Recovery of molybdenum, cobalt and nickel from spent hydrodesulphurization catalyst through oxidizing roast followed by sodium persulfate leaching

Hasan Arslanoğlu [a,*], Ali Yaraş [b]

[a] Kırşehir Ahi Evran University, Faculty of Engineering and Architecture, Department of Chemical and Process Engineering, 40200 Kırşehir, Turkey
[b] Bartın University, Faculty of Engineering, Architecture and Design, Department of Metallurgy and Material Engineering, 74110 Bartın, Turkey

ABSTRACT

The spent hydrodesulphurization (HDS) catalyst is an important secondary source for Ni, Mo, Co and Al metals. The high yield recovery of these metals is quite difficult due to the carbon accumulated on the catalyst surface and the stability of the metal oxides. Therefore, the leaching process in the presence of sodium persulfate ($Na_2S_2O_8$) was carried out after the roasting pre-treatment to remove the carbon from the spent HDS catalyst structure and convert the metal oxides to the soluble form in this study. The optimum experimental conditions were determined as roasting temperature, 500 °C; roasting time, 120 min.; particle size, $+75–30$ μm; liquid/solid ratio, 12.5 mL/g; $Na_2S_2O_8$ concentration, 0.4 M; leaching temperature, 50 °C; leaching time, 90 min and stirring speed, 400 r/min. Recovery of Mo (89.8%), Co (86.5%) and Ni (81.2%) from leach solution were achieved by precipitation method. The liquid film diffusion control mechanism best represents the proposed leaching process. On the other hand, the magnitude of E_a values (<20 kJ/mol) for Mo, Co, Ni and Al metals indicates that the leaching process is controlled by liquid film diffusion mechanism.

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1. Introduction

A large amount of inorganic solid catalysts is used in oil refineries to accelerate chemical reactions in various processes known as thermo-chemical catalytic processes [1]. These catalysts are used to remove sulfur, nitrogen and other metals in the crude oil structure during the petroleum refining process. They are generally alumina-based and contain metals such as molybdenum (Mo), cobalt (Co) and nickel (Ni) [2]. They lose their catalytic activities during different catalytic processes due to the accumulation of impurities in the petroleum to the catalyst surface [3,4].

The amount of catalyst consumed by the oil industry all over the world is estimated to be $150 \times 10^3 - 170 \times 10^3$ per year [5]. The spent catalysts in petroleum refineries constitute only 4% of the total refinery wastes and it is classified as a hazardous waste to the environment and human health by various organizations [1,6]. Therefore, the valorization or disposal of the spent catalysts containing various metals are highly important. There are different applications for the storage, disposal, regeneration and recovery of precious metals [7]. The landfilling is not generally preferred due to the strict laws and regulations related to

the environment are very strict and the large area requirement [3,8]. Although regeneration is an attractive method, it is not preferred because this technology is not available for petroleum refineries and can be performed for a limited number of cycles [9]. However, it is not possible to regenerate the catalysts which have lost their activity in processes, especially in the case of thermal degradation and phase separation [10].

Recovery of metals from the spent catalysts is a very convenient method in terms of reduce environmental pollution, to minimize the need for storage space and to meet the metal needs of the market. Furthermore, the spent catalysts can be considered as an important secondary source because they contain valuable metals such as Co, Mo, Ni and Al [11,12]. In order to recover precious metals from the spent catalysts, two different methods are applied: hydrometallurgical and pyrometallurgical [13,14]. Hydrometallurgical processes are more preferred than pyrometallurgical method because of low energy consumption and low gas emission and recovery of metals by high efficiency [15]. In hydrometallurgical processes, pre-treatments such as oxidation and roasting are applied to the spent catalyst to ensure that precious metals are passed to the solution in high yields [16,17]. However, leaching process of the spent catalyst may be directly carried out in the presence of acid or alkali leaching agents [15].

