Efficient chromium removal from aqueous solutions by precipitate flotation using rhamnolipid biosurfactants

Vahideh Shojaei, Hamid Khoshdast

Department of Mining Engineering, Higher Education Complex of Zarand, Zarand, Iran

Corresponding author: shojaei.vahideh@gmail.com (Vahideh Shojaei)

Abstract: In the present research study, the efficient removal of hexavalent chromium from aqueous solutions by precipitate flotation method was investigated. The experiments were carried out with the use of ferrous sulfate as a precipitating agent for chromium and rhamnolipid bio surfactant (RL) as a precipitate collector. The effects of rhamnolipid and co-precipitate concentrations, aeration rate, solution pH, and salt addition on the chromium removal were studied using a full factorial design. The chromium removal and water recovery to foam products were analyzed as process responses. Statistical analyses showed that the effects of all factors on the chromium removal followed a non-linear trend with a peak at the middle level. After the process optimization, the maximum chromium removal of $96.75\pm0.3\%$ was obtained at pH value of 8, RL/Cr ratio of 0.01, Fe/Cr ratio of 3, and aeration rate of 50 cm^3/min. Addition of salt with different cationic and anionic groups negatively influenced the removal efficiency. Kinetic studies suggested that the process of chromium removal by the precipitate flotation followed the first-order process with a rate constant of about 0.018 sec^{-1}. Given the good removal capacity and kinetics, rhamnolipid biosurfactants can be a promising environmental-friendly bio collector for the removal of chromium ions from aqueous solutions.

Keywords: chromium, rhamnolipid biosurfactant, precipitate flotation, wastewater, kinetics

1. Introduction

The generation of effluents containing valuable metals continues to increase while the reserves in ores of economically recoverable metals decrease. Chromium ion, for example, is considered as a very toxic water pollutant. Chemicals industries, leather tanning, cement industries, dyes, electroplating, steelworks and other metals alloys, photographic material, and corrosive paints produce high content chromium wastes (Medina et al., 2005). Currently, numerous treatment methods and techniques have been developed in order to remove chromium ions from aqueous solutions. The most widely used method is foam flotation in which metal removal process is carried out based on reaction between chromium ions and an oppositely charged ionic surface-active reagent (collecting surfactant) (Ehrampoush et al., 2011). The ability of synthetic surfactants to bind with heavy metal ions has been reported by researchers who have conducted experiments involving water and wastewater treatment with different synthetic surfactants (Monem El Zeftawy and Mulligan, 2011).

Today, it is well known that some microorganisms are able to produce surface-active compounds that can vary in their chemical structure and size. Since the last decade of the past century, the concern about environmental protection has led to an increased interest in the production and properties of these natural products. These surfactants, often called microbial surfactants or biosurfactants, are considered nowadays as potential substitutes of synthetic surfactants from petrochemical origin. The main advantages of biosurfactants over their chemical counterparts are their lower toxicity, better environmental compatibility, biodegradability, and effectiveness in a wide range of temperatures and pH. Last, but not least, their production by renewable resources provides a further impetus for serious consideration of biological surfactants as possible alternatives of the commonly used industrial

chemicals (Cohen and Exerowa, 2007; Vilinska et al., 2008). Due to the high binding capacity with metal ions, the biosurfactants are widely used for the remediation of soils contaminated by heavy metals such as Zn and Cu by surfactant (Mulligan et al., 1999), Pb (Hong et al., 2000), and Cd and Zn (Hong et al., 2002) by saponin, Cd and Ni by rhamnolipid (Mulligan and Wang, 2006), Cu, Zn, and of Ni by rhamnolipid (Dahrazma and Mulligan, 2007), Cr, Cd, and Cu by di-rhamnolipid (Juwarkar et al., 2008), Cd, Co, Pb, Ni, Cu, and Zn by surfactin and fengycin mixture (Singh and Cameotra, 2013), and Cu, Cd, Pb, and Cr by rhamnolipid (Chen et al., 2017). The removal efficiency values reported in these studies varied from 13% to 100% depending on bio surfactant dosage and other operating parameters.

Although there is rather a large body of literature regarding the use of synthetic collectors in foam separation of heavy metal ions such as Cr(VI) and Cr(III) bi-mixture (Zouboulis and Goetz, 1991), Zn and Ag (Charewicz et al., 1999), Zn and Cd (Kozlowski et al., 2000), Cu, Ca, and Pb (Liu and Doyle, 2001), Zn and Cd (Ulewicz and Walkowiak, 2003), Cu, Zn, Cr, and Ag (Polat and Erdogan, 2007), and Cd (Ehrampoush et al., 2011) with the removals varying from 40% to 90%, few scientific researches, which apply biosurfactants have been found (Zouboulis et al., 2003; Bodagh et al., 2013). Precipitate flotation is an efficient process, in which heavy metal ions are first precipitated using a suitable precipitating agent, and the precipitates are then removed from aqueous solution using an appropriate collector. The present study focuses on the efficient application of rhamnolipid bio surfactant as a metallic precipitate collector for the precipitate flotation to remove hexavalent chromium ions from aqueous solution. The main and interaction effects of factors influencing the removal efficiency, including pH, rhamnolipid concentration, precipitant concentration, aeration rate, contact time, and salt type and concentration were investigated using a systematic experimental design. The flotation modeling, optimization, and kinetics were also evaluated.

2. Materials and methods

2.1 Reagents

Rhamnolipid (RL), which is a biologically produced surface-active glycolipid, was examined as an alternative collector to common chemical surfactants. This bio surfactant was prepared at the National Institute of Genetic Engineering and Biotechnology (Tehran, Iran). Details on structure and surface activity of the used bio surfactant are available in our previous works (Khoshdast et al., 2011; 2012). It is shown that rhamnolipid biosurfactants have been powerful frothing characteristics. Khoshdast and Shojaei (2012) compared the dynamic frothability index (DFI) of rhamnolipid biosurfactants with conventional industrial frothers such as DF-250 and methyl isobutyl carbinol (MIBC). It was shown that RL with DFI value of 597091 $s.mol.dm^{-3}$ produced more elastic and stable foams than DF-250 (DFI 208000 $s.mol.dm^{-3}$) and MIBC (DFI 37000 $s.mol.dm^{-3}$) frothers. Therefore, no further frother was added to the flotation system as preliminary studies showed that RL produced appropriate foam volume. The following chemicals, purchased from Merck as analytical grade, were also used: Sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$) as a metal species source; ferrous sulfate ($FeSO_4.7H_2O$) as a co-precipitant; hydrochloric acid (HCl) and sodium hydroxide (NaOH) as solution pH-regulators; and sodium chloride (NaCl), calcium chloride ($CaCl_2$), calcium carbonate ($CaCO_3$), and calcium sulfate ($CaSO_4.2H_2O$) as electrolyte sources.

