Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.862009

53 (2015) 1664–1674
February

Taylor & Francis
Taylor & Francis Group

Continuous foam fractionation of chromium(VI) ions from aqueous and industrial effluents

M. Arulmozhi[a], K.M. Meera S. Begum[b,*], N. Anantharaman[b]

[a]*Department of Petrochemical Technology, Anna University of Technology, Tiruchirappalli, Tiruchirappalli 24, India*
[b]*Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli, Tiruchirappalli 15, India*
Tel. +91 09600330944; email: meera@nitt.edu.in

Received 16 October 2012; Accepted 6 October 2013

ABSTRACT

The purpose of this study was to investigate the use of foam fractionation to recover Cr(VI) ions from simulation aqueous solution and tannery effluent. The effects of operation parameters, such as air flow rate, liquid pool height, feed concentration, surfactant concentration, pH of the feed, and feed flow rate on the separation characteristics were studied in the continuous operation. Enrichment ratios of 5.2 and 4.8 with percentage removal of 65% and 61% were achieved for the removal Cr^{6+} ions from simulation aqueous solution and tannery effluent on the basis of optimization of parameters, respectively. As the optimized results, the air flow rate and liquid pool height were 0.1 lpm and 30 cm, feed concentration and surfactant concentration were 10 ppm and 0.1 % (w/v), pH of the feed was 6 and feed flow rate was 4 lph. The Cr(VI) concentration in the effluent was around 0.5 ppm which could meet the Bureau of Indian standards (BIS2490) wastewater discharge standards. Box–Behnken model and Analysis of Variance (ANOVA) were applied to the experimental foam fractionation studies. Response surface method with three levels of variances was used in the identification of significant effects and interaction of the above mentioned six variables in the continuous foam fractionation studies. A second order polynomial regression model has been developed using experimental data. From the results it was found that the selected variables have a strong effect on the foam fractionation and also the experimental values were in good agreement with predicted values.

Keywords: Foam fractionation; Sodium lauryl sulphate (SLS); Metal ion (Cr^{6+}); Tannery effluent; Box–Behnken response surface method

1. Introduction

Toxic metals, such as Cd, Hg, Pb, Cr, Ni, Zn, and Co at trace concentrations in water bodies are detrimental to human health and ecosystem stability. Metal ions are characterized by their mobility in the liquid phase of the eco system and are toxic to higher life forms even at low concentrations. In addition these ions are nondegradable and thus lead to both ecological and health problems. Chromium is one of the heavy metal ion that does not undergo biodegradation. Chromium is found in various oxidation states ranging from +2 to +6 in which trivalent and hexavalent states are most predominant in the environment. The toxic hexavalent chromium anions

---

*Corresponding author.

such as chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and dichromate ($Cr2O_7^{2-}$) are not strongly sorbed in many soils under alkaline to slightly acidic conditions. Hexavalent chromium compounds are highly toxic and are considered as mutagens and carcinogens. This pollutant is introduced into natural water by a variety of industrial processes, such as textile, dyes and pigments, leather tanning, electroplating, metal finishing, and wood preserving industries.

Foam fractionation is a simple and low cost method, belonging to the adsorptive bubble separation techniques [1–3] and plays a major role in wastewater treatment, especially from dilute streams for the removal of trace metals, such as cadmium, chromium, copper, iron, mercury, nickel, and zinc with the aid of surfactants. In foam fractionation, the surface active compounds are attached by adsorption to gas bubbles, which then rise to the top of the liquid at the surface (Fig. 1). When these bubbles rise out of the solution, foam is formed. Only a small fraction of the liquid is carried with the bubbles into the foam phase due to gravity drainage. The foam phase can be collapsed into a new liquid foamate by releasing the gas bubbles. The concentration of the metal ions in the new liquid is several times of that in the initial liquid solution. Surface inactive components can be removed from a solution if an appropriate surface active material is added to unite with the surface inactive material so that it can be adsorbed on the bubble surface [4]. This can occur either through the formation of a chelate or other compound, or through electrostatic (counter ionic) attraction by the surfactant layer adsorbed at the surface or by both the types of mechanisms.

Foam fractionation is rapidly becoming an effective method to separate surface active and nonsurface active species. Walkowiak and Grieves [5] investigated the batch foam fractionation of the cyanide complex anions of Zn(II), Cd(II), Hg(II), and Au(II) from alkaline aqueous solutions using cationic surfactant, hexadecyltrimethylammonium chloride. The selectivity sequence of metal ions, $Au(CN)_4^- < Hg(CN)_4^- > Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$ were established. Foam separation of Cd^{2+} with sodium lauryl sulfate and sodium nitrate solution was studied by Jukiewicz [6–8]. Moussavi [9,10] used three types of chelating agents EDTA, NDDTC, and CA with different concentration ratios with respect to the metal ions to separate the heavy metals from water by foaming. Choi and Choi [11] carried out foam separation experiments for the removal of Direct Red from an aqueous solution. Chang et al. [12,13] recovered tributyl phosphate (TBP) from dilute aqueous solution by foam separation with sodium lauryl sulfate (SLS) or cetyl trimethyl ammonium bromide (CTAB) as surfactant. It was observed by them that when the surfactant concentration was so low as just enough to maintain the foam stability, the TBP concentration in the foam has the higher enrichment (5–7 times that of TBP in aqueous feed) under the experimental conditions. Kinoshita et al. [14,15] studied the foam separation of Au(III) from its hydrochloric acid solutions in batch and continuous modes using a nonionic surfactant (PONPE 20). The surfactant showed a strong affinity to Au(III) in HCl media and it was observed that the recovery increased with the increase in the surfactant concentration and air flow rate. Kumpabooth et al. [16] reported a continuous mode foam fractionation to recover surfactant present at low concentrations in aqueous streams. Three surfactants were chosen for this study were sodium lauryl sulphate, cetylpyridinium chloride, and sodium n-hexadecyl diphenyl oxide disulfonate. Desai and Kumar [17,18] developed a model to predict the liquid hold-up profiles in semi-batch cellular foams. The model was

