Cerium Extraction from Solution
by Adsorbing Colloid Flotation (ACF)

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ABSTRACT: *In this research, cerium recycling was studied by Adsorbing Colloid Flotation (ACF). Ten important parameters including collector type and dosage, cerium and colloid concentrations, frother type, activator type, preparation and frothing time, air flowrate and pH, each in two levels, were investigated. Statistical design of experiment was implemented for process modelling and analysis of variance showed that factors pH, collector type, collector and cerium dosage and colloid concentration were the most significant factors which effecting Ce recovery and grade. Results showed that the cerium maximum recovery was 99.84 %. The feed initial concentration was 500 ppm in each test and the final concentrate grade was enhanced to 25.1 % by Adsorbing colloid flotation. The SEM (Scanning Electron Microscope) analysis before and after adsorbing flotation showed that ACF was a great method for cerium extracting from solutions and waste waters. Finally, results showed an economical optimum point to achieve maximum recovery and grade simultaneously under minimum consumption of flotation reagents.*

KEYWORDS: *Cerium flotation; Adsorbing colloid flotation; Colloid; Fractional factorial design; REE elements.*

INTRODUCTION

The high-tech application of Rare earth elements (REEs) such as hard-disk drives, smartphones, flat-screen televisions and monitors, rechargeable batteries (household and automotive) and tiny earphones and other uses contain lasers, strong permanent magnets for electrical generators, glass-polishing powders and energy-saving lamps [1-4] become REEs more attractive than last decades. Cerium is used in the polishing compounds, and fluid catalytic cracking, catalytic convertor, a component in special glass (Anti-radiation glasses), alloys, pigment are the most widely applications of Cerium [3]. There are four methods for REE separation includes selective oxidation/ reduction, fractional crystallization, ion exchange, and solvent extraction but they are inefficient when the rare earth concentration is low [5].

One method which is used for extraction of metal ions from dilute solutions is Adsorbing Colloid Flotation (ACF) that has a great ability to remove these elements from wastewaters[6], [7]. Depends on the type and quantity of heavy and precious metals in wastewater, they require special chemicals and adsorbent to remove. Precipitate flotation and Adsorbing Colloid Flotation (ACF) are novel waste removal techniques that based on flotation and the immobilization of pollutants as precipitates or adsorbates [7]. Adsorbing Colloid Flotation (ACF)

is the removal of metal ions by adsorption onto a precipitate, which named as an adsorbing carrier. The loaded carrier is then floated by a surfactant as a collector. Carriers include ferric or aluminum hydroxides and collector is SDS (Sodium Dodecyl Sulfate) [8-10].

Because of increasing the number of experimental runs, economic, time or other constraints in full factorial experiments, even in two-level factors, "fractional factorial" is the best way to study more factors within a given experimental budget. In addition, experiments that involve many factors are not necessary to test all possible factor–level combinations to estimate the important factor effects, generally the main effects and low-order interactions [11-13].

According to the databases [7, 14-33] Some research studies have been done on heavy metals adsorbing colloid flotation so far but rare earth is not examined which results in a lack of an appropriate and effective method for the recovery of these elements in flotation methods.

The aim of this study was to find the best physical and chemical conditions for adsorbing colloid flotation method to enhance recovery and grade of cerium.

EXPERIMENTAL SECTION

In this study, the most effective factors of cerium flotation were investigated. The important factors of cerium flotation and main low-order interactions was recognized and after analyzing the results and graphs, the validation test which the software suggested, was conducted.

Colloid preparation

Ferric hydroxide forms a lyophobic sol with water which is the dispersion medium. It is prepared by hydrolysis of ferric chloride using boiling distilled water as per reaction equation (1). It was prepared by adding 1.28 g $FeCl_3.6H_2O$ to boiling water and obtained $Fe(OH)_3$ was stable and it did not need any dialysis.

$$FeCl_3(aq) + 3H_2O \rightarrow Fe(OH)_3 + 3HCl(aq) \qquad (1)$$

Equipment

Cerium flotation teste were conducted in a Plexiglas cell with 1 m height and 30 cm diameter. A Plexiglas sparger with 500-micrometer holes installed at the bottom of the cell and an air flow meter with compact air attached to the sparger and cell. Reagents addition and pH adjustment performed through a hole on the body of the cell. A valve at the bottom of the cell did discharging of cell and floated concentrate overflew at the top of the cell without wash water.

Adsorbing colloid flotation

In the experiments, various dosages of Fe colloid and cerium (350 and 500 ppm respectively) added to 1000 mL water and after preparation time (nearly 2-5 min), SDS (Sodium dodecyl Sulfate) or Armac T was added as collector. Sodium sulfide and pine oil was also added to the pulp as activator and frother, respectively. While the air entered the cell, a froth column formed and complex of metal and colloid which attached to the bubbles overflowed as a concentrate.

Experimental design

The Experiments were designed by the use of "Design experiment 8" (DX8) software. The design contained 32 tests ($2^{10-5}=32$) that had 10 factors in which 7 factors were Numeric and 3 factors were Categoric. Levels of each factor are shown in Table 1.

RESULTS AND DISCUSSION

Adsorption of cerium on the colloid surface

Cerium adsorption takes place on the surface of colloid by physisoprtion by forming electrostatic forces. After cerium adsorption, hydroxide floc has a positive charge which attached to rising bubbles by the specific amount of collector such as SDS. Fig. 1 shows the prepared $Fe(OH)_3$ colloid surface at a zoom of 30000x. As it is shown in Fig. 1 a, the surface of Fe colloid is extended, so it is expected to have favorable adsorption of cerium. Fig. 1 b shows adsorbed cerium particles on the surface after adsorption. The SEM picture shows that there has been a marked growth of adsorbed cerium on the iron colloid surface and vacant surface that could be filled by an adsorbent.

