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OPTIMIZATION OF GOLD SORPTION FROM AMMONIACAL THIOSULPHATE SOLUTION ON ANION EXCHANGE FIBER USING TAGUCHI EXPERIMENTAL DESIGN

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ABSTRACT. Taguchi experimental design was used to optimize the experimental parameters for Au sorption from ammoniacal thiosulfate solutions containing 2 mg/L Cu complexed as cuprous thiosulfate $[Cu(S_2O_3)_3]^{5-}$ onto anion exchange fiber (METALICAPT® MFH11). An L_9 orthogonal array was chosen to study the effect of three parameters, namely Au initial concentration (10-30 mg/L), fiber quantity (0.05-0.55 g) and temperature (20-30°C). The sorption tests were carried out in batch mode at a stirring rate of 500 rpm and pH of 9.3. The experimental data were processed using signal-to-noise ratio and the analysis of variance was used to determine the most significant parameters. The optimal conditions for Au sorption were found to be 30 mg/L Au concentration, 0.05 g of fiber and temperature of 20°C. The obtained results indicated fiber quantity as the most influential parameter on Au sorption with a contribution of 66%, followed by Au initial concentration with a contribution of 33%. In the optimal conditions, the sorption capacity of the fiber was found to be 16.8 mg/g, in good agreement with the predicted result by Taguchi method (16.7 mg/g). Further investigations are necessary to examine the elution behavior of gold from the fiber.

Keywords: *gold sorption, anion exchange fiber, Taguchi experimental design, ANOVA*

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INTRODUCTION

The technologies for precious metal recovery have gained considerable interest, as gold (Au) resources are limited while Au is frequently used in various fields due to its outstanding thermal and electrical conductivity, high catalytic performance and photothermal conversion efficiency [1,2].

Gold leaching using thiosulfate solutions has emerged as an innovative and eco-friendly alternative to cyanide leaching, for gold containing wastes. However, the recovery of gold thiosulfate complex from pregnant leachate solution proved to be challenging. Thus, development of appropriate methods to effectively recover gold thiosulfate complex are still unavailable [3]. Although there are several papers on gold leaching from wastes, only few studies reported the recovery of Au from pregnant thiosulfate leaching solution. Literature data suggest that activated carbon adsorption, cementation, electrowinning and solvent extraction are likely inapplicable for the separation of gold from thiosulphate solutions, especially in case of the presence of competitive metal ions. Activated carbon presents low affinity for $[Au(S_2O_3)_2]^{3-}$ probably due to weak interaction between carbon active sites and $S_2O_3^{2-}$. The recovery of gold using activated carbon can be improved by the addition of cyanide, which is not environmentally friendly. Through cementation process, gold can be precipitated, yet the recycling solution is difficult. The main disadvantages of electrowinning process for gold recovery are the high energy consumption and the low efficiency. Solvent extraction is a time-consuming process and expensive to achieve a complete solid-liquid separation [4]. Compared to other separation techniques, like electrolysis, solvent extraction and membrane separation, adsorption using ion exchange resins presents several advantages, like fast adsorption, high loading capacity, simultaneous elution and regeneration as well as operation at ambient temperature [4,5]. Moreover, it generates fewer toxic by-products and the adsorbent can be regenerated and reused several times [2]. Although, few information related to resin regeneration is available [6].

The efficiency of gold recovery is dependent on physical and chemical properties of the adsorbent and is influenced by the sorption conditions, such as pH of the solution, contact time, the quantity and initial gold concentration. Weak and strong base anion exchange resins are presently used in gold recovery [5]. In general, the pH of ammoniacal thiosulfate solution used for gold leaching is in the range of 9-11, thus at this pH both the thiosulfate and copper ammonia complexes formed during gold leaching are simultaneously stabilized [4]. Consequently, the weak-base resins are not adequate to recover Au from ammoniacal thiosulfate solution since their ion-exchange ability is damaged at a pH higher than 8. The strong base anion exchange resins are more resistant to the competing anions and aurothiosulfate complex can be efficiently removed at low concentrations. Nonetheless, these resins have a poor selectivity, $[Cu(S_2O_3)_3]^{5-}$ will strongly compete with $[Au(S_2O_3)_2]^{3-}$ for the active sites on resin surface [4]. The elution of gold and copper from the adsorbent is a two-stage process: in the first stage, Cu is selectively eluted by a solution containing oxygenated ammonia-ammonium sulfate or ammonium thiosulfate and in the second stage, Au is effectively eluted by thiocyanate, polythionates, perchlorate or nitrate containing solutions or by mixtures of thiourea and sulfuric acid or sulfite and chloride [4].