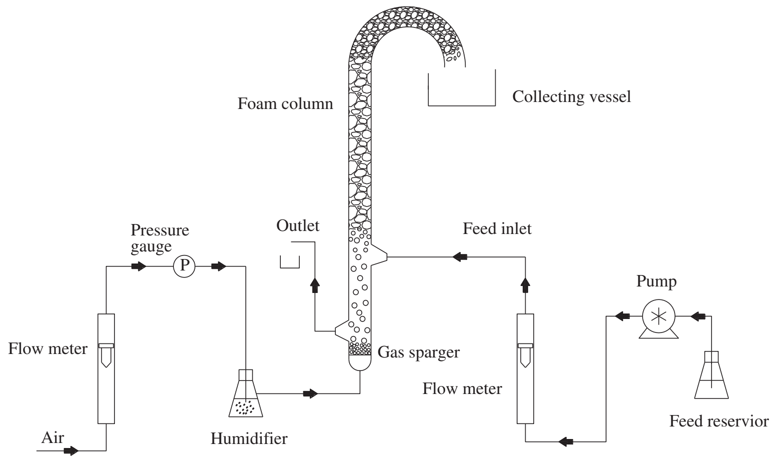

Fig. 1. Experimental setup of a continuous foam column.

based on two basic processes of film thinning and flow through plateau borders. Bhattacharjee et al. [19] investigated the separation of proteins from their binary mixtures (BSA-casein, BSA-lysozyme) and they found that the adsorption is kinetically controlled and not attained equilibrium. Boonyasuwat et al. [20] investigated the recovery of a cationic surfactant (cetylpyridinium chloride, CPC) and an anionic surfactant (sodium lauryl sulphate, SDS) from water by multistage foam fractionation in a bubble cap tray column with four stages operated in steady-state mode for surfactant concentration less than critical micelle concentration (CMC). Alan and Wilbert [21] investigated the removal of lead(II) using sodium lauryl sulphate as a collector. Despite these large number of publications, the use of foam fractionation for recovery of valuable metal ions from real industrial effluents has seldom been reported. In this study, we designed and built a continuous foam fractionator and investigated a continuous operation in the recovery of Cr(VI) ions from synthetic aqueous solution and tannery effluent. The effects of conditions of feed solution (feed and surfactant concentration, pH of feed) and the operational parameters of the column (air and feed flow rate, liquid pool height) on the enrichment ratio were investigated. Box–Behnken model and analysis of variance (ANOVA) were applied to the experimental foam fractionation studies. Response surface method with three levels of variances was used in the identification of significant parameters and their interaction in the continuous foam fractionation studies. A second-order polynomial regression model has been developed to describe the experimental results.

2. Materials and methods

2.1. Materials

Analytical grade potassium dichromate, sodium lauryl sulphate (SLS) surfactant, Diphenyl carbazide (coloring agent for analysis of chromium(VI) in UV-spectrophotometer) were purchased from Sigma chemicals (P) Ltd. Effluent from chrome tanning industry was collected from nearby industrial unit whose characteristics are given in Table 1. Double Distilled water was used in all experiments.

Table 1
Characteristics of chrome tanning effluent

Parameters	Chrome tanning effluent (raw)	Chrome tanning effluent (after pretreatment)
pH	2.5–3.5	3.5
Cr(VI) (ppm)	3,000	2,500
Odour	Very high	High
Colour	Dark brown	Dark brown

2.2. Equipment and method

The continuous foam column comprises of a cylindrical glass tube (1,000 mm in height and 160 mm in diameter) with a sintered glass sparger of pore size ranging from 15 to 40 microns mounted at the bottom of the column which is used as a gas distributor. The basic configuration of the experimental setup of a continuous foam fractionator is shown in Fig. 1.

Air flow was measured using a rotameter and then passed through the distributor. The feed solution was continuously fed into the column through an inlet port and the residual solution was discharged from the outlet port near the bottom of the column. The range of variables studied is given in Table 2.

Foamate was collected continuously at the top of the column and it was collapsed by warming them slightly, and the collapsed liquid samples were then analyzed to determine the metal ion concentration. The foam fractionation was studied under steady state and all runs were carried out for a minimum of 2 h. Steady state was ensured when all measured parameters were invariant with time.

2.3. Analytical methods

The concentration of chromium(VI) ions was measured in UV-Spectrophotometer at a wavelength of 540 nm (JASCO make) using diphenyl carbazide as the coloring agent. The pH of the feed was measured using the digital pH meter (VSI-01 ATC Deluxe, Pricillab).

Table 2
Range of parameters studied for continuous foam fractionation of chromium(VI)

Variables	Range studied
Air flow rate (lpm)	0.1, 0.2, 0.3 0.4, and 0.5
Liquid pool height (cm)	10, 15, 20 , 30, and 40
Feed concentration (ppm)	10, 20, 30, and 40
Sodium lauryl sulphate surfactant concentration (% w/v)	0.1, 0.2, 0.3, and 0.4
pH of feed	4, 5, 6, 7, and 8
Flow rate of feed (lph)	1, 2, 3, 4, and 5

2.4. Calculation

The performance of foam fractionation is expressed in terms of enrichment ratio or separation factor, E and percentage removal (P.R. %)

$$\text{Enrichment ratio } (E) = \frac{\text{Concentration of metal ions in foamate } (C_p)}{\text{Concentration of metal ions in feed solution } (C_f)} \tag{1}$$

$$\text{Percentage removal (P.R \%)} = \frac{\text{Amount of metal ions recovered } (C_f - C_b)}{\text{Amount of metal ions in feed solution } (C_f)} \times 100 \tag{2}$$

3. Results and discussion

3.1. Effect of air flow rate

The effect of air flow rate on enrichment ratio of Cr(VI) ions for synthetic aqueous solution and tannery effluent at fixed other conditions of 30 cm liquid pool height, 10 ppm of feed concentration, 0.1% (w/v) sodium lauryl sulphate concentration, 6 pH of feed, and 4 lph of feed flow rate is shown in Fig. 2. As the air flow rate was increased from 0.1 to 0.5 lpm, the enrichment ratio decreased from 5.2 to 1.7 for synthetic solution and from 4.8 to 1.4 for tannery effluent. With increase in air flow rate, the bubble size decreased and coalescence as well as drainage decreased. In other words the wetness of the foam increases which leads to decrease in enrichment ratio. These observations agreed well with those of Brown et al. [22].

