Physicochem. Probl. Miner. Process., 59(5), 2023, 183176 | Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp | ISSN 1643-1049

Metallurgical evaluation of copper ore flotation performance in the presence of Rhamnolipid biosurfactant produced from Pseudomonas aeruginosa. Part 1: Copper-bearing minerals

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Abstract: The present research work studies the effect of rhamnolipid biosurfactant (RL) produced from *Pseudomonas aeruginosa* bacteria on the metallurgical response of a copper ore sample flotation through an extensive full factorial experimental design. Key influential factors including feed particle size, pulp solid content, pH, and dosages of collector, frother and RL biosurfactant were considered. The surface activity of the RL biosurfactant was also studied based on a D-optimal experimental design. Surface activity results revealed that increasing pH and electrolyte concentrations negatively impacted the RL surface activity, while the effect of electrolyte source was dependent on their ionic strength. Metallurgical investigations showed that operating parameters significantly influence the copper grade and recovery with considerable interaction among various parameters. RL biosurfactant was found to negatively decrease the copper grade (~0.5%) and positively enhance the recovery (~3%). Effect of RL was attributed to two potential mechanisms, i.e., being ineffective on copper minerals and/or interaction with gangue minerals, as well as increasing the rate of entrainment due to high foamability, both of which increased non-selective recovery of gangue minerals. Interestingly, regardless of the structural similarities, no interaction between the flotation reagents and rhamnolipid was observed. Fourier-transform infrared (FTIR) spectroscopic analysis of copper minerals, both pure and RL-exposed, showed that there was actually no molecular interaction between RL molecules and particle surface.

Keywords: copper ore, bioflotation, rhamnolipid biosurfactant, metallurgical response, surface adsorption

1. Introduction

Today, there is no room for doubt that froth flotation is one of the most efficient and widespread methods for processing various minerals, especially fine particles. This technological boom is due to the ability of flotation to provide a selective beneficiation process. The simultaneous presence of three phases solid, liquid, and gas, although increases the complexity of the process, provides the possibility of managing different aspects of the operation to improve the efficiency and selectivity of the concentration process. The principal method of altering flotation phases is the use of chemicals that directly affect the physicochemical properties of phases. The most important of these chemicals, so-called flotation reagents, are collectors and frothers, which are used to modify solid (mineral particles) and gas phases (to improve the characteristics of air bubbles in the pulp and froth zones), respectively (Khoshdast, 2019; Bulatovic, 2020).

DOI: 10.37190/ppmp/183176

Due to the importance of these two flotation reagents, many efforts have been made during the last decade to produce and market the most efficient industrial reagents. The noteworthy point in these commercial efforts is that all the reagents that are currently used on an industrial scale are of petroleum origin. Regardless of the application and efficiency of these petroleum-based reagents, the most important challenge is the environmental impacts of these reagents, both in the work and natural environments, especially underground water (Wang et al., 2022). In this regard, several attempts have been made to introduce green alternatives, that is, reagents with minimal health risks and more compatible with the environment. During the last two decades, the efficiency of various types of microorganisms and biological products as reagents in the flotation processes of minerals and coal has been investigated (Rawlings and Johnson. 2019; Moosakazemi et al., 2022). Each approach, that is, the direct use of microorganisms or the use of bioproducts, has its advantages and disadvantages; However, bioproducts namely biosurfactants are superior to direct flotation methods due to ease of production, much higher physical and chemical stability, better biocompatibility, and structural characteristics very similar to conventional chemical surfactants (Asgari et al., 2022).

To shorten a long story, research on the application of biosurfactants to coal and mineral flotation has been summarized in Table 1. In general, biosurfactants, like chemical surfactants, contain one or more hydrophilic groups and one or more hydrophobic hydrocarbon chains. The hydrophilic head of biosurfactants consists of a complex structure of carbon and hydrogen, which receives its hydrophilic nature from the presence of several hydroxyl and oxidryl groups. The hydrophobic effect of biosurfactants is also due to the presence of one or more long and multi-branched chains of various hydrophobic compounds such as lipids. According to Table 1, biosurfactants have been used in various roles, including collector, frother, and depressant in flotation processes.

Table 1. Summary of researches conducted on the role of bioproducts in coal and mineral flotation

Generative microorganism	Biosurfactant	Mineral	Role	Reference(s)
Pseudomonas aeruginosa	Rhamnolipid	Coal	Collector	Fazaelipoor et al. (2010); Gholami and Khoshdast (2020)
		Hematite	Depressant	Szymanska and Sadowski (2010)
		Phosphate ore	Depressant	Khoshdast et al. (2011)
		Iron ore	Collector	Khoshdast et al. (2012a)
		Copper ore	Frother	Khoshdast et al. (2012a)
		Iron concentrate	Depressant	Khoshdast and Sam (2012)
Bacillus circulans	N.D.*	Serpentinite	Collector	Didyk and Sadowski (2012)
Streptomyces sp.	N.D.	Quartz	Collector	Didyk and Sadowski (2012)
Citrobacter sp.	N.D.	Pyrite	Depressant	Wahyuningsih et al. (2020)
Rhodococcus opacus	N.D.	Hematite	Collector	Simões et al. (2020)
Yeast	Sophorolipid	Copper sulfide	Collector	Dhar et al. (2020)
Bacillus subtilis	Surfactin	Calcite	Frother	Aytar Çelik et al. (2021)
		Magnesite	Collector	Öz Aksoy et al. (2022)

*The type of the bioproduct was Not Detected (N.D.)

Regardless of the type and degree of effect of the biosurfactant used in the studies, two important points can be extracted from the review of the conducted research. First, most studies are related to rhamnolipid biosurfactants. These biosurfactants include one or two hydrophilic rhamnose agents and several lipid chains that have high surface activity due to their high molecular weight. However, the main reason for paying more attention to this biosurfactant compared to other types of bioproducts is the significant development of its production technology, especially on an industrial scale, while the production of other biosurfactants is limited to the laboratory scale. Also, many studies have been published regarding the characterization of this type of biosurfactant. The second point is that despite the general conclusion about the effect of the biosurfactant on the behavior of the coal and mineral flotation process, the interaction of the biosurfactant with other operational parameters has not been investigated. Likewise, the mechanism of action of biosurfactant on the surface of different particles is not well known. It should be noted that the conducted research works are all limited to feasibility studies with the one-factor-at-the-time (OFAT) approach, and therefore, the obtained results are not of favorable reliability.

Therefore, in this research, extensive studies have been conducted on the effect of rhamnolipid biosurfactants on copper ore flotation behavior. For this purpose, in the first part of this research, in addition to investigating the physicochemical properties of the produced biosurfactant, its behavior in a copper ore flotation system was investigated in the form of a detailed experimental design and the interaction of biosurfactant with other operating parameters, especially conventional reagents were evaluated. Moreover, the metallurgical response of the process in terms of possible interaction of biosurfactant with pure copper minerals was also assessed by particle surface analysis. In the second part of the paper, the effect of biosurfactant on gangue minerals in copper ore flotation system has been investigated and analyzed in detail.