In the literature, there are studies conducted in the presence of different acid and alkali solvents to recover valuable metals from the

* Corresponding author.
E-mail addresses: hasan.arslanoglu@ahievran.edu.tr (H. Arslanoğlu), aliyaras@bartin.edu.tr (A. Yaraş).

spent catalysts; mixture of H_2SO_4, HNO_3 and HCl solutions [18,19], $H_2C_2O_4$ and H_2O_2 solutions [20], Na_2O_2 and H_2O_2 solutions [21], $H_2C_2O_4$ solutions [22]. In addition, there are also studies in which the roasting process was applied followed by leaching process [1,3,4,23]. However, there is no study in the presence of sodium persulfate ($Na_2S_2O_8$) leaching agent for the recovery of valuable metals from the spent catalyst after roasting pre-treatment. The aim of the present study is to perform recovery of Co, Ni, Mo and Al metals from the spent hydrodesulfurization catalyst in $Na_2S_2O_8$ solution medium; to investigate the effects of roasting temperature and time, particle size, liquid/solid ratio, $Na_2S_2O_8$ concentration, leaching temperature and time, stirring speed on the dissolution efficiency of metals and to determine optimum experimental conditions.

2. Experimental

2.1. Material and characterization

The spent Mo-Co-Ni/Al_2O_3 powder catalyst was obtained from an oil refinery industry in Romania. High purity $Na_2S_2O_8$ used as leaching agent was provided from Merck. Prior to characterization and leaching, the powder sample was milled to ensure homogeneity. It was then sieved to obtain the desired particle size. The prepared samples were dried at 105 °C for 2 h and kept in capped plastic bottles for subsequent leaching experiments.

The chemical composition of the spent catalyst was determined by the microwave dissolution process as shown Table 1. Phase analysis of the roasted sample was carried out with XRD (Fig. 1). The surface morphology and elemental analysis of the unroasted, roasted sample and the leached residue were determined by SEM-EDS (Fig. 2). Based on SEM-EDS analysis, all samples have an irregular morphology. It demonstrates that the spent catalyst contains Mo, Co, and Ni, especially Al. However, there is sulfur in its structure due to oil refining process. The results also indicate that metal sulfides are converted to metal oxides by roasting pretreatment. The surface area and pore volume values of unroasted, roasted and leaching residue were determined by BET analysis as 148.9 m²/g, 225.7 m²/g, 387.7 m²/g; 0.97 mL/g, 0.59 mL/g and 0.26 mL/g, respectively.

All leaching experiments were performed using a shaker incubator (Zhcheng ZHWY-200D) adjustable the stirring speed and temperature. The amount of metal passed to the solution was find out using atomic absorption spectrophotometer (Perkin Elmer AAnalyst-400) and ICP-MS (Agilent 7500ce Octopole).

2.2. Experimental procedure

The spent catalyst sample was firstly roasted with a heating rate of 10 °C/min. at different temperatures (300-700 °C) and time (30–360 min), while all other experimental parameters constant (Particle size: +150–75 μm; liquid/solid ratio: 10 mL/g; $Na_2S_2O_8$ concentration: 0.3 M; leaching temperature: 40 °C; leaching time: 90 min; stirring speed: 300 r/min). For all leaching experiments, different concentrations of $Na_2S_2O_8$ solutions were prepared in 500 mL erlenmeyer flasks, the solution temperature was adjusted and the powder sample was added. Then, it was stirred during the desired reaction time and filtered. The amount of metal passed to the leaching solution was analyzed by an atomic absorption spectrophotometer (Perkin Elmer AAnalyst-400)
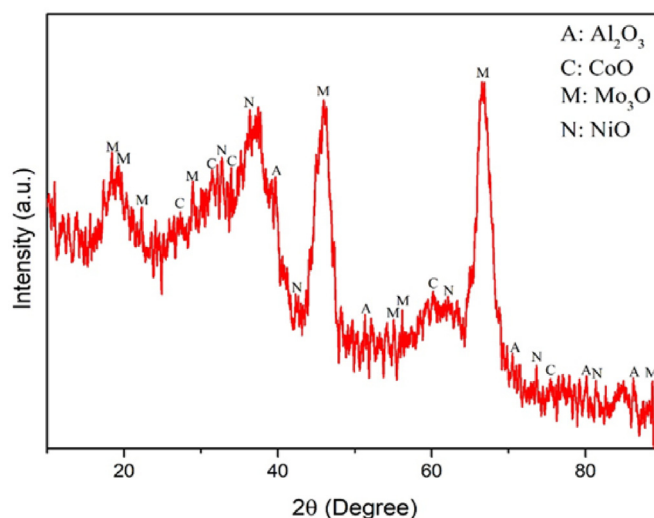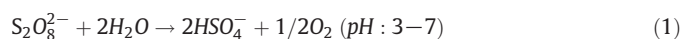