3.2. Effect of liquid pool height

The effect of liquid pool height on enrichment ratio of chromium(VI) ions for both synthetic solution and tannery effluent at optimum conditions of other parameters using sodium lauryl sulphate surfactant is shown in Fig. 3. As the liquid pool height was increased from 10 cm to 40 cm, the enrichment ratio increased from 2.7 to 5.2 for synthetic solution and from 2.1 to 4.8 for tannery effluent, respectively.

The residence time of bubbles in the liquid pool is high when the height of the liquid pool is more. This leads to a higher enrichment of metal ions on the bubble surface and it could reach an equilibrium beyond which enrichment may not increase. In the present study, this equilibrium is reached at a pool height of 30 cm. The results are in agreement with the reported literatures by Qu et al. [2].

3.3. Effect of feed concentration

Experiments were carried out to find the effect of metal ion concentration in feed on enrichment ratio and the results obtained for synthetic solution and tannery effluent using sodium lauryl sulphate surfactant are shown in Fig. 4. The enrichment ratio

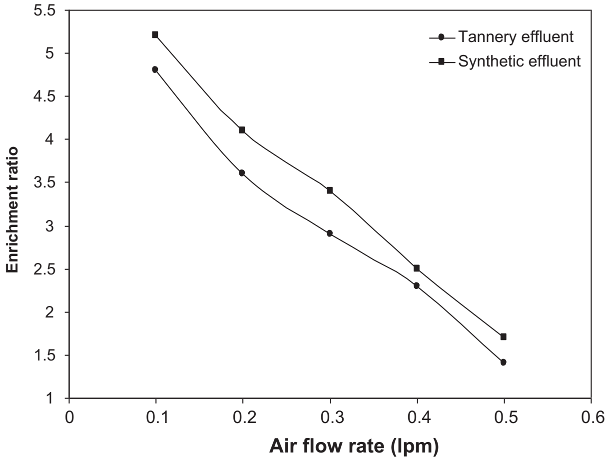

Fig. 2. Effect of air flow rate on enrichment ratio of chromium(VI). Liquid pool height = 30 cm, feed concentration = 10 ppm, SLS surfactant concentration = 0.1% (w/v), pH of the feed = 6, and feed flow rate = 4 lph.

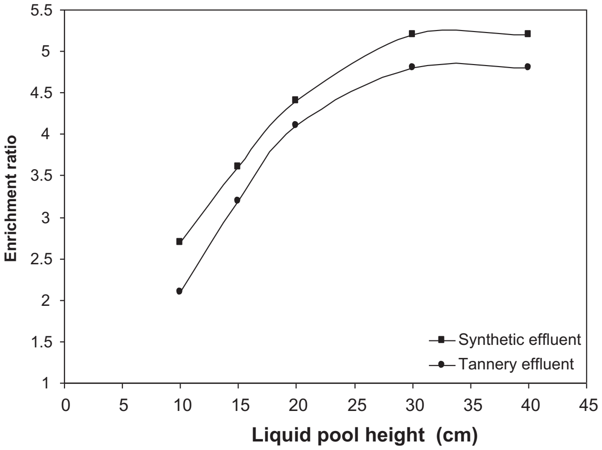

Fig. 3. Effect of liquid pool height on enrichment ratio of chromium(VI). Air flow rate = 0.1 lpm, feed concentration = 10 ppm, SLS surfactant concentration = 0.1% (w/v), pH of the feed = 6, and feed flow rate = 4 lph.

decreased from 5.2 to 2.1 for synthetic solution and from 4.8 to 1.6 for tannery effluent.

As the feed concentration increases, the viscosity of the solution increases which intern decreases the surface tension. This leads to quite stable bubbles and decrease in coalescence as well as drainage from foam. Hence, the wetness of foam is higher which decreased the enrichment ratio and percentage removal. The results are in agreement with the reported literatures by Wong et al. [23], Arulmozhi et al. [24,25]. The reason for decrease in enrichment with increase in feed concentration as per the reported literatures of Farooq Uraizee et al. [26] are due to the nature of adsorption isotherm. It is to be noted that enrichment $e = 1 + \Gamma/C_f$, where Γ and C_f are surface and bulk concentration of metal ion, respectively. Γ/C decreases with an increase in concentration thus leading to a lower enrichment at higher concentration.

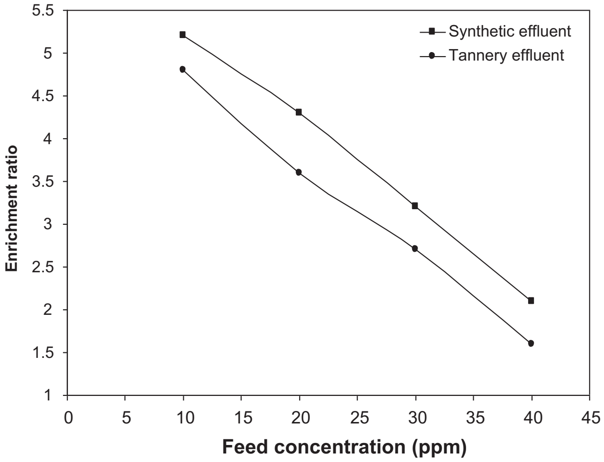

Fig. 4. Effect of feed concentration on enrichment ratio of chromium(VI). Air flow rate = 0.1 lpm, liquid pool height = 30 cm, SLS surfactant concentration = 0.1% (w/v), pH of the feed = 6, and feed flow rate = 4 lph.