Fig. 1 c reveals the EDS of Fe surface and Fig. 1 d shows the EDS analysis of adsorbed cerium on the colloid. As predicted, 85 wt. percentage of those white particles were analyzed was cerium (EDS 2) and gray color particles (EDS 1) was colloid surface.

Analysis of Variance

The Analysis of Variance (ANOVA) for Ce recovery revealed that the model was significant. Also, Values of "Prob > F" less than 0.0500 indicates model terms are significant.

Table 1: Factors and their levels in the fractional factorial design.

Factor	Name	Minimum	Maximum
A	pH	2	5
B	Collector type	Armac T	SDS
C	Collector concentration	350	500
D	Colloid concentration	350	500
E	Cerium concentration	350	500
F	Air flow rate	18	24
G	Preparation time	2	5
H	Frothing time	5	7
J	Sodium sulfide (activator)	without Na2S	Na2S
K	Pine oil (frother)	without Pine Oil	Pine Oil

EDS 1

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc
Cl	Ka	30.79	2.865	74.915 wt.%
Fe	Ka	3.56	0.974	25.085 wt.%
				100.000 wt.% Total

EDS 2

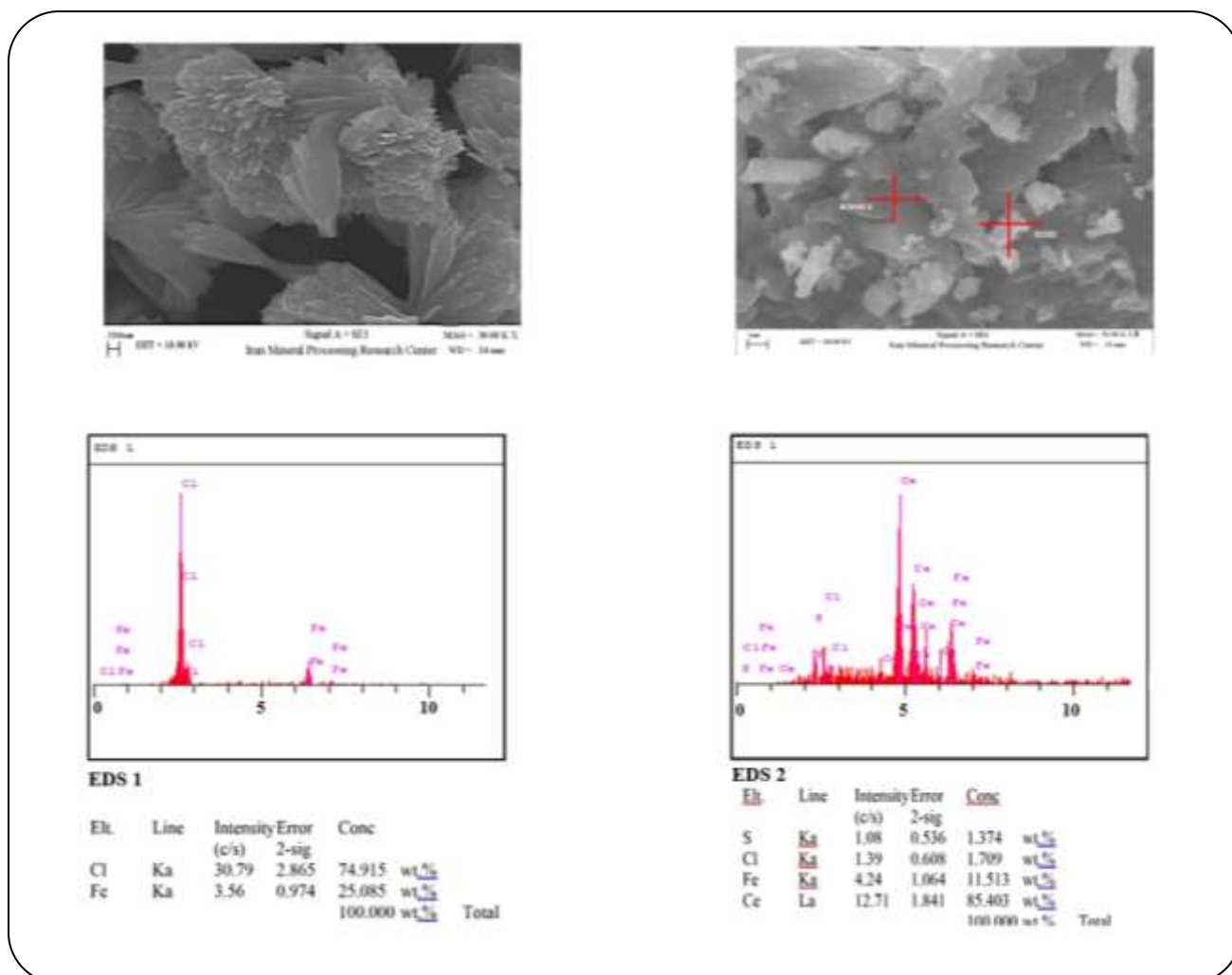| Elt.	Line	Intensity (c/s)	Error 2-sig	Conc
S	Ka	1.08	0.536	1.374 wt.%
Cl	Ka	1.39	0.608	1.709 wt.%
Fe	Ka	4.24	1.064	11.513 wt.%
Ce	La	12.71	1.841	85.403 wt.%
				100.000 wt.% Total

Fig. 1: a) Iron colloid SEM with 30000x zoom b) iron colloid with adsorbed cerium on its surface with 50000x zoom after adsorption c) the results of EDS1 and ESD2 analysis (SEM) shown in part b.

The ANOVA for grade showed that the model was significant and Model F-value was 26.69. Also Values of "Prob > F" less than 0.0500 (<0.0001) indicates the significance of model terms. In this case, A, C, D, F, G, AH, BK, CD, CG, are significant model terms.

