The Effect of Kinetics Parameters on Gold Extraction by Lewis Cell: Comparison Between Synthetic and Leach Solution

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ABSTRACT: *Modern hydrometallurgical techniques have been adopted to produce high-purity gold. Many extractants were used for the extraction of gold from various synthetic solutions from which DiButyl Carbitol (DBC) had a unique superiority. Kinetics of process was studied in this paper and the influence of several parameters such as stirring speed, agitation time, impeller type, interfacial area, $[AuCl_4]^-$ and DBC concentrations, pH and temperature on gold extraction were investigated. The increase in the stirring speed up to 300 rpm increased the extraction rate that means the process is diffusion control. Agitation time and interfacial area had a direct effect on gold extraction. It was found that using 4-blade impeller was better than 2-blade impeller. DBC and gold concentrations had positive effect on the extraction but pH had a negative. Enthalpy was obtained 14.27 kJ mol^{-1} indicating that the extraction of gold (III) in the investigated system was endothermic process. Similar study was carried out for leach solution obtained from aqua regia leaching of copper anode slimes. The results were compared, a correlation for gold extraction percent was then released using software.*

KEY WORDS: *Kinetics, Gold extraction, Lewis cell, Synthetic solution, Comparison.*

INTRODUCTION

Developing of modern industry and high technology leads to producing various rare elements and other matters with high purity. Solvent extraction method has some advantages, such as large capacity, simple equipment, easy auto control, quick and safe operation and low cost. Therefore it has been employed for the recovery of precious metals from chloride solutions or real solution widely [1]. It is important to study effective parameters for solvent extraction process. Lewis cell is a method used for research about extraction processes and optimizing operating conditions.

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Many extractants have been reported for gold extraction which include oxygenated extractants DiButylCarbitol (DBC), thio extractants [2], ammonium extractants [3], phosphorus extractants such as TriButyl Phosphate (TBP) [4], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) [5], TriButyl Phosphine Oxide (TBPO) [6] as well as Methyl IsoButyl Ketone (MIBK) [7,8], monoamid compounds [1] and amine extractants [9]. In addition, the extraction of Au (III) from chloride media using thio-caprolactam as extractant was studied by Nunez [10]. The gold extracted by DBC can follow by direct reduction with a chemical reductant to granular metallic gold (>99.9%).

Comparative study on solvent extraction process of gold with DBC in both leach and synthetic solutions has not been accomplished yet. In this paper, the influence of several parameters on gold extraction was studied in both solutions. Also data analysis was done by DATAFIT and EVIEWS software for both synthetic and leach solutions.

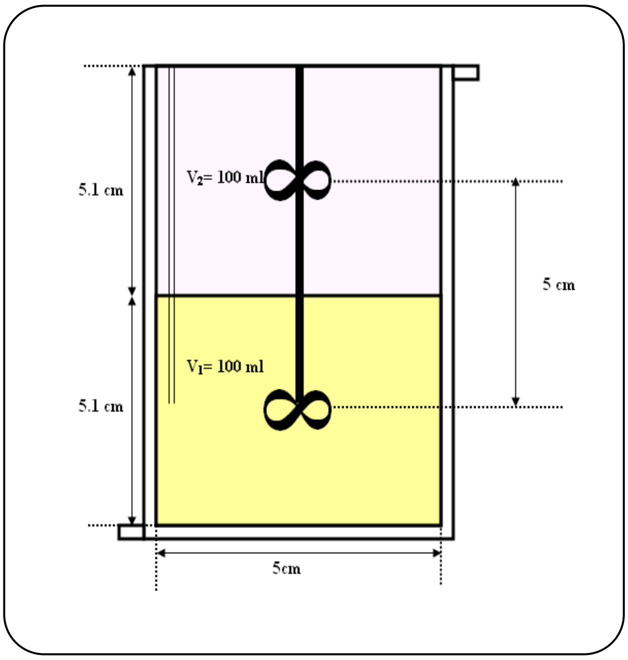

Fig. 1: Structure of a Lewis cell.

EXPERIMENTAL SECTION

Reagent

DBC (99%) was obtained from Shuyang Hengrun Fine Chemical Co. Ltd, China. Kerosene was bought from Fluka, which was colorless and mostly aromatic free. Au powder (99%), nitric acid (65%) and hydrochloric acid (37%) were from Merck (Germany).

For preparation of gold solution, an accurate weight (200 mg) of the gold powder was poured in a 3 liter beaker containing 1500 mL of hydrochloric acid (2 M) and 500 mL of nitric acid (3 M). Then the mixed solution was stirred at 90˚C for 30 minutes in a covered beaker to protect the contents from evaporation.

Apparatus

The structure details of the Lewis cell used in this investigation was described earlier by *Danesi & Chiarizia* [11], *Danesi et al.* [12], *Aparicio & Muhammed* [13] and *Biswas et al.* [14]. It consists of a cylindrical jacketed glass vessel having a double-bladed paddle one in each phase, which allows the equal individual mixing of each phase without disturbing the interface (Fig. 1). Identical aliquots (100 mL) of the aqueous phase containing $[AuCl_4]^-$ at a definite pH and the organic phase containing DBC were introduced into the cell gradually not to disturb the interface. The stirrer speed was fixed at 200 rpm in order not to disturb the interface (remains stable). After certain intervals of time (usually 2-6 minutes depending on reaction parameters), 3 mL of the aqueous phase was withdrawn from the cell by syringe for analysis. The sampling was done without disturbing the interface of two phases.

The amount of $AuCl_4^-$ transferred into the organic phase was caculated from the gold content remained in aqueous phase. All experiments were carried out at 293° K, unless tests related to temperature effects study. In the most of experiments, the interfacial area was kept at 15.9×10^{-4} m^2, which can be reduced by setting circular rings within the cell where the interface is formed.

For the determination of Droplet diameter in each test, a 10 Megapixel with 12 optical zoom digital camera was used. Also the interfacial tension was determined by TE3, LAUDA (Germany).

Analytical

The gold content in the aqueous phase was determined by Atomic Absorption Spectrophotometer (A.A.S) 240 Varian. Gold concentration in the organic phase was obtained by mass balances. The pH of the solution was adjusted by addition of sodium hydroxide solution. During the experiments, the pH was controlled using a Metrohm 827 pH meter (Switzerland).

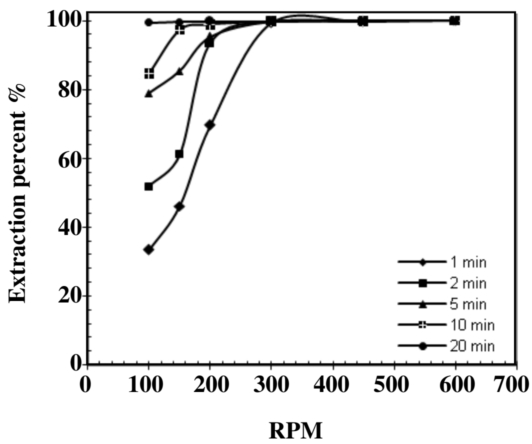

Fig. 2: Effect of Stirring Speed on E % in various contacting time V_o=V_a= 25ml, $[Au]_{(ini)}$ = 93.5 ppm, [DBC] =4 M, [Cl^-] = 2 M, Temp. =25°C.

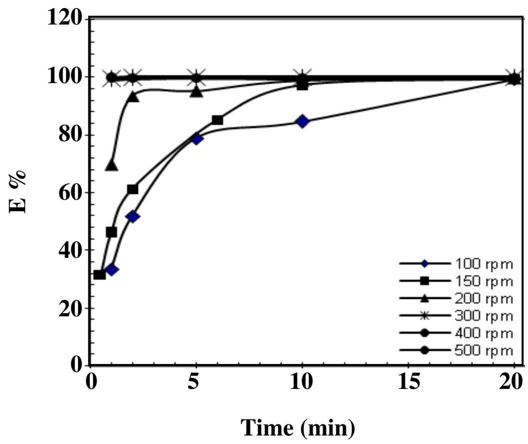

Fig. 3: Effect of agitation time on the E % in various stirring speed V_o=V_a= 25ml, $[Au]_{(ini)}$ = 93.5 ppm, [DBC] =4 M, [Cl^-] = 2 M, Temp. =25°C.

RESULTS AND DISCUSSION

Extraction of gold from synthetic solution

Synthetic gold solution (100 ppm) was prepared by dissolving gold powder. All experiments were done in ambient temperature and phase volume was fixed at 25 mL. For gold analysis, a sample (3ml) was taken from aqueous phase in different time intervals (1, 2, 5, 10 and 20 minutes). After sampling, 3 mL of bulk solution was added to cell for keeping phase volume constant.

Extraction of gold was calculated by the following equation:

$$E = \frac{C_{AuCl_4^-,f} - C_{AuCl_4^-,raff.}}{C_{AuCl_4^-,f}} \times 100 \quad (1)$$

Where subscripts of $AuCl_{4,f}^-$ and $AuCl_4^-{}_{,raff}$ are related to gold concentration in aqueous feed and raffinate respectively.

The effect of stirring speed

An increase in the stirring speed resulted in an increase in the extraction rate for diffusion controlled systems till it reaches a plateau region where the rate remains constant. In that region, the diffusion contribution is minimized and the rate of extraction was mainly controlled by chemical reactions in bulk phase or at interface [15].

In this study, the plot of extraction versus stirring speed gave a plateau region over a 300 rpm (Fig. 2). Considering Fig. 2, it found that extraction has been increased by raising stirring speed up to 300 rpm. Therefore diffusion controls system.

In the Lewis cell tests, the stirrer speed was kept at 200 rpm in order not to disturb the interface (remains stable) because this condition is vital in this technique.

Effect of agitation time

It is clear that an increase in agitation time results in more contact between two phases, consequently mass transfer will be increased. Samples were taken in different times and analyzed by A.A.S. These experiments were performed at different speeds as well. By increasing agitation time, gold extraction has been increased. It was observed that extraction reached to 100% after 20 minutes. The equilibrium has been occurred at short time but in higher stirring speed. Results were illustrated in Fig.3.

Impeller type effect

Since operation was affected by impeller type, two types of impellers, 2-blade and 4-blade, were going on to study. Tests (Figs 2 and 3) were done by 2-blade, repeated by 4-blade impeller. Effect of stirring speed and time on extraction using 4-blade was shown in Figs. 4 and 5 respectively. By increasing the agitation time from 1 to 5 minutes, gold extraction has been increased from 38% to 78%.

The results for both impellers effect were compared in Fig. 6. It is clear that, extraction percent has been increased much more by 4-blade compared to 2-blade

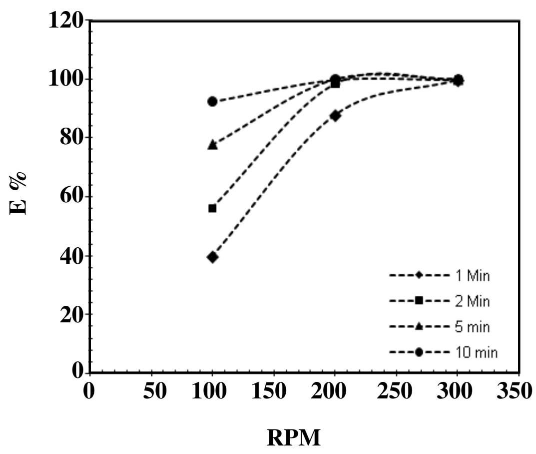

Fig. 4: Effect of Stirring Speed on the Extraction by 4- blade. Conditions is the same as Fig. 1.

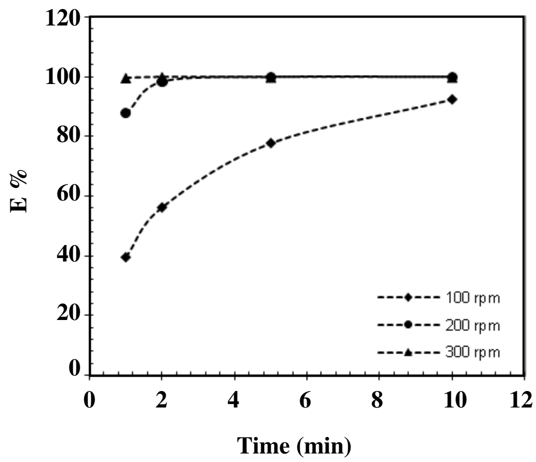

Fig. 5: Effect of agitation time on the Extraction by 4- blade. Conditions is the same as Fig. 2.

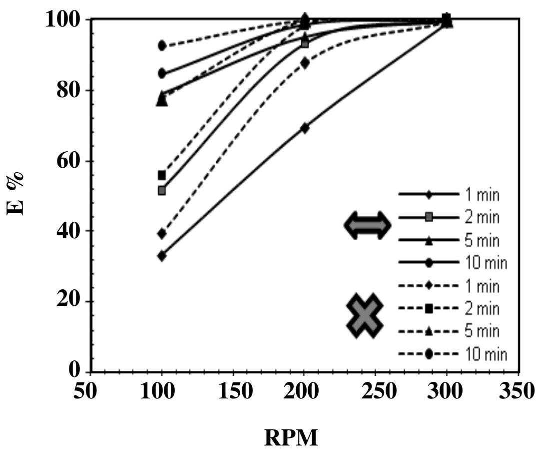

Fig. 6: Comparison of agitation effect on the gold extraction for 2 and 4-blade impellers.

under same conditions. Generally using 4-blade impeller, extraction percent was increased 5% more. This increase is a very important point in industry so selection of proper impeller can be attributed to high extraction efficiency and low energy consumption.

As mentioned, the whole gold content was extracted at high stirring speed. So under this condition, the effect of impeller type on extraction was negligible. On the other hand, impeller type had no effect on extraction at high stirring speed.

Effect of time on extraction for both 2 and 4-blade were shown in Fig. 7. It was found that it's possible to reach the equilibrium sooner using 4-blade impeller. So residence time will be reduced for industrial equipment and maximum throughput will be achieved.

Effect of interfacial area in Lewis cell

In a given system, the effect of interfacial area is usually studied to distinguish chemical reaction taking place in the bulk or at the interface. In the bulk, the rate of extraction is independent of the interfacial area, while at the interface, the extraction rate increases with the increase of interfacial area [16].

In this respect, the effect of the interfacial area was studied in Lewis cell with different interfacial areas in the range of 3.4–15.9 cm^2 by placing some ring inside the cell while keeping the volume of each phase constant at 100 mL.

100 mL of aqueous phase was poured into cell. Then organic phase was slowly added into the cell through funnel not to cause any turbulence in the interfacial. The mixer was turned on at 200 rpm, two samples were taken after 2 and 6 minutes. The results are illustrated in Fig. 8. Plotting extraction (%) against the corresponding interfacial area showed that the values of E has been increased by extending the interfacial area.

It was indicated that the rate of extraction was dependent on the variation of interfacial area and the rate controlling reaction takes place at the interface rather than in the bulk phase. Further experiments carried out at the maximum interfacial area (15.9 cm^2).

Effect of DBC concentration

By adding various volume of kerosene as a diluent to DBC, different concentrations of solvent were prepared. Tests were carried out under following conditions in Lewis cell: room temperature (20°C); gold concentration,

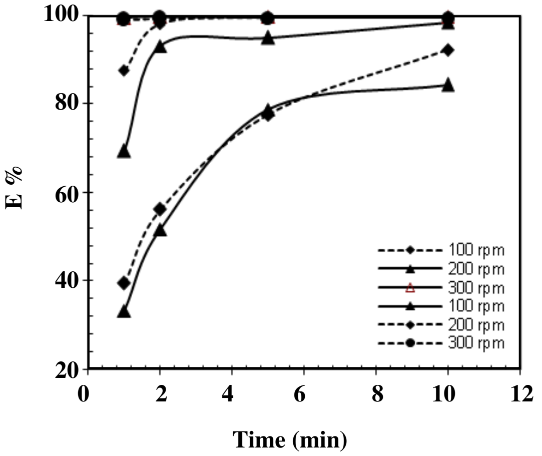

Fig. 7: Comparison of time effect on gold extraction for 2 and 4-blade impellers.

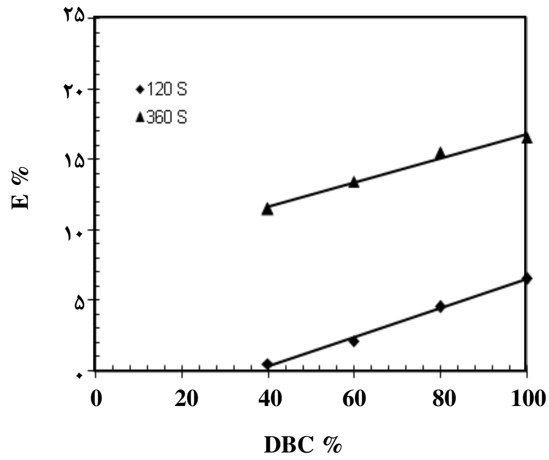

Fig. 9: Effect of DBC concentration on gold extraction in Lewis cell ([Au]$_{ini}$:93.5ppm, temp.:20°C,pH: -0.3, A:15.9cm^2,200rpm).

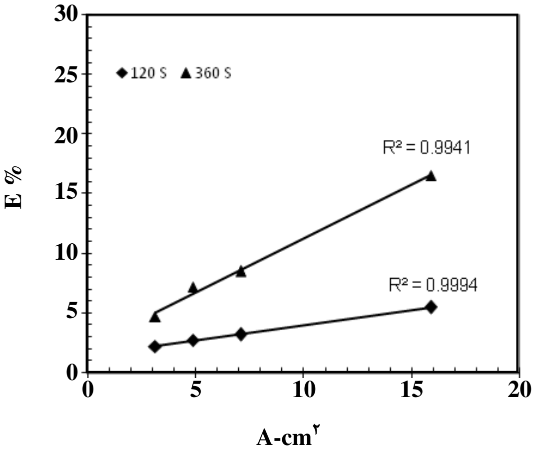

Fig. 8: Effect of interfacial area on gold extraction in Lewis cell ([Au]ini:: 93.5ppm, temp.:20◦C, pH: -0.3, DBC:4M, 200rpm)..

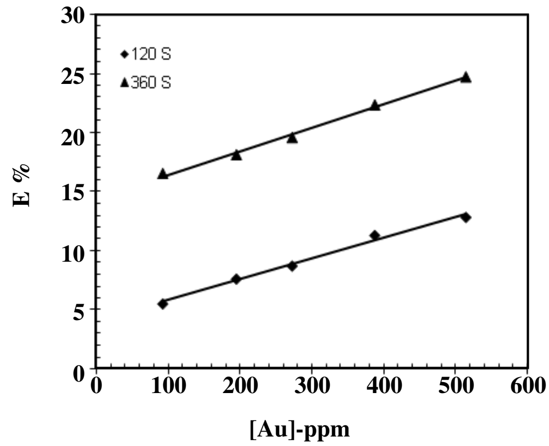

Fig. 10: Effect of gold concentration in aqueous phase on gold extraction in Lewis cell(DBC: 4M, temp.:20°C, pH: -0.3, A: 15.9cm^2, 200rpm).

93.5 mg/L; pH of aqueous phase, -0.3, phase ratio(O/A), 1:1; mixing time, 2 and 6 minutes. The procedure was the same as previous section (3.1.3). It was observed that by increasing the DBC concentration, the gold extraction has been regularly raised (Fig.9). An important reason for this phenomena may be relevant to the amount of available DBC molecules for extracting each molecule of gold chloride complex from aqueous phase. It means by increasing DBC content the probability of reaction between gold in the form of chloride complex and DBC molecules increases. In mixer-settler, there is also another reason. By measuring the interfacial tension between two immiscible liquids, it was found that interfacial tension was affected by diluent content. Therefore droplets size of organic phase increases and, consequently, contact area between two phases decreases. So gold extraction diminishes considerably.

Effect of gold concentration

One of the most important parameter that should be studied in solvent extraction systems is the concentration of desired metal. For this purpose, some experiments in different concentrations of gold were done. As shown in Fig. 10, when the gold concentration was increased from 100 to 500 ppm, the extraction percent has been increased from 15 to 25% in 6 minutes. This is because of high loading capacity of DBC and high concentration of gold in aqueous phase. Also by changing agitation time from 2 to 6 minutes the same results have been observed.

Effect of pH

The effect of aqueous phase acidity on gold extraction is shown in Fig. 11. All experiments were carried out at 4M DBC and ambient temperature. The extraction efficiency decreased with increasing pH up to 2.3. This effect should be attributed to the fact that the gold (III) ion exists as tetrachloroauric in hydrochloric acid solution especially at a lower pH, while at a higher pH gold (III) hydroxide forms that can not be extracted by DBC [17].

Effect of temperature

The temperature effect on the rate of extraction controlled by diffusion is less pronounced than that of controlled by the chemical process and the activation energy in the former case does not usually exceed 20.9 kJ/mol [15]. The most satisfactory method for expressing the influence of temperature on extraction is Van't Hoff equation. Enthalpy can be derived by plotting log D values against the reciprocal of the absolute temperature 1000/T. The results are represented as a straight line with slope minus one(-1) (Fig. 12).

$$\log D = \frac{-\Delta H}{2.303\,RT} \qquad (2)$$

Where D is distribution coefficient, R the universal gas constant and *T* the absolute temperature. The enthalpy was calculated from the slope of the line and found to be 14.27 kJ/mol indicating that, the extraction of gold (III) in the investigated system is endothermic process.

Gold extraction from leach solution

The same parameters were investigated for the leach solution as well. Real solution was provided by aqua regia leaching of copper anode slimes. For the preparation of gold leach solution, an accurate weight (50g) of copper anode slimes was placed in a 500mL beaker containing 375 mL of hydrochloric acid (2 M) and 125 mL of nitric acid (3 M). The mixture was then stirred at 90˚C for one hour and the filtrate was diluted by distill water to obtain a solution containing 100 ppm gold.

Effect of interfacial area, DBC concentration, gold concentration in aqueous phase, pH and temperature were shown in Figs 13-17 respectively. As observed, the curves obtained for leach solution are similar to synthetic solution's curves but there is a little difference for tests carried out for 2 minutes due to unsteady of system.

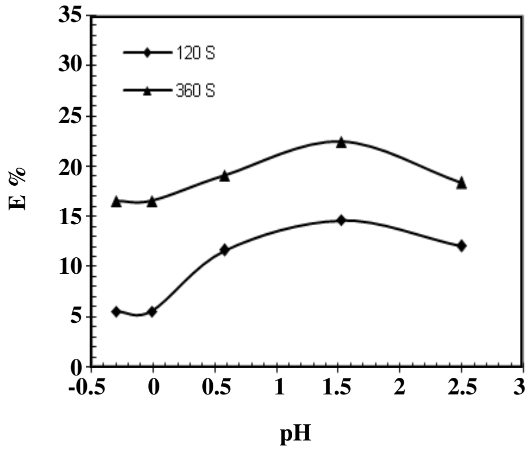

Fig. 11: Effect of pH in aqueous phase on gold extraction in Lewis cell (DBC: 4M, temp.:20°C, $[Au]_{ini}$:93.5ppm, A: 15.9cm^2, 200rpm).

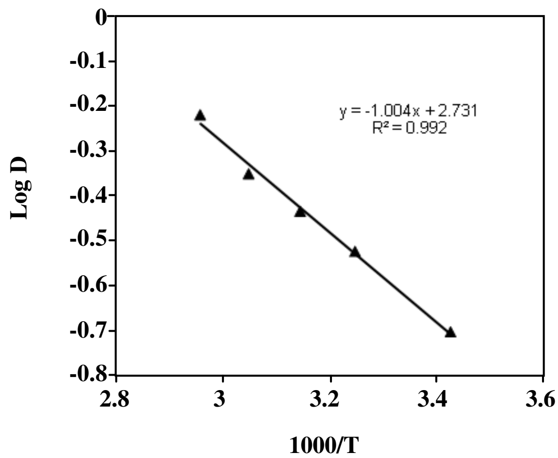

Fig. 12: Effect of temperature on gold extraction in Lewis cell(DBC: 4M,pH: -0.3, $[Au]_{ini}$:93.5ppm, A: 15.9cm^2, 200rpm).

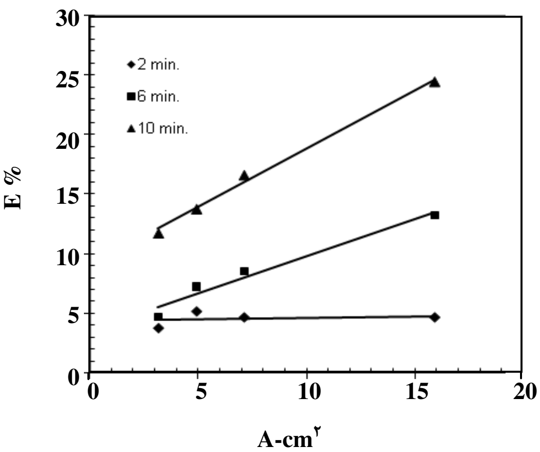

Fig. 13: Effect of interfacial area on gold extraction ($[Au]_{ini:}$:101ppm, temp.:20°C,pH: 0.5, DBC:4M, 200 rpm).

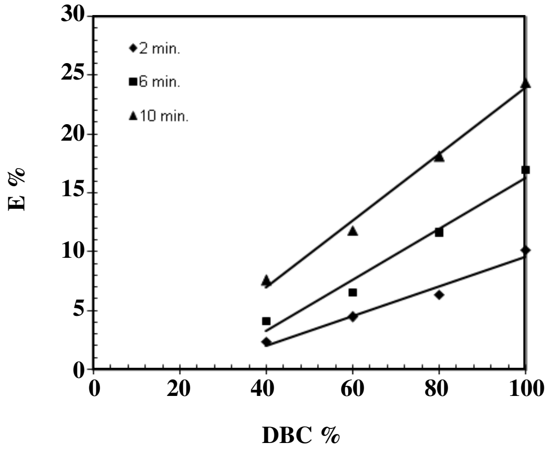

Fig. 14: Effect of DBC concentration on gold extraction ($[Au]_{ini:}$:101ppm, temp.:20°C,pH: 0.5, A: 15.9cm^2, 200 rpm).

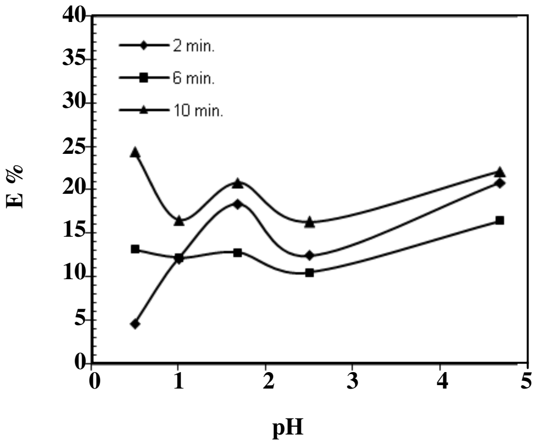

Fig. 16: Effect of pH on extraction ($[Au]_{ini:}$:101ppm, temp.:20°C , DBC:4M A: 15.9cm^2, 200 rpm).

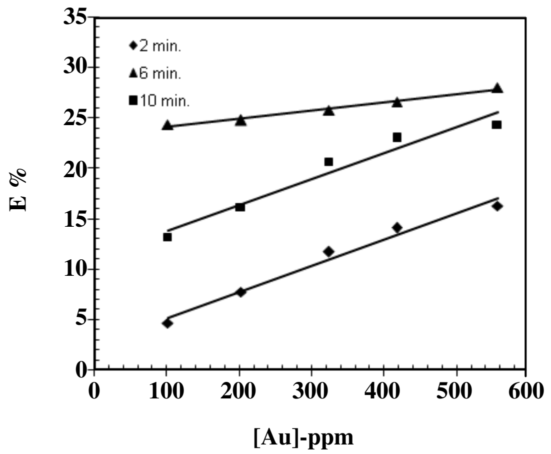

Fig. 15: Effect of gold concentration on extraction (temp.:20°C, pH: 0.5, DBC:4M A: 15.9cm^2, 200 rpm).

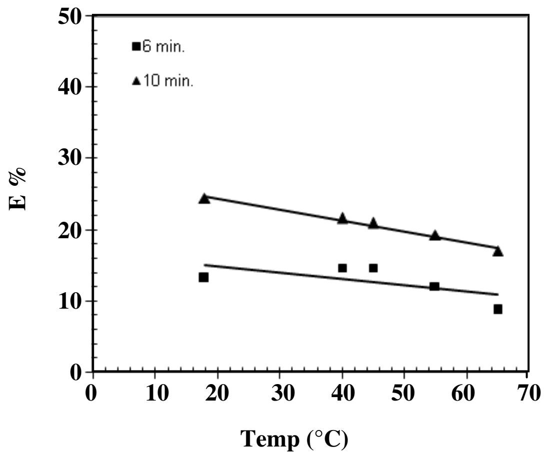

Fig. 17: Effect of temperature on gold extraction ($[Au]_{ini:}$:101ppm, pH: 0.5, DBC:4M A: 15.9cm^2, 200rpm).

Fig. 17 shows that temperature has negative effect on gold extraction that probably is due to the existence of various elements in leach solution.

Correlation of gold extraction by DATAFIT and EVIEWS software

First, parameters and their values were introduced to the software. A logical relationship between the variables was given. The coefficients related to each parameter and also the correlation coefficients based on the given relationship has been calculated.

All equations were derived by strong DATAFIT software which had good accordance for all correlation coefficient value. Then by selecting the best equation, the constants of model were determined based on ordinary least square (O.L.S) method by "EVIEWS". In EVIEWS software [18], various examinations are done for analyzing and fitting of data and the models are developed based on the statistical function such as R^2. It is the most important parameter to determine the model ability in fitting of various models provided on basis of experimental data. In general, the amount of this parameter is between 0.0 and 1.0. There is a suitable correlation between data and model when R^2 is close to 1.0. Another parameter in EVIEWS is "probability value". In fact, when the probability value is less than 0.05, the coefficient will be reliable.

According to Figs 8-12 for synthetic and Figs 13-17 for leach solution, we found that efficiency does not change by most variables (such as Au, DBC …) and it is as a linear equation. But few variables are dependent on each other. So a simple relationship is given as follow:

$$E= a_1 + a_2T + a_3C_{AuCl_4^-} + a_4pH + a_5A + a_6C_{DBC} \qquad (3)$$

Where E is extraction percent and T is the temperature and C_{AuCl4-}, A and C_{DBC} refer to gold concentration in aqueous phase, interfacial area and DBC concentration respectively. The results are given in Tables 1 & 2 for synthetic and leach solution, respectively.

The probability value related to pH for leach solution is 0.0787 and so is not reliable. Therefore pH effect was eliminated and coefficients for other parameter were achieved the same as previous stage. Results were shown in Table 3. As shown, the coefficients for leach and synthetic solution (tables 3 and 1) were the same.

CONCLUSIONS

The extraction rate has been increased by the increase of stirring speed up to 300 rpm. So in this condition diffusion controls systems. Also at high stirring speeds (>300 rpm) equilibrium occurred for a few seconds.

The results of impeller type effect (2 and 4 blades) confirmed that the extraction efficiency using 4 blades impeller was higher than that of 2 blades. While the effect of different DBC and gold concentration on extraction was the same for both impellers and the extraction has been gradually increased.

Gold (III) ion exists as tetrachloroauric in hydrochloric acid at a lower pH, while at a higher pH, gold (III) hydroxide forms that can not be extracted by DBC.

Plotting E% versus interfacial area showed that the rate controlling reaction takes place at the interface rather than in the bulk.

The influence of temperature on the extraction was studied by using Van’t Hoff equation. Enthalpy was calculated and was equal to 14.27 kJ/mol indicating that, the extraction of gold (III) in the investigated system is endothermic process.

For real solution all parameters had similar effects to that of synthetic solution on gold extraction. Only temperature had a different effect that may be due to the existence of various elements in leach solution.

Correlation of extraction by EVIEWS 5 software was done for synthetic and leach solution. The coefficients for both solutions were found the same.

Table 1: Coefficients related to each parameter for synthetic solution by EVIEWS.

Prob.	Coefficient	
0.0000	-16.15555	a_1
0.0000	0.413810	a_2
0.0000	0.017665	a_3
0.0112	1.288344	a_4
0.0000	0.941747	a_5
0.0004	0.090892	a_6
0.975207		R-squared

Table 2: Coefficients related to each parameter for leach solution by EVIEWS.

Prob.	Coefficient	
0.0008	-15.37857	a_1
0.0135	-0.107106	a_2
0.0178	0.011408	a_3
0.0787	-0.997107	a_4
0.0000	0.839722	a_5
0.0000	0.263519	a_6
0.872058		R-squared

Table 3: Coefficients related to each parameter for real solution by EVIEWS without pH effect.

Prob.	Coefficient	
0.0000	-16.80018	a_1
0.0000	0.374561	a_2
0.0005	0.014055	a_3
0.0000	0.998098	a_5
0.0008	0.104290	a_6
0.954435		R-squared

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