2.2 Experimental design

Different types of experimental designs have been developed by statisticians. The choice of appropriate design depends on the objectives of investigations and the number of parameters to be investigated. In this study, a full factorial design was selected. Full factorial is a suitable design technique which is commonly used for process analysis and modeling (Obeng et al., 2005; Aghajani et al., 2013). Such a statistical design helps researchers to generate mathematical equations that describe how studied variables affect the target response(s). Additionally, full factorial design allows us to estimate interaction effects, and nonlinear relations between variables and response if exist (Montgomery, 2001). The precipitate flotation experiments were conducted based on a double replicated 2-level full factorial experimental design to evaluate the effects of the initial solution pH, the rhamnolipid to the chromium ratio (RL/Cr), the co-precipitant to the chromium ratio (Fe/Cr), and aeration rate (Q). To investigate

possible non-linear effects, a center point with four replications was also considered at levels with middle values. The chromium removal and water recovery were treated as responses. The levels of variables studied are presented in Table 1.

2.3 Precipitate flotation tests

The precipitate flotation tests were carried out in a 100 cm in height acrylic column cell with an internal diameter of 5 cm. Bubbles were generated carefully by sparging air through a sintered glass frit (10–15 µm, porosity 4), installed at the base of the column, at a controlled pressure of 1±0.05 atm. The air compressor was supported with an in-line air filter (0.2-0.4 µm) to avoid sparger blockage and a manometer (Dwyner model RMA-12-SSV, USA) to control airflow at required rates. A port 7 cm above the sparger was used for sampling.

For each test, 1000 cm³ of initial solution containing 50 ppm chromium and requisite amounts of FeSO₄ and rhamnolipid was prepared using double distilled water. After pH adjustment, the solution was mixed with a magnetic stirrer for 20 min to ensure consistent mixing of all reagents. Bubble generation was begun just after the solution was introduced into the column, filling it with bubbles. The movement of the bubbles upward was turbulent. Immediately, a foam layer formed at the top of the solution, creating a distinct interface. Initially, the flotation time was of 5 min with the solution samples taken at six 15 sec and seven 30 sec periods. Before each sampling, about 3 cm³ of solution was drained from the sampling port to withdraw an actual sample. To minimize entrainment of air bubble, samples were withdrawn very slowly. All experiments were conducted at room temperature, about 25–27°C. Effect of salt addition on separation efficiency was also studied after the optimum conditions on the maximum chromium removal were determined.

2.4   Analysis methods

The chromium content of the samples taken from the bulk solution was measured by an atomic absorption instrument (Varian model SperctAA 220, Mulgrave, Victoria, Australia). The removal efficiency of ion flotation, R_{Cr} was defined in Eq. 1 (Yuan et al., 2008):

$$R_{Cr}, \% = \frac{(C_0 - C_t)V_{wt}}{C_0 V_{w0}} \times 100 \tag{1}$$

where C_0 is the initial concentration of heavy metal ion, C_t the concentration after t minute, V_{w0} the initial volume of solution, and V_{wt} is the volume of solution after t minute.

As seen in Eq. (1), liquid removal to the froth zone plays a significant role in removal determination. The recovery of water depends on the stability of the froth phase (Engelbrecht and Woodburn, 1975). The stability of the froth phase is determined by the stability of liquid lamellae between gas bubbles, which in turn affects the froth water content (Neethling and Cilliers, 2002). Therefore, the water recovery of the discharged froth can be used as a parameter to evaluate the stability of a froth zone (Ekmekci et al., 2006). The water recovery was calculated using Eq. (2):

$$R_w, \% = \frac{H_0 - H_f}{H_0} \times 100 \tag{2}$$

where H_0 and H_f are initial and final solution heights in the column, respectively.

3   Results and discussion

3.1   Statistical analysis of experimental design

According to the basic 2^4 full factorial design, 16 runs are needed for a non-replicated case. For the present case involving two replications at center points, the total number of tests is 36. Table 1 shows variables entered in their actual form as an input data along with Cr removals (R_{Cr}, %) and water removal (R_w, %) obtained for each test.

In general, the experimental data obtained from the full factorial design experiment can be analysed by nonlinear regression procedure using the following multi-variable equation:

$$y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \varepsilon \tag{3}$$

where y is the predicted response, b_0 represents the constant coefficient, b_i is the linear coefficients, b_{ij} denotes the nonlinear coefficients, x_i and x_j are coded values of the independent process variables, and ε is the residual error. The values of the coefficients were calculated by using Design Expert v.7 (DX7) software. The best fitted model equation was obtained for Cr removal as follows:

$$\text{Chromium Removal (\%)} = 79.11 + 1.86A + 3.03B + 8.05C - 2.19D - 5.94AB + 3.27AC$$
$$+ 1.64BC + 1.50BD - 1.58CD - 2.05ABC - 3.98ABD \tag{4}$$

and for water recovery as below:

$$\text{Water Recovery (\%)} = 3.96 + 1.82A + 1.89B + 0.38C + 1.65D + 1.01AB + 1.04AD$$
$$+ 1.65BD + 0.99ABD \tag{5}$$

