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Surface properties of neutral components in copper column bioleaching of black shale samples

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Abstract: The behaviour of glass beads and polyethylene pellets as the extra bacteria support in the fine black shale ore in the column bed bioreactor was compared. Capillary rise experiments enabled the calculation of the contact angle and the surface free energy of glass beads and polyethylene pellets. The results showed that the support material made up of polyethylene pellets yielded a higher copper extraction, which could be explained by conditions favourable to cell adhesion on the polyethylene surface.

Keywords: biohydrometallurgy, column bioleaching, adhesion, surface energy, bacteria cell, glass beads, polyethylene pellets

1. Introduction

The heap bioleaching process may be considered as a heterogeneous fixed bed reactor where bacteria suspension circulates in the packed bed column. During the flow of leaching solution through the porous canals bacteria cells are attached to the mineral surface and their adhesion depends on the physicochemical parameters of this surface and hydrodynamic conditions. The effect of the latter on the black shale bioleaching was considered (Sadowski and Baranska, 2015). Since bacteria cells can be recognized as an organic colloid, the colloid filtration theory (CFT) can be used for the description of bacteria cell deposition (Torkzaban et al., 2007).

An irrigation rate depends on bed porosity which in turn is contingent on the mineral particle size. A heap bioleaching material particle has a size ranging from 5 to 40 mm (Wang et al., 2015). The black shale material was fine powder with a mean particle size of 34.1 μm. The bed which is made of such fine particles is not permeable to leaching solution without special pressure. This disadvantage can be overcome with support material (big particles) which forms beds with very different hydrodynamic characteristics (Sokolovic et al., 2009).

Authors who have investigated adhesion of *Acidithiobacillus ferrooxidans* cells to the surface of sulphur, pyrite and chalcopyrite (Devasia and Natarajan 2010) suggest that bacteria cells are attached to the mineral surface by the "enzymatic machinery" i.e. a special "glue" in the form of exposed polysaccharide which immobilizes cells. The adsorption of polysaccharides changes both cell surface and mineral particles. The atomic force microscope (AFM) measured the adhesion forces acting between bacteria cells used in bioleaching (*Acidithiobacillus ferrooxidans, Acidithibacillus thiooxidans* and *Leptospirillum ferrooxidans*) and chalcopyrite surface. The results showed that both surface charge and hydrophobicity of bacteria cells influence adhesion (Zhu et al., 2012). Determination of adhesion forces of acidophilic bacteria adsorbed onto the mineral surface were studied using silica and pyrite. The magnitude of adhesion forces was strongly influenced by the ionic strength and pH of the solution applied. Some authors have suggested a correlation between adhesion forces and solution properties (Diao et al., 2014).

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This paper focuses on the correlation between surface properties of support materials such as glass beads and polyethylene pellets and the adhesion of microbial cells and copper recovery from bioleaching black shale ore samples.

2. Materials and methods

2.1. Materials

The black shale material is middlings-tailings from 1st flotation cleaning circulation obtained from the KGHM Concentration Plant. The size distribution of black shale material is presented in Fig. 1.

The surface area of black shale powder measured by means of the BET technique (FlowSorb II 23000) was equal to 4.128 m^2/g.

Research was done using glass beads, which have a uniform size with a diameter of 2 mm (Fig. 2A), and polyethylene pellets, which have a medium size of 2.5 mm and do not have a uniform shape (Fig. 2B).

