. 2 for the magnesite solid waste suspensions with addition of different quantities of rhamnolipid. The same plot of  $\log Q$  against the solid concentration was made for other investigated surfactant and biosurfactant.

Figure 2 shows that a large amount of the biosurfactants caused destabilization of the suspension. The molecules of surfactant adsorbed onto magnesite solid waste particles surface and it lead to aggregation of particles by strong hydrophobic interaction. The aggregates settle with high velocity. At the low surfactants concentration stabilization of a suspension was observed. The presence of a small amount of biosurfactant disturbs formation of flocs and particles settle slower than without that compound.

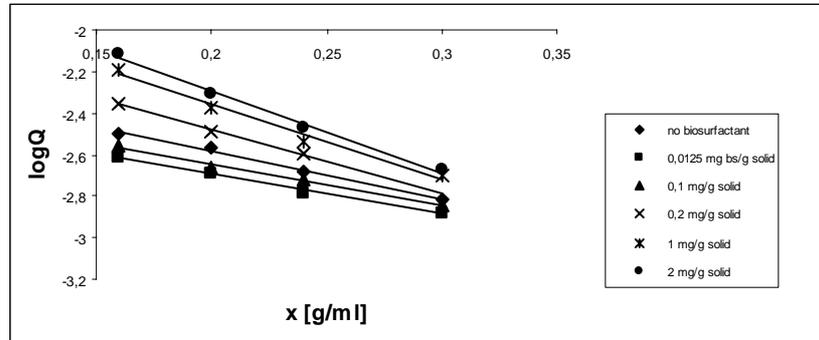


Fig. 2. Settling velocity versus suspension concentration at the presence of rhamnolipid

The values of settling velocity and diameter of particles were shown in Table. 1.

Table 1. The mean diameters of magnesite solid waste particles in the presence of surfactants

Amount of surfactants	witout	Rh 0.00125 mg/g	Rh 0.1 mg/g	Rh 0.2 mg/g	Rh 1.0 mg/g	Rh 2.0 mg/g
Diameter of particles [ $\mu\text{m}$ ]	2.89	2.38	2.54	4.03	5.15	6.01
Settling velocity [cm/s]	0.00735	0.00493	0.00561	0.0142	0.0231	0.0315

broth 80 % 1 ml/g	broth 60 % 1 ml/g	broth 40 % 1 ml/g	broth 20 % 1 ml/g	broth 5 % 1 ml/g	SDS 1,0 mg/g	SDS 2,0 mg/g
4.74	3.99	3.40	2.85	2.69	4.0	3.23
0.0196	0.0139	0.0101	0.00707	0.00631	0.0139	0.00909

The addition of a small quantity of biosurfactants caused the stabilization of magnesite solid waste suspension. The particles repel each other and disturb the formation of aggregates. It causes a rise of an energetic barrier, which particles have to overcome if they want to collide. When the concentration of surfactants increased, the suspension became less stable and at the critical concentration and above it the destabilization of suspension was observed. The critical concentration of compounds was:  $0.1 < c < 0.2$  mg/g solid for rhamnolipid, 20 % for cell filtrate. The presence of biosurfactant caused coagulation of the investigated suspension. The molecules of surfactant interact with particle surface and change its properties. It leads to the formation of aggregates, which settle with high velocity. Probably the monolayers of surfactants increase dispersion interaction and it decreases stability of suspension.

Surface activity compounds interact with solid surface and destroy a hydration sheath by replacing the molecules of water. The diameter of particle settling in pure water was 2.98  $\mu\text{m}$ , but in non-polar solvent was 1.40  $\mu\text{m}$ . It means that water molecules surround the solid particle.

The largest value was observed with the rhamnolipid presence (2.0 mg/g solid) in the mineral suspension. The addition of a large amount of the supernatant (80 %, 60 %, 40 %) caused destabilization of a suspension. However, the values of particle diameters were smaller than those with a pure rhamnolipid but it was comparable with particle size when a chemical surfactant (SDS) was added. The concentration of rhamnolipid was difficult to estimate because it contained many metabolic compounds. The concentration of supernatant in suspensions was chosen to be like the surface tension of pure rhamnolipid solutions.

In addition, the presence of surfactant affects the structure and height of sediment.