where parameters are in the coded form. Model Eqs. (4) and (5) were used to evaluate the influence on the flotation variables on Cr removal and water recovery. Analysis of Variance (ANOVA) was performed to assess significance of the models. ANOVA results for the regression models suggested that both models were highly significant, as was evident from Fisher's F-test (F model = 102.38 and 63.37) with a very low probability value (p model < 0.0001). Significance of each variable was also determined by p-values. "Prob > F" values of less than 0.05 (for confidence interval of 95%) indicate that model terms are significant. As indicated by ANOVA, all the single effects were significant terms for both Cr removal and water recovery. In addition, the significant curvature term means that all the factors have nonlinear effects on responses. Normal probability plot of the residuals is a useful tool which can be used to detect the normal distribution and independency of model errors and the homogeneity of the error variance (Yetilmezsoy et al., 2009). Normal probability of the residuals for Cr removal presented in Fig. 1(a) showed that almost no serious violation of the assumptions underlying the analyses, which confirmed normality assumptions and independence of the residuals. All of above considerations confirmed the adequacy of the developed relationship. A high value of R^2 (98%) indicates high correlation between the measured and predicted values of the response. Moreover, a closely high value of the adjusted correlation coefficient (Adj R^2 = 97.04%) also shows high significance for the model; also, total variation of about 97% for Cr removal was attributed to the independent variables and only about 3% of total variation could not be explained by developed model. This fact was also confirmed from the predicted versus observed values plot for Cr removal in Fig. 1(b). The Pred R^2 was 94.93%, implying that it could explain variability in predicting new observations. This was in reasonable agreement with the Adj R^2 of 97.04%. Adeq precision shows the signal to noise ratio; a ratio of greater than 4 is a desirable value (Montgomery, 2001). In this investigation, the ratio was 29.09, which indicates an adequate signal. The model could be used to navigate the design space. In the case of water recovery, a same model description can also be presented and normal probability and prediction plots shown in Figs. 2(a) and (b), respectively.
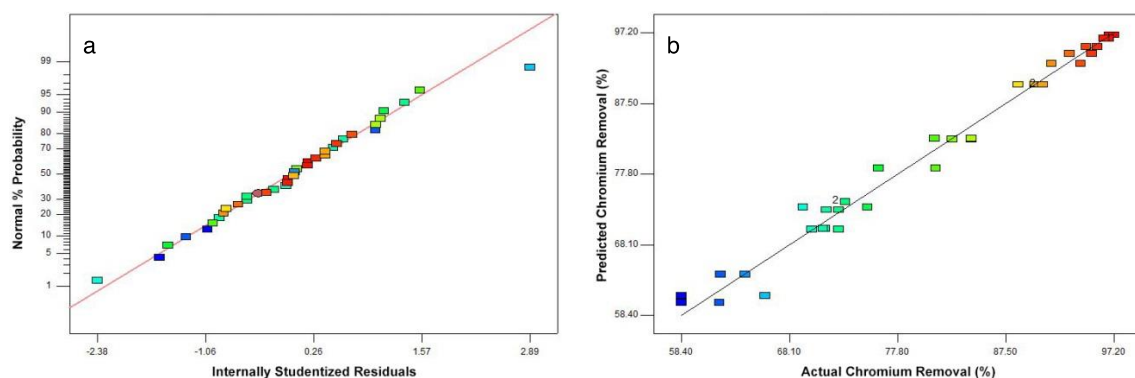

Fig. 1. Normal probability plot of the residuals (a) and relation between observed and predicted chromium removal values (b)
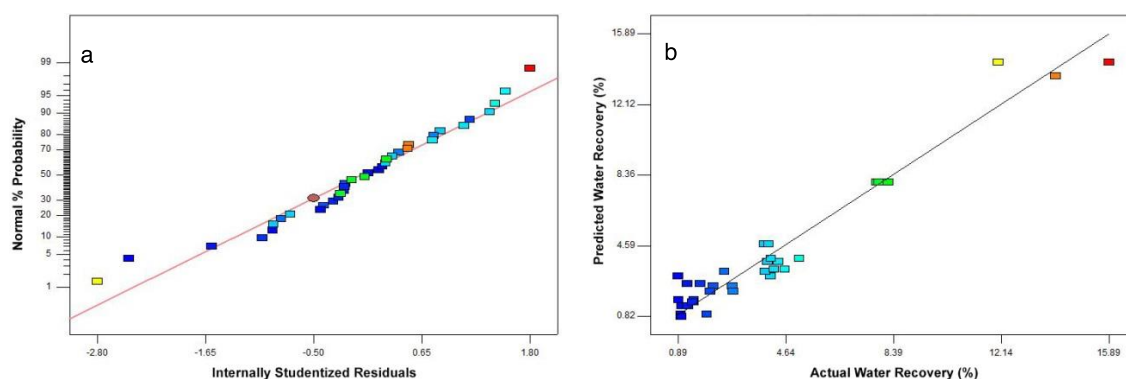
Fig. 2. Normal probability plot of the residuals (a) and relation between observed and predicted water recovery values (b)

Table 1. Process variables for 2^4 full factorial design and experimental results

Run	A: pH	B: RL/Cr ratio	C: Fe/Cr ratio	D: Aeration rate (cm³/min)	Cr Removal (%)		Water recovery (%)	
					R. 1	R. 2	R. 1	R. 2
1	5	0.01	3.0	50	76.1	81.2	0.90	1.44
2	5	0.01	1.5	200	65.9	58.4	0.98	1.01
3	5	0.01	3.0	200	61.8	58.4	1.44	1.39
4	5	0.01	1.5	50	75.1	69.3	0.98	1.89
5	5	0.1	3.0	50	94.2	91.6	2.01	2.80
6	5	0.1	1.5	200	82.7	84.4	4.12	5.10
7	5	0.1	3.0	200	96.3	96.7	4.04	3.89
8	5	0.1	1.5	50	72.5	71.4	1.23	1.02
9	8	0.01	3.0	50	96.8	97.2	3.92	2.50
10	8	0.01	1.5	200	73.1	73.1	1.21	1.66
11	8	0.01	3.0	200	95.2	93.2	4.23	4.60
12	8	0.01	1.5	50	71.1	71.3	2.11	2.78
13	8	0.1	3.0	50	94.7	95.7	4.37	4.01
14	8	0.1	1.5	200	64.1	61.9	14.04	14.03
15	8	0.1	3.0	200	81.1	84.4	15.89	12.03
16	8	0.1	1.5	50	72.5	70.1	4.11	0.89
17	6.5	0.06	2.25	125	88.6	90.1	7.79	7.89
18	6.5	0.06	2.25	125	90.8	90.8	8.01	8.21

3.2 Effect of variables on Cr(VI) removal

The individual effect of operating variables on process response(s) can be evaluated using main plots in which the response variation is drawn for variables' levels considered in experimental design. Design Expert software uses, as default, the developed prediction models (Eqs. (4) and (5)) to calculate the response values for variables varying within their experimental levels (three levels in this study, Table 1) while other variables are maintained at their mid-levels. The following discussions are based on main plots directly prepared by DX software.