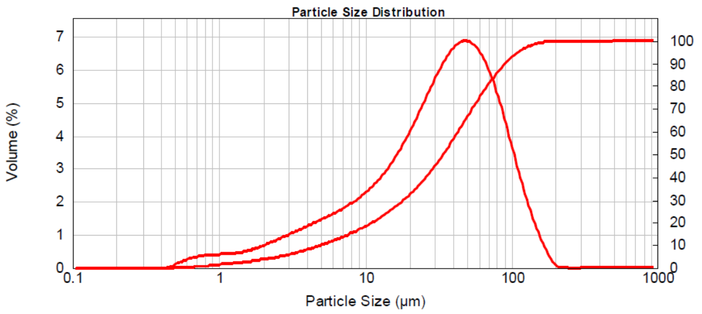

Fig. 1. Size distribution of black shale powder

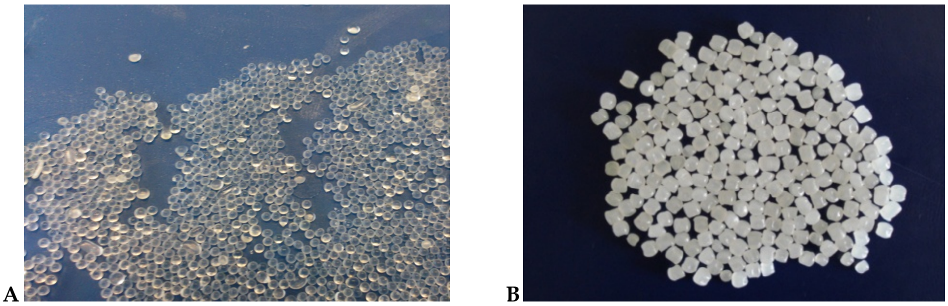

Fig. 2. (A) Glass beads, (B) Polyethylene pellets

2.2. Column bioleaching

Bioleaching experiments were conducted in a small column (37 cm/5.0 cm) with a total volume of 680 cm^3 which was charged with black shale, the mixture of black shale and supported materials. Air was pumped to the solution above the bed. The leaching solution was re-circulated into the column. Fig. 3 shows a schematic drawing of the column set-up.

2.3. Zeta potential

The average values of electrophoretic mobility measurements were automatically converted to zeta potential according to the Smoluchowski equation. The zeta potential of glass and polyethylene powder was determined by the Zeta Analyzer (Malveren Instrument). A sodium chloride solution with a concentration of 10^{-3} mol/dm^3 was used as a supporting electrolyte to maintain the ionic strength constant. An average value of at least ten measurements for each suspension was reported.

2.4. Surface area

The Flowsorb II apparatus (Mitrometrics) was used to measure the particle specific surface. The laser diffractometer Mastersizer 2000 (Malvern Instruments G.B) yielded particle size distribution.

2.5. Capillary rise measurements and contact angle determination

The Washburn capillary rise method was employed to measure the contact angles for glass and polyethylene. The experimental setup, described by Dang-Vu and Hupka (2005), consisted of an electronic balance and glass tube. The tube, which the bottom had the filter paper cork to support the powder bed, was connected to an electronic balance. The whole enabled weight data gathering over time during the rise of the liquid.

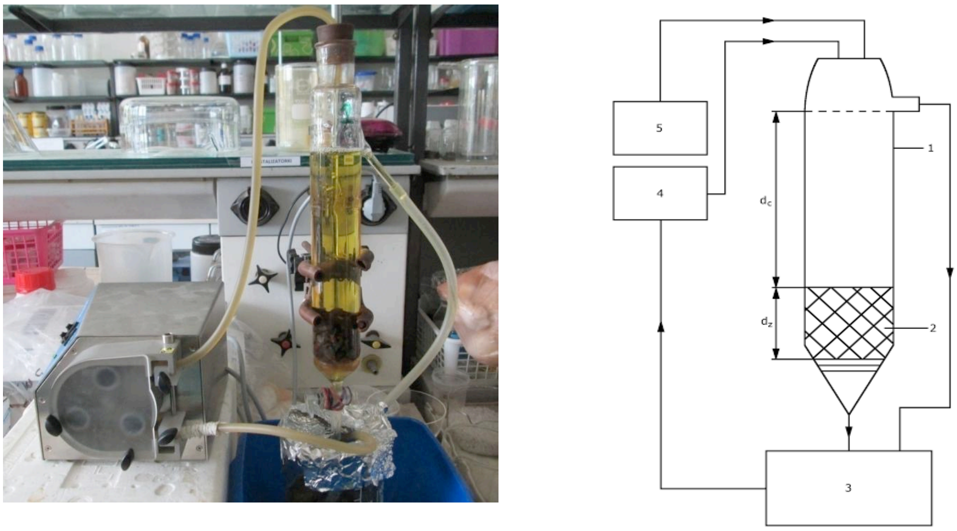

Fig. 3. Bioleaching column: 1 - bioreactor, 2 - bed, 3 - container with leaching solution, 4 - peristaltic pomp, 5 – air pomp