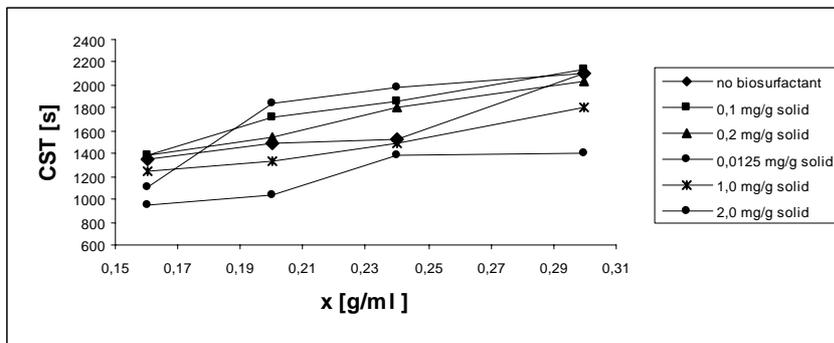


Fig. 3. CST versus suspension concentration in the presence of rhamnolipid

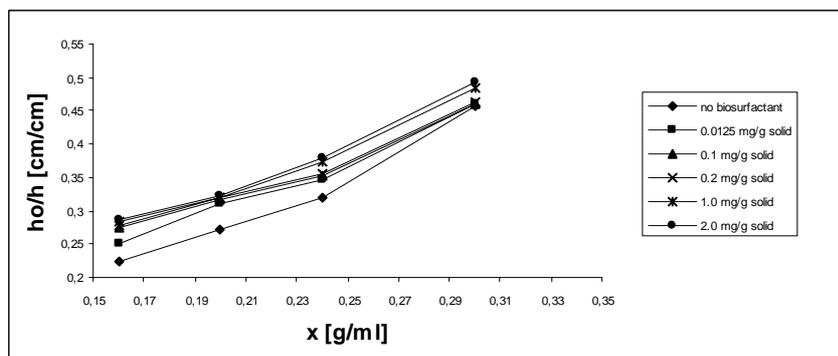


Fig. 4. The height of sediment versus suspension concentration in the presence of rhamnolipid

Figure 4 shows that the presence of rhamnolipid affects the height of sediment. The addition of biosurfactants causes an increase of sediment height of mineral suspension. The settling aggregates form the sediment, which is less packed. The highest sediment

was observed for suspension consisted of 0.3 g/ml mineral, and 2.0 mg/g solid rhamnolipid.

Experimental results (Fig. 3.) show that the value of capillary suction time is depended on the concentration of rhamnolipid and suspension. The CST decreases with the decreasing suspension concentrate. The highest value was observed for concentrated suspension. It is also shown that the addition of large amount of particles into slurry causes increasing the specific resistance of the cake and the capillary suction time is larger. At the low concentration of rhamnolipid (0.0125 mg/g solid, 0.1 mg/g solid) the rise of CST was observed. But the large amount of rhamnolipid caused decreasing of CST because of formation aggregates. Those structures have larger diameter than mineral particles. The cake made for aggregates is characterized by higher porosity and less resistance of flow. The smallest value of capillary suction time (946 s) was observed for suspension consisting of 0.16 g/ml mineral and 2.0 mg/g solid rhamnolipid.

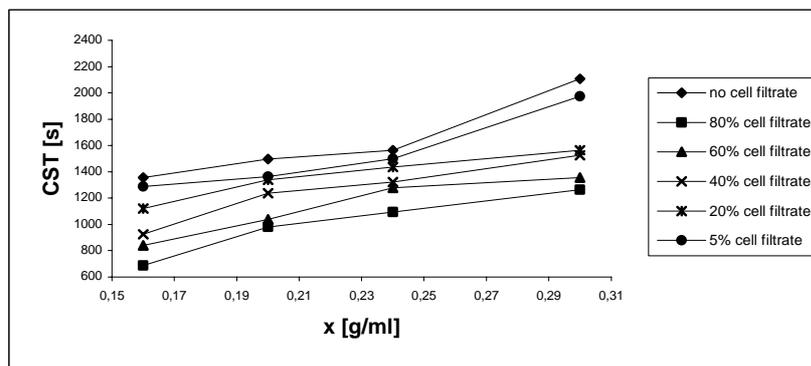


Fig. 5. CST versus suspension concentration at the presence of cell filtrate

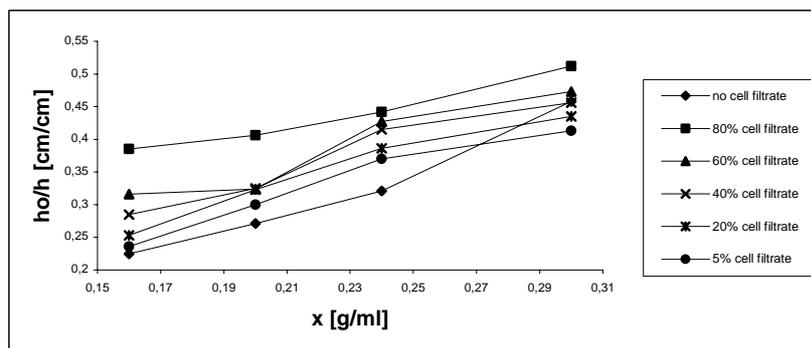


Fig. 6. The height of sediment versus suspension concentration at the presence of cell filtrate

The figure 5 and 6 show that the addition of cell filtrate affects the sediment height and structure of investigated suspension. The height of sediment rises with the increasing cell filtrate concentration, whereas the capillary suction time decreases with the increasing the concentration of supernatant. The effect of addition SDS was comparable with the effect when biosurfactants were added.