2. Materials and methods

2.1. Biosurfactant production and characterization

2.1.1. Production and characterization of rhamnolipid

The bacterial strain of *Pseudomonas aeruginosa* was used as a biosurfactant generative source. Cultivation was performed in a rich nourishment composed of 40 g/L soybean oil as a hydrocarbon source and a blend of 0.25 g/L KH_2PO_4, 0.25 g/L $MgSO_4.7H_2O$, and 3 g/L $NaNO_3$ as mineral nutrition. The nourishment was then mixed with 1 g/L yeast extract, as organic basement, in 1000 ml distilled water and left overnight while stirring via a rotary mixer at 200 rpm and 30 °C (Khoshdast et al., 2012b). Afterwards, a needle of cultivation seed was added to 700 mL of fermentation medium contained at the ratio of 2% by volume and left to stir for 10 days. The resultant cultivated suspension was then clarified by cold centrifuging (6–16 K, Sigma, Germany) for 15 min at the rate of 16,000 ×g. To separate the rhamnolipid biosurfactant, the cell-free supernatant was first acidified down to pH 2 using 1 N HCl, next left overnight in a refrigerator for RL precipitation, and finally, cold centrifuged for 50 min at the rate of 18,000 ×g. The rhamnolipid precipitate was then purified by washing using acidic distilled water, cold centrifuging, rewashing by an equal volume of ethyl acetate, and finally, concentration by evaporating under vacuum (R-200, Buchi Rotary Evaporator, Germany) at 35 °C. The obtained rhamnolipid product was also analyzed using the Fourier-transform infrared (FTIR) technique (Nicolet 6700, Thermo Fisher, USA) for its composition verification (Mirshekari et al., 2023).

2.1.2. Surface activity of rhamnolipid biosurfactant

To investigate the surface activity of the produced biosurfactant, two experimental groups were considered. In the first group, the surface tension changes of the solution containing different concentrations of biosurfactant at different pH values were measured using a Tensiometer (TD1C model, Lauda Scientific Co., Germany) according to the Du Nouy ring method. The effect of variables on the surface tension of solution was assessed through a full factorial experimental design and results were analyzed based on analysis of variance (ANOVA) approach. In the second experimental group, the effect of electrolytes on the surface activity of the biosurfactant was evaluated by a D-optimal factorial experimental design. The variables and their investigated levels are presented in Table 2. In order to adjust the pH, NaOH and HCl (KFK® Chemicals, Iran) with analytical purities were used. Electrolyte salts were obtained from Merck (Germany) with an analytical purity.

Table 2. Variables and their levels used in surface activity measurement of the RL product

Experimental set	Variables	Levels
pH sensitivity	RL concentration (ppm)	5, 10, 25, 50
	Solution pH	3, 5, 7, 9, 11
Electrolyte sensitivity	Electrolyte source	NaCl, KCl, CaCl2, MgCl2, FeCl2, AlCl3
	Electrolyte concentration (ppm)	0.01, 0.1, 1, 10
	RL concentration (ppm)	5, 10, 25, 50

2.2. Preparation and characterization of copper ore sample

To prepare a bulk sample for conducting flotation tests, 1000 kg of samples were collected from the stockpile of feed to the processing plant of Sarcheshmeh Copper Complex (SCC, Rafsanjan, Iran) by an automatic sampler for three working days. The subsamples were taken and blended by the automatic sampler based on its default settings; finally, based on the needs of the studies, 200 kg of representative samples were prepared by the automatic rotary sampler. To prepare the required samples for characterization studies and flotation tests, the representative sample was divided into 1.7 kg sub-samples using a riffle sample divider. Then, samples were sent to the SCC analysis laboratory to measure the mineralogy and chemical composition of the ore sample.

X-ray diffractometer (XRD), Bruker D8 ADVANCE model, equipped with Copper Anticathode in configuration Bragg-Brentano optics with fixed slits, Ni filter, and ultrafast linear detector was used for mineralogical analysis. The radiation employed was a Cu K-α with a wavelength of 1.540598 Å within the values of 2θ from 0–80° Bragg's angle. The XRD was used to identify the mineral phases present in the ore. The mass of the sample was required to be about 3 g with a particle size of <30 μm. The sample was pressed to obtain a flat and uniform surface and after that, it was put into the XRD equipment to start detection (Fozooni et al., 2017). A pressed pellet prepared from a representative sample was analyzed to identify the chemical composition by the X-ray fluorescence (XRF) technique using a Bruker-Axs: S8 TIGER X-ray spectrometer. Loss on ignition (L.O.I.) was obtained by heating the sample powder to 1000 °C for 2 h (Khoshdast and Shojaei, 2012).

2.3. Flotation experiments

2.3.1. Operating variables and experimental design

The operational goal of the flotation process in the Sarcheshmeh copper processing plant is to concentrate valuable copper sulphide minerals. The metallurgical efficiency of the flotation process is also determined by the copper grade and recovery. According to the nature of the flotation process, several factors such as ore characteristics (grade, type of valuable minerals, type and amount of gangue minerals, hardness, etc.), type of chemicals and their consumption dosage, grinding rate (degree of liberation) as well as process factors such as pulp solid content, pH, froth height, etc. may influence the grade and recovery. Therefore, following the consultation with the plant's process control unit, in order to achieve the optimal conditions for copper grade and recovery, input feed size, feed pulp solid content, collector concentration, frother concentration, and pulp pH in the presence of rhamnolipid biosurfactant were considered as operating parameters. The operating levels of each parameter were selected based on three-month monitoring of the factory, and the flotation test program was designed in the form of a two-level full factorial experimental design. To investigate the non-linear effects of the parameters, a central point with 6 replications was defined in the experimental design (DOE). The values of the parameter levels for the central points are defined as the middle values of the lower and upper levels in DOE. The parameters and their level values are presented in Table 3. The target size of the feed was obtained following a set of extensive grinding tests to indicate the optimal grinding time (data are available upon request). It should be noted that in order to check the net effect of each flotation reagent, the low concentration level of the reagents was considered zero. Finally, flotation tests were performed based on the full-factorial DOE with two replications (a total of 134 tests, available upon request) and considering copper grade and recovery as process responses.

Table 3. Variables and their levels used for developing flotation tests DOE

Factor	Name	Unit	Type	Low Level	Middle Level	High Level
A	Particle size	μm	Numeric	75	90	105
B	Solid content	%	Numeric	20	25	30
C	Frother dosage	g/t	Numeric	0	10	20
D	Collector dosage	g/t	Numeric	0	20	40
E	RL dosage	g/t	Numeric	0	10	20
F	pH	-	Numeric	9	10.5	12

2.3.2. Flotation test works, elemental analyses, and metallurgical calculations

To perform flotation tests, a standard flotation machine (D10 model, Denver®, USA) equipped with a 4 L cell was used. To perform each test, the copper ore sample was first mixed with the appropriate amount of tap water in the cell to prepare the solid percentage corresponding to the test conditions in the experimental design. Then, the pH of the pulp was adjusted using lime corresponding to the experimental design for each test. After preparing the pulp, the appropriate concentration of rhamnolipid biosurfactant was added to the cell and stirred for 3 minutes. Afterwards, sodium isopropyl xanthate collector (Z11) with the concentration defined in the DOE was added to the pulp and stirred for another 3 minutes. At the end, frother was also added to the pulp and stirred for a further 2 minutes. The frother used in the plant is a mixture of 40% methyl isobutyl carbinol (MIBC) and 60% polypropylene glycol methyl ether (F742). After the conditioning step, the air valve was gently opened to let the foam form. The foam was collected for 16 minutes. The stirrer speed was kept at 1100 rpm in all stages of conditioning and flotation test. At the end of each experiment, collected froths and tailings were filtered, dried, weighed, and sent for chemical analysis. The amount of metal in the samples was measured using atomic absorption spectrometry (SpectrAA 220 FS, Varian, Australia). Copper recovery (R, %) was also calculated for each test based on the grade and weight of the samples using equation (1) (Khoshdast, 2019):

$$R\ (\%) = \frac{Cc}{(C+T)f} \times 100 \quad (1)$$

where C, and T are the weight (g) of concentrate and tailing, and f and c are the copper grade (%) in the test feed and concentrate, respectively.