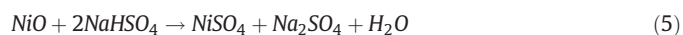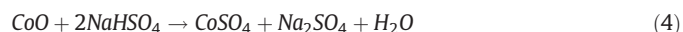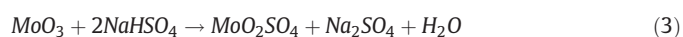**Fig. 1.** XRD patterns of the roasted spent HDS catalyst.

and ICP-MS (Agilent 7500ce Octopole). The recovery values of Mo, Co and Ni were carried out by the precipitation method in terms of Fig. 3. The flow diagram of the process applied to the recovery of metals from the HDS spent catalyst is shown in Fig. 3.

2.3. Dissolution reactions

The pH of the leaching medium was measured to about 5.9 in the concentration range of $Na_2S_2O_8$ in this study. Therefore, the its reaction depending on the pH can be given as follows;

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + 1/2O_2 \ (pH:3-7) \tag{1}$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2 \ (Diluted \ acid \ medium) \tag{2}$$

Dissolution reactions between the roasted spent catalyst and $Na_2S_2O_8$ solution:

$$MoO_3 + 2NaHSO_4 \rightarrow MoO_2SO_4 + Na_2SO_4 + H_2O \tag{3}$$

$$CoO + 2NaHSO_4 \rightarrow CoSO_4 + Na_2SO_4 + H_2O \tag{4}$$

$$NiO + 2NaHSO_4 \rightarrow NiSO_4 + Na_2SO_4 + H_2O \tag{5}$$

$$Al_2O_3 + 6NaHSO_4 \rightarrow Al_2(SO_4)_3 + 3Na_2SO_4 + 3H_2O \tag{6}$$

A series of preliminary tests were carried out for roasted and unroasted spent HDS catalysts due to the formation of H_2O_2 and O_2 according to the above-mentioned reaction 1 and reaction 2. The aim here is to oxidize the sulfur into the MeS (Me = Mo, Co and Ni) structure in the unroasted catalyst due to H_2O_2 and O_2 released by degradation of $Na_2S_2O_8$ in aqueous medium the following reactions;

$$MoS_2 + 9H_2O_2 \rightarrow MoO_2^{2+} + 2SO_4^{2-} + 2H^+ + 8H_2O \tag{7}$$
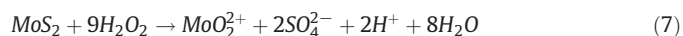
Table 1
Chemical composition of roasted Mo-Co-Ni /Al_2O_3 spent catalyst.