According to the ANOVA table, the most important factor affecting recovery are: A, B, C, D, E, F, G and the main interactions are: AC, BJ, CD, CG, ABE, ABJ and the most effective factors for the grade are :A, C, D, F, G, and the main interactions are: AC,AD, AG, AH, BE, BK, CD,CG, ABE, ABJ.

Effective factors on Cerium recovery and grade
Effect of pH (A)

The maximum recovery was achieved at a minimum level of pH (pH=2). Fig. 2a shows the recovery variation from pH=2 to 5. The Ce recovery in all experiments shows such decrease from pH=2 to 5.

As can be observed from Fig. 2b, the pH=2 led to more recovery in comparison of pH=5 despite changing collector to Armac T.

As can be seen from Fig. 2c by increasing pH, the grade saw a marked decrease. Similar to recovery, the impact of low pH on the obtaining maximum grade was very powerful. The zeta potential of Fe colloid is in pH=6.7, the surface charge below this pH is positive and above of 6.7 is negative. So in acidic pH, the colloid could be float by SDS easily. The colloid has a positive charge at pH=2 and the collector ionize in water to $R-SO_4^{3-}$ and Na^+. The nonpolar part of collector attached to colloid and the polar head of hydrocarbon part of collector ($CH_3(CH_2)_{11}SO4$) face to the water and then attached to the bubble and rise to froth zone. Therefore, pH=2 to have the optimum mechanism of attaching bubble to the collector is the best pH.

Collector type effect (Factor B)

The results showed 87.01 % recovery using Armac (Fig. 2d) and 97.22 % recovery for SDS (Fig. 2e). In SDS collector, it was found that cerium concentration should be in minimum value (cerium concentration=350 ppm) to have the maximum recovery as shown in Fig. 2f.

The effect of collector concentration (Factor C)

For Armac T, maximum recovery obtained in minimum collector concentration (Collector

concentration=350 ppm) as per c a and for SDS collector, the highest amount of collector (Collector concentration= 500 ppm) led to maximium recovery (Fig. 3b). Fig. 3c revealed that there has been a slight rise in cerium grade in increasing collector concentration. In contrast to recovery, changes in this parameter didn't have a profound effect on the grade. Flotation takes place only over a finite range of surfactant concentration; concentrations above and below this range yield hydrophilic surfaces to which bubbles cannot attach.

Armac T is the first type of Amine collectors in which micelle formation is the main feature of amine type 1. If the concentration of Armac T(as a surfactant) is further increased, the exposed hydrocarbon tails may permit a second layer of surfactant to adsorb, forming a micellar layer on the solid surface. This second monolayer will be attached by van der Waals forces to the first layer and will present an ionic or hydrophilic surface, preventing bubble attachment and flotation so the minimum concentration for Armac leads to the best recovery but in SDS collector, the fenamenon doesn't ocuur, therfore the best recovery is in the maximum concentration of SDS.

The effect of Fe concentration (factor D)

When SDS was used as collector, the Fe concentration had the most effect on the results, therefore in the highest level of Fe (colloid concentration=500 ppm), 85.70 % recovery was obtained (Fig. 3d). looking at Fig. 3e, it is apparent that colloid concentration has more impact on grade than recovery. By increasing the Fe colloid, the sites of solid adsorbing will be increased. That is, the probability of adsorbing for cerium will be increased and the amount of adsorbed cerium on colloid will be raised. On the other hand, because of increased colloid, attaching of the collector to colloid increase strongly. Thus, adsorbing capacity capacity will be increase and recovery and grade increase simultaneously.

The effect of Cerium concentration (Factor E)