The value of CST depends on the height of sediment too. The CST decreases with the rising sediment height. The particles of magnesite solid waste in the presence of biosurfactants are coagulated and are characterized by a large size. It leads to formation of a close-packed sediment. The strong hydrophobization of surface particle at the presence of surfactants is reflected by the adsorption isotherms (Fig. 10).

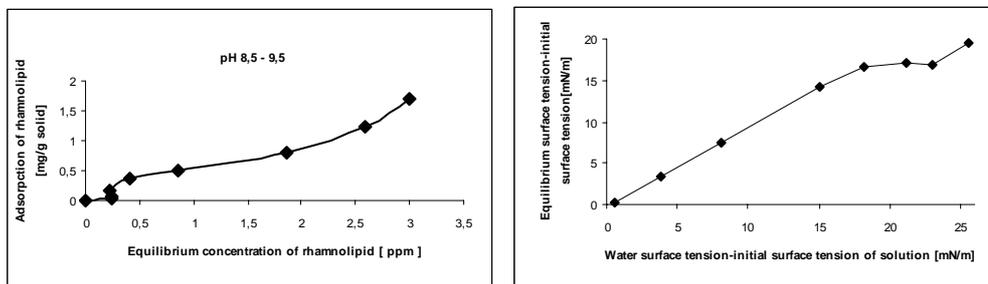


Fig. 10. Adsorption isotherms of rhamnolipid and compounds of cell filtrate on the magnesite particles

Those compounds adsorbed onto particle surface as monolayer, which is characterized by strong hydrophobic interaction.

## CONCLUSIONS

- Experimental data showed that the addition of surfactants (SDS) and biosurfactants (rhamnolipid and cell culture filtrate) had a strong effect on behaviour of magnesite solid waste suspension.
- In the cases when the large amount of biosurfactants was added, the values of settling velocity and particles diameter were greater than those without surfactant (0.00735 cm/s, 2.89  $\mu\text{m}$ , respectively).
- The low concentration of biosurfactants causes the values of settling velocity to be smaller than those without surfactant – stabilization of suspension.
- The largest particle diameter (6.01  $\mu\text{m}$ ) was obtained when the natural pure biosurfactant (rhamnolipid) was used.
- The effect of destabilization in the presence of natural surfactant (rhamnolipid, cell filtrate) was greater than that with the chemical surfactant (SDS).
- Experimental data show that the height of sediment increases with the rising quantity of surfactants.

- The highest sediment was observed in the case when suspension consisted of 80 % supernatant and 0.3 g/ml mineral. The height was 0.512 cm/cm.
- The presence of chemical compounds lowered the value of CST and the smallest value of CST (687 s) was observed for suspension consisted of 80 % supernatant.
- The capillary suction time is inversely proportional to the height of sediment.

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**Bastrzyk A., Polowczyk I., Sadowski Z.**, *Wpływ adsorpcji surfaktantów na kolektywną sedymentację odpadów magnezytowych*, Physicochemical Problems of Mineral Processing, 39 (2005) 211-218 (w jęz. ang).

Proces kolektywnej (gromadnej) sedymentacji został wykorzystany do badania wpływu surfaktantu i biosurfaktantu na stopień agregacji drobnych ziaren odpadów magnezytowych. W badaniach został użyty płyn po hodowli mikroorganizmu *Pseudomonas aeruginosa* oraz odczynnik dostarczony przez firmę Jeneil Biosurfactant Company JBR599. Oba produkty zawierają rhamnolipid, będący biosurfaktantem. Dla porównania, część prac przeprowadzono z syntetycznym surfaktantem (dodecylosiarczan sodu - SDS). Badania przeprowadzono używając wodnej zawiesiny odpadów magnezytowych (frakcja  $-45\ \mu\text{m}$ ). Doświadczenia sedymentacyjne były przeprowadzone w szklanych cylindrach sedymentacyjnych, przy użyciu których określano prędkość przesuwania granicy supernatant/zawiesina. Do badania struktury przestrzennej osadu użyto metody ssania kapilarnego (CST). Otrzymane wyniki świadczą, że dodanie biosurfaktantu powodowało przyspieszenie sedymentacji i wzrost wysokości osadu. Ustalono, że małe wartości czasu ssania kapilarnego były odwrotnie proporcjonalne do ilości dodanego surfaktantu.