Component (wt%)													
Al	Mo	Co	Ni	Ca	Fe	Zn	Cr	Cu	Cd	Pb	C	S	P
36.15	8.72	1.97	1.04	0.38	0.022	0.01	0.008	0.009	0.021	0.003	12.92	0.68	0.19
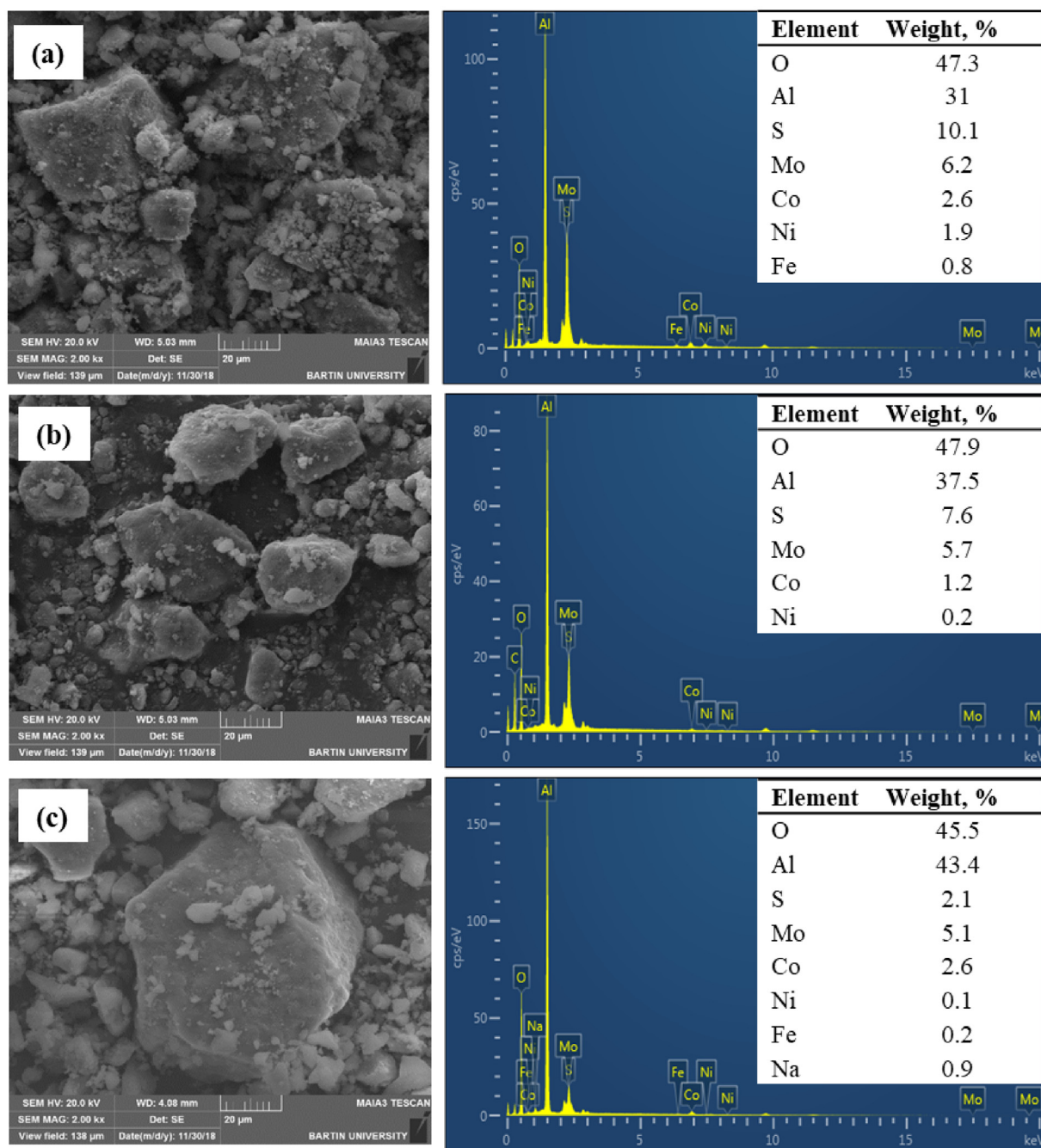
Fig. 2. SEM-EDX images of unroasted (a), roasted (b) and leaching residue (c), respectively.

$$Co_3S_4 + 15H_2O_2 \rightarrow 3Co^{2+} + 4SO_4^{2-} + 2H^+ + 14H_2O \tag{8}$$

$$NiS + 4H_2O_2 \rightarrow Ni^{2+} + SO_4^{2-} + 4H_2O \tag{9}$$
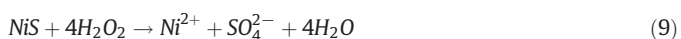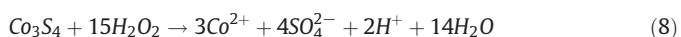
The results of the preliminary experiments are given in Fig. 4. It is clearly seen that the leaching efficiency of the roasted catalyst is about 10% higher than the unroasted catalyst for all metals. On the other hand, more metal was extracted per unit quantity than the raw spent catalyst in the roasted product. That is, when 10 g of catalyst is roasted at 500 °C, a weight loss of about 20% occurs. In addition, the organic substances which are contaminated with the unroasted catalyst also pass to the solution during leaching. However, in the leaching process where roasted catalyst was used, the leaching solution was found to have lower pollution and the final pH of solution was measured as 5.9. For

this reason, the roasting treatment was applied to the spent HDS catalyst and the affecting independent variables on the process are optimized.