2.3.3. Pure mineral samples and FTIR analysis

To investigate the interaction of the biosurfactant with the surface of minerals, pure samples of dominant copper minerals, i.e., chalcopyrite and covellite, were collected from the Sarcheshmeh copper mine by hand. It should be noted that studies related to other gangue minerals have been studied in detail in part 2 of this paper. After grinding in a ceramic planetary grinder to sizes finer than 100 µm, pure mineral samples were washed with deionized water to remove any external dirt. Then, washed samples were dried and placed in vacuum bags for further investigation. On the other hand, 100 g of washed samples was mixed with 20 g/t of rhamnolipid in the flotation cell containing 1 L of deionized water by gently stirring for 30 min. Afterwards, the RL-exposed mineral was dewatered using the procedure served in the sample preparation step. Finally, the surface properties of RL-exposed and raw mineral samples were analyzed using the FTIR method (Mirshekari et al., 2022).

3. Results and discussion

3.1. Structural verification of rhamnolipid biosurfactant

The FTIR spectrum of the produced rhamnolipid is shown in Fig. 1 and reveals characteristic features suggestive of rhamnolipid molecular structure. Notably, the spectrum exhibits a broad absorption band in the region from 3725 cm^{-1} to 3600 cm^{-1}, indicative of O–H stretching vibrations associated with hydroxyl groups (Hasanizadeh et al., 2023a). The broad observed in the regions 2958 to 2854 cm^{-1} infers the presence of aliphatic with small, symmetrical, and asymmetrical CH_3, CH_2, and –C–H– vibrations in lipids. The spectrum displays absorption bands between 2200 cm^{-1} and 1550 cm^{-1}, representing C–O–C stretching vibrations, typically attributed to the sugar moiety, particularly rhamnose. Those C–O–C stretching vibrations could correspond to the glycosidic linkage type. The presence of aliphatic hydrocarbon chains is supported by the absorption band in the 830 cm^{-1} to 730 cm^{-1} range, corresponding to C–H stretching vibrations. As mentioned, certain observable features in the FTIR spectrum provide strong evidence for the glycolipid nature of the rhamnolipid product, with this conclusion founded upon the inherent structural composition of rhamnolipids. In some studies, similar results were found with the rhamnolipid biosurfactant (e.g., Jadhav et al., 2011; Deepika et al., 2017; Zarandi et al., 2020).

3.2. Characterization of copper ore sample

The chemical composition of the bulk representative sample is presented in Table 4. As seen, the ore

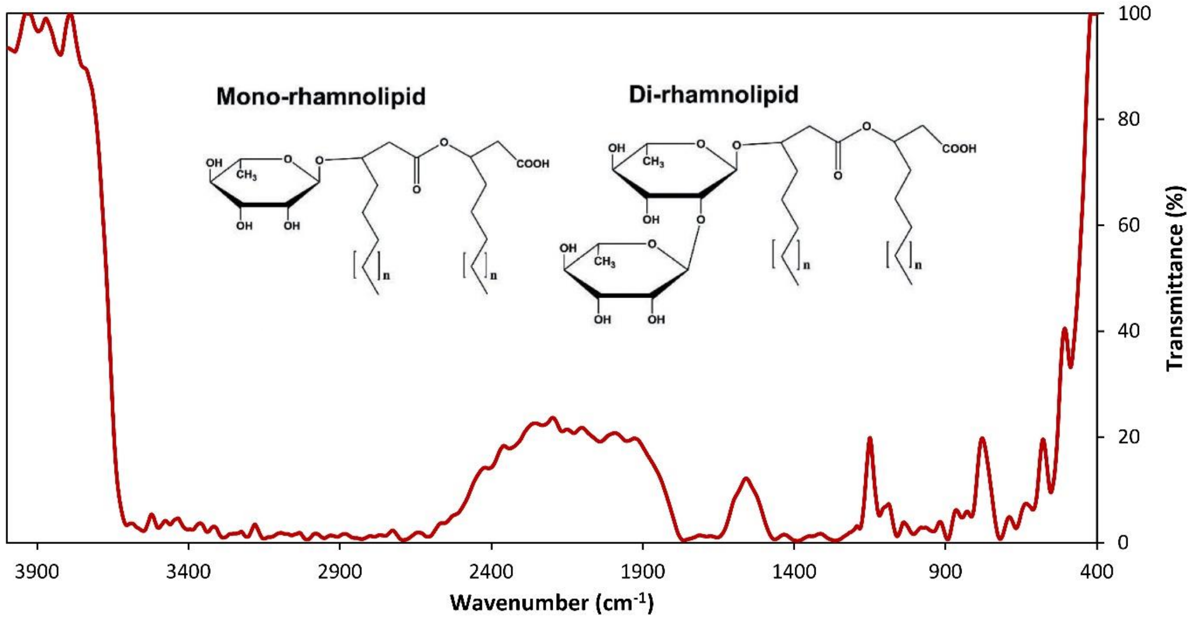

Fig. 1. FTIR spectrum of rhamnolipid biosurfactant produced from Pseudomonas aeruginosa strain

sample contains 0.6wt% copper with 54.39 wt% SiO_2 and 17.92 wt% Al_2O_3. The mineralogical composition of the ore sample is listed in Table 5 showing that chalcopyrite and chalcocite are the major copper minerals. The presence of pyrite is significant, and the main non-metallic minerals are muscovite and illite as well as quartz. According to the results given in Table 4, since the Cu/S ratio is lower than 0.7 (Cu/S = 0.14), the studied ore sample can be considered a high-pyritic (elevated-pyritic) feed which is relatively difficult to treat. Further information in terms of this type of ore and its floatation behavior can be found elsewhere (Hassanzadeh et al., 2020).

Table 4. Chemical composition of the copper ore representative sample

Component	Cu	CuO	Fe	S	Mo	SiO_2	Al_2O_3	K_2O
Amount (%)	0.60	0.03	7.40	4.04	0.03	54.39	17.92	4.45
Component	MgO	CaO	Na_2O	TiO_2	MnO	P	BaO	ZnO
Amount (%)	3.89	1.07	1.00	0.89	0.17	0.13	0.06	0.06

Table 5. Mineralogical composition of the copper ore representative sample

Mineral	Chalcopyrite	Chalcocite	Covellite	Bornite	Molybdenite	Sphalerite	Pyrite
Amount (wt%)	1.09	0.17	0.04	0.06	0.05	0.27	19.98
Mineral	Muscovite	Quartz	Illite	Kaolinite	Clinochlore	Albite	Amorph
Amount (wt%)	22.96	13.14	21.48	3.84	9.32	3.67	3.93

3.3. Surface activity analysis of biosurfactant

To investigate the effect of operating variables on the surface activity of the biosurfactant, experimental designs related to the sensitivity of biosurfactant to pH and electrolyte were analyzed using the analysis of variance (ANOVA) method at the 95% confidence level. The summary of ANOVA results is presented in Table 6. Details of ANOVA tables and model parameters are available upon request. As can be seen in Table 6, the statistical models for both experimental designs are significant (p-value < 0.05) and therefore can be used for the analysis of the experimental design. Also, as presented in Table 7, the fitting parameters of the models are also very accurate (Gholami et al., 2021). The results of ANOVA in Table 6 show that the effect of all variables on the response of the experimental designs (i.e., the surface tension of the solution) is significant (p-value < 0.05). Therefore, their effect can be interpreted physically (Khoshdast et al., 2017).