3.3 Effect of solution pH

Fig. 3(a) shows the effect of initial solution pH on the chromium removal. As seen from Fig. 3(a), Cr removal increased up to middle level of pH and then decreased. The surface activity of rhamnolipids

was directly affected by the pH of the solution. Therefore, the degree of dissociation of the rhamnolipid molecules, associated with pH, controlled the repulsion forces between the rhamnolipid molecules, and hence the compaction of the monolayer at bubble surfaces. In addition, the elasticity is inversely proportional to the compressibility of the rhamnolipid. Ozdemir et al. (2004) showed that rhamnolipid molecules at acidic environment are more surface active due to the increase of electrostatic repulsion forces on rhamnolipid head groups. Therefore, RL molecules at more acidic conditions can form a more compact monolayer in the air/water interface. However, the higher compaction on the surface film causes a more rigid foam film, decreasing the foam stability slightly. Effect of pH on the water recovery, as a measure of foam stability, is shown in Fig. 3(b). A more rigid foam film means a less elastic film which disrupts more readily as it expands under air flow. The effect of alkaline pH can be attributed to electrolytic effect of sodium cations dissociated from NaOH used as pH-regulator, as will be discussed later.

3.4 Effect of rhamnolipid concentration

The effect of rhamnolipid concentration on the chromium removal and water recovery is shown in Fig. 3. Fig. 3(c) shows a non-linear trend in removal efficiency by rhamnolipid concentration with a maximum value at the mid-point. In the present study, rhamnolipid bio surfactant acts as the collector for collecting chromium from the solution. Thus, as the collector concentration increases, more chromium precipitates will attach to rising bubbles loaded by rhamnolipid molecules. In addition, froth stability increases by rhamnolipid concentration due to the increase in liquid film elasticity of bubbles (Fig. 3(d)) (Khoshdast et al., 2012). Higher froth stability lower coalescence of bubble and consequently, lower drop-back of precipitates to the solution. The removal efficiency decreased at high level of rhamnolipid concentration. Mass concentration values corresponding to low, mid, and high level of rhamnolipid concentrations are 4, 24.4, and 44.4 ppm, respectively. The critical micelle concentration of the used rhamnolipid product was reported to be 10.1 ppm (Khoshdast et al., 2011). The formation of micelle in the solution prevents individual rhamnolipidic anions to adsorb at bubble surfaces which this, in turn, decreases chromium removal using bubbles. In addition, the suppression of the species removal for raised collector concentrations can be due to competition between coligand-collector complex and free ion collectors for a place on the surface of the bubble (Pinfold, 1972).

3.5 Effect of FeSO₄ concentration

Fig. 3 shows the effect of precipitant concentration on chromium removal and water recovery. There are a number of studies on the reduction mechanism of hexavalent to trivalent chromium by ferrous salts (Eary and Rai, 1989; Fendorf and Li, 1996; Buerge and Hug, 1997; Sedlak and Chan, 1997; Li et al., 2009; Døssing et al., 2011). At neutral condition, the chromium (VI) reduction occurs as follows:

$$CrO_4^{2-} + 3Fe^{2+} + 4OH^- \leftrightarrow Cr(III)OOH_{(s)} + 3Fe(III)OOH_{(s)} \tag{6}$$
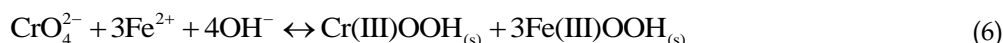
Cr(III)OOH and Fe(III)OOH are then dissociated into hydroxyl ions and monovalent oxygenated complexes of Cr(III)O⁺ and Fe(III)O⁺ which interact with rhamnolipid anions and are removed from the column by rising bubbles. As seen in Fig. 3(e), the removal efficiency increases by increasing of Fe/Cr ratio from 1.5 to 2.25 and then approaches to a relatively constant trend at ratio 3 which is corresponding to the optimum stoichiometric ratio of Fe(II) to Cr(VI) as shown in Eq. (10). The fairly decrease of chromium removal at Fe/Cr ratio of 3 can be ascribed to the competitive adsorption of Cr(III) and Fe(III) complexes by rhamnolipid anions. In addition, free Fe(II) cations may directly interact with rhamnolipid and decrease the froth stability, i.e. water recovery in Fig. 3(f), through electrolytic effect. This, in turn, affects the removal process in a negative manner as will be discussed later.

3.6 Effect of aeration rate

The stability of foams can be described in terms of thin liquid film between bubbles in foam phase. Foam formation is a dynamic phenomenon and caused by monomer surfactant molecules. Therefore, the thin liquid film characteristics of rhamnolipids molecules adsorbed at the bubble surface determine the foamability of rhamnolipid adsorption layer. The elasticity must be adequately low to allow expansion