The effects of cerium concentration on recovery are similar to those of Fe concentration factor. When the collector SDS used, in maximum cerium concentration (cerium concentration=500 ppm), the most recovery was observed as Fig. 3f illustrates. As a result of Sodium dodecyl sulfate (SDS) hydrocarbon tail, and its anionic head group it has amphiphilic properties. SDS
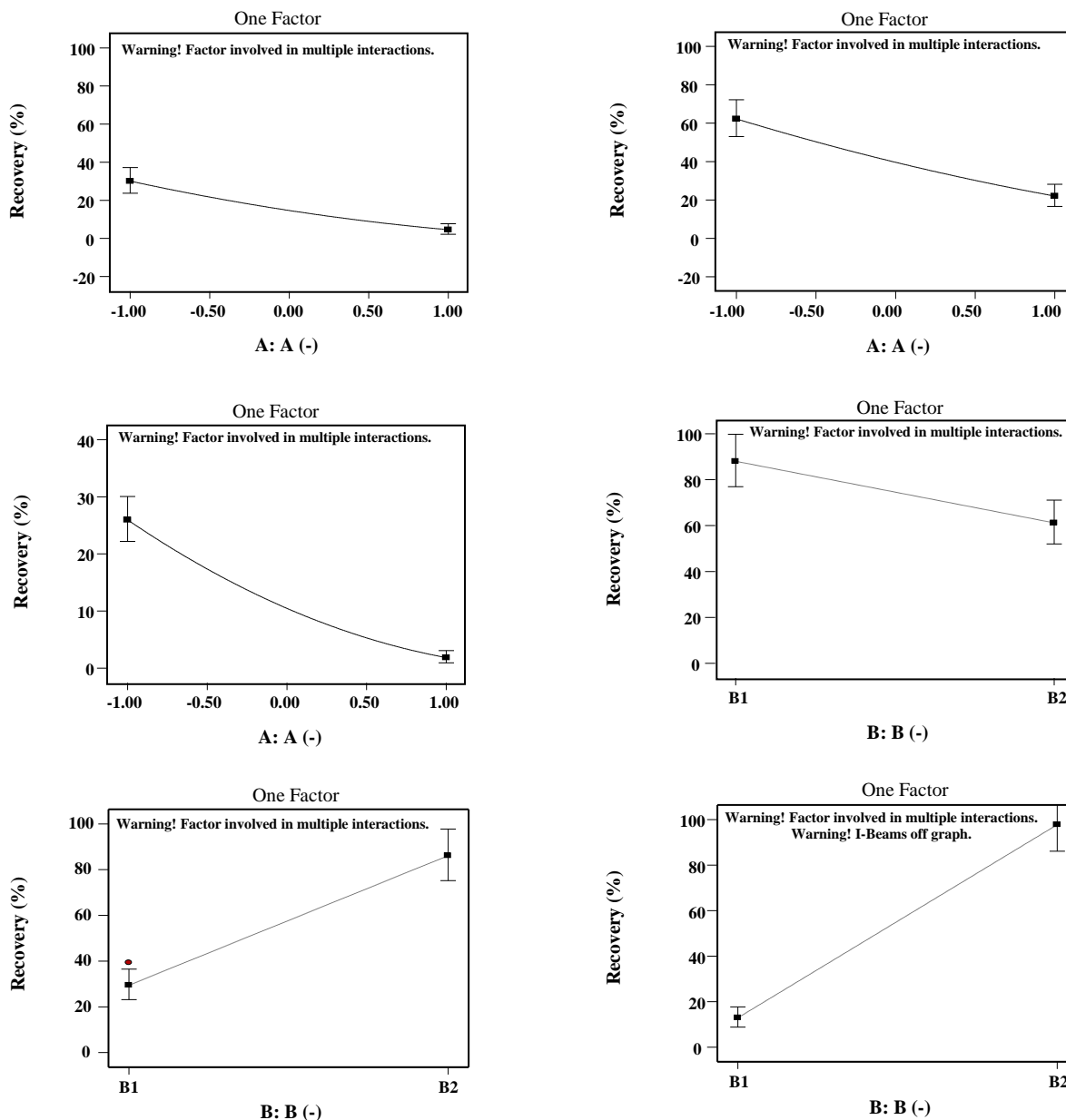
Fig. 2: a) the effect of pH (factor A) on the recovery of cerium in the presence of SDS collector. Level -1 is pH=2 and level +1 is pH=5; b) the effect of pH (factor A) on the recovery of cerium in the presence of Armac T collector c) Cerium grade to pH changes d) Armac T (B1) effect on recovery; e) SDS effect on grade with E=350 ppm; f) 85.70 % recovery for SDS collector with E=500 ppm.

is adsorbed on the surface of cerium adsorbed on Fe Colloid which is also negatively charged. Although the magnitude of negative charge density increases with the increase of the collector concentration (Collector concentration=500 ppm), the electrostatic repulsion becomes smaller with more than 500 ppm concentration, because the screening effect is strong and the magnitude of the potential near the surface decreases.

The effect of air flow rate (factor F)

