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Research article

Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation

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A B S T R A C T

Rhamnolipid (RL) is a biosurfactant which is produced by the bacterial species *Pseudomonas aeruginosa*. Although applications of this material have been examined in various fields, its applications in the flotation of heavy metals remain to be explored. In this research, rhamnolipid was applied as a collector in the flotation of Cr(III) from aqueous solutions. FeSO4 was used for the precipitation of Cr(VI) to Cr(III) which was subsequently removed by flotation. A two level full factorial design (with center points) was used to evaluate the effects of pH, air flow rate, RL/Cr and Fe/Cr molar ratios on the performance of the flotation system. The results showed that the biosurfactant was highly effective in the removal of chromium, and all of the factors had significant effects on the flotation performance. The chromium removal efficiencies of greater than 95% were obtained with the initial chromium concentration of 40 ppm within 5 min. Kinetic studies showed that a first order kinetic model was appropriate to describe the precipitate flotation of Cr(III) using rhamnolipid as a collector. The interference of NaCl, $CaCl_2$, $CaSO_4$, and $CaCO_3$ on the Cr removal was also investigated, and it was demonstrated that $CaSO_4$ and $CaCO_3$ as sparingly water soluble salts, and $CaCl_2$ as a contributor to water hardness had significant negative impacts on Cr removal efficiency of rhamnolipid.

1. Introduction

Chromium exists in nature in a variety of forms with predominant forms of Cr(VI) as chromate and Cr(III) as hydroxide. While chromate is soluble in water and toxic, chromium hydroxide is only sparingly soluble in water, and is generally considered as a non toxic chemical. Conversion of Cr(VI) to Cr(III), therefore, can be a remediation process. Flotation has been shown to be an efficient way for the removal of chromium from wastewaters. Various studies exist in the literature for the removal of chromium by flotation. A precipitant (usually ferrous salts) is used to convert Cr(VI) to Cr(III) which is subsequently removed by precipitate flotation.

Following equations show the precipitation of chromium:

$$Cr(VI)\,(aq) + 3Fe(III)\,(aq) \rightarrow Cr(III)\,(aq) + 3Fe\,(III) \quad (1)$$

$$x\,Cr\,(III)_{(aq)} + (1\text{-}x)\,Fe\,(III)_{(aq)} + 3H_2O \rightarrow (Cr_xFe)_{(1\text{-}x)}(OH)_{3(s)} + 3H^+ \quad (2)$$

x varies from 0 to 1. The reactions are stoichiometric at pH < 10, and complete within 5 min. The precipitates appear brown in the solution (Fendorf, 1995).

A surfactant is used as the collector in flotation. Sodium dodecyl sulfate (SDS) has been widely used in the flotation of chromium (Grieves and Lee, 1971; Huang et al.,1995). Due to the environmental concerns about the use of synthetic surfactants, alternative surfactants are being sought by researchers. Biosurfactants are produced by various microbial species. They have low toxicity, good environmental compatibility, biodegradability, and effectiveness in a wide range of temperatures and pHs. Recent research works have shown promising results for the replacement of synthetic surfactants by biosurfactants (Cohen and Exerowa, 2007; Khaje-Bafghi and Fazaelipoor, 2012). Rhamnolipid is a biosurfactant produced by the bacterial species *Pseudomonas aeruginosa*. Its molecule contains one or two molecules of rhamnose and a lipid with varying chain length. Extensive research works have been done on the production and characterization of this biosurfactant. The

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applications of rhamnolipid have also been examined in various fields (Fazaelipoor et al., 2010; Khoshdast et al., 2011).

A few studies can be found in the literature on the application of biosurfactants in foam flotation for chromium removal (Zouboulis et al., 2003). Little published data, however, exist on the application of rhamnolipid in foam flotation of heavy metals. This study investigates the potential application of rhamnolipid as a novel (bio)surfactant in the flotation of chromium from solutions.

2. Materials and methods

2.1. Chemicals

Rhamnolipid (RL) was obtained from a research group at the National Institute of Genetic Engineering and Biotechnology (Iran). The structure and surface activity of this biosurfactant were characterized by Khoshdast et al. (2011, 2012). The biosurfactant was a mixture of mono and dirhamnolipid with the average molecular weight of 577 g/mol.

The following analytical grade chemicals from Merck were also used: $Na_2Cr_2O_7.2H_2O$; FeSO4.7H_2O; HCl; NaOH; NaCl; $CaCl_2$; CaCO3; CaSO4.2H_2O.

2.2. Flotation column

A glass column with the height of 60 cm and the internal diameter of 5.7 cm was used for the flotation tests. A compressor was used to inject air to the flotation column. The air entered the column through a sintered glass sparger, with the average pore size diameter of 12 μm. The system was equipped with a manometer to regulate air flowrate. The column had a sampling port 5 cm above the sparger.

2.3. Flotation tests

The experiments were conducted in duplicates based on a 2 level full factorial experimental design to evaluate the effects of initial pH, rhamnolipid to chromium molar ratio (RL/Cr), Fe(II) to chromium molar ratio (Fe/Cr), and air flow rate(Q). The levels of the variables are presented in Table 1. Chromium removal percentage was considered as the response. For initial pH the lower level was selected in the acidic range, the higher level in the basic range, and the middle level is a near neutral pH. The levels of RL/Cr molar ratio were selected small enough to be economical in the case of scale up. The lower level is below the critical micelle concentration (CMC) of the biosurfactant (CMC of the biosurfactant was reported to be 10.1 ppm by Koshdast et al.(2012)), and the two other levels are above the CMC of the biosurfactant. The levels of Fe/Cr are equal or less than the stoichiometric ratio based on the equation (1). The levels of air flow rate were selected, based on trials, to give high density of bubbles in the flotation column. For each flotation test, 1000 mL of distilled water containing 40 ppm Cr(VI) and the required amounts of FeSO4 and rhamnolipid (based on the ratios in Table 1) was prepared. After pH adjustment, the solution was stirred with a magnetic stirrer for 30 min. The solution was then introduced to the column and flotation was started. The process was terminated after 5 min and samples were taken in duplicates from the remaining solution in the column immediately after the termination of the process. For kinetic studies, samples were taken at specified time intervals (Shown in Fig. 2). All of the experiments were conducted at room temperature (25–27 °C). The run with the highest removal efficiency (No.13 in Table 2) was selected for the investigation on the effect of interfering salts on the chromium removal. NaCl, $CaCl_2$, $CaCO_3$, and $CaSO_4$ were the sources of interfering ions. Each salt was tested separately at two concentrations of 0.001 and 0.002 M. The flotation procedure was exactly as described before, except that the interfering salts were added before stirring the solution.

Table 1
Level of variables chosen for 2^4 full factorial experimental design for Cr flotation.

Flotation variables	Lower level	Middle level	Higher level
pH	5	6.5	8
RL/Cr (molar ratio)[a]	0.01	0.055	0.1
Fe/Cr (molar ratio)	1.5	2.25	3
Air flow rate (mL/min)	50	125	200

[a] The initial concentration of Cr in solution was 40 ppm.

2.4. Chromium analysis

Chromium content of the samples was measured by an atomic absorption instrument (Varian model SpectrAA 220) at 357.9 nm wavelength. The removal efficiency of flotation (*R*Cr%) was defined as below:

$$R_{Cr}\% = 100(C_0 - C_t)V_t/(C_0V_0)$$

Where C and V stand for the concentration of chromium and the volume of solution, respectively. The subscripts 0 and t indicate the values at zero and t minutes, respectively.

3. Results and discussions

3.1. Factorial analysis and regression model

The basic 2^4 full factorial design involves 16 runs. Performing each run in duplicate and using 2 center points, 34 tests were performed totally. Table 2 shows the average values for chromium removal of each run. The results of analysis of variance (using Minitab 16) for Cr removal ($R_{Cr}\%$) have been presented in a supplementary file. The results indicate that all of the factors have significant effects on the Cr removal percentage at 95% confidence intervals, and for two way interactions only the effects of air flow rate (Q) and pH are independent. All other two way interactions are

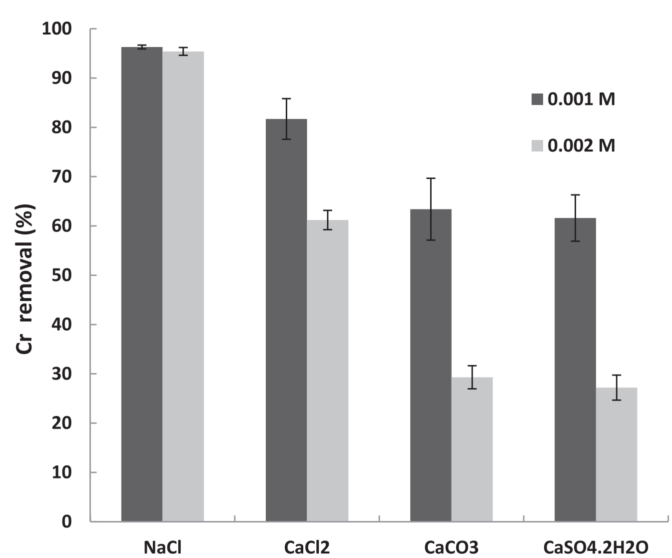

Fig. 1. Effect of salts on the flotation of Cr using rhamnolipid. Initial Cr concentration: 40 ppm. Air flow rate: 50 mL/min, Rhamnolipid/Cr molar ratio: 0.01, Fe/Cr molar ratio: 3, pH = 8.