Table 6. Variables and their levels used in surface activity measurement of RL product

Experimental set	Source	p-value	State
pH sensitivity	Model	< 0.0001	Significant
	RL concentration (ppm)	< 0.0001	Significant
	Solution pH	< 0.0001	Significant
Electrolyte sensitivity	Model	< 0.0001	Significant
	Electrolyte source	0.00542	Significant
	Electrolyte concentration (ppm)	0.00557	Significant
	RL concentration (ppm)	< 0.0001	Significant

Table 7. Significance and determination coefficients for pH and electrolyte sensitivity models

Response	F value	p-value	R^2 (%)	Adj R^2 (%)	Pred R^2 (%)	Adeq Precision
pH sensitivity	42.87	< 0.0001	96.15	93.91	89.32	21.65
Electrolyte sensitivity	27.72	< 0.0001	94.06	90.67	85.22	17.99

The main effect plots for the pH sensitivity experiments are shown in Fig. 2. As can be seen, with the increase in biosurfactant concentration, the surface tension has decreased. Rhamnolipid biosurfactants have a multi-branched structure and consist of several hydrocarbon chains and therefore have high surface activity (Champion et al., 1995; Benincasa et al., 2010; Khoshdast et al., 2012b). For this reason, with the increase in the concentration of this biosurfactant, the surface tension decreases rapidly. In most of the research, the maximum decrease in surface tension of solutions containing rhamnolipids has been reported to be about 25 mN/m, which is consistent with the results of this research (e.g., Ozdemir et al., 2004; Patel et al., 2019). The highest activity of rhamnolipids has been reported in acidic environments (Shojaei and Khoshdast, 2018). As the pH increases towards the alkaline environment, the hydroxyl groups in the molecular structure of rhamnolipids are neutralized by the cations released from the pH regulator (in this study, Na^+ from NaOH) and as a result, the surface activity of the biosurfactant decreases (Bodagh et al., 2013; Boveiri et al., 2019).

The effect of the type and concentration of electrolyte on the surface activity of biosurfactant is shown in Fig. 3. In this research, only chloride salts were used in order to avoid anionic effects and identify

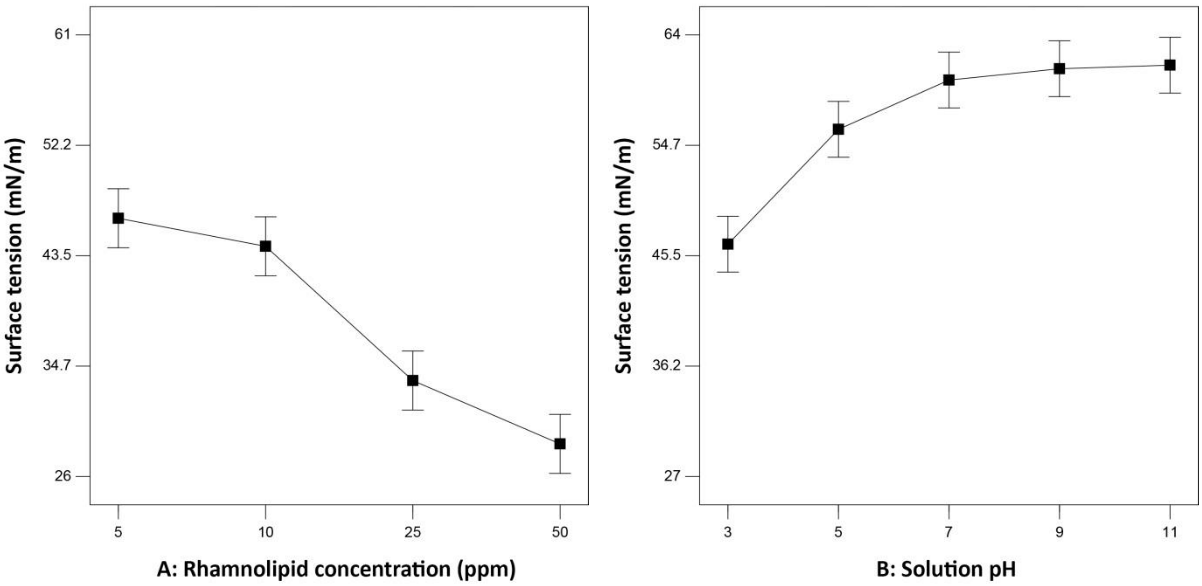

Fig. 2. Main effect plots showing the influence of selected variables on RL surface tension

the direct effect of electrolytes. As can be seen in Fig. 3, the surface tension of the biosurfactant is not very sensitive to the type of electrolyte and it changes only in a range of about 2 units. This low sensitivity can be seen in the small value of probability value (*p*-value of 0.00542) in Table 3. The reason for this phenomenon can be attributed to the large rhamnolipid molecules and the large number of hydroxyl groups in them. Although according to Fig. 3, it seems that in general, the surface activity of rhamnolipid decreases with the reduction of reactivity of the electrolyte. The order of reactivity of the electrolytes used in this research is $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+} > Fe^{2+}$ (Haynes, 2016). Although exceptional responses are also observed in the case of iron and potassium, which require more specialized studies. The effect of electrolyte concentration also shows a completely nonlinear but limited (*p*-value of 0.00557) trend. Theoretically, it is expected that the surface tension will increase with the increase of the concentration of the electrolyte and the subsequent increase in the number of neutralizing agents (cations) of the hydroxyl groups in the biosurfactant structure. However, this expectation changes periodically. In order to evaluate these unexpected behaviors, more detailed studies are needed.

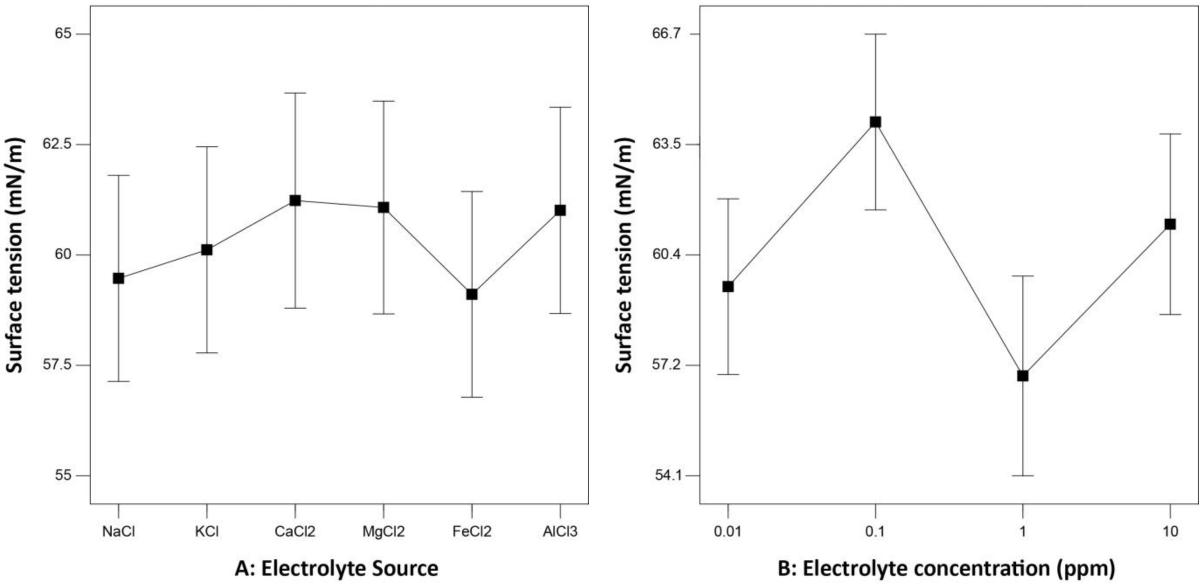

Fig. 3. Main effect plots showing the influence of electrolytes on RL surface activity

3.4. Results of flotation experiments

3.4.1. Statistical analysis of DOE

The first step in the analysis of any DOE is the development of an efficient prediction model based on the relationship between the experimental results obtained during the tests and the levels of operational parameters. The task of this model is to predict changes in the response of the process in the space of the DOE and for new values of the parameter levels in the range determined in the DOE. Then, using the model, one can draw plots of the individual and interaction effects of the parameters. The continuity of the points in these plots is the values predicted by the model, which sit between the experimental values obtained during the test work (Mahmoodabadi et al., 2019; Khoshdast et al., 2021). Considering that in the first part of this research, copper grade and recovery are considered as flotation responses, two prediction models for grade and recovery were developed, whose fitting parameters are presented in Table 8. The relevant equations are not present due to the limited length of the paper, and they can be provided upon request. According to Table 8, it can be seen that both models are significant due to very small probability values and high Fischer values. Also, the high values of the determination coefficients indicate the very favorable accuracy of the models for predicting grade and recovery in different values of operational parameters. The Adequate precision factor is also much larger than 4 for both models and therefore, the models are very reliable (Montgomery, 2020).