of the interface during foam formation; and it should be high enough to maintain the rigidity which is vital for the stabilization of the foam. The effect of aeration rate on chromium removal and water recovery is shown in Fig. 3. The removal efficiency is improved by increasing the air flow rate since the effective carrying capacity of bubbles increases due to the increase of bubble density (number of bubbles per unit volume of solution). Below the optimum flow rate, foam formation collapses due to the resistance of the surface film to expansion. The monolayer elasticity as the main characteristic of the liquid film is responsible for this behaviour. At the highest air flow rate the removal efficiency decreases because of the foam instability and rupture causing lower surface area to carry the chromium precipitates.
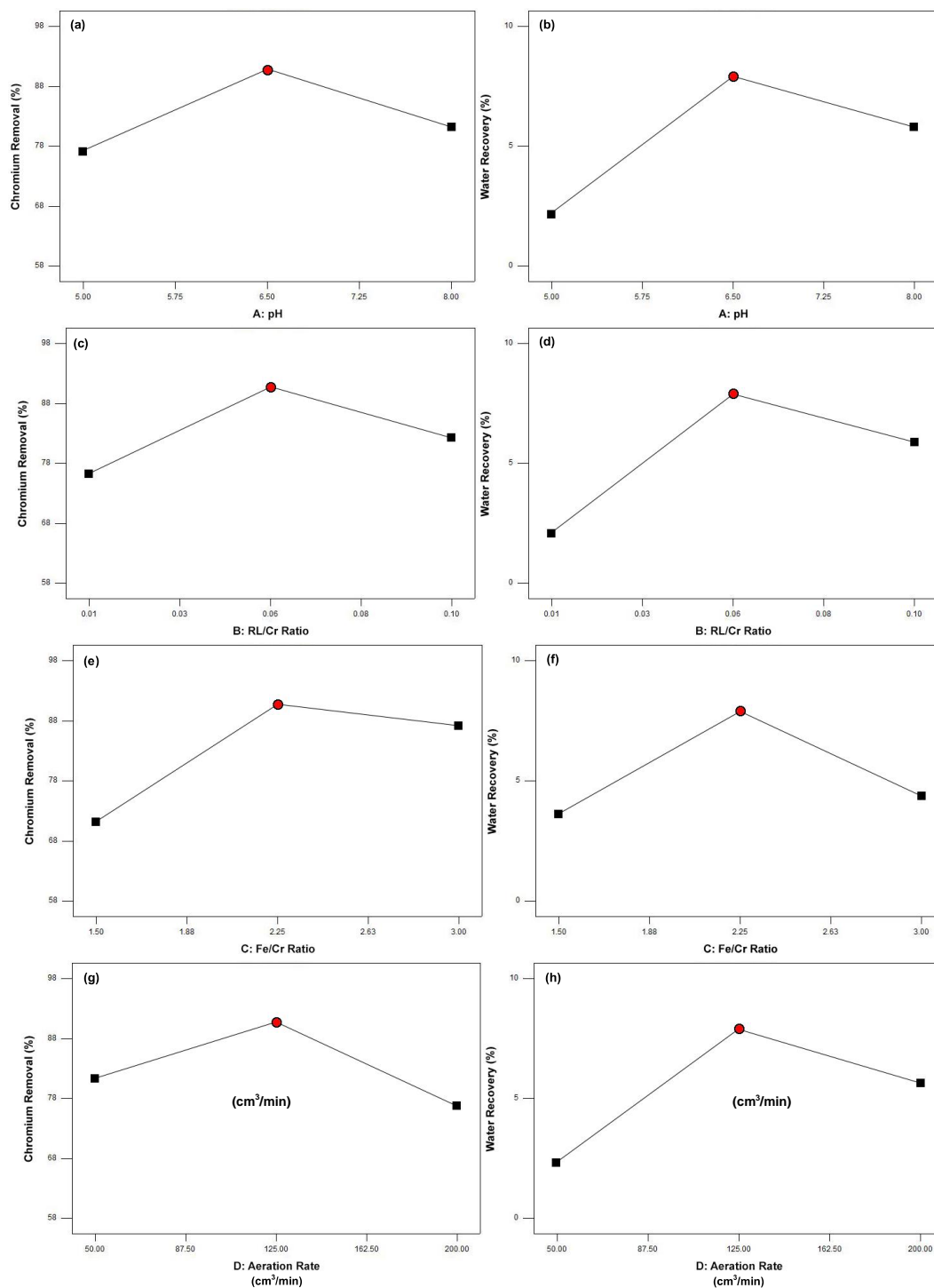

Fig. 3. Effect of (a) pH (b) RL/Cr ratio (c) Fe/Cr ratio (d) aeration rate on chromium removal and water recovery

3.7 Analysis of interaction effects

The three-dimensional (3D) response plots of the model response vs. two independent variables varying within their experimental levels while maintaining other variables at their mid-levels can give useful information about their relationships (Liu and Chiou, 2005). Therefore, in order to gain better understanding of individual effects of the studied operating variables and their corresponding interaction effects on the other variables, 3D response plots for the chromium removal were constructed based on the nonlinear model proposed by DX7 software. Since the model for this study had four independent variables, two variables were held constant at their mid-level for each plot. The significant double effects were interactions between pH and RL/Cr ratio (AB) and Fe/Cr ratio (AC), RL/Cr ratio and Fe/Cr ratio (BC) and aeration rate (BD), and Fe/Cr ratio and aeration rate (CD). The corresponding 3D surface plots are visualized in Fig. 4. The key point emerged from response plots is that the effect of RL/Cr ratio depends on the effect of other factors such that at the lower level of each factor, Cr removal does not change by RL/Cr ratio. This implies that maximum Cr removal can even be obtained at lower RL/Cr ratios. In the case of other factors, Fig. 4 reveals that maximum Cr removal may be obtained when all other factors take values around their mid-level.
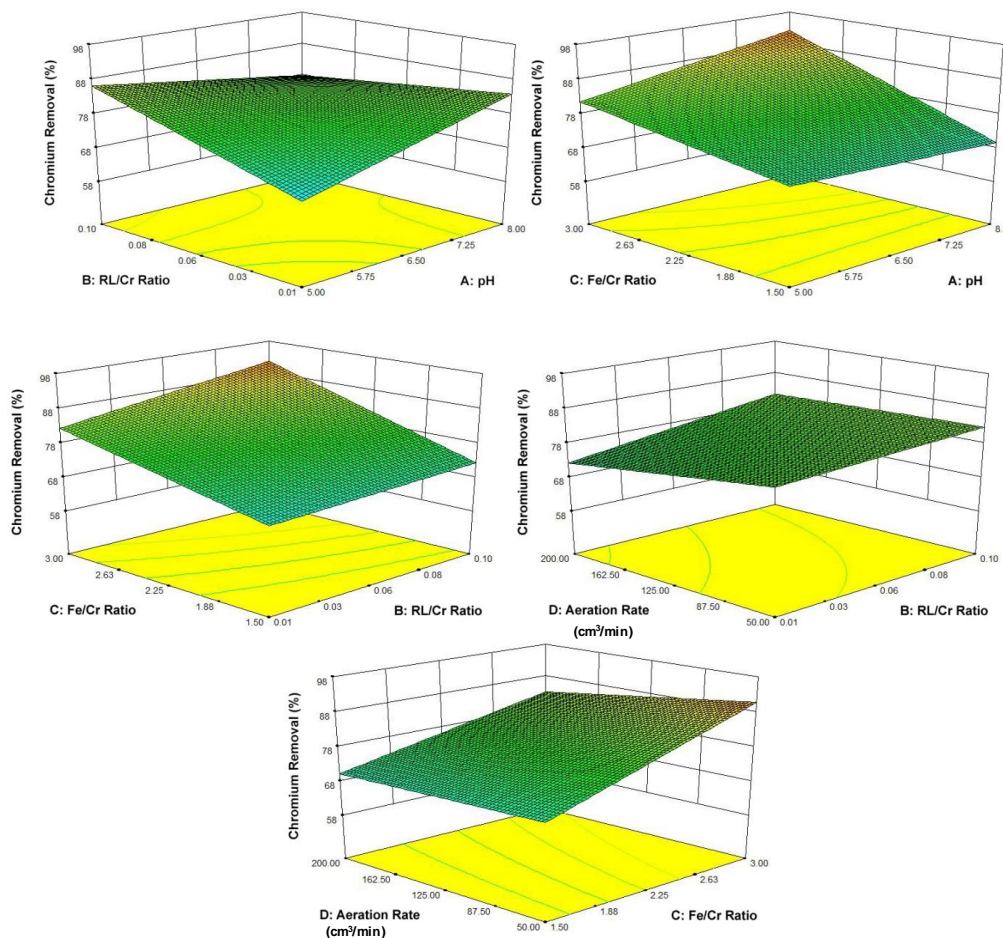