3. Results and discussion

A bioleaching column can be treated as a flooded packed bed bioreactor in which some of the bacteria are immobilized inside a biofilm on the solid surface. It was observed that suppo3rt materials added to the black shale bed accelerated the immobilization of microbial cells and consequently improved the bioleaching results. The bacteria concentration profiles for both supported materials were similar. However, when the polyethylene pellets were used, the pregnant leach solution contained low quantities of bacterial cells (Table 1). These bacteria abundance changes in pregnant leach solutions suggested a strong adhesion of bacterial cells to the polyethylene pellet surface.

Higher bacteria affinity to the polyethylene pellet surface corresponds to a higher copper recovery. In the case of black shale ore with polyethylene pellets the copper recovery was 78%($\pm$2.6) whereas for black shale ore and glass beads it was 65%%($\pm$1.8).

The surface free energy and its components are characterized by the solid surface properties. Both the contact angle and the surface free energy of supported materials were estimated by means of the capillary rise method. The contact angle values were calculated by the following equation:

$$m^2 = \frac{C\,\rho^2 \gamma_L cos\theta}{\eta} t \qquad (1)$$

where m is the mass of liquid, ρ is density of liquid, Υ_L is surface tension of liquid, Θ is contact angle, C is constant, η is viscosity of liquid and t is time of migration liquid. Two tested liquids were used for surface free energy determination. Table 2 presents some physicochemical parameters of used liquids.

Our experimental results clearly showed that the surface of glass beads is hydrophilic whereas the surface of polyethylene pellets is hydrophobic. The large difference in glass beads and polyethylene pellets contact angle could be associated with free surface energy.

The adhesion of bacteria cells to the solid surface can be related to the differences in the surface electric properties of both bacteria cells and support material. Tables 5 and 6 present zeta potentials of glass and polyethylene for pure powder and that with bacteria cells.

Tables 5 and 6 show the variation of zeta potential of support materials as a function of pH. The zeta potential of pure glass particles has negative values in the whole pH (1.5 -11.5) range. The contact of glass particles with the cells of *Acidithiobacillus ferroxidans* caused a decrease in negative values of zeta potential. The isoelectric point (iep) of glass particles occurred at the vicinity of pH 2. The behaviour of polyethylene particles was different. Within the acid pH range (pH 1.5 – 5.0), polyethylene particles had minimal positive zeta potentials. Therefore, bioleaching was only possible within the acidic pH range.

Table 1. Bacterial cell quantity transported by the mineral bed

Materials	Leaching solution flow (cm^3/s)	Bacterial cell quantity × 10^7					
		0	5 min	30 min	60 min	120 min	24 h
Polyethylene pellets	0.0505	12.3	5.67	2.6	1.2	1.5	10.1
Glass beads	0.0495	12.5	11.0	10.1	8.3	1.2	14.3

Table 2. Values of surface free energy of liquids and its components

Liquid	Surface tension Υ (mJ/m^2)	Dispersion component Υ^d (mJ/m^2)	Polar component Υ^p (mJ/m^2)	Density ρ (g/cm^3)	Viscosity η (mPa)
water	72.8	21.8	51.0	0.998	1.0002
diiodomethane	51.0	48.6	2.4	3.325	2.702