2.4. Effect of roasting temperature and time

The metals in the spent catalyst structure are generally present in the form of metal sulfides. Prior to leaching process, the roasting pre-treatment is converted metal sulfides into metal oxides. Then, it is converted to soluble metal sulfates according to the dissolution reactions given above during the leaching reaction. The results of the roasting experiments carried out at different temperatures (300-700 °C) and time (30–360 min) are illustrated in Fig. 5 and Fig. 6, respectively. According to the results, it is clearly seen that the extraction efficiencies of all
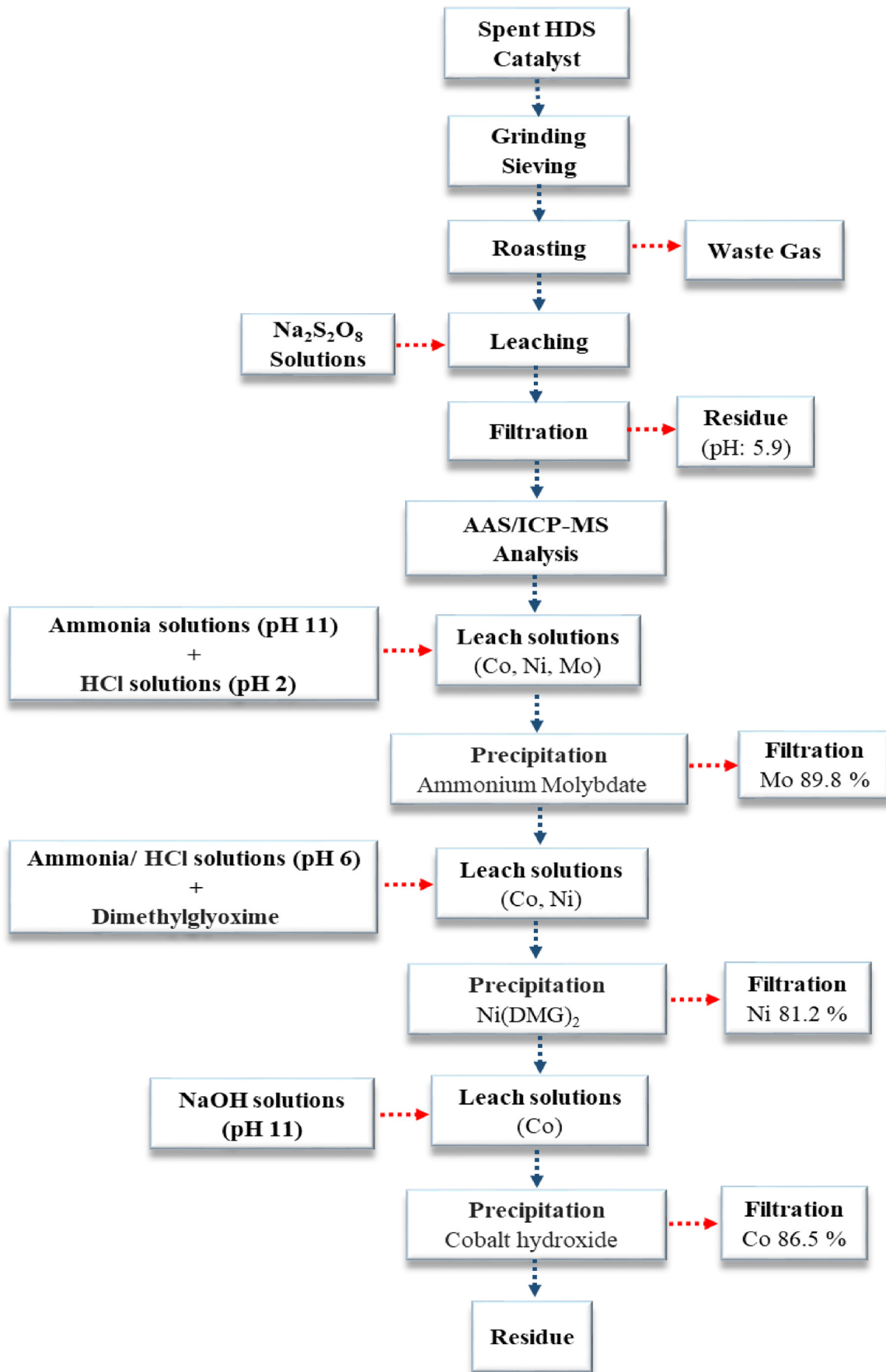
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                              │    Sieving      │
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                              │ Cobalt hydroxide │         │  Co 86.5 %   │
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Fig. 3. The flow diagram of the process applied to the recovery of metals from the HDS spent catalyst.
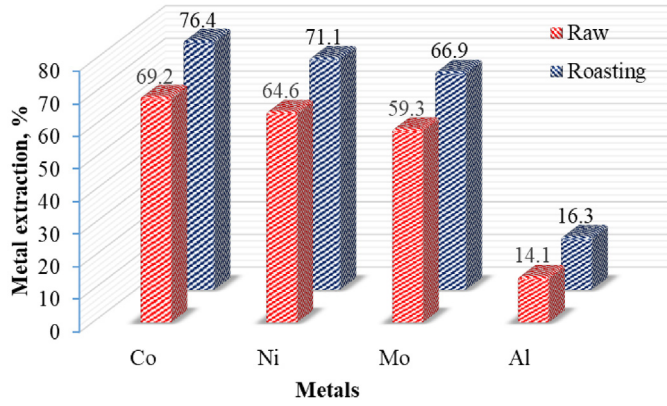
Fig. 4. Effect of thermal degradation on percentage dissolution of metals.