Fig. 4. 3D response plots showing the interaction effects of process variables on chromium removal

3.8 Process optimization

Design Expert is a powerful tool for prediction of optimal conditions under which maximum response value would be obtained. The software uses the predication model developed on the basis of statistical analysis and then, presents a list of optimal conditions with their corresponding response values. After setting the value limits for all model parameters, DX7 suggested the optimal conditions sets with maximum Cr removal of about 97% as shown in Table 2. As seen from Table 2, all suggested conditions are actually the same. In addition, these conditions are those used for conducting runs 6 and 24 in Table

1. To confirm the accuracy of DX7 prediction, two new experiments were conducted under these conditions and Cr removals of 96.4% and 96.6% were obtained. Thus, the optimum conditions to achieve maximum Cr removal would be pH value 8, RL/Cr ratio 0.01, Fe/Cr ratio 3, and aeration rate of 50 cm³/min, i.e. the levels predicted using 3D response plots.

Table 2. Optimal conditions suggested by DX7 to achieve maximum chromium removal

Number	pH	RL/Cr ratio	Fe/Cr ratio	Aeration rate (cm³/min)	Predicted Cr Removal (%)
1	8	0.01	3	50	96.89375
2	7.999998	0.010169	2.999753	50.63992	96.87511
3	7.99329	0.010329	2.993174	50.00007	96.72605
4	7.963658	0.01	3	52.09588	96.63359
5	7.932297	0.010001	2.999105	50.0007	96.46585

3.9 Effect of salt addition

Effect of salt addition on the chromium removal was also investigated by adding different concentrations of various types of Na and Ca salts under optimal conditions. Fig. 5 shows the effects of type and concentration of salt on chromium removal. As seen in Fig. 5, the Cr removal decreases in the presence of all types of salt added. The effect of salt on Cr flotation behavior can be explained for the case of both cationic and anionic effects. The anionic character of the rhamnolipid molecules is from its carboxyl group. The majority of the carboxyl groups of RL are dissociated to form negatively charged carboxylate groups in the absence of an electrolyte. With the addition of an electrolyte, the ionic strength of the solution increases and the carboxylate groups are shielded by a diffuse layer of counterions. Therefore, the addition of electrolytes neutralizes the head groups by reducing head repulsion and causes more compact foam films (i.e. surfactant molecules come into the vicinity of each other) (Helvaci et al., 2004). Compaction of RL molecular monolayer at a bubble surface means a less elastic film which disrupts more readily as it expands under air flow as observed with a similar effect at high acidic condition. The structure of the foam will be then with larger bubbles causing less foam volume and less surface area for interaction with Cr ions. Besides the interaction of RL on the foam film with cations reduces the interaction with Cr ions remarkably. At constant electrolyte concentration, Ca^{2+} cations are able to reduce chromium removal more effectively compared to Na^+ ions. In other words, equal number of double charged Ca^{2+} ions can neutralize higher numbers of carboxylate groups, which consequently, cause more rigid foam films. Salt anions can also decrease the Cr removal by competition with rhamnolipidic anions to adsorb cationic chromium complexes. Such a competitive adsorption is directly influenced by ionic strength of anions. The ionic strengths of various anions, calculated by Ionic Strength Calculator at concentration of $1 \cdot 10^{-3}$ mol/dm³, follow the order of $Cl^- \approx COO^-$ ($5 \cdot 10^{-4}$ mol/dm³) $< CO_3^{2-} \approx SO_4^{2-}$ ($2 \cdot 10^{-3}$ mol/dm³). Therefore, CO_3^{2-} and SO_4^{2-} can interrupt the removal process more effectively compared to Cl^- and COO^- groups. In addition, it can be observed from Fig. 5 that anions with equal ionic strength value yield the relatively same removal efficiency.

3.10 Kinetics study

Flotation kinetic studies the variation of floated concentration according to flotation time. Studies of flotation kinetics are useful for the elucidation of the mechanism of the process, and serve as predictive tools in the implementation of flotation technology. Chemical kinetics principles are used for the modeling of flotation processes, particularly in the formulation of the basic rate equation (Medina et al., 2005):

$$R_t = R_\infty \left(1 - \exp(-kt)\right) \tag{11}$$

where R_t is the chromium removal at time t, R_∞ is the maximum chromium removal at practical time, t is the flotation time, and k is the flotation rate constant. Calculations showed that chromium removal

kinetics is in a good agreement with Eq. (11) with a correlation coefficient (R^2) of 99.88%. The rate constant and R_∞ were also found to be 0.018 sec^{-1} and 96.82%, respectively.
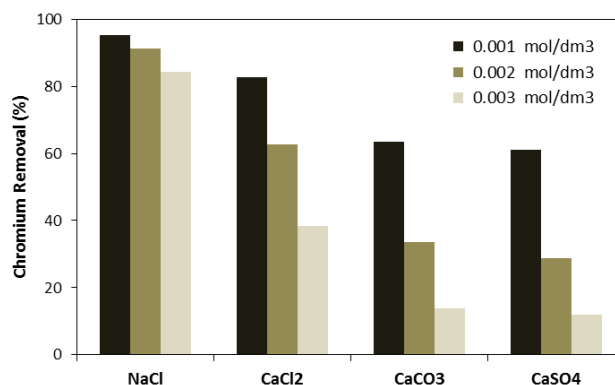