It had a a linear relationship with recovery and grade, by increasing air flow rate, cerium recovery and grade were increased (Fig. 3g for recovery and Fig. 3h for a grade). The height of froth was increased with increaing air flow rate. However, it was observed that at air flow rates higher than 32 cc/min, the froth was not continuous although the formation of froth was more. When the air
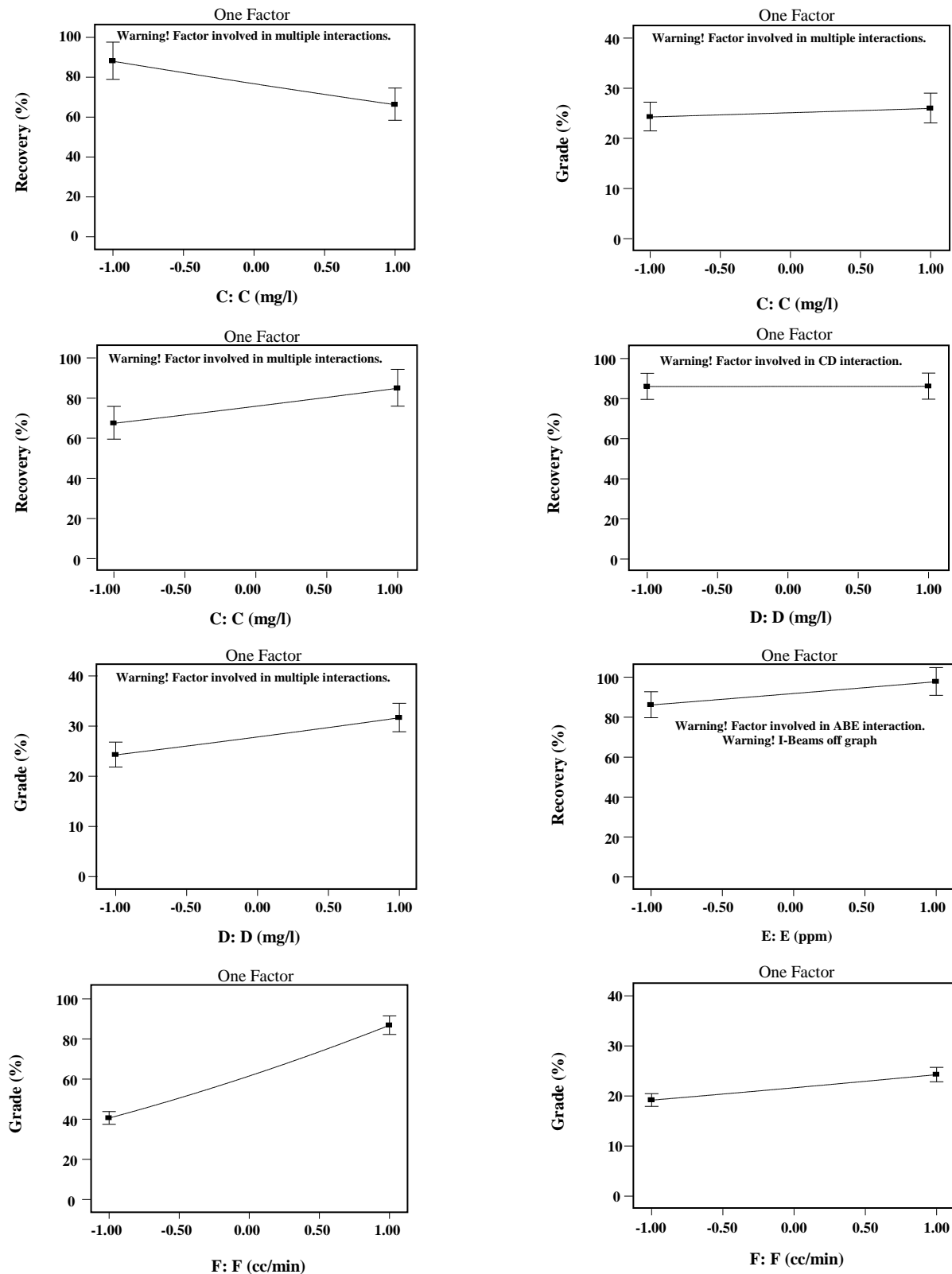
Fig. 3: Effect of the collector on recovery; a: Armac T; b: SDS; c: cerium grade versus collector concentration.
d) Fe concentration effect on recovery e) the impact of Fe concentration on grade f) recovery versus cerium concentration
(factor E) g) recovery versus air flow rate(Factor F) h) air flow rate effect on cerium grade.
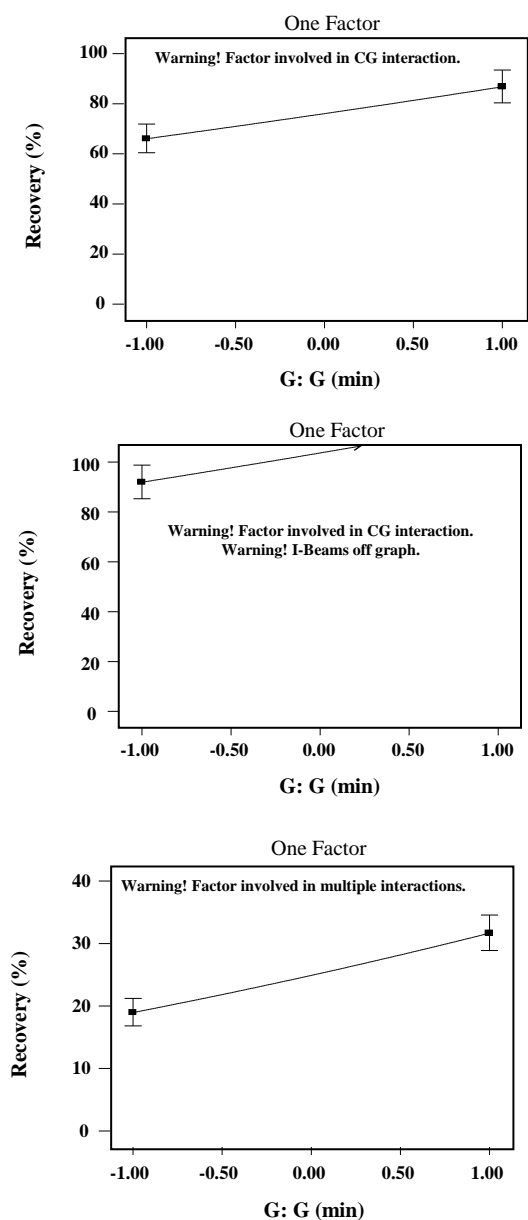
Fig. 4: a) preparation time effect on recovery without using activator and frother b)effect of preparation time on recovery using activator and frother c)grade versus prepation time (factor G) and its linear relationship.

flow rate is below or above of optimum air flow rate, the pulp and water are in plug flow system (not continuous), the collector has no suitable time to attach to the bubble and the bubble carry no concentrate to the froth zone but in a perfect mixed system, colloid and collector attached to the bubble in a specific time and because of contionuous flow of water (for appropriate air flow rate, as mentioned) the buubles carry the colloid and cerium that adsorbed on the cooloid.

The effect of preparation time (factor G)

As shown in Fig. 4a, the recovery increased in the longest preparation time (preparation time=5 min) while activtor and frother were not used. On the other hand, it is apparent from Fig. 4b when activator and frother was used (K2 and J2), maximum recovery was in the shortest preparation time (preparation time=2 min). The effects of preparation time on grade are similar to those of recovery as shown in Fig. 4c.

Adsorption mechanism steps are involved in three steps: mass transfer step:

"1. Mass transfer step: mass transfer from the bulk of the fluid to the surface of the adsorbent particle through the boundary layer around the particle.

2. Diffusion step: internal diffusion through the adsorbent pores.

3. Adsorption step: adsorption onto the surface of the particle" [34]. Therefore, preparation time is a vital parameter for the adsorption mechanism and the optimum time, will lead to the best recovery and grade.

The effect of interactions on Cerium recovery

The maximum point of AC (pH-collector concentration) interaction was observed in pH=2 and collector concentration=350 ppm (Fig. 5a). so the factors should be at minimum levels simultaneously. A glance at the BJ (Collector type- activator interaction) graph provided reveals that for J1 and K1(without frother and activator), recovery of Armac T is 44.17 % and for SDS is 86.36% While using frother and activator (J2 and K2), recovery for Armac T reduces to 23.11 % and increase to 99.8 % (Fig. 5b) for SDS. Armac T (as an Amine collector) has the frothing characterization [35], so if the frother adds to the pulp, it acts reversely and the froth does not have selective froth. While in SDS collector, it has a positive effect and stable the froth to form a mixed flow instead of plug flow.