3.4. Effect of sodium lauryl sulphate surfactant concentration

The effect of surfactant concentration on enrichment ratio of metal ions from synthetic solution and tannery effluent is shown in Fig. 5. The results indicated that the enrichment ratio decreased from 5.2 to 2.4 for synthetic solution and from 4.8 to 1.6 for tannery effluent.

A primary advantage of foam separation is the small volume of foamate necessary to perform separations which would otherwise require much larger volumes by other techniques. The production of a large amount of foam is both unnecessary and undesirable. An excess collector can reduce the separation by competing against the collector-colligen complex for the available surface. It can also reduce the separation by forming micelles in the bulk solution which adsorb some of the colligen, thus keeping it away from the surface. These observations agree with those of Chang et al. [12,13].

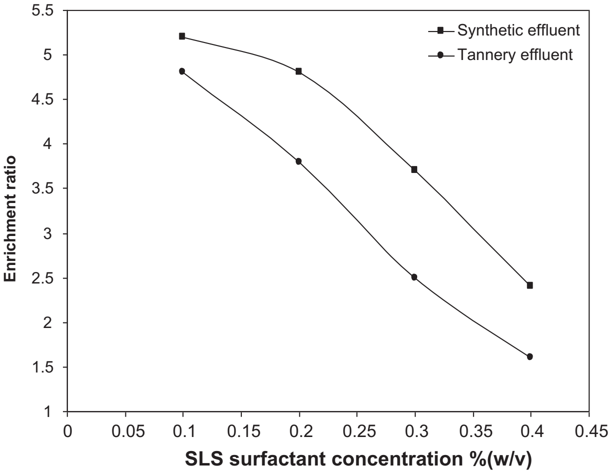

Fig. 5. Effect of SLS surfactant concentration on enrichment ratio of chromium(VI). Air flow rate = 0.1 lpm, liquid pool height = 30 cm, feed concentration = 10 ppm, pH of the feed = 6, feed flow rate = 4 lph.

3.5. Effect of pH of feed

The effect of pH of feed on enrichment ratio of chromium(VI) ions from synthetic solution and tannery effluent using sodium lauryl sulphate (SLS) surfactant is shown in Fig. 6. The maximum enrichment ratio of 5.2 and 4.8 occurred at a pH of 6 indicating that the best separation can be obtained at that pH. The reason for the best separation at pH 6.0 is due to the charge reversal of chromium ions (isoelectric point).

3.6. Effect of feed flow rate

The effect of feed flow rate on enrichment ratio of chromium(VI) ions from both synthetic and industrial effluent using sodium lauryl sulphate surfactant is shown in Fig. 7.

Fig. 7 indicates that with increase in feed flow rate from 1 to 4 lph, the enrichment ratio of chromium(VI) ions increased from 2.1 up to a maximum value of 5.2 and then decreased to five for synthetic chromium solution and from 1.7 up to a maximum value of 4.8 and then decreased to 4.5 for tannery effluent.

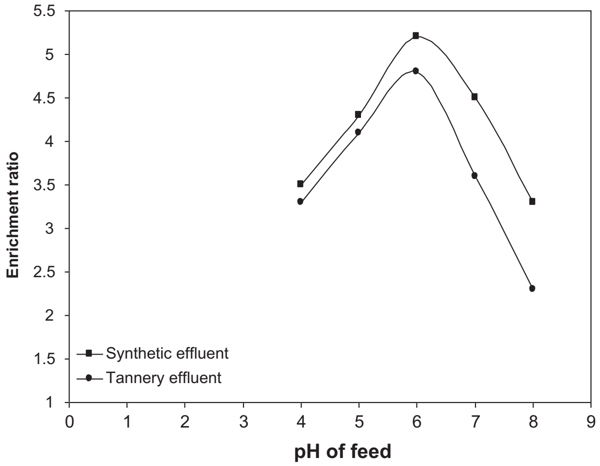

Fig. 6. Effect of pH of feed on enrichment ratio of chromium (VI). Air flow rate = 0.1 lpm, liquid pool height = 30 cm, feed concentration = 10 ppm, SLS surfactant concentration = 0.1% (w/v), and feed flow rate = 4 lph.

An increase in the feed flow rate from 1 to 4 lph results in more availability of metal ions, which leads to an increase in the enrichment ratio.

Subsequent increase in feed flow rate leads to lower residual time of bubbles in the column causing lesser drainage, and thus decreasing the enrichment ratio.

3.7. Effect of bubble diameter

The bubble diameter was determined experimentally using bubble image analyzer interfacing with BIOVIS software. The bubble diameter was analyzed for two different air flow rates by keeping the other parameters at liquid pool height of 30 cm, feed concentration of 10 ppm, SLS surfactant concentration of 0.1% (w/v), pH of feed as 6 and feed flow rate as 4 lph and are reported in Table 3.

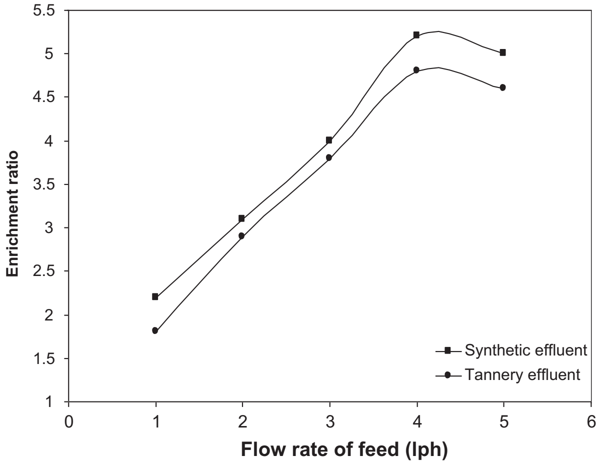

Fig. 7. Effect of feed flow rate on enrichment ratio of chromium(VI). Air flow rate = 0.1 lpm, liquid pool height = 30 cm, feed concentration = 10 ppm, SLS surfactant concentration = 0.1 % (w/v), and pH of feed = 6.