Taguchi method is a simple and effective experimental design technique used for optimizing process parameters [7]. The optimum experimental conditions are determined using an orthogonal array which aims to maximize the experimental results using a small number of experiments. Consequently, the signal-to-noise (S/N) ratio is used to analyze the experimental results and to determine the optimal levels of each parameter [8,9]. S/N represents the ratio of desirable results (signal) to undesirable results (noise) obtained [10]. Thus, using S/N ratio, the control factors that reduce the variability of the Au removal by minimizing the effects of uncontrollable factors can be identified [11]. Through Taguchi method, the effects of multiple parameters and their interaction can be investigated in a time- and cost-effective manner [12].

The objective of the present study was to maximize the total amount of Au as $[Au(S_2O_3)_2]^{3-}$ adsorbed on METALICAPT® MFH11 fiber from a synthetic aqueous solution containing ammonium thiosulfate (0.1 M) and 2 mg/L Cu complexed as $[Cu(S_2O_3)_3]^{5-}$ by optimizing the selected process parameters using Taguchi method. The METALICAPT® MFH11 fiber is a newly developed anion exchange fiber containing ammonium ($-NR_3^+$) and tertiary amine ($-NR_2$) functional groups that has not been previously studied for Au sorption from ammoniacal thiosulphate solution. The research was carried out in four steps. In the first step, three parameters, namely Au initial concentration, fiber quantity and temperature were selected to be optimized in batch experiments due to their significant effect on aurothiosulfate complex sorption. An appropriate orthogonal array was chosen based on the considered parameters and their levels. In the second step, the experiments were performed using the selected 9 experimental trials. For each experiment conducted, the total amount of Au as $[Au(S_2O_3)_2]^{3-}$ sorbed on METALICAPT® MFH11 fiber was calculated. In the third step, the obtained results were processed with larger-the-better equation (S/N output) to determine the optimum conditions for the considered process and to maximize the response in terms of the total amount of $[Au(S_2O_3)_2]^{3-}$ sorbed on METALICAPT® MFH11 fiber. Finally, in the fourth step, confirmation experiments were carried out to verify the experimental conclusions.

RESULTS AND DISCUSSION

Taguchi Experimental Design

The experimental results express in terms of sorption capacity and removal efficiency obtained based on Taguchi's orthogonal array are presented in Table 1. Based on the obtained results, it can be seen that as initial Au concentration increased the q_e values increased and the removal efficiency decreased. The initial Au concentration offers the necessary driving force to overcome the mass transfer resistance of adsorbate [13]. The q_e decreases as the fiber quantity increases because more sorption sites are available. As the temperature increases, q_e decreased suggesting an exothermic process for Au sorption [12]. The Minitab software was used to calculated the equivalent S/N ratio of the experiments based on the obtained q_e values using larger-the-better equation to maximize the response [11].

Table 1. The experimental results obtained based on Taguchi's orthogonal array and the corresponding S/N ratio for each experiment

Experiment number	**Experimental result**		**S/N ratio**
	q_e (mg/g)	**Au removal (%)**	
1	8.1	40.8	18.12
2	2.9	73.3	9.24
3	1.6	88.0	3.98
4	16.8	37.6	23.96
5	6.5	73.0	16.12
6	3.5	87.2	10.83
7	19.9	31.8	25.92
8	8.9	71.5	19.02
9	4.9	85.7	13.75

The S/N ratio response (the average value of S/N ratio of each parameter at levels 1, 2 and 3) for Au sorption onto METALICAPT® MFH11 fiber is given in Figure 1. The greatest S/N ratio represents the optimal level of the considered parameter. Based on the difference between the highest S/N and lowest S/N for each parameter, the delta value can be calculated and compared. The following series was depicted based on the obtained delta values: fiber quantity (13.15) > Au concentration (9.12) > temperature (0.65). Thus, fiber quantity has a strong influence on Au sorption, followed by concentration and temperature has a low influence on Au sorption onto METALICAPT® MFH11 fiber. Consequently, concentration has the highest effect on the Au sorption at level 3 and fiber quantity and temperature had the highest effect at level 1. The optimum conditions for Au sorption were found to be initial Au concentration of 30 mg/L, fiber quantity of 0.05 g and temperature of 20°C.