After the development of prediction models, the significance of the effect of each parameter on the responses can be evaluated using ANOVA. In short, at the 95% confidence level, if the probability value is less than 5% (i.e., 0.05), the effect of that parameter is significant and meaningful and can be interpreted physically (Shami et al., 2021; Hasanizadeh et al., 2023b). Further detailed information regarding the stepwise application of this approach can be found elsewhere (Azizi et al., 2020). The ANOVA results of copper grade and recovery models are summarized in Table 9. Detailed results are available upon request. As can be seen in Table 9, the effect of all operational parameters on the grade is significant, while in the case of recovery, the effect of particle size and pH is not significant. In addition to the main effects, the significance of the interaction effects can also be evaluated in the ANOVA results. In the following sections, significant interaction effects have also been investigated.

Table 8. Fitting coefficients for copper grade and recovery model equations

Response	F value	*p*-value	R^2 (%)	Adj R^2 (%)	Pred R^2 (%)	Adeq Precision
Cu grade (%)	48.89	< 0.0001	95.80	93.84	90.53	22.782
Cu recovery (%)	87.31	< 0.0001	98.10	96.97	94.94	31.575

Table 9. Summary of ANOVA results of effect significance analysis for copper grade and recovery

Source	Cu grade		Cu recovery	
	p-value	State	*p*-value	State
Model	< 0.0001	Significant	< 0.0001	Significant
A-Particle size (μm)	0.0242	Significant	0.9179	Insignificant
B-Solid content (%, w/w)	< 0.0001	Significant	0.0003	Significant
C-Frother dosage (g/t)	< 0.0001	Significant	< 0.0001	Significant
D-Collector dosage (g/t)	< 0.0001	Significant	< 0.0001	Significant
E-RL dosage (g/t)	0.0303	Significant	0.0050	Significant
F-pH	< 0.0001	Significant	0.1396	Insignificant

3.4.2. Effect of operating variables on copper grade

The main and interactional effects of operating parameters on copper grade are shown in Figs. 4 and 5, respectively. As can be seen in Fig. 4, with the increase in the size of the particles, the grade of the concentrate has increased slightly. However, it was expected that the grade decreases with the increase of the particle size due to the decrease in the degree of liberation of the copper minerals. One reason can be attributed to the activation of pyrite particles in the presence of copper ions which was discussed in detail by Agheli et al. (2018). As seen in Fig. 5, the particle size has a significant interaction with the frother concentration and the pH of the pulp; therefore, the unusual effect of particle size with a low quantitative variation can be attributed to its interaction with other parameters. With an increase in pH, the grade has improved due to the depression of pyrite by lime. On the other hand, increasing the concentration of frother has also caused an increase in the grade. The direct relationship between grade and frother dosage can be attributed to the effect of frothers on the kinetic rate of the process; if the concentration of frother increases, the kinetics of the process is improved, and as a result, the flotation rate of copper minerals is enhanced (Gholami et al., 2022).

According to Fig. 5, the effect of frother concentration has the opposite relationship with the effect of particle size; as the increase in the size of the particles improves the grade in low concentrations of frother, but it slightly decreases it in high dosages of frother. This behavior is reversed for the interaction of particle size and pulp pH. Also, the interaction plot of pH and frother dosage shows that the highest copper grade is obtained at the highest pH value and frother concentration.

By comparing these interaction plots, the unusual behaviour of the particle size can be explained as follows: with increasing pH, the depression rate of pyrite increases, but due to the improvement of frother performance at high pH, the flotation rate of coarse particles increases. The distribution of copper and iron in different particle size fractions of flotation feed is listed in Table 10. As can be seen, although the copper grade is higher in the finer size fractions, the iron content of the coarser fractions is much lower and as a result, with the transferring of coarse particles to the concentrate, the iron grade has decreased and the copper grade has increased (Zahab-Nazouri et al., 2022).

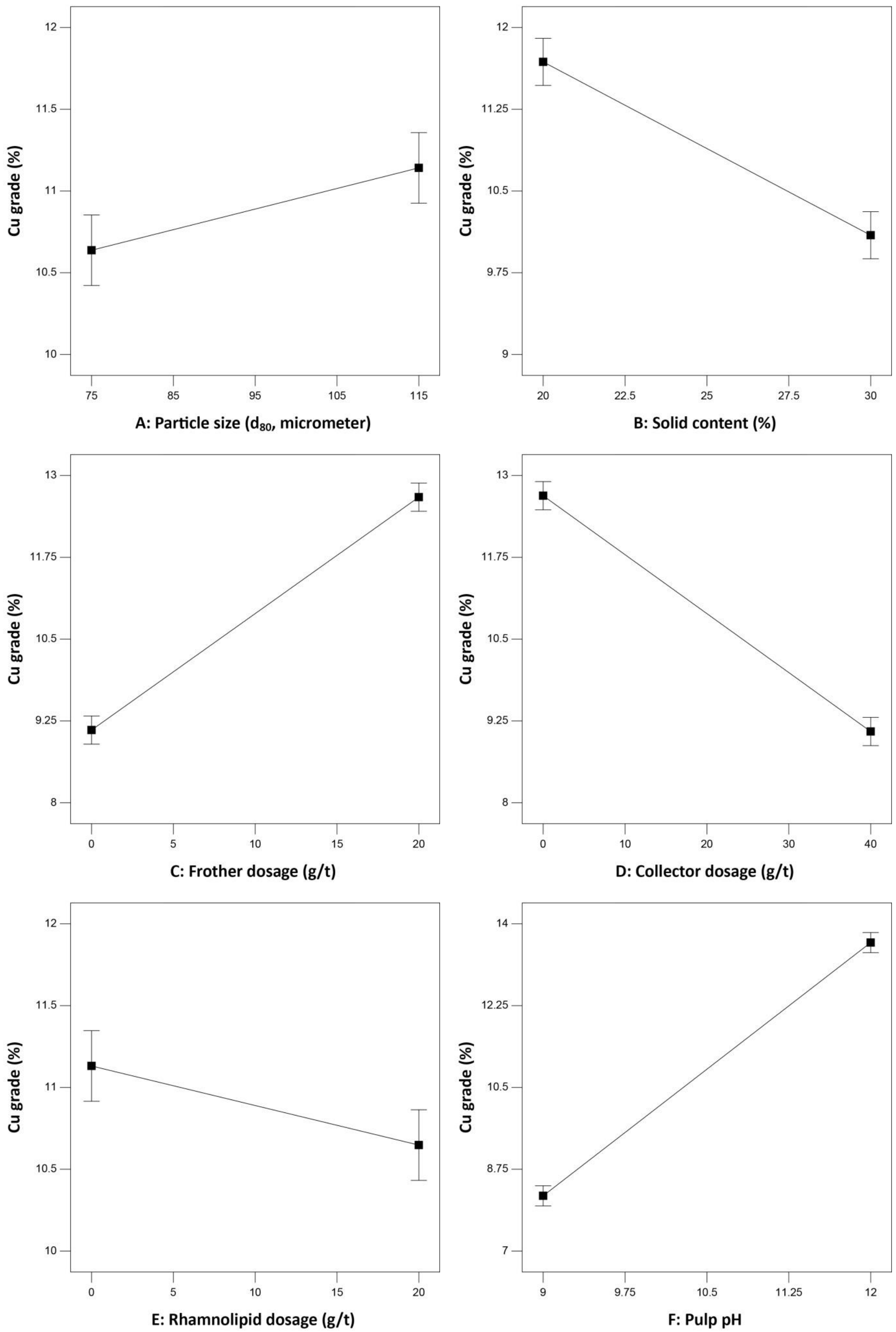

Fig. 4. Main effect plots showing the influence of operating variables on copper grade