The enrichment ratio was found to be higher for larger bubble sizes. As the bubble size was decreased, coalescence and drainage decreased whereas for larger bubbles, liquid drainage in the foam was faster, resulting in a smaller liquid holdup.

3.8. Statistical analysis of results obtained from continuous foam fractionation of chromium(VI)

Box–Behnken method helps in exploring the best operating conditions for the removal of metal ions. Box–Behnken design requires a number of experimental runs according to $N = K^2 + K + C_P$, where K is the factor number and C_P is the replicate number of central point. This design leads to study the effects of six factors in a single block of 54 sets of test conditions and 3 central points The order of the experiments is fully randomized. In this study, the Box–Behnken experimental design is chosen to estimate the relationship between enrichment ratio of metal ions and parameters like superficial air velocity (X_1), liquid pool height (X_2), feed concentration (X_3), surfactant concentration (X_4), pH of feed (X_5), and superficial liquid feed velocity (X_6). A 3^6 full factorial central composite design with three coded levels leading to 54 sets of experiments were performed.

For statistical computation, the variables were coded according to Eq. (3)

$$X_i = \frac{U_i - U_0}{\Delta U_i} \tag{3}$$

where X_i is the independent variable coded value, U_i independent variable- real value U_0 independent variable real value on the centre point, and ΔU_i step change value.

Experimental data obtained on the enrichment of chromium(VI) ions in tannery effluent, the range, and

Table 3
Effect of bubble diameter on enrichment ratio of chromium(VI)

Air flow rate (lpm)	Bubble diameter (m)	Enrichment ratio
0.2	0.00002	4.1
0.5	0.000008	1.7

the levels of the variables used for factorial design are given in Table 4.

3.8.1. Prediction of regression equation

The mathematical relationship between the six variables and response is approximated by the second-order polynomial equation

$$Y_c = a_0 + \Sigma a_{ii} x_i + \Sigma a_{ii} x_i^2 + \Sigma a_{ij} x_i x_j \tag{4}$$

where Y_c is the predicted response (enrichment ratio) by the model; X_1, X_2, X_3, X_4, X_5, and X_6 are independent variables; a_0 is a constant; a_i, a_{ii}, a_{ij} are regression coefficients of the model. The accuracy and general ability of the second-order-multiple regression models could be evaluated by the coefficient of determination (R^2). The coefficients, a_i and two interaction factors a_{ii} and a_{ij} have been estimated from the experimental results by applying least-square method using the software MINITAB^{TM} (version 15). The regression equation (second-order polynomial) relating enrichment ratio with process variables, such as air velocity (X_1), liquid pool height (X_2), feed concentration (X_3), surfactant concentration (X_4), pH of feed (X_5), and liquid feed velocity (X_6) with enrichment ratio is given in Eq. (5).

$$\begin{aligned}&\text{Enrichment ratio of chromium(VI)}\\ &\quad = -13.5237 - 0.0136X_1 + 0.025X_2 + 0.0007X_3\\ &\qquad - 0.0506X_4 + 5.8488X_5 + 0.061X_6 - 0.033X_1^2\\ &\qquad - 2.8205X_4^2 - 0.4871X_5^2 - 0.0015X_6^2 - 0.0017X_1X_3\\ &\qquad - 0.0025X_1X_6 + 0.0024X_3X_4 + 0.0037X_4X_6\end{aligned}$$

These statistical analysis are done by means of Fisher's "F" test and Student"t" test. The student"t" test was used to determine the significance of the regression coefficients of the parameters as per Khuri and Cornell [27] and Merz [28].

Table 4
Operating variables and experimental levels by factorial experimental design

Factors	Symbol	Range and level −1	0	+1
Air flow rate (lpm)	X_1	0.1	0.3	0.5
Liquid pool height (cm)	X_2	10	25	40
Feed concentration (ppm)	X_3	10	25	40
Surfactant concentration (% w/v)	X_4	0.1	0.25	0.4
pH of feed	X_5	4	6	8
Feed flow rate (lph)	X_6	1	3	5

The statistical analysis of results given in Table 5 for the enrichment of chromium(VI) from tannery effluent using sodium lauryl sulphate surfactant in continuous column indicate the regression coefficient, t and P values for all the linear, quadratic, and interaction effects on enrichment ratio of chromium(VI). The larger the magnitude of t and smaller the value of P, the more significant is the corresponding coefficient term. The significance of each coefficient was determined by t-values and P-values which are listed in Table 5.

It is observed that the coefficients of linear effects of liquid pool height (p = 0.025), pH of feed (p = 0) and liquid feed velocity (p = 0.001) are significant. The coefficients of quadratic effects of pH of feed (p = 0) and liquid feed velocity (p = 0) are significant. However, the coefficients of interactive effects of none of the variables are significant.

3.8.2. Analysis of Variance (ANOVA)

The ANOVA results are represented in Table 6 for the enrichment of chromium(VI) ions. The high value of F indicates that most of the variation in the response can be explained by the regression equation. A P-value lesser than 0.05 (i.e. α = 0.05, or 95% confidence) indicates that the model is considered to be statistically significant.

The value of F (26, 27) = 3.47 at α = 0.05 [29]. As the calculated value of F is 851.03 > 3.47 the results are significant. It indicates that the fitted model exhibits a good fit at 95% confidence level.

3.9. Effect of process variables on enrichment ratio of chromium(VI) from tannery effluent using sodium lauryl sulphate surfactant

3.9.1. Contour plot showing the effect of feed concentration and pH of feed on enrichment ratio of chromium(VI)

The data required for contour plots are calculated from regression equation. The results of the calculation are shown as contour plot in Fig. 8. It represents infinite number of combinations of two variables feed concentration and pH of the feed to obtain constant enrichment ratio of chromium in tannery effluent using sodium lauryl sulphate surfactant at specified conditions of air velocity, liquid pool height, surfactant concentration, and feed velocity.