Maximum recovery for nearly all experiments was acheived by SDS collector, As a result, only related data was considered. Fig. 5c indicated that recovery of 99.48 % in CD (collector -colloid concentration) interaction graph, was obtained in collector concentration=350 ppm and colloid concentration=500 ppm and at collector concentration=350 ppm and Colloid concentration=350 ppm, recovery was 78.29 %, for collector concentration=500 and colloid concentration=500 ppm. So the best result for SDS
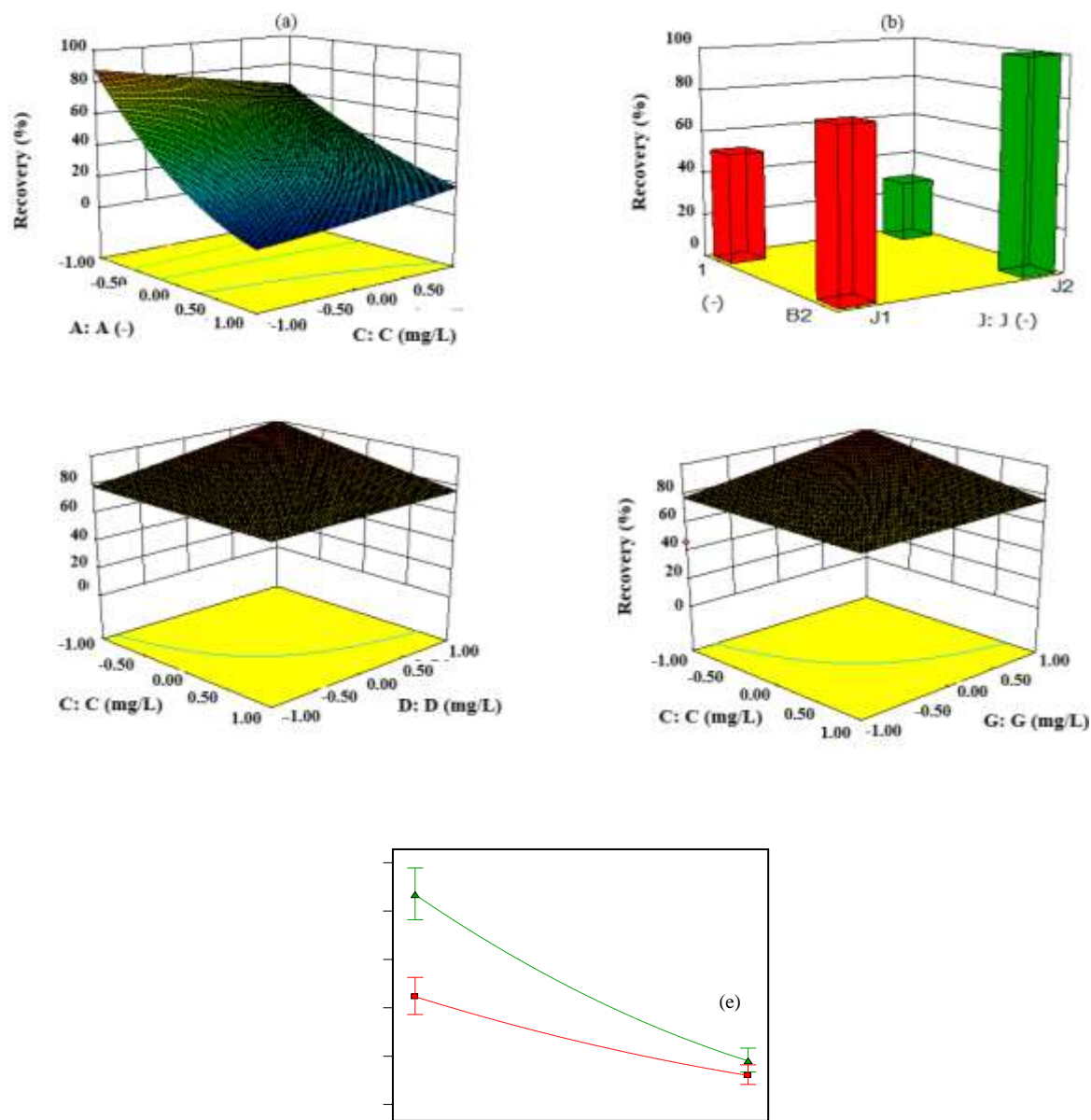
Fig. 5: The effect of interactions on cerium recovery; a) AC interaction b) BJ interaction c) CD interaction
d) CG interaction e) ABE interaction.

collector (99.48 % of cerium recovery), owing to the presence of activator (J2) and frother (K2), with the highest dosage of Fe (colloid concentration=500) and the minimum level of the collector (Collector concentration=350).

as Fig. 5d depicts, using activator (J2), SDS collector, the minimum level of the collector (collector concentration=350) and the shortest preparation time (preparation time=2 min), the recovery of 98.45 % for CG interaction gained. As aforementioned, the best recovery related to SDS

collector thus, from Fig. 5e, it is apparent that for collector concentration=500 ppm, air flow rate=24, preparation time=5 min and in the presence of activator (J2), absence of frother (J1) and at the lowest pH (pH=2), recovery was 86.22 %.