Table 10. Distribution of copper and iron grades in different particle size fractions of flotation feed

Size (µm)	149	125	105	88	74	53	44	33	23	15	11	<11
Cu (wt%)	0.30	0.31	0.32	0.70	0.52	0.45	0.61	0.78	1.10	0.75	0.45	0.49
Fe (wt%)	3.89	4.12	5.08	7.21	7.38	6.79	7.97	7.39	10.95	6.86	6.65	6.60

According to Fig. 4, with the increase of pulp solid percentage, the grade decreases which is in line with the results presented by Asghari et al. (2015). An increase in pulp concentration causes an increase in the state of suspension of particles (Jarkani et al., 2014), and as a result, the rate of entrainment of particles to froth and concentrate increases, and thus, the grade decreases. Paryad et al. (2017) showed that thicker flotation feeds can increase the rate of entrainment with swarm mechanism due to increased turbulent conditions in the pulp environment. As seen in Fig. 5, pulp solid content and frother concentration have an opposite relationship. In thinner pulp, increasing the concentration of frother increases the flotation rate due to reducing the size of the bubbles and improving their performance, but with the increase of the solid percentage, the flow of rising bubbles is disturbed, and the efficiency of selective flotation is also reduced. Increasing the concentration of the collector also reduces the grade. In general, increasing the concentration of the collector causes a decrease in the grade due to the decrease in the selectivity of the process. However, by increasing the pH due to the increase in lime concentration as a pyrite depressant, the negative effect of increasing the collector can be reduced. This positive effect of pH can be seen in the interaction diagram of pulp pH and collector concentration in Fig. 6. Another noteworthy point is the interaction between the dosages of the collector and frother. As can be seen in Fig. 6, the performance of the frother at high concentrations of the collector is greatly reduced. This phenomenon can be attributed to the interaction of collector and frother molecules in the aqueous phase, which has been studied in detail in various references (e.g., Khoshdast et al., 2022; Asgari et al., 2023).

As the concentration of rhamnolipid increased, the copper content in the concentrate decreased (Fig. 4). However, comparing the interaction plots of rhamnolipid concentration with solid percentage and frother concentration (Fig. 5) shows that increasing the concentration of rhamnolipid in low solid percentage and high frother concentration has improved the grade. Therefore, it seems that rhamnolipid has no special interaction with copper minerals and its effect is partly due to the interaction with other minerals and partly due to its foaming function. The former will be examined in detail in part 2 of this paper. The strong foaming effect of rhamnolipid biosurfactants in two-phase systems has been investigated in detail by Khoshdast et al. (2012b) and in three-phase systems by Asgari et al. (2023).

3.4.3. Effect of operating variables on copper recovery

Figs. 6 and 7 show the individual and interaction effects of operating parameters on copper recovery, respectively. In general, grade and recovery in any process have an inverse relationship. Therefore, if a parameter increases the grade of the process, the recovery subsequently decreases. Based on the results of the analysis of variance (Table 8), the effect of particle size and pulp pH on recovery was not significant. According to Fig. 6, the increase in solid percentage increases the recovery due to the increase in entrainment rate. Referring to Fig. 7, the interaction between solid percentage and particle size shows that the increasing effect of solid percentage decreases with the increase of particle size, so that at the highest level (i.e., 115 microns), the increase of solid percentage does not affect the grade. This relationship clearly confirms the role of entrainment at high solid percentages as the entrainment rate increases as the particle size decreases. The interaction effect of solid percentage and pH also shows a completely non-linear behaviour so that with increasing pH, the effect of solid percentage also grows significantly. At high pH values, although locked particles and gangue, especially pyrite, are depressed, an increase in the non-selective flotation rate is more evident due to an increase in the solid percentage and entrainment rate. According to Figs. 4 and 6, increasing the frother concentration has increased both the grade and recovery. Although increasing the concentration of the frother improves the kinetic rate, it also increases the rate of entrainment by the swarm mechanism due to the increase in the number of bubbles (Paryad et al., 2017, Khoshdast et al., 2023). This effect can be observed based on the given plots indicating the interaction effects of frother concentration with solid percentage and with pulp pH (as discussed earlier).

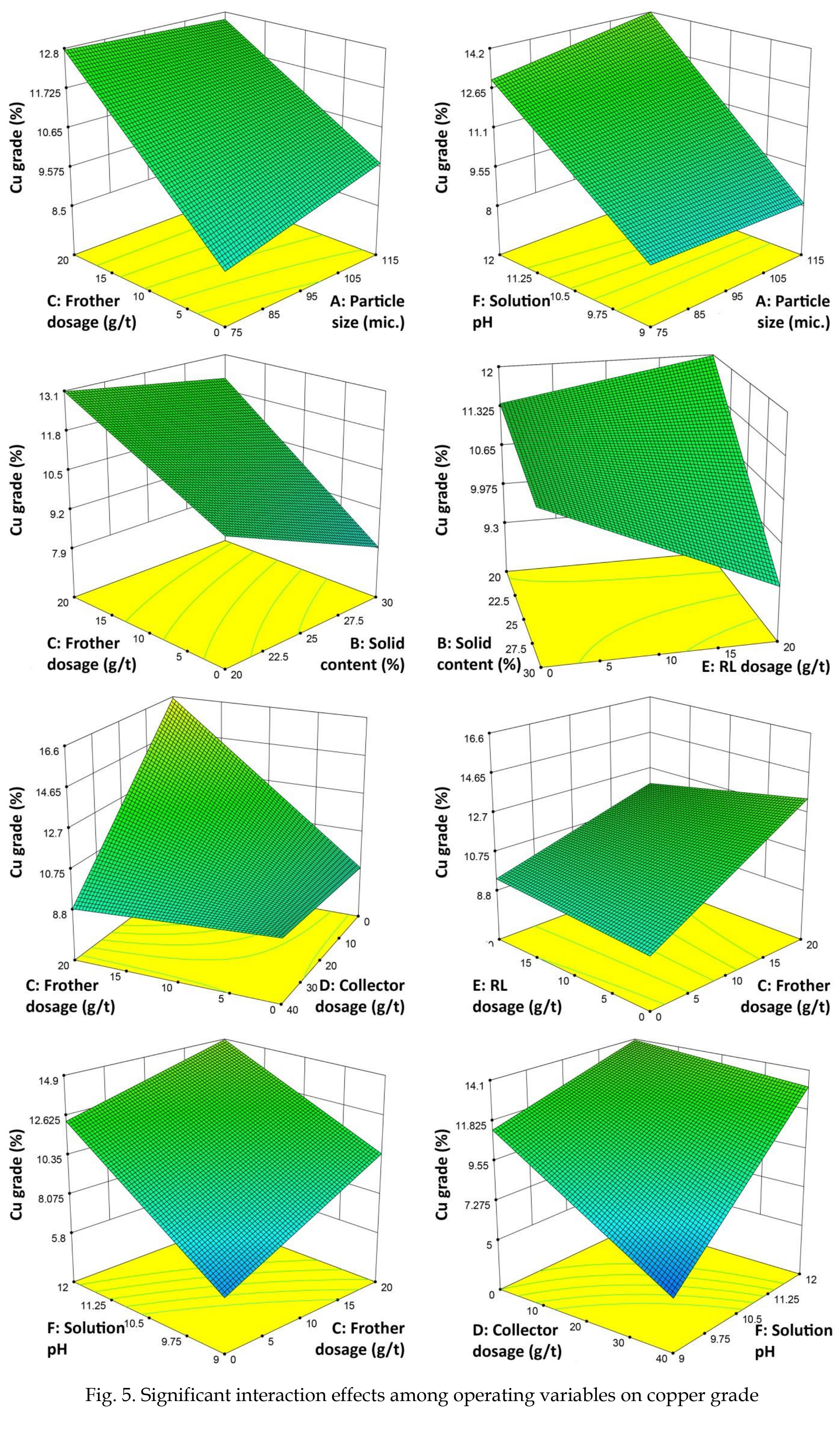

Fig. 5. Significant interaction effects among operating variables on copper grade