It is seen from Fig. 8 that at the optimum pH of 6, an enrichment ratio of around 4.6 is achieved at a maximum concentration of 25 ppm and as the feed concentration increases, the enrichment ratio decreases. For example, at a pH of 5, the enrichment

Table 5
Statistical t and P values for percentage removal of chromium(VI)

Parameters/terms	Regression coefficient	Standard error of coefficient	*t*	*P*
Constant	−13.5237	0.50639	−26.706	0
Superficial air velocity	−0.0136	0.16055	−0.085	0.933
Liquid pool height	0.025	0.0105	2.384	0.025
Feed concentration	0.0007	0.01113	0.064	0.95
Surfactant concentration	−0.0506	1.0975	−0.046	0.964
pH of feed	5.8488	0.10045	58.227	0
Superficial liquid feed velocity	0.061	0.01606	3.798	0.001
(Superficial air velocity)^2	−0.0333	0.02876	−1.159	0.257
(Liquid pool height)^2	−0.0002	0.00012	−1.757	0.091
(Feed concentration)^2	−0.0002	0.00013	−1.735	0.095
(surfactant concentration)^2	−2.8205	1.2976	−2.174	0.039
(pH of feed)^2	−0.4871	0.00687	−70.91	0
(Superficial liquid feed velocity) ^{2}	−0.0015	0.0003	−5.208	0
Superficial air velocity × Liquid pool height	0	0.0021	0	1
Superficial air velocity × Feed concentration	−0.0017	0.0021	−0.797	0.433
Superficial air velocity × surfactant concentration	0	0.14858	0	1.0
Superficial air velocity × pH of feed	0	0.01576	0	1.0
Superficial air velocity × Superficial liquid feed velocity	−0.0025	0.00317	−0.797	0.433
Liquid pool height × Feed concentration	0	0.00015	0	1.0
Liquid pool height × surfactant concentration	0	0.01394	0	1
Liquid pool height × pH of feed	−0.0002	0.00076	−0.211	0.834
Liquid pool height × Superficial liquid feed velocity	0	0.0002	0	1.0
Feed concentration × surfactant concentration	0.0024	0.01569	0.155	0.878
Feed concentration × pH	0	0.0011	0	1.0
Feed concentration × Superficial liquid feed velocity	0.0001	0.00015	−0.393	0.698
Surfactant concentration × pH of feed	0	0.10454	0	1.0
Surfactant concentration × Superficial liquid feed velocity	0.0037	0.02366	0.155	0.878
pH of feed × feed flow rate	0	0.00152	0	1.0

Table 6
Analysis of variance

Source	DF	SS	MS	*F*	*P*
Regression	27	53.4754	1.98057	251.7	0
Residual Error	26	0.2046	0.00787		
Total	53	53.6800			

ratio decreases from 4.15 to 3.75 for variation in feed concentration from 10 to 40 ppm. The results are in agreement with the experimental values obtained.

3.9.2. Contour plot showing the effect of liquid pool height and feed velocity on enrichment ratio of chromium(VI)

The data required for contour plots was calculated from regression equation. The results of the calculation are shown as contour plots as in Fig. 9 for specific values of air velocity, feed concentration, surfactant concentration, and pH of the feed. This plot represents infinite number of combinations of two variables with liquid pool height and feed velocity to obtain constant enrichment ratio.

As the liquid pool height increases, the enrichment ratio increases. For example, at a feed velocity of 5 cm/h, with increase in liquid pool height from 13.5 cm to 40 cm, the enrichment ratio increases from 4.2 to 4.56. Similarly with increase in feed velocity, the enrichment ratio increases up to a feed velocity of 20 cm/hr and then decreases slightly.

3.9.3. Contour plot showing the effect of surfactant concentration and feed flow rate on enrichment ratio of chromium(VI)

The data required for contour and surface plots are calculated from regression equation. The results of the calculation are shown as contour plots in

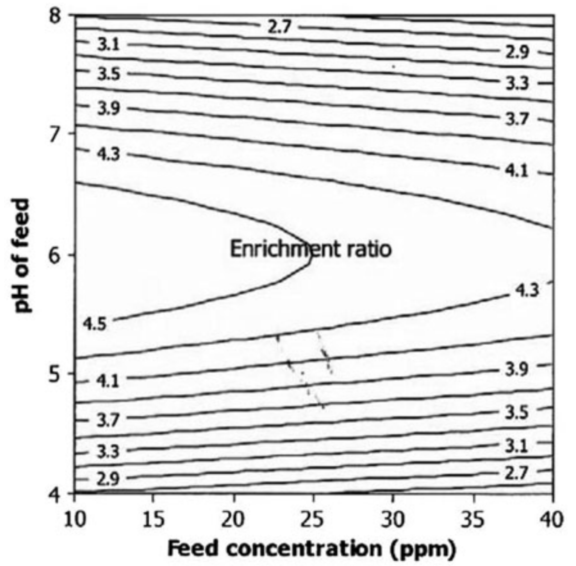

Fig. 8. Contour plot for enrichment ratio of chromium(VI) in tannery effluent. Air flow rate = 0.1 lpm, liquid pool height = 30 cm, surfactant concentration = 0.1% (w/v), and feed flow rate = 4 lph.

Fig. 10. It represents infinite number of combinations of two variables surfactant concentration and feed velocity to obtain constant enrichment ratio of chromium in tannery effluent using sodium lauryl sulphate surfactant at specified conditions of air velocity, liquid pool height, feed concentration, and pH of the feed.

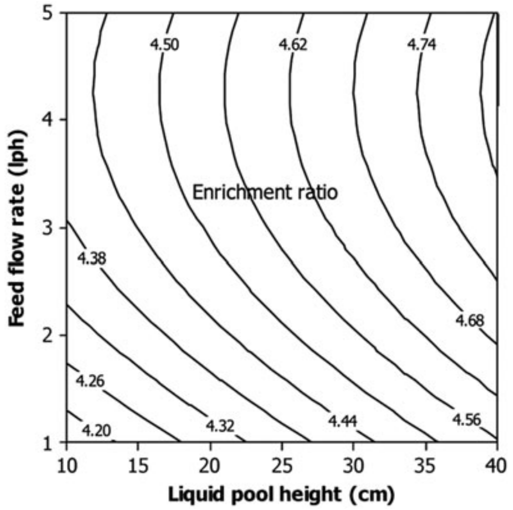

Fig. 9. Contour plot for enrichment ratio of chromium(VI) in tannery effluent. Air flow rate = 0.1 lpm, feed concentration = 10 cm, surfactant concentration = 0.1% (w/v), pH of feed = 6).

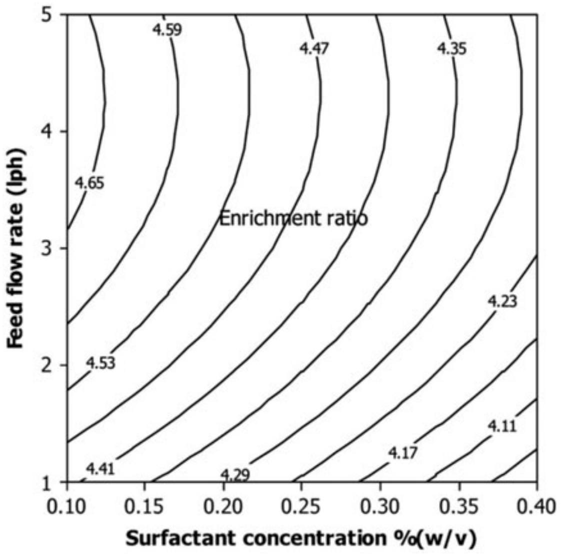

Fig. 10. Contour plot for enrichment ratio of chromium(VI) in tannery effluent. Air flow rate = 0.1 lpm, liquid pool height = 30 cm, feed concentration = 10 ppm, pH of feed = 6.

It is inferred from Fig. 10 that with increase in surfactant concentration, enrichment ratio decreases. For example, at a feed velocity of 5 cm/h, with increase in surfactant concentration from 0.11 to 0.33% (w/v), the enrichment ratio decreases from 4.41 to 4.11. The results are in agreement with experimental findings.

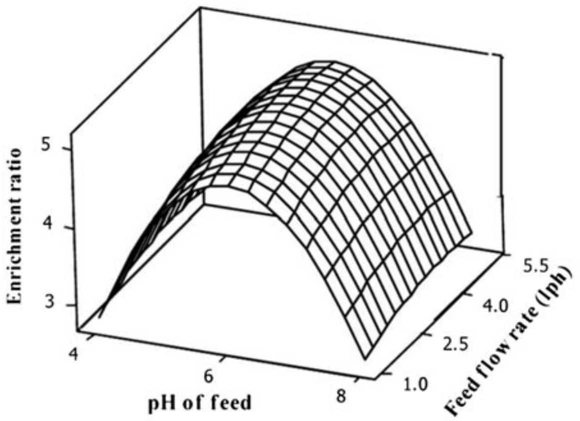

Fig. 11. Surface plot for enrichment ratio of chromium(VI) in tannery effluent. Air flow rate = 0.1 lpm, liquid pool height = 30 cm, surfactant concentration = 0.1% (w/v).

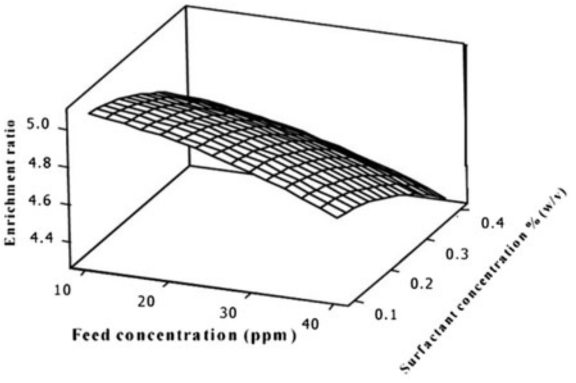

Fig. 12. Surface plot for enrichment ratio of chromium(VI) in tannery effluent. Air flow rate = 0.1 lpm, liquid pool height = 30 cm, pH of feed = 6, feed flow rate = 4 lph.

3.9.4. Surface plots showing the effects of variables on enrichment ratio of chromium(VI)

Figs. 11 and 12 show the effects of pH of feed and feed flow rate, feed concentration and surfactant concentration, respectively on the enrichment ratio of chromium(VI) in tannery effluent using sodium lauryl sulphate surfactant under specified conditions.

4. Conclusions

Foam fractionation is effective in the removal of chromium(VI) ions from synthetic aqueous solution and tannery effluent. The effects of parameters like air flow rate, liquid pool height, feed concentration, surfactant concentration, and pH of feed and feed flow rate on enrichment ratio were investigated in single-stage continuous foam column. At the optimum conditions of 0.1 lpm of air flow rate, 30 cm of liquid pool height, 10 ppm of feed concentration, 0.1 %(w/v) of SLS concentration, 6 pH of feed, and 4 lph of feed flow rate, an enrichment ratio of 5.2 and 4.8 with a percentage removal of 65 and 61% were achieved for synthetic aqueous solution and tannery effluent, respectively. The statistical analysis of the experimental data using MINITAB^{TM} (version 15) has demonstrated the use of Box–Behnken design by determining the conditions leading to the optimum enrichment ratio of Cr(VI) ions. This methodology could therefore be successfully employed to any process (especially with three levels), where an analysis of the effects and interactions of many experimental factors are referred. Box–Behnken designs maximize the amount of information that can be obtained, while limiting the number of individual experiments required. Response surface plots are very helpful in visualizing the main effects and interaction of its factors. Thus, smaller and less time consuming experimental designs could generally suffice the optimization of many foam fractionation processes.