Table 3. Values of cos Θ and contact angle of support materials

Support material	Cosine of wetting angle (cos Θ)			
Liquid	water		diiodomethane	
Conditions	without bacteria contact	after bacteria adhesion	without bacteria contact	after bacteria adhesion
Glass beads	0.9336 Θ=21°	0.9511 Θ=18°	0.7880 Θ=38°	0.8192 Θ=35°
Polyethylene pellets	0.2419 Θ=76°	0.3090 Θ=72°	0.8829 Θ=28°	0.9063 Θ=25°

Table 4. Surface free energy of support materials before and after contact with bacteria

Support material	Conditions	Dispersion component (Υ^d) (mJ/m^2)	Polar component (Υ^p) (mJ/m^2)	Total free surface energy (Υ) (mJ/m^2)
Glass beads	without contact with bacteria	43.4	30.78	74.18
	after contact with bacteria	45.33	30.72	76.05
Polyethylene pellets	without contact with bacteria	13.33	5.15	18.48
	after contact with bacteria	15.86	3.72	19.58

The attachment of bacteria cells plays an important role in bioleaching and weathering. The bacteria adhesion onto the solid surface can be described by the classic DLVO theory (Hong et al., 2018), which posits that the main interaction forces that dominate the adhesion of bacterial cells are electrostatic force, Lifshitz-van der Waals interactions, and acid-base interactions. Consequently, the adhesion of bacteria cells to the solid surface can be related to electric properties of both bacteria cells and support materials. As revealed by zeta potential measurements, mutual electrostatic repulsion between bacteria cells and the glass surface should be expected within the acid pH range. A positive zeta potential of polyethylene particles favours the adhesion of negative charged bacteria cells.

Although hydrodynamics seems to be a crucial factor for column and heap bioleaching, also the interaction between bacteria and the solid surface plays an important role (Sadowski and Szubert 2010; Sadowski and Baranska 2015; Govende-Opitz et al., 2017). A much better copper extraction of 78% was achieved in the bioleaching column system when polyethylene pellets were used as a support material.

Adhesion forces between bacteria cells and the surface of support material were responsible for the cell attachment. Immobilization of bacterial cells inside the porous solid bed improved copper extraction. The physicochemical parameters of both bacteria cells and mineral (support) surface contributed to a high degree to bacteria cell immobilization.

Table 5. Zeta potential of glass particles

Pure glass particles								
pH	1.0	1.8	2.7	4.0	7.2	9.3	10.0	11.2
Zeta potential (mV)	-4.5 ±0.5	-17.2 ±4	-19.8 ±3	-52 ±4.2	-58.5 ±4	-59.3±5	-55.6 ±4	-60 ±5.2
Glass particles after adhesion of bacteria								
pH	1.2	1.8	2.6	4.0	7.0	9.2	10.0	11.1
Zeta potential (mV)	+6.3 ±1.5	+2.5 ±2.1	-3.2 ±1.7	-10.4 ±3.2	-24.3 ±6.8	-20.3 ±7.5	-56 ±4.8	-58.2 ±4.3

Table 6. Zeta potential of polyethylene particles

Pure polyethylene particles								
pH	1.1	1.8	2.4	4.0	5.0	9.1	10.3	11.5
Zeta potential (mV)	+0.4 ±0.2	+0.4 ±0.5	0.4 ± 0.2	-0.3 ±0.5	0.0	-5.2 ±0.4	-6.9±0.7	-8.9 ±0.9
Polyethylene particles after adhesion of bacteria								
pH	1.2	1.8	2.4	5.1	7.6	9.2	10.1	11.0
Zeta potential (mV)	1.8 ±0.2	1.0 ±0.2	0.0	-0.7 ±0.1	-2.4 ± 0.3	-4.2 ±0.6	-6.8 ±0.6	-8.9 ±0.4

4. Conclusions

Support materials made bioleaching more effective in terms of copper recovery from the black shale ore. These support materials showed different surface properties, which can be determined by contact angle and zeta potential measurements. Polyethylene pellets possess a small value of surface free energy and small positive zeta potential within the bioleaching pH range. Physicochemical parameters of polyethylene pellets created convenient conditions for bacteria cells attachment.

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