Fig. 5. Effect of salt addition on chromium removal by rhamnolipid aided precipitate flotation

4 Conclusions

The efficient applicability of rhamnolipid bio surfactant as a collector for hexavalent chromium removal from aqueous solution by precipitate flotation was reported. Effects of various operating factors, including aeration rate, rhamnolipid to a chromium ratio, co-precipitate to the chromium ratio, and initial solution pH were found to be significant with respect to chromium removal and water recovery as the process responses. The negative effect in the presence of different types of cations and anions in the solution was also confirmed. The results obtained under the optimum conditions during the study were compared with those reported in literature for both synthetic and microbial collectors and listed in Table 3 which clearly confirms that rhamnolipid can compete with its counterparts in the chromium removal. The superiority of rhamnolipid can be attributed to lower collector and precipitant Fe(II) consumption, which is beneficial from economic point of view. Among various advantages of biosurfactants, environmental compatibility of rhamnolipid can be denoted as its major advantageous over chemical surfactants. More detailed investigations are required to confirm the general applicability of rhamnolipid biosurfactants in heavy metal polluted wastewaters. For example, the bio surfactant uptake is another important factor that should be evaluated to further assess its potential for chromium extraction.

Table 3. Comparison between precipitate flotation results of this study and others reported in literature

Collector	Collector dosage (ppm)	Initial conc. of Cr (ppm)	Co-precipitant and dosage (ppm)	Final conc. of Cr (ppm)	Removal (%)	Reference
Sodium dodecyle sulfate (SDS)	56	100	HSO$^-_3$, 200	16.6	83.4	Grieves and Lee (1971)
	40	5	Fe(III), 100	0.21	95.8	Huang et al. (1982)
	64	5	Al(III), 100	0.14	97.2	Huang et al. (1982)
	60	50	Fe(II), 150	0.24	99.51	Huang et al. (1982)
	60	50	Fe(II), 175	0.09	99.82	Huang et al. (1995)
Surfactin-105[a]	175	50	Fe(III), 600	0.25	99.5	Zouboulis et al. (2003)
Lichenysin-A[a]	250	50	Fe(III), 600	1	98	Zouboulis et al. (2003)
Lichenysin-A[a]	50	50	FeO(OH), 3000	2.5	95	Zouboulis et al. (2003)
Rhamnolipid[a]	0.5	50	Fe(II), 150	0.23	96.75	Present study

[a] biosurfactant

References

AGHAJANI, S.A., SOLTANI, G.A., EBRAHIMZADEH, G.M., SARAFI, A., RAZMIRAD, M., ABDOLLAHI, H., 2013. *Application of response surface methodology and central composite rotatable design for modeling the influence of some operating variables of the lab scale thickener performance*. Int. J. Mining Sci. Technol. 23, 717–724.

BODAGH, A., KHOSHDAST, H., SHARAFI, H., ZAHIRI, H.S., AKBARI NOGHABI, K., 2013. *Removal of cadmium(II) from aqueous solution by ion flotation using rhamnolipid biosurfactant as ion collector*. Ind. Eng. Chem. Res. 52(10), 3910–3917.

BUERGE, I.J., HUG, S.J., 1997. *Kinetics and pH dependence of chromium(VI) reduction by Iron(II)*. Environ. Sci. Technol. 31, 1426–1432.

CHAREWICZ, W.A., HOLOWIECKA, B.A., WALKOWIAK, W., 1999. *Selective flotation of zinc(II) and silver(I) ions from dilute aqueous solutions*. Sep. Sci. Technol. 34(12), 2447–2460.

CHEN, W., QU, Y., XU, Z., HE, F., CHEN, Z., HUANG, S., LI, Y., 2017. *Heavy metal (Cu, Cd, Pb, Cr) washing from river sediment using biosurfactant rhamnolipid*. Environ. Sci. Pollut. R. 24(19), 16344–16350.

COHEN, R., EXEROWA, D., 2007. *Surface forces and properties of foam films from rhamnolipid biosurfactants*. Adv. Colloid Interface. Sci. 134–135, 24–34.

DAHRAZMA, B., MULLIGAN, C.N., 2007. *Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration*. Chemosphere. 69, 705–711.

DOSSING, L.N., DIDERIKSEN, K., STIPP, S.L.S., FREI, R., 2011. *Reduction of hexavalent chromium by ferrous iron: A process of chromium isotope fractionation and its relevance to natural environments*. Chem. Geol. 285, 157–166.

EARY, L.E., RAI, D., 1989. *Kinetics of chromate reduction by ferrous ions derived from hematite and biotite at 25 degrees C*. American J. Sci. 289(2), 180–213.

EHRAMPOUSH, M.H., GHANEIAN, M.T., SALMANI, M.H., DAVOUDI, M., FALLAHZADEH, M.H., 2011. *Selectivity in removal of cadmium (II) from mixed metal effluents using ion flotation*. World Appl. Sci. J. 13(1), 52–59

EKMEKCI, Z., BRADSHAW, D.J., HARRIS, P.J., BUSWELL, M.A., 2006. *Interactive effects of the type of milling media and CuSO4 addition on the flotation part II: froth stability*. Int. J. Miner. Process. 78, 164–174.

ENGELBRECHT, J.A., WOODBURN, E.T., 1975. *The effects of froth height, aeration rate and gas precipitation on flotation*. J. S. Afr. Inst. Min. Metall. 76, 125–132.

FENDORF, S.E., LI, G., 1996. *Kinetics of chromate reduction by ferrous iron*. Environ. Sci. Technol. 30, 1614–1617.

GRIEVES, R.B., LEE, R.W., 1971. *Continuous precipitate flotation of chromium(III) hydroxide*. Ind. Eng. Chem. Process. Des. Develop. 10, 390–395.

HELVACI, S.S., PEKER, S., OZDEMIR, G., 2004. *Effect of electrolytes on the surface behavior of rhamnolipids R1 and R2*. Colloids Surf. B: Biointerfac. 35, 225–233.