Symbols

X_i	independent variable coded value
U_i	independent variable-real value
U_o	independent variable -real value on the centre point
ΔU_i	step change value
Y_c	predicted response (enrichment ratio)
a_o	a constant
a_i, a_{ii}, a_{ij}	regression coefficients
Γ	surface concentration of metal ion
C_f	concentration of metal ions in feed solution
C_p	concentration of metal ions in foamate

References

[1] R. Lemlich, Adsorptive bubble separation methods, Ind. Eng. Chem. 60 (10) (1968) 16–29.

[2] Y.-H. Qu, G.-M. Zeng, J.-H. Huang, K. Xu, Y.-Y. Fang, X. Li, H.-L. Liu, Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionator, J. Hazard. Mater. 155 (1–2) (2008) 32–38.

[3] R. Konduru, Adsorptive studies of aqueous zinc ions by foam fractionation in simple mode, J. Chem. Eng. Jpn. 25 (5) (1992) 555–560.

[4] P.A. Schweitzer, Handbook of Separation Techniques for Chemical Engineers, 3rd ed., McGraw-Hill, Singapore, 1997 pp. 2–130 to 2–172.

[5] W. Walkowiak, R.B. Grieves, Foam fractionation of cyanide complex anions of Zn(II), Cd(II), Hg(II) and Au(III), J. Inorg. Nucl. Chem. 38 (1976) 1351–1356.

[6] K. Jurkiewicz, Study on the separation of Cd from solutions by foam separation I, Sep. Sci. Technol. 19 (1984) 1039–1050.

[7] K. Jurkiewicz, Study on the separation of Cd from solutions by foam separation of complex cadmium anions, Sep. Sci. Technol. 20 (1985) 179–192.

[8] K. Jurkiewicz, Adsorptive bubble separation of zinc and cadmium cations in presence of ferric and aluminium hydroxides, J. Colloid Interface Sci. 286 (2005) 559–563.

[9] M. Moussavi, Effectiveness of chelating agents upon foam separation of heavy metals from waters, Amer. Inst. Chem. Eng., National Meeting 29D (1986) 16–20.

[10] M. Moussavi, Separation of cyanide ions by foam fractionation, Sep. Sci. Technol. 27 (6) (1996) 783–792.

[11] S.J. Choi, Y.H. Choi, Removal of direct red from aqueous solution by foam separation techniques of ion and adsorbing colloid flotation, Sep. Sci. Technol. 31 (15) (1996) 2105–2116.

[12] Z.-D. Chang, H.-Z. Liu, J.-Y. Chen, Foam separation of tributyl phosphate from aqueous solutions Part I. Experiment, Sep. Purif. Technol. 19 (2000) 131–136.

[13] Z.-D. Chang, H.-Z. Liu, J.-Y. Chen, Foam separation of tributyl phosphate from aqueous solutions Part II. Simulation, Sep. Purif. Technol. 19 (2000) 137–143.

[14] T. Kinoshita, S. Akita, S. Osawa, S. Nii, F. Kawaizumi, K. Takahashi, A study on Gold(III) recovery via foam separation with nonionic surfactant in batch mode, J. Miner. Mater. Char. Eng. 2 (2003) 71–82.

[15] T. Kinoshita, S. Akita, S. Osawa, S. Nii, F. Kawaizumi, K. Takahashi, Continuous recovery of Gold(III) via foam separation with nonionic surfactant, J. Miner. Mater. Char. Eng. 3 (2004) 53–63.

[16] K. Kumpabooth, J.F. Scamehorn, S. Osuwan, J.H. Harwell, Surfactant recovery from water using foam fractionation: Effect of temperature and added salt, Sep. Sci. Technol. 34 (1999) 157–172.

[17] D. Desai, R. Kumar, Flow through a plateau border of cellular foam, Chem. Eng. Sci. 37 (1982) 1361–1370.

[18] D. Desai, R. Kumar, Liquid holdup in semi-batch cellular foams. Chem. Eng. Sci. 38 (1983) 1525–1534.

[19] S. Bhattacharjee, R. Kumar, K.S. Gandhi, Prediction of separation factor in foam separation of proteins, Chem. Eng. Sci. 52 (1997) 4625–4636.

[20] S. Boonyasuwat, S. Chavadej, P. Malakul, J.F. Scamehorn, Anionic and cationic surfactant recovery from water using a multistage foam fractionator, Chem. Eng. Sci. 93 (2003) 241–252.

[21] A.J. Rubin, W.L. Lapp, Foam separation of lead(II) with sodium lauryl sulphate, Anal. Chem 41 (1969) 1133–1135.

[22] L. Brown, G. Narsimhan, P.C. Wanket, Foam fractionation of globular proteins, Biotechnol. Bioeng. 36 (1990) 947–959.

[23] C.H. Wong, M. Monwar, Hossain C.E. Davies, Performance of a continuous foam separation column as a function of process variables, Bioprocess. Biosyst. Eng. 24 (2001) 73–81.

[24] M. Arulmozhi, K.M. Meera, S. Begum, N. Anantharaman, Removal of chromium (VI) ions by foam separation: Aqueous and industrial effluent, Int. J. Environ. Cult. Econ. Soc. Sustain. 4 (2008) 69–76.

[25] M. Arulmozhi, K.M. Meera, S. Begum, N. Anantharaman, Continuous foam separation of heavy metal ions from electroplating industrial effluent, Chem. Eng. Commun. 198 (2011) 541–551.

[26] F. Uraizee, G. Narsimhan, Effects of kinetics of adsorption and coalescence on continuous foam concentration of proteins, Biotechnol. Bioeng. 51 (1996) 384–398.

[27] A.I. Khuri, J.A. Cornell, Response Surfaces (design and analysis). Marcel Dekker, New York, NY, 1987.

[28] J. Merz, H. Zorn, B. Burghoff, G. Schembecker, Purification of a fungal cutinase by adsorptive bubble separation: A statistical approach, Colloids Surf. A 382 (2011) 81–87.

[29] O.L. Davies, P.L. Goldsmith, Statistical Methods in Research and Production. 4th ed., Tweddale court, Edinburg, Imperial Chemical Industries, 1972 pp. 125–128.