As aforemntioned, each parameter has its effects on flotation that their synergitic effects cause double effects on the surface of colloid, bubble satability and the maximum recovery.
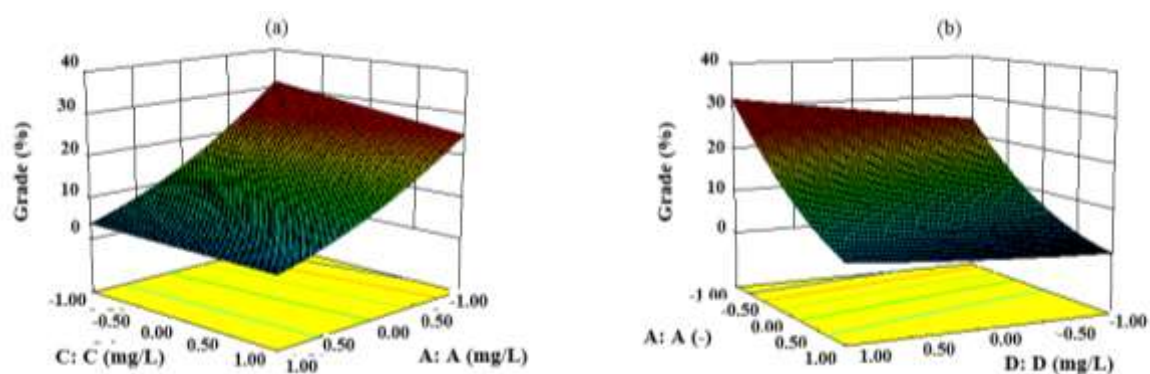
Fig. 6: a) Interaction of pH and collector dosage b) pH and Fe (Colloid) concentration interaction.

The effect of interactions on Cerium grade

At low pH value (pH=2), the results are better in comparison with other pH levels. In AC (pH-collector concentration) interaction, If collector Concentration=350 ppm and pH=2, the Ce grade for Armac T is 14.16 % and for SDS is 7.39 %. If the cerium concentration increase (collector concentration=500 ppm), for Armac T, the grade is 16.64 and 9.2 % for SDS. Therefore, Armac T has a better effect for grade increasing (Fig. 6a). Fig. 6b (AD inteaction) represnts that increasing pH and decreasing Fe concentration at the same time and using the activator and frother reduced Ce grade. Conversely, in similar conditions, by increasing Fe concentration and low values of pH, the outcome is high cerium grade.

Like other interactions, In AG (pH-preparation time) interaction**,** there is a notable decrease in the cerium grade using Armac T with activator and pine oil. Besides, high amounts of pH (pH=5) had a negetive effect on the grade. Fig. 7a revealed that using Armac T, without activator and frother, For pH=2 at 500 ppm, the maximun grade was 18.41 %. On the other hand, obtaining the same grade by SDS, it should be used Na2S and pine oil (J2 and K2). At minium levels of pH and frothing time (pH=2 and Frothing time =-1) in AH (pH-frothing time) interaction, the grade of cerium was maximum (Fig. 7b). In BE (Collector type-Cerium concentration) interaction consideing, the grade in pH=2 (pH=2) was maximum like previous interactions. For Armac T and the minimum level of cerium (cerium concentration=350 ppm), the maximum grade was 17.72 %. For obtaining this grade with SDS, the frother and activator and maximum cerium level should be applied (J2 and K2 and cerium concentration=500 ppm respectively).

From the data in Fig. 7c, it is apparent that at pH=2 and without activator, the maximum grade for Armac T was 25.74% and for obtaining the same grade with SDS (grade=25.83, Fig.7d), activator and frother should be used in pH=2.

In Fig. 7e, activator has no effect on flotation and the results seem to be well without using the frother. The maximum grade for this case (20%) would get with Armac collector, the highest collector concentration (C =500 ppm) and maximum Fe colloid (colloid concentration=500 ppm). At collector concentration=500 ppm and colloid concentration=500 ppm and SDS collector, the grade was 5.96%.

If collector concentration in CG (Collector concentration- Preparation time) interaction would be at the highest level (collector concentration=500 ppm) and preparation time=2 min, the maximum grade is 2.9 % so the results seem weak.

The effect of main parameters and their mechanism explained above. Therfore changing the effective parameters, have synergitic effect on adsrption and finally on the cerium grade.