metals increase due to the increase in roasting temperature and time. There was not much increase in the dissolution yields of metals at temperatures higher than 500 °C and the roasting temperature was chosen as 500 °C for subsequent experiments to prevent the formation of more complex structures at high temperatures [14]. In terms of roasting time, it is clearly shown that metal dissolution percentages are an uptrend to 120 min and there is no significant increase after this value. Consequently, the extraction yields of Co, Mo, Ni and Al dissolution were obtained as 75.7%, 67.1%, 70.1% and 14.1% at 500 °C roasting temperature and 120 min. Roasting time, respectively.

2.5. Effect of particle size

The particle size plays a critical role on metal dissolution efficiency in the leaching process [24]. Experiments were performed at particle sizes ranging from +600–300 μm to +30–20 μm and the results were plotted in Fig. 7. As seen from Fig. 7, the extraction values of all metals increase
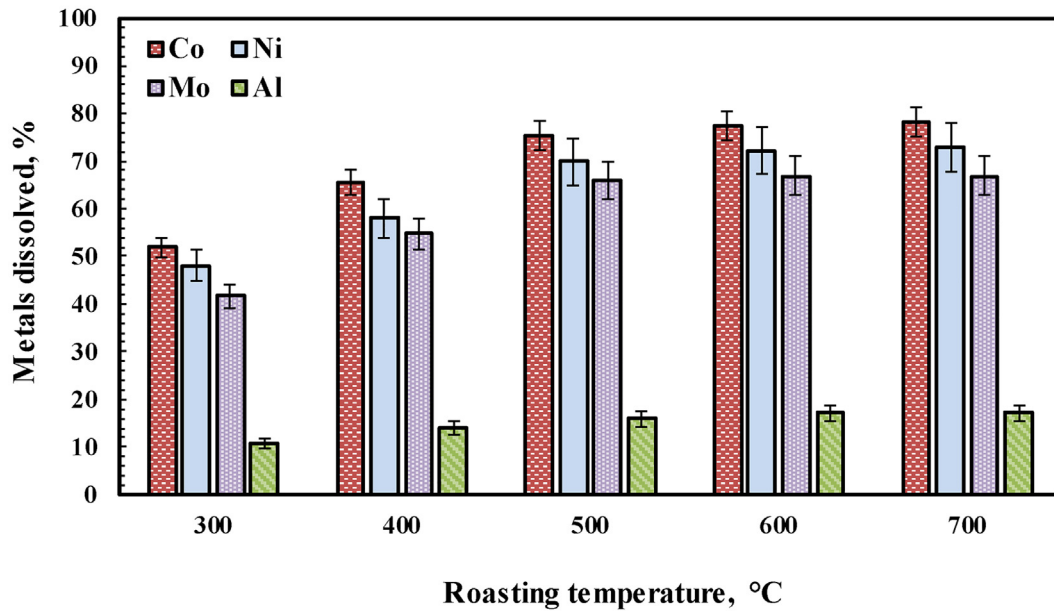
Fig. 5. Effect of roasting temperature on percentage dissolution of metals.
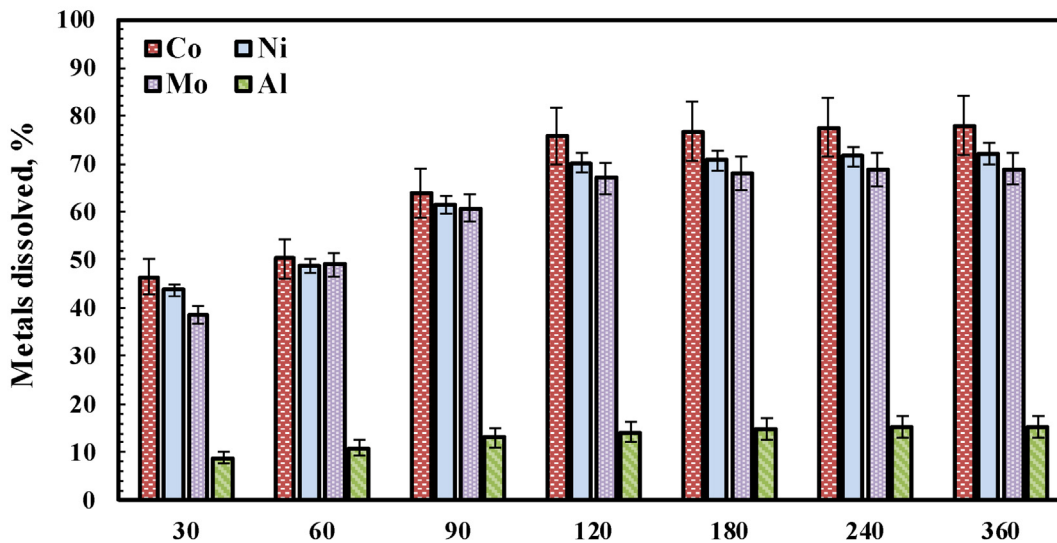
Fig. 6. Effect of roasting time on percentage dissolution of metals.
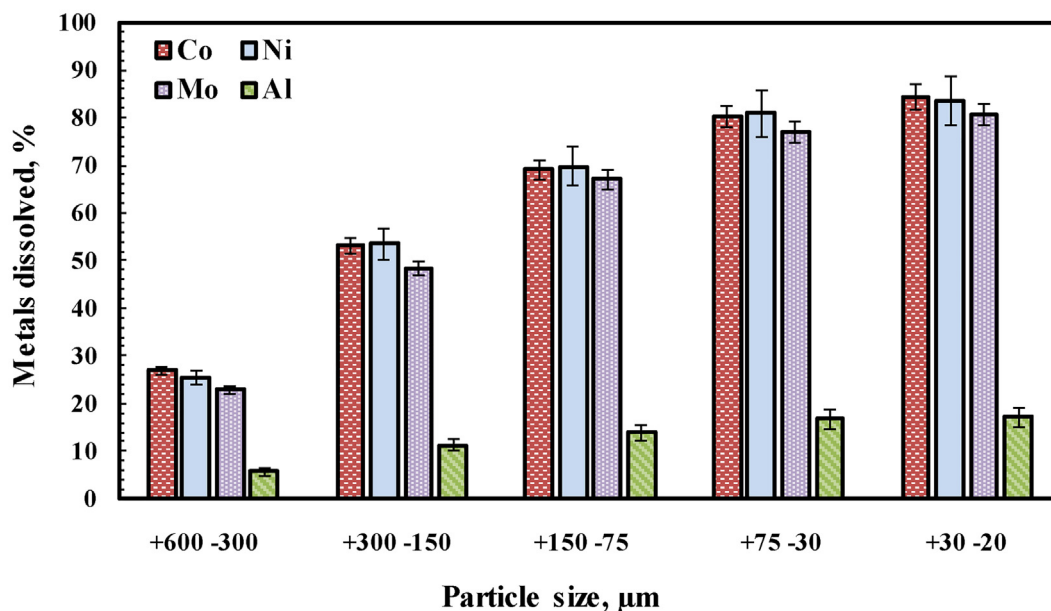
Fig. 7. Effect of particle size on percentage dissolution of metals.

with decreasing particle size. This phenomenon is attributed to the greater of the particle surface area by smaller particle size and the more efficient reaction between the solvent and the material [25]. The highest dissolution efficiencies of Co (80.3%), Mo (77.1%), Ni (80.9%) and Al (16.8%) were obtained in +30–20 μm particle size. On the other hand, a minor raise was observed in dissolution rates in case of particle size finