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Selective Extraction of Molybdenum from the Spent HDS Catalysts using Cyanex272 Extractant

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ABSTRACT

Selective extraction of Mo from the spent HDS (Hydro desulfurization) catalysts was studied using Cyanex272 extractant. The required experiments were designed by RSM (Response Surface Methodology) method according to CCD (Central Composition Design), and four independent parameters were examined, including Cyanex272 concentration, H^+ concentration of leach solution, temperature, and Mo concentration in the leach solution. A quadratic equation was derived for the prediction of Mo recovery with R^2 equal to 0.98, which verified this equation for fitting the experimental results. The value of Mo recovery in different conditions showed that the effect of the leach solution acidity is insignificant at a low concentration of Cyanex272. The optimum value for Cyanex272 concentration, H^+ concentration of leach solution, temperature, and Mo concentration was obtained at 0.27 M, 3.4 M, 30 °C, and 279.74 mg/L, respectively. The Mo recovery was 99.05% in these conditions, which had a 0.74 error from the software predicted value.

1. Introduction

Molybdenum (Mo) is a strong metal with a high melting point that increases tensile strength, abrasion resistance, and corrosion resistance in various industries. It has uses in steel alloys, cast iron, and super alloys, in radios, thermocouples, tubular anticathodes, X-rays, etc. This metal also has a unique application in medicine, including magnetic resonance imaging of the brain and analysis as a target element in X-ray diffraction (XRD) [1-3]. Also, molybdenum with other metals such as cobalt and nickel on the alumina-silica base acts as a catalyst in the oil and petrochemical industries [2]. After several cycles of reduction and use, Catalysts practically lose a significant part of their activity and become irreversibly unusable. In this case, the catalyst must be removed from the reactor and replaced [1]. These spent catalysts are critical because not only are they abundant and of great economic value, but

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in most cases, the cost of resumed metals is up to ten times the investment required for the recovery process. There are also environmental concerns about the disposal of heavy metals [4].

Hydrodesulfurization (HDS) catalysts are widely used in oil refining operations to remove sulfur, resulting in pure flow, heavy hydrocarbon breakdown, and increased process efficiency. As global demand for heavy fuel and oil increases, so the use of HDS catalysts is increasing, leading to a global increase in the number of HDS catalysts used. In general, the management of spent HDS catalysts varies depending on the volume of waste generated as well as national regulations. In many cases, spent HDS catalysts are disposed of under continuous monitoring to prevent adverse effects on the environment at specific locations. Because of the strict environmental regulations associated with spent HDS catalysts and their increasing production, research on various methods of recovering hazardous metals in various sources has been conducted by researchers.

The two main separation processes (hydrometallurgical and pyro metallurgical) have been used to separate precious metals from spent catalysts. High energy consumption and release of harmful gases in the pyro metallurgical process have led researchers to use the hydrometallurgical method [3]. In hydrometallurgical processes, spent catalysts are first introduced into the furnace to reduce the number of hydrocarbons, coke, and sulfur in them, and then enter the leaching process by acid or base. In this method, catalysts are immersed in acid or base or other solvents to recover the metal. Metals are recycled pure or metallic compounds [1]. One of the hydrometallurgical techniques is solvent extraction, which is widely used to recover metals from various solutions. Solvent extraction is a confirmed method with a high mass transfer rate that can be used to extract metal ions on an industrial scale [5].

Mo recovery from spent catalysts was performed using Cyanex-272 and Cyanex301 [3], LIX 84-I [2], LIX 63 [4], Alamine 306 [6], TOPO and Alamine 308 [7], TBP and Alamine 308 [8], LIX-84I [9], LIX-84I and Cyanex 272 [10], Cyanex272, PC88A and TR-83 [11], (bis (2-ethylhexyl) phosphinic acid) PIA-8 [12], mixture of TOA/Cyanex272 [13], Trioctylmethylammoniumchloride (TOMAC) [14] and TBP [15]. The extraction of Mo from other solutions also was investigated using PC-88A [16], the combination of tertiary amine (N-235) and secondary alcohol caprylic [17], Alamine 304-I [18], the combination of tributyl phosphate (TBP) and tri-alkyl phosphine oxide (TRPO) [19], LIX 973 N [20], and LIX 63 [21]. Park et al. recovered the metals from the HDS spent catalyst by solvent extraction method. They used LIX 84-I and Cyanex272 for the separation of Mo and Al, respectively [10]. Padhan and Sarangi used Cyanex272 and Cyanex301 for the separation of Mo and Co from the leach liquor of the spent catalyst containing 1.74 g/l Co, 12.52 g/l Mo and 9.98 g/l Al [3].

In this investigation, the solvent extraction method was used for the separation of Mo from spent HDS catalysts leach solution containing Mo, Ni, Fe, and Al using Cyanex272 extractant for the first time. The important parameters including Cyanex272 concentration, H^+ concentration of leach solution, temperature, and Mo concentration of leach solution were optimized using RSM for maximum extraction of Mo ions.

2. Experiments

2.1. Materials

Cyanex272 extractant and kerosene solvent were purchased from Sigma Aldrich and Alpha Acer, respectively. The spent catalysts used for this investigation were obtained from Tehran Oil and Gas Refinery. Table 1 displays the component of the spent catalysts leach solution. Other chemicals including NH_4F, NH_4OH, $(NH_4)_2CO_3$, NH_4Cl, H_2SO_4, and HCl were provided by Merck. All the chemicals were used with no purification.

Table 1. The concentration of metal ions in the spent HDS catalysts leach solution [22]

Metal ions	Al(III)	Mo(VI)	Ni(II)	Fe(III)	Ca(II)	As(III)	Ti(IV)	Cr(III)	V(V)
Concentration (ppm)	1093.2	280	136.62	16.29	7.147	6.418	0.19	0.173	0.006

2.2. Apparatus and procedure

For extraction of Mo, 20 mL of the catalysts leach solution and the organic phase (O/A = 1) were blended in a shaker with a given temperature. After a certain time and reaching equilibrium, the solution was separated into two phases in a funnel. The concentration of Mo ions in the aqueous phase was specified by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Optima 7300 DV, America). The extraction efficiency (Ex%), extraction distribution coefficient (D), stripping efficiency (St%) and separation factor (SF) were estimated using the following equations:

$$Ex\% = \frac{D}{1+D} \times 100 \tag{1}$$

$$D = \frac{[M]_{org}}{[M]_{F,t}} \tag{2}$$

$$St\% = \frac{[M]_{S,t}}{[M]_{org}} \times 100 \tag{3}$$

$$S_{F(Mo/X)} = \frac{([M]_{Mo} / [M]_X)_S}{([M]_{Mo} / [M]_X)_F} \tag{4}$$

where $[M]_{F,t}$ and $[M]_{S,t}$ are the final concentration of the metal ions in the feed and stripping phases, respectively. $[M]_{org}$ is the metal ion concentration in the organic phase after extraction. $[M]_{Mo}$ and $[M]_X$ are the concentrations of Mo and other metal ions in the aqueous solutions, respectively. Subscripts F and S represent the feed phase and the stripping phase, respectively. For determining the acidity of the aqueous phase, a pH meter (Sartorius) was utilized.

2.3. Experimental design

To inquire the effect of the selected parameters on the Mo ions extraction from the spent HDS catalysts, a set of experiments was designed using the RSM with Design Expert software version 7. This method was used based on Central Composite Design (CCD) with four independent parameters (Cyanex272 concentration (M) (X_1), H^+ concentration of leach solution (M) (X_2), temperature (˚C) (X_3), and Mo concentration (ppm) (X_4)) at three levels. The 30 experiments were designed including 16 factorial points, 8 axial points and 6 replicates at the center points.

3. Results and discussion

3.1. Selection of contact time

Contact time of aqueous and organic phases has the main role in the amount of Mo ions extraction. So, at first, a set of experiments were conducted to select the best time for the maximum separation of Mo ions from the spent catalysts leach solution. In these experiments, 0.4 M Cyanex272 was used for the extraction of Mo ions from leach solution with acidity of 1 M H^+. The obtained results in Fig. 1 show that after 15 minutes, about 85% of molybdenum and

after 120 min, 98% of molybdenum is extracted. Therefore, in all subsequent experiments, the contact time was adjusted to be 120 min.

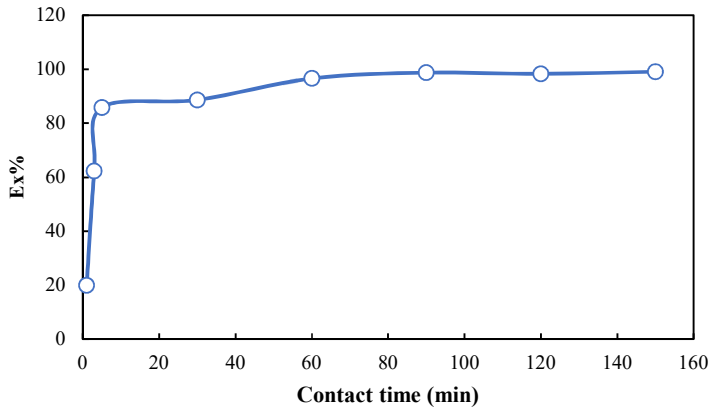


Fig. 1. The effect of the contact time on the extraction of Mo from spent HDS catalyst

3.2. Experimental design analysis

The obtained results of the 30 runs for the optimization of Mo extraction from spent catalysts leach solution are reported in Table 1. These results were fitted to the quadratic model and the obtained equation with R^2 of 0.98, and R^2 adj of 0.97 was the appropriate model for the prediction of experimental data, as follows:

$$Ex\% = 87.207 + 18.064X_1 - 0.687X_2 + 0.262X_3 - 6.880\times10^{-3}X_4 + 8.202X_1X_2 + 0.315X_1X_3 + 0.0518X_1X_4 + 0.021X_2X_3 - 1.993\times10^{-3}X_2X_4 + 3.365\times10^{-4}X_3X_4 - 77.797X_1^2 - 0.222X_2^2 - 6.632\times10^{-3}X_3^2 + 8.247\times10^{-6}X_4^2 \quad (5)$$

Table 2 shows the linear, quadratic, and binary interactions of the parameters. The Model F-value of 71.03 mentions the model is meaningful. The significant terms of the model have the P-values less than 0.0500; in this case, X_1, X_2, X_3, X_4, X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_3X_4, X_1^2, X_3^2 are meaningful terms. Values higher than 0.1000 demonstrate the model terms are negligible; So, X_2X_4, X_2^2, and X_4^2 are insignificant and can be eliminated from the presented model.

$$Ex\% = 87.664 + 20.221X_1 - 1.875X_2 + 0.286X_3 - 8.118\times10^{-3}X_4 + 8.202X_1X_2 + 0.315X_1X_3 + 0.0518X_1X_4 + 0.021X_2X_3 - 3.365\times10^{-4}X_3X_4 - 82.591X_1^2 - 6.922\times10^{-3}X_3^2 \quad (6)$$

The "Lack of Fit P-value" of 0.1467 indicates the model fits the data well. Fig. 2 also shows the relationship between the obtained experimental results and the values calculated by the proposed model. It can be seen there is a slight difference between the experimental and calculated values, which verifies the ability of the presented model for fitting the experimental results.

3.3. Effects of Cyanex272 concentration, H^+ concentration, temperature, and Mo concentration

The effect of extractant concentration in the organic solution and the H^+ concentration of the leach solution is displayed in Fig. 3(a). The results show that by adding more Cyanex272, the extraction efficiency of Mo increases at all concentrations of H^+. As the carrier concentration increases, the amount of organic base (-R) in the medium increases, and as a result more metal cations are collected from the aqueous solution. The results also show that increasing the acidity of the leach solution leads to enhancement of extraction efficiencies at high concentrations of Cyanex272. On the other hand, this effect is insignificant at a low concentration of Cyanex272. Fig. 3(b) presents the

influence of Cyanex272 and temperature on the efficiency of the extraction process. The results show that at all concentrations of Cyanex272, raising the temperature reduces the extraction efficiency. This indicates that the reaction of Cyanex272 and Mo ions is exothermic.

Table 1. The experimental design parameters, values and results for the optimizing the recovery of Mo from spent HDS catalysts

Run	Cyanex 272 conc. (M) (X_1)	H^+ conc. (M) (X_2)	Temperature (°C) (X_3)	Mo conc. (mg/L) (X_4)	Mo extraction efficiency (%)	
					Experimental	Predicted
1	0.05	1.95	42.5	160.67	89.13	89.09
2	0.225	1.95	20	160.67	95.97	95.26
3	0.4	0.5	20	280	94.97	94.36
4	0.225	3.4	42.5	160.67	96.86	96.49
5	0.4	3.4	20	280	97.78	99.63
6	0.05	0.5	20	280	91.23	91.56
7	0.225	1.95	42.5	160.67	95.11	95.26
8	0.4	3.4	20	41.33	96.00	95.01
9	0.4	0.5	20	41.33	89.30	89.73
10	0.225	1.95	42.5	160.67	95.97	95.26
11	0.05	0.5	20	41.33	91.21	91.27
12	0.4	1.95	42.5	160.67	96.90	96.36
13	0.4	0.5	65	41.33	82.20	82.92
14	0.4	3.4	65	41.33	91.35	90.91
15	0.05	3.4	65	41.33	79.69	79.17
16	0.225	1.95	42.5	280	98.70	97.39
17	0.05	0.5	65	280	83.56	83.41
18	0.225	1.95	42.5	41.33	92.33	93.13
19	0.225	1.95	65	160.67	88.11	88.69
20	0.225	1.95	42.5	160.67	94.69	95.26
21	0.225	0.5	42.5	160.67	93.00	94.03
22	0.225	1.95	42.5	160.67	94.42	95.26
23	0.05	0.5	65	41.33	80.09	79.51
24	0.05	3.4	20	41.33	87.70	88.23
25	0.4	0.5	65	280	91.80	91.17
26	0.225	1.95	42.5	160.67	95.97	94.82
27	0.225	1.95	42.5	160.67	95.00	95.26
28	0.05	3.4	20	280	89.00	88.52
29	0.4	3.4	65	280	98.97	99.15
30	0.05	3.4	65	280	82.23	83.07

Table 2. The results of the analysis of variance (ANOVA)

Parameter	Sum of Squares	Df	Mean Square	F-Value	P-Value	
Model	878.32	14	62.74	71.03	<0.0001	Significant
X_1	14.53	1	14.53	16.45	0.0010	
X_2	69.95	1	69.95	79.19	<0.0001	
X_3	23.65	1	23.65	26.78	0.0001	
X_4	19.38	1	19.38	21.94	0.0003	
X_1X_2	69.31	1	69.31	78.46	<0.0001	
X_1X_3	24.6	1	24.6	27.85	<0.0001	
X_1X_4	18.79	1	18.79	21.28	0.0003	
X_2X_3	7.32	1	7.32	8.28	0.0115	
X_2X_4	1.9	1	1.9	2.16	0.1627	
X_3X_4	13.07	1	13.07	14.79	0.0016	
X_1^2	14.71	1	14.71	16.65	0.0010	
X_2^2	0.57	1	0.57	0.64	0.4358	
X_3^2	29.21	1	29.21	33.07	<0.0001	
X_4^2	0.036	1	0.036	0.04	0.8433	
Residual	13.25	15	0.88			
Lack of fit	11.15	10	1.11	2.65	0.1467	Not significant

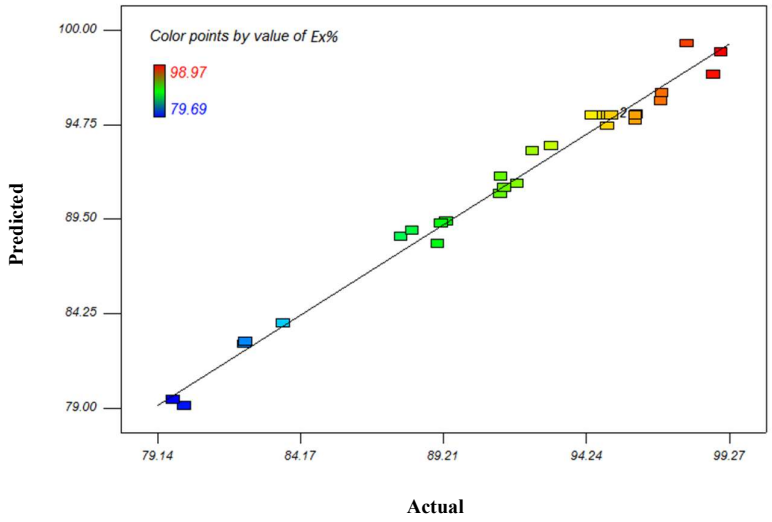


Fig. 2. Comparison of experimental and predicted results for the extraction of Mo from spent HDS catalysts

By drawing the diagram of log D versus 1/T (Fig. 4), the ΔH of the reaction was calculated using Van't Hoff Equation as follows:

$$\log D = \left(\frac{-\Delta H}{2.303RT}\right) + C \tag{7}$$

where D, ΔH, and R are the distribution coefficient, enthalpy change, and universal gas constant, respectively. C is a constant which includes the equilibrium constant of the extraction reaction. The negative value of ΔH (-39.32 kJ/mol) verifies the exothermic nature of the extraction reaction. The concentration of the Mo ions was varied from 280 to 41.33 ppm by dilution of the leach solution and was examined for extraction at different concentrations of Cyanex272. As shown in Fig. 3(c), diluting the leach solution reduces the extraction efficiency. Because at low concentrations, low metal ions are available to form a complex with the carrier molecules. However, this effect is not more sensible at a low concentration of Cyanex272. The simultaneous effects of temperature and H^+ concentration of the leach solution in Fig. 3(d) and Mo concentration of the leach solution and temperature in Fig. 3(f) reveal that the influence of temperature on the extraction rate is almost independent of leach solution acidity and concentration. The interaction of the Mo and H^+ ions concentration of the leach solution in Fig. 3(e) indicates that at low Mo concentrations, the influence of the leach solution acidity is more meaningful.

3.4. Optimization of the presented model

The proposed model (Eq. 6) was solved using the software and the optimal amounts of Cyanex272 concentration, H^+ concentration of leach solution, temperature, and Mo concentration were determined 0.27 M, 3.4 M, 30 ˚C, and 279.74 mg/L, respectively. In the obtained optimal conditions, the maximum extraction of Mo ions from the leach solution was equal to 99.76%. The experimental and estimated values of the proposed model for three experiments and the optimum point are presented in Table. 3. The calculated error values demonstrate that the proposed model is appropriate for predicting the experimental results with high accuracy.

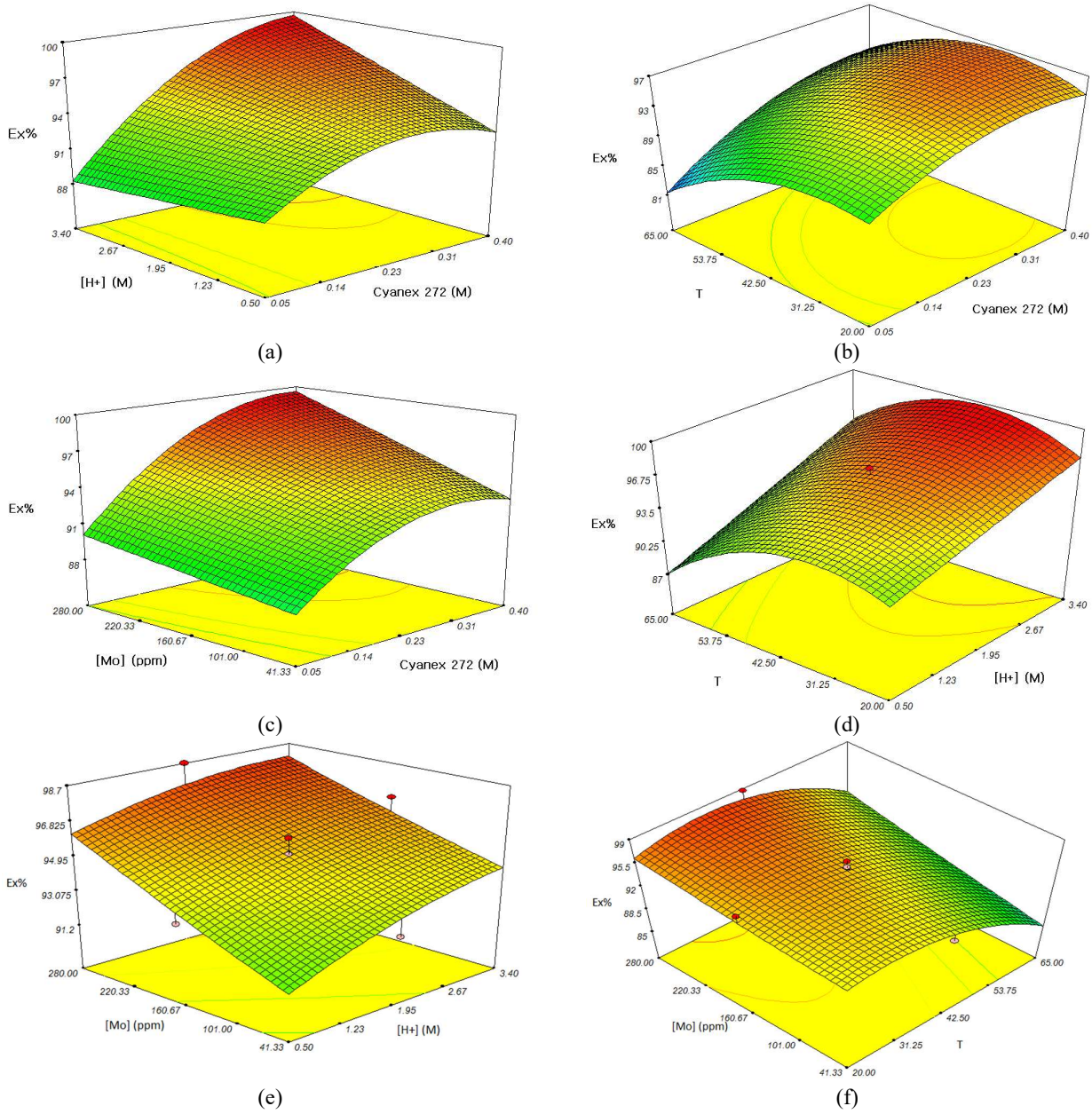


Fig. 3. Response surface plot of Mo extraction as a function of (a) Cyanex272 concentration of the organic phase and the H^+ concentration of the leach solution, (b) Cyanex272 concentration of the organic phase and temperature, (c) Cyanex272 concentration of the organic phase and Mo concentration of the leach solution, (d) H^+ concentration of the leach solution and temperature, (e) H^+ concentration and Mo concentration of the leach solution, (f) temperature and Mo concentration of the leach solution

3.5. Selection of stripping agent type and concentration

The high ability of Cyanex272 for extracting the Mo(VI) ions from an acidic solution is a reason why mineral acids cannot be a suitable strippant for these ions from the organic phase. On the other hand, molybdenum can form non-extractable anionic species by Cyanex272 only in an alkaline environment or with the help of anions such as fluoride ions in near-neutral or alkaline media. Therefore, stripping experiments were performed with alkaline solutions such as ammonium carbonate and ammonium hydroxide or with fluoride ion complexing agent and also in almost neutral media of fluoride ion complexing agent such as ammonium fluoride solution, but in different concentrations. As can be seen in Fig. 5, most recovery occurs with a molar solution of ammonium fluoride and ammonium hydroxide. It is

also worth noting that in the use of pure alkaline agents, namely ammonium hydroxide and ammonium carbonate, the separation of phases was not done properly.

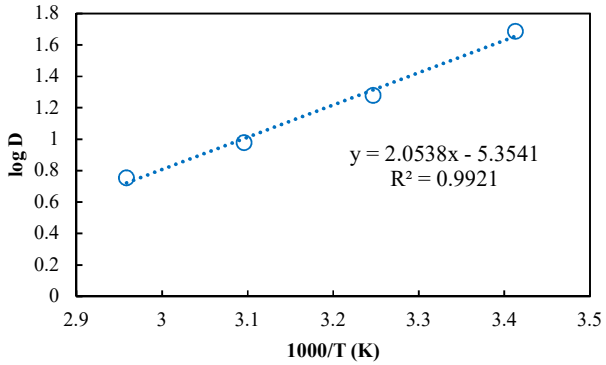


Fig. 4. The effect of temperature on the distribution coefficient of Mo ions

Table 3. The results of the proposed model accuracy and validity

Run	Cyanex 272 conc. (M) (X_1)	H^+ conc. (M) (X_2)	Temperature (°C) (X_3)	Mo conc. (mg/L) (X_4)	Mo extraction efficiency (%)		Error (%)
					Experimental	Predicted	
1	40	2	25	250	97.22	97.78	0.57
2	27	3.4	25	250	95.61	96.21	0.62
3	27	2	40	100	93.98	94.92	1.00
Opt	27	3.4	30	279.74	99.05	99.79	0.74

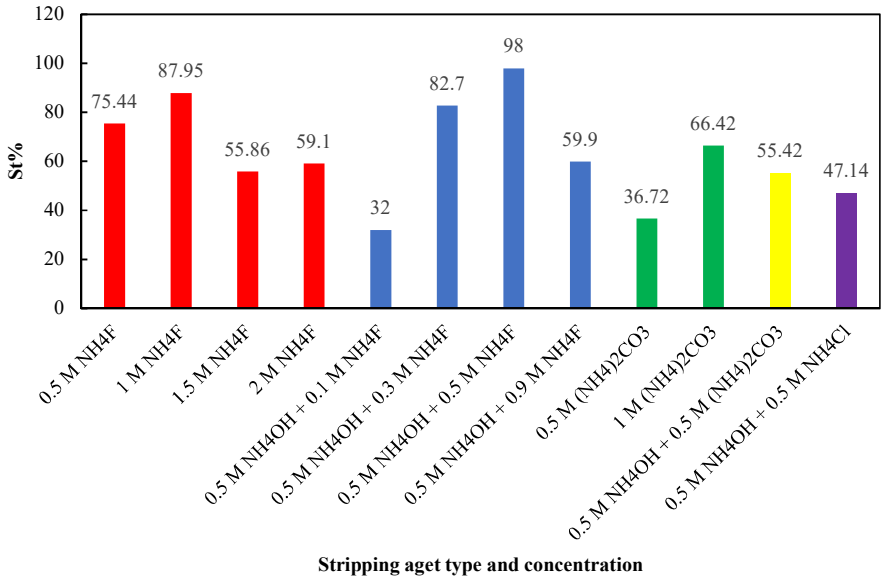


Fig. 5. The effect of stripping agent type and concentration on the Mo stripping from the organic phase

3.6. Calculating the separation factor at the achieved optimum conditions

To study the selectivity of the Cyanex272 in the sulfuric acid leach solution, the extraction of the other metal ions (Al^{+3}, Ni^{+2}, and Fe^{+3}) under optimum conditions were determined. The achieved results (Table 4) showed a high selectivity of the Cyanex272 towards Mo ions from the sulfuric acid leach solution.

Table 4. Results of the transport of Mo and other metal ions in a competitive transport experiment

Parameter	Cyanex272 conc. (M)	H+ conc. (M)	Temperature (˚C)	Mo conc. (ppm)	Mo Ex%	Al Ex%	Ni Ex%	Fe Ex%	S_F (Mo/Al)	S_F (Mo/Ni)	S_F (Mo/Fe)
Value	0.27	3.4	30	279.74	99.05	1.1	2.3	0.75	10323.96	5113.09	13816.57

4. Conclusion

In this study, the RSM was used for the optimization of the molybdenum recovery from the HDS catalysts using the solvent extraction method. The four independent parameters were investigated, including Cyanex272 concentration (X_1), H^+ concentration of the leach solution (X_2), temperature (X_3), and Mo concentration (X_4). The RSM proposed an equation for the prediction of Mo recovery with R^2 equal to 0.98 with a non-significant lack of fit, which verified the ability of that for fitting the experimental results. This equation showed that the interaction of H^+ concentration and Mo concentration of leach solution did not have a significant effect on the Mo recovery. The value of Mo recovery in different conditions showed that the effect of the leach solution acidity is insignificant at low concentrations of Cyanex272. The results also revealed that raising the temperature reduces the extraction efficiency, which indicates that the reaction of Cyanex272 and Mo ions is exothermic with ΔH value of -39.32 kJ/mol. The optimum value for Cyanex272 concentration, H^+ concentration of leach solution, temperature, and Mo concentration was obtained at 0.27 M, 3.4 M, 30˚C, and 279.74 mg/L, respectively. The Mo recovery was 99.05% in these conditions, while the equation had predicted 99.79%. The separation factor of Mo/Al, Mo/Ni, and Mo/Fe was calculated to be 10323.96, 5113.09, and 13816.57, respectively. The stripping experiments were performed with alkaline solutions. 98.0% of Mo ions were stripped from the organic phase with a molar solution of ammonium fluoride and ammonium hydroxide.

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