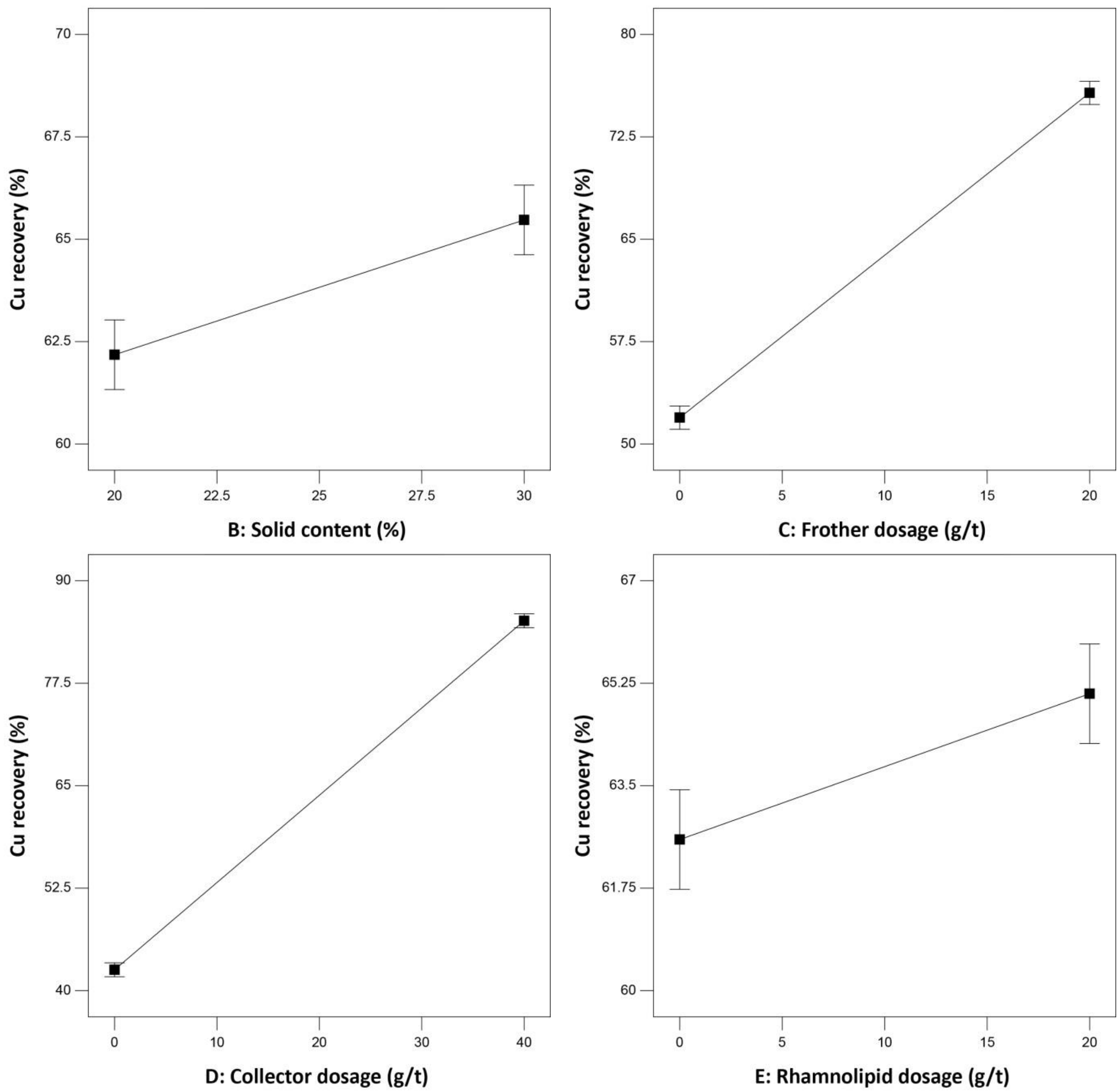

Fig. 6. Main effect plots showing the influence of operating variables on copper recovery

The effect of frother concentration on the entrainment phenomenon can be verified by referring to the plot of its interaction with collector concentration. So that in the absence of the collector, increasing the concentration of frother has greatly increased the recovery, while with the significant growth of the effect of the collector at high concentrations, the effect of the frother dosage has decreased significantly. Increasing the concentration of the collector also increases the recovery due to the increase of the non-selective hydrophobicity of gangue, especially at low pH values (interaction between the concentration of the collector and the pH of the pulp in Fig. 7). However, this effect decreases slightly with increasing particle size (interaction of collector concentration and particle size in Fig. 7).

As seen in Fig. 6, the effect of rhamnolipid concentration on recovery is incremental. As mentioned earlier, the effect of rhamnolipid can be attributed to two possibilities, i.e., being ineffective on copper minerals and/or interaction with gangue minerals, as well as increasing the rate of entrainment due to high foamability, both of which increase non-selective recovery of gangue minerals. The first effect can be observed in the interaction of rhamnolipid concentration and solid percentage with a similar interpretation to that of the interaction effect of frother concentration with solid percentage. Another noteworthy point is the very strong and non-linear effect of rhamnolipid and pulp pH, so that with increasing pH, the effect of rhamnolipid decreases drastically. Several research works have shown that with the increase in pH due to the increase in the activity of hydroxyl ions in the solution and therefore,

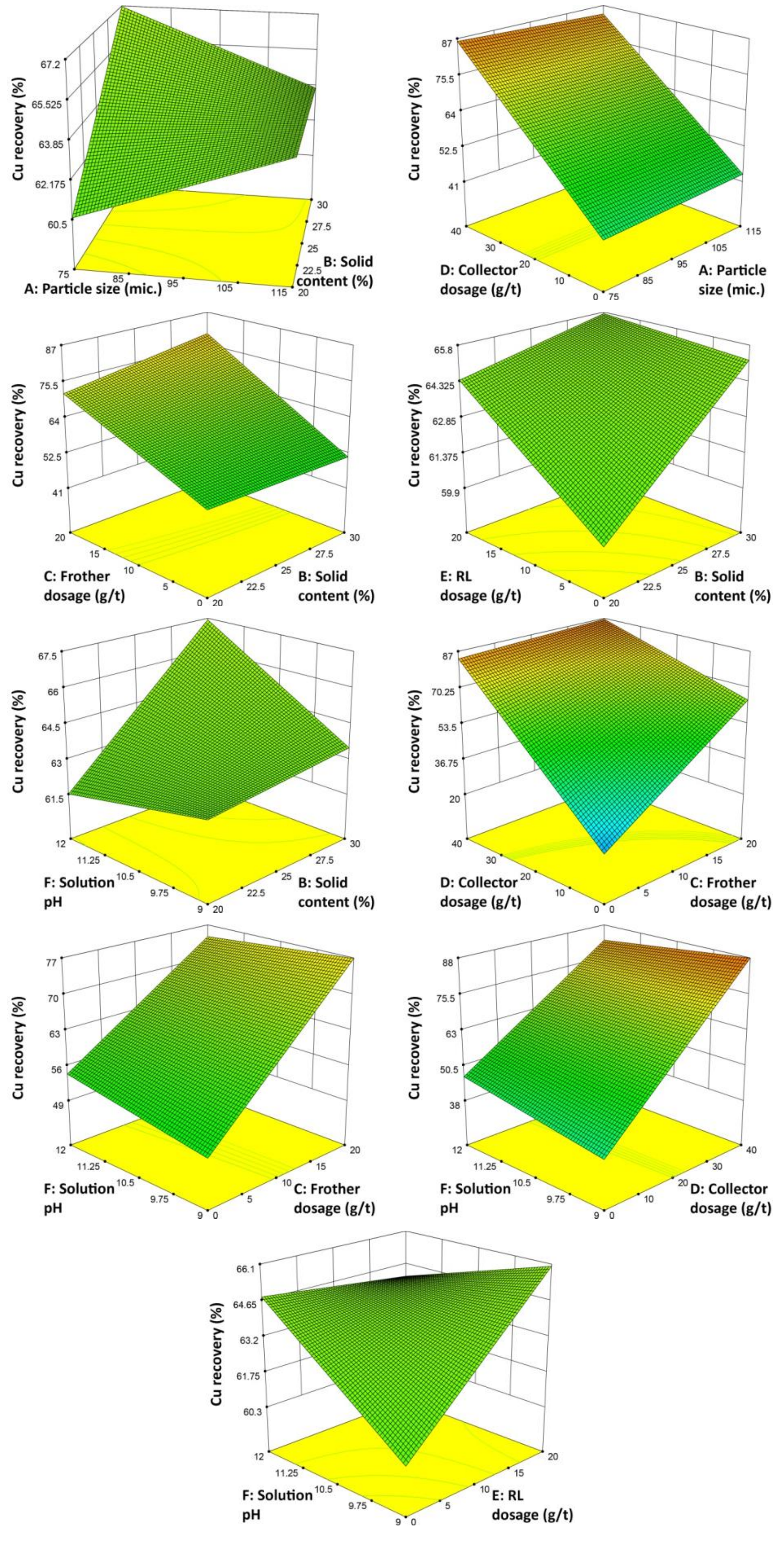

Fig. 7. Significant interaction effects among operating variables on copper recovery

the decrease in the activity of oxidryl functional groups in the rhamnolipid structure, the rate of rhamnolipid micelle formation increases and its effectiveness (both physical and chemical) reduces (Boveiri et al., 2019; Asgari et al., 2022). The interesting point in these studies is that despite the structural similarities, no interaction was observed between the flotation reagents and rhamnolipid.

3.4.4. Interaction between RL and pure copper minerals

The FTIR spectra of pure chalcopyrite and chalcocite minerals, both prior to and after exposure to rhamnolipid, were analyzed to investigate potential interactions between the minerals and the biosurfactant. Results are presented in Fig. 8. In the pristine mineral samples, characteristic bands associated with sulfide minerals were observed, including metal-sulfur vibrations and sulfur-hydrogen groups. Notably, no significant changes were observed in the FTIR spectra after the introduction of rhamnolipid. There were no new bands or shifts in the bands associated with their surface functional groups. To be more specific, there were no alterations in metal-sulfur vibrations, which typically occur in the lower wavenumber region (below 1500 cm^{-1}). This suggests that neither the chalcocite nor the chalcopyrite samples adsorbed rhamnolipid. The spectra retained their initial features, suggesting that the rhamnolipid samples had no discernible impact on the surface chemistry of chalcocite and chalcopyrite. This outcome implies a lack of substantial chemical alterations or mineral-biosurfactant interactions, highlighting the chemical stability of the minerals when exposed to rhamnolipid. These results are in good agreement with metallurgical findings. Thus, the effect of rhamnolipid can be ascribed to its potential interaction between gangue minerals and/or powerful frothing properties.

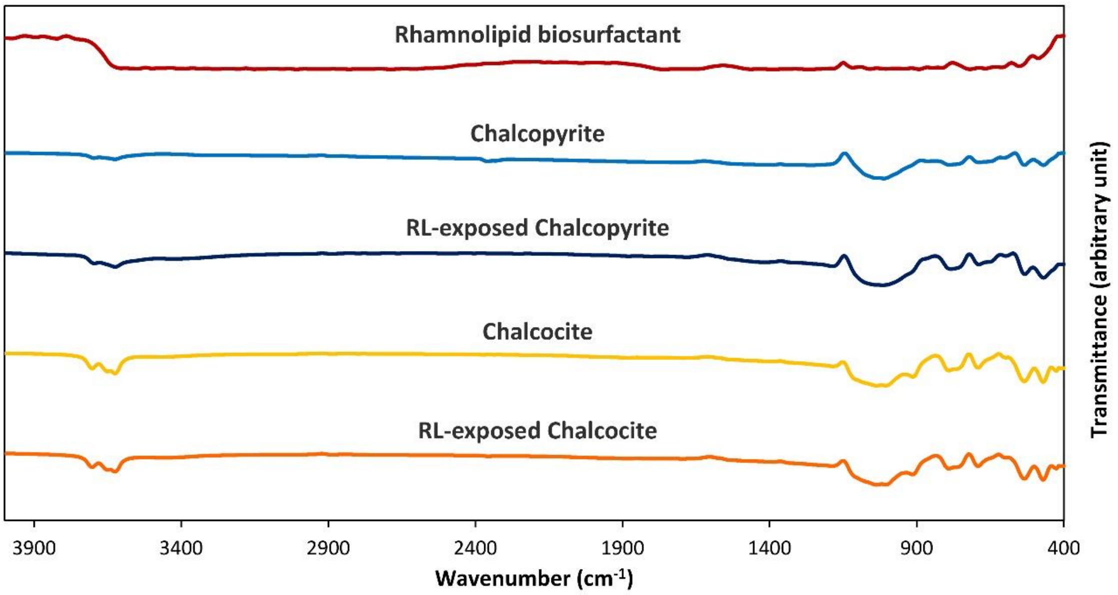

Fig. 8. FTIR spectra of pure copper minerals and rhamnolipid polluted mineral particles

4. Conclusions

The metallurgical response of a copper ore flotation in the presence of rhamnolipid biosurfactant was assessed following a detailed experimental design. The effect of some important operational parameters namely the particle size, solid content, and pH of feed pulp as well as the concentration of flotation reagents and rhamnolipid biosurfactant were investigated. The surface activity of biosurfactant was also evaluated using a set of DOE-based tests. The key remarks emerged from this research work can be summarized as follows:

- Surface activity of the RL was negatively influenced by solution pH and the presence of electrolytes. As pH was increased, the surface tension of the RL-bearing solution was decreased by about 20 units. However, the effect of electrolyte type was directly originated from their ionic activity in the aqueous environment.

- ANOVA results revealed that the effects of operating parameters on flotation responses, i.e., copper grade and recovery, were significant. Moreover, many interactional effects were found to be meaningful when interpreting the individual effect of each parameter.
- Generally speaking, the effect of conventional operational parameters on grade and recovery was opposite and mostly follows the route reported in many investigations. However, expirations were found in regard to the effect of particle size.
- Rhamnolipid addition showed a negative impact on grade (about 0.5% decrease) and accordingly, a positive effect on recovery (about 3% increase). The effect was ascribed partially to potential interaction between RL and the surface of gangue minerals, and in part, to the high foamability of the RL.
- Investigating the functional groups participated in the system of RL and pure copper minerals, i.e., chalcopyrite and chalcocite, using FTIR analyses showed that there was no interaction between RL molecules and the surface of minerals.

It should be noted that detailed investigations have been performed on the effect of RL on the metallurgical response of gangue minerals which will be presented in the second part of this paper.

Acknowledgments

Authors would like to acknowledge technical support from Sarcheshmeh Copper Complex (Rafsanjan, Iran) and the collaboration of Dr. Yarahamdi for his kind comments. The authors would like to express their sincere gratitude to Prof. Juan Yianatos`s significant scientific contributions to developing our understanding of mineral processing concepts from several aspects.

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