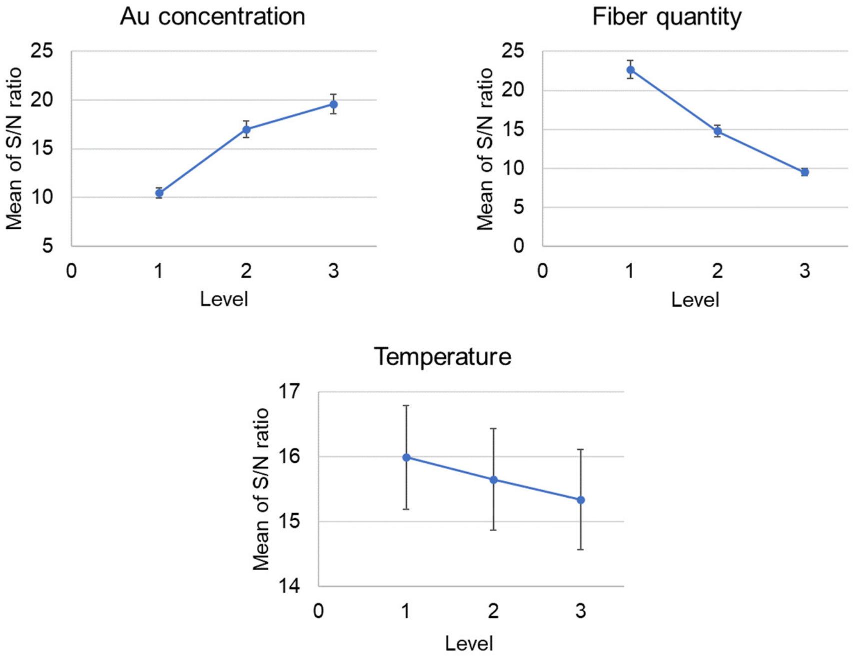

Figure 1. The effects of process parameters on Au sorption onto METALICAPT® MFH11 fiber

Analysis of variance (ANOVA)

ANOVA is one of the statistical models used to distinguish the performance of parameters and their interactions. ANOVA analysis was used to identify the significant parameters for Au sorption onto METALICAPT® MFH11 fiber by the sum of the squared deviations from the total mean of S/N ratio [11].

The degrees of freedom (*DF*), sum of squares (*SS*), mean square (*MS*), distribution of the ratio (*F)* and *p* value are shown in Table 2. Further, the percent contribution (*PC*) of each parameter [14] was calculated and the results are given in Table 2.

Table 2. Analysis of Variance for S/N ratio

Parameter	*DF*	*SS*	*MS*	*F*	*p*	*PC*
Concentration	2	132.48	66.24	197.95	0.005	33.42
Fiber quantity	2	262.65	131.32	392.46	0.003	66.25
Temperature	2	0.64	0.32	0.95	0.512	0.16
Residual Error	2	0.67	0.34			0.17
Total	8	396.43				

The *p* value for concentration and fiber quantity is very small which means that there is significant evidence against null hypothesis (H_0). The most significant parameters ($p<0.01$) for Au sorption are initial Au concentration and fiber quantity (Table 2). The *p* value for temperature was 0.512, thus this parameter can be ignored as it is insignificant for Au sorption. Fiber quantity (PC% = 66.25) was the most important parameter on Au sorption, followed by Au initial concentration (PC% = 33.42). The mean response for larger-the-better used to predict the optimum q_e value is given in Table 3.

Table 3. The mean response for larger-the-better (average q_e values)

Level	Concentration	Fiber quantity	Temperature
1	3.51	**14.24**	**6.17**
2	8.93	6.10	8.19
3	**11.22**	3.32	9.30
Delta	7.71	10.92	3.14
Rank	2	1	3

Three experiments were carried out to validate the obtained results using the levels of the optimal process parameters for Au sorption onto anion exchange fiber. The results obtained are presented in Table 4. As it can be seen in Table 4 the predicted optimal q_e value and the average of confirmation experiment was 16.7 mg Au/g fiber and 16.8 mg/g, respectively. As it can be observed the obtained values are very close. Thus, the results predicted by Taguchi method were validated by the confirmation experiments. Further, the fiber can be burned to obtain Au. Also, the purity of the Au depends on the concentration of other concurrent anions present in the solution subjected to treatment.

Table 4. Predicted optimal q_e values and the results of confirmation experiment

Adsorbent	Predicted optimal q_e value	Mean predicted	Average of confirmation experiment (q_e)
	mg/g	mg/g	mg/g
METALICAPT® MFH11	16.7	18.0	16.8

CONCLUSIONS

In the current study, the Taguchi method was used to investigate the effects of Au initial concentration, fiber quantity and temperature on Au sorption from ammoniacal thiosulfate solutions containing 2 mg/L Cu onto an anion exchange fiber. The experimental results were analyzed using the signal to noise ratio and ANOVA to identify the optimum and to most significant parameters. The most prominent parameter affecting the Au sorption was fiber quantity, followed by initial concentration. The data suggested that temperature was insignificant for Au sorption. The predicted optimal value was confirmed through the confirmation experiments performed using the optimal conditions identified by Taguchi method.

EXPERIMENTAL SECTION

Description and Characteristics of the Sorbent

METALICAPT® MFH11, an anion exchange fiber supplied by AJELIS SAS was used for Au sorption. Its characteristics are given in Table 5.

Table 5. Characteristics of the METALICAPT® MFH11 fiber

Ionic form	Chloride (Cl^-)
Functional group	Ammonium ($-NR_3^+$), Tertiary amine ($-NR_2$)
Total exchange capacity (eq /L)	1.25-2.5 ($-NR_3^+$), 1-1.5 ($-NR_2$),
Maximum operating temperature (°C)	90
Density (kg/dm^3)	~0.2-0.3
Appearance	Staple
Regenerant	1-4%NaOH or Na_2CO_3

Reagents and solutions

Analytical grade reagents, such as copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), ammonium thiosulfate $(NH_4)_2S_2O_3$ and sodium hydroxide (NaOH) were used for the preparation of the solutions. All used chemicals were of analytical purity and purchased from Merck (Darmstadt, Germany). Au as $AuCl_4^-$ was introduced in 0.1 M ammoniacal thiosulfate solutions, which was reduced to $Au(S_2O_3)_2^{3-}$. The pH of the solution was adjusted to 9.3 with NaOH, and then Cu (2 mg/L) was added to simulate the effluent obtained after leaching of gold from ores.

Taguchi experimental design

Three parameters with three levels each (Table 6) were taken into consideration to identify the optimum conditions for Au sorption using METALICAPT® MFH11 fiber.

Table 6. Selected parameters and their levels used in the Taguchi experimental design

Symbol	**Parameters**	**Units**	**Levels**		
			1	**2**	**3**
A	Au initial concentration	mg/L	10	20	30
B	Fiber quantity	g	0.05	0.25	0.55
C	Temperature	°C	20	25	30

Based on the considered parameters and their levels, the Minitab software generated the L_9 orthogonal array (Table 7).

Table 7. Design of experiments using Taguchi orthogonal array

Experiment number	**Experiment Design**		
	Au **concentration (mg/L)**	**Fiber quantity (g)**	**Temperature (°C)**
1	10	0.05	20
2	10	0.25	25
3	10	0.55	30
4	20	0.05	25
5	20	0.25	30
6	20	0.55	20
7	30	0.05	30
8	30	0.25	20
9	30	0.55	25

Sorption and confirmation experiments

The optimization of gold sorption on METALICAPT® MFH11 fiber using Taguchi experimental design is detailed in Figure 2.

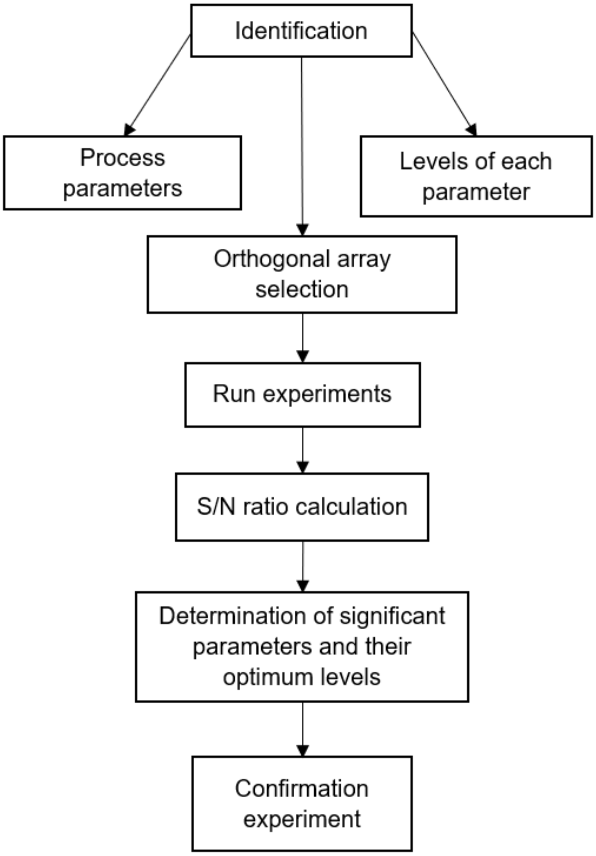

Figure 2. Optimization of gold sorption on METALICAPT® MFH11 fiber using Taguchi experimental design

The sorption experiments were performed in triplicate according to Table 7 for 240 min at a stirring rate of 500 rpm. Preliminary tests showed that equilibrium was reached up to 240 min. The Au concentration was analyzed using an Optima 5300 DV Perkin-Elmer inductively coupled plasma optical emission spectrometer. At the end of each experiment, the sorption capacity of the fiber (q_e) and removal efficiency (percent of sorption, E) were calculated [15] according to Equation 1 and 2, respectively.

$$q_e(mg/g) = \frac{C_o - C_e}{m} \cdot \frac{V}{1000} \quad (1)$$

$$E(\%) = \frac{C_o - C_e}{C_o} \cdot 100 \quad (2)$$

where, C_o, C_e are the initial and equilibrium Au concentrations (mg/L); V is the volume of Au solution (mL) and m is the mass of the fiber (g).

Based on the obtained q_e values, the S/N ratio (using the larger-the-better equation) was calculated to analyze the combined effects of control and noise factors [14]. The larger-the-better equation to maximize the response is given below [11,14].

$$S/N = -10\ log \left[\left(\sum \frac{1}{Y^2}\right)/n\right] \quad (3)$$

where, Y is the value of the response and n is the total number of repetitions in a trial [14].

Further, the ANOVA analysis was conducted to identify the significant parameters of the sorption process. Three confirmation experiment were conducted using the optimal levels of the process parameters. The average value was compared with the predicted value. After determination of the optimum conditions, the mean (μ) was estimated from the significant parameters identified by ANOVA analysis [12,16].

$$\mu = \bar{U} + (A_3 - \bar{U}) + (B_1 - \bar{U}) \quad (4)$$

where, $\bar{U}$ is the overall mean of the response (mean of q_e value of the experiments performed according to L_9) and A_3, B_1 represent average values of response at their optimum levels.

The predicted optimum value of q_e was calculated as follows:

$$\mu_{fiber} = \bar{U}_{fiber} + (A_3 - \bar{U}_{fiber}) + (B_1 - \bar{U}_{fiber}) + (C_1 - \bar{U}_{fiber}) \quad (5)$$

where, μ_{fiber} is the predicted optimum value of q_e for the anion exchange *fiber*, $\bar{U}_{fiber}$ is the overall mean of q_e, and A_3, B_1, C_1, are the average q_e values at their optimum levels [12,16].

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