HONG, K.J., TOKUNAGA, S., ISHIGAMI, Y., KAJIUCHI, T., 2000. *Extraction of heavy metals from MSW incinerator fly ash using saponins*. Chemosphere 41, 345–352.

HONG, K.J., TOKUNAGA, S., KAJIUCHI, T., 2002. *Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils*. Chemosphere. 49, 379–387.

HUANG, S.D., FANN, C.F., HSIEH, H.S., 1982. *Foam separation of chromium(VI) from aqueous solution*. J. Colloid. Interface Sci. 89(2), 504–513.

HUANG, S.D., LI, H.H., LIN, C.S., 1995. *Adsorbing colloid flotation of heavy metal ions from aqueous*. Environ. Sci. Technol. 29, 1802–1807.

JUWARKAR, A.A., DUBEY, K.V., NAIR, A., SINGH, S.K., 2008. *Bioremediation of multi-metal contaminated soil using biosurfactant − a novel approach*. Indian J. Microbiol. 48(1), 142–146.

KHOSHDAST, H., ABBASI, H., SAM, A., AKBARI NOGHABI, K., 2012. *Frothability and surface behavior of a rhamnolipid biosurfactant produced by Pseudomonas aeruginosa MA01*. Biochem. Eng. J. 64, 127–134.

KHOSHDAST, H., SHOJAEI, V., 2012. *Ash removal from a sample coal by flotation using rhamnolipid biosurfactants*. J. Min. World Express. 1(2), 39–45.

KHOSHDAST, H., SAM, A., VALI, H., AKBARI NOGHABI, K., 2011. *Effect of rhamnolipid biosurfactants on performance of coal and mineral flotation*. Int. Biodeter. Biodeg. 65, 1238–1243.

KOZLOWSKI, C., ULEWICZ, M., WALKOWIAK, W., 2000. *Separation of zinc and cadmium ions from aqueous chloride solutions by ion flotation and liquid membranes*. Physicochem. Probl. Miner. Process. 34, 141–151.

LI, Y., LOW, G.K.C., SCOTT, J.A., AMAL, R., 2009. *The role of iron in hexavalent chromium reduction by municipal landfill leachate*. J. Hazard. Mater. 161, 657–662.

LIU, H.L., CHIOU, Y.R., 2005. *Optimal decolorization efficiency of reactive red 239 by UV/TiO₂ photocatalytic process coupled with response surface methodology*. Chem. Eng. J. 112, 173–179.

LIU, Z., DOYLE, F.M., 2001. *Modeling metal ion removal in alkylsulfate ion flotation systems*. Miner. Metal. Process. 18, 167–171.

MEDINA, B.Y., TOREM, M.L., DE MESQUITA, L.M.S., 2005. *On the kinetics of precipitate flotation of Cr III using sodium dodecylsulfate and ethanol*. Miner. Eng. 18, 225–231.

MONEM EL ZEFTAWY, M.A., MULLIGAN, C.N., 2011. *Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF)*. Sep. Purif. Technol. 77, 120–127.

MONTGOMERY, D.C., 2001. *Design and analysis of Experiments*. John Wiley & Sons, New York.

MULLIGAN, C.N., WANG, S.L., 2006. *Remediation of a heavy metal-contaminated soil by a rhamnolipid foam*. Eng. Geol. 85, 75–81.

MULLIGAN, C.N., YONG, R.N., GIBBS, B.F., 1999. *Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin*. J. Soil Contam. 8, 231–254.

NEETHLING, S.J., CILLIERS, J.J., 2002. *Entrainment of solids into flotation froths*. Int. J. Miner. Process. 64, 123–134.

OBENG, D.P., MORRELL, S., NAPIER-MUNN, T.J., 2005. *Application of central composite rotatable design to modeling the effect of some operating variables on the performance of the three-product cyclone*. Int. J. Miner. Process. 76, 181–192.

OZDEMIR, G., PEKER, S., HELVACI, S.S., 2004. *Effect of pH on the surface and interfacial behavior of rhamnolipids R1 and R2*. Colloids Surf. A: Physicochem. Eng. Aspects 234, 135–143.

PINFOLD, T.A., 1972. *Precipitate flotation*. in: Adsortive Bubble Separation Techniques, Academic Press, South Africa. 75–90.

POLAT, H., ERDOGAN, D., 2007. *Heavy metal removal from waste waters by ion flotation*. J. Hazard. Mater. 148, 267–273.

SANG-JUNE, C., SON, K., 1988. *Removal of Cu(II) from aqueous solutions by the foam separation techniques of precipitate and adsorbing colloid flotation*. Sep. Sci. Technol. 23(4/5), 363–374.

SEDLAK, D.L., CHAN, P.G., 1997. *Reduction of hexavalent chromium by ferrous iron*. Geochim. Cosmochim. Acta. 61, 2185–2192.

SINGH, A.K., CAMEOTRA, S.S., 2013. *Efficiency of lipopeptide biosurfactants in removal of petroleum hydrocarbons and heavy metals from contaminated soil*. Environ. Sci. Pollut. R. 20(10), 7367–7376.

ULEWICZ, M., WALKOWIAK, W., 2003. *Separation of zinc and cadmium ions from sulfate solutions by ion flotation and transport through liquid membranes*. Physicochem. Probl. Miner. Process. 37, 77–86.

VILINSKA, A., RAO, K.H., FORSSBERG, K.S.E., 2008. *Microorganisms in flotation and flocculation of minerals–an overview*. in: 24th Int. Miner. Process. Cong. Proc., China. 22–39.

YETILMEZSOY, K., DEMIREL, S., VANDERBEI, R.J., 2009. *Response surface modeling of Pb(II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design*. J. Hazard. Mater. 171, 551–562.

YUAN, X.Z., MENG, Y.T., ZENG, G.M., FANG, Y.Y., SHI, J.G., 2008. *Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation*. Colloids Surfaces A: Physicochem. Eng. Aspects 317, 256–261.

ZOUBOULIS, A.I., GOETZ, L., 1991. *Ion flotation as a tool for speciation studies selective separation in the system Cr^{3+}/Cr^{6+}*. Toxic. Environ. Chem. 31(1), 539–547.

ZOUBOULIS, A.I., MATIS, K.A., LAZARIDIS, N.K., GOLYSHIN, P.N., 2003. *The use of biosurfactants in flotation: application for the removal of metal ions*. Miner. Eng. 16, 1231–1236.