Conclusion for Recovery

The maximum recovery of the Armac T was 88.84% and the highest value for the collector type 2 (SDS) was 99.84%. Factor F (gas flow rate), has a linear relationship with recovery but pH has inverse proportion, that is acidic pH enhances the recovery. when the collector SDS is used, the concentration of iron and cerium is most effective. Factor G also depends on the activator and frother using. When none of them used, the minimum time for maximum recovery was appropriate.
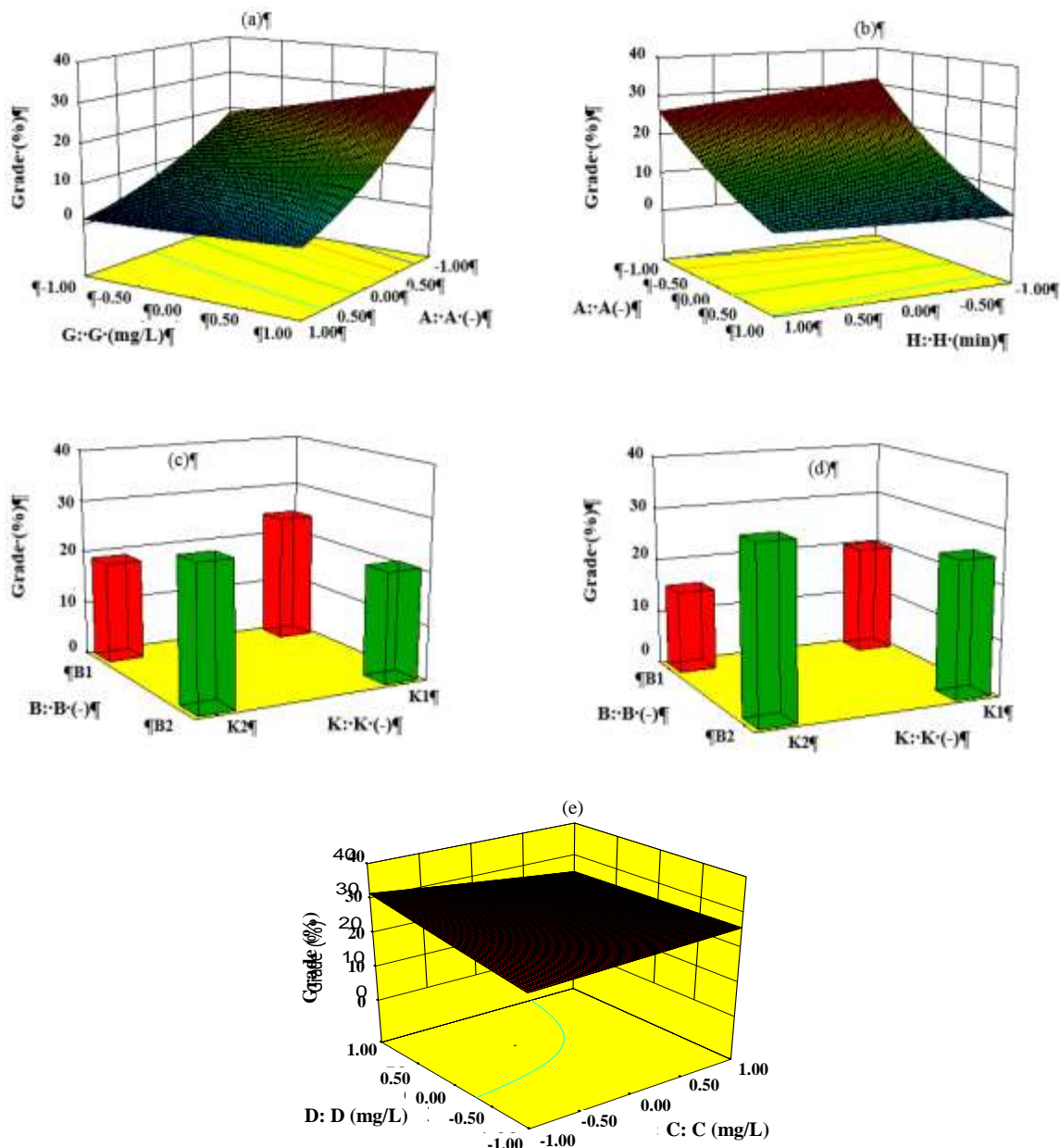
Research Article

Fig. 7: The effect of interactions on cerium grade: a) AG interaction; b) AH interaction c,d) effects of BK interaction in which both factors B and K are catagoric on cerium grade e)3D graph of CD interaction effect on cerium grade.

In interaction BJ, the major influenced factors are the activtor presence (J2) with the absence of the frother (K1). The highest recovery, when J2 and K1, is also related to the collector SDS. While the low level of the collector SDS (C = 350 ppm), the presence of Na_2S without pine oil (as frother) and the highest concentrations of iron, the maximum recovery was obtained. Coded Model for Recovery is shown in equations 2.

Sqrt(Recovery + 1.00) = + 4.47 -1.19 A +1.17*B + 0.80*C + 0.28* D - 0.30* E + 1.47* F + 0.31* G + 0.86* A * C + 0.33* B * J -0.28* C * D - 0.28* C * G - 0.60* A * B * E - 0.26* A * B * H - 0.58 A * B * J + 0.18* A * B * K   (2)

Conclusion for Grade

The highest grade was on the condition that the collector type 1 (Armac T) and the lowest pH was used

Table 2: The validation test conducted according to the suggested point of software and comparising validation and prediction test.

predicted point versus validation test			
Response	Software Prediction	Validation test	Error
Grade	19.78	18.93	4 %
Recovery	91.30	88.32	3 %

without the presence of activator and frother. Armac T has frothing properties, so it doesn't need any frother. By adding Na2S, the armac T was deactivated and the froth was reduced markedly. On the other hand, Na2s and pine oil helped to SDS to float better.

Parameters D, F, and G have a direct effect on the grade, while the factors A and C have the opposite effect. On the other hand, the interaction of these factors, have increasing effects on the grade trend. When pH leads to grade enhancing, by increasing the factor C, the grade would be increased.

In general, to increase the grade, according to the graphs, the best collector is Armac T. As mentioned above, due to its properties does not need to use a frother or activator. In the best case, the grade of cerium with Armac T was 25.10 % and, up to 16.1 % achieved with SDS using frother and activator.

Coded Model for a grade is shown in Equations (3).

$$Sqrt(Grade + 0.25) = + 2.39 - 1.04 * A + 0.29 * C + 0.30 * D + 0.27 * F + 0.25 * G + 0.13 * A * C + 0.15 * A * D - 0.12 * A * G + 0.25 * A * H + 0.13 * B * E + 0.29 * B * K - 0.20 * C * D - 0.27 * C * G - 0.20 * A * B * E - 0.22 * A * B * J \quad (3)$$

OPTIMIZATION

In optimization, the main goal is the simultaneous increasing of recovery and grade. Therefore, with regard to minimum reagent dosages, the software suggested the optimum conditions (Table 2). According to the suggested software points, the validation test implemented and the results comparised to the software result as per Table 2. As seen, the same results with less than 5% error were acheived.

CONCLUSIONS

This research was undertaken to conduct cerium flotation and define the most important factors affects on adsorbing colloid flotation of cerium. Some factors which are thought to contribute to ACF were examined and finally recovery and grade as responses were optimized. The most obvious finding to emerge from this study is that the maximum recovery was 99.84% and the grade increased up to 25.10 % from the initial 500 ppm cerium. pH, collector type, collector and cerium dosage and colloid concentration are the most significant factors which effecting Ce recovery and grade. After optimization, when the final aim was floating of cerium with maximum recovery and grade simultaneously, the suggested points of software was parctically done and the results were in accordance with predicted points of the software. The SEM (Scanning Electron Microscope) analysis before and after adsorbing flotation showed that ACF is a great method for extracting of cerium from solutions and wastewaters.

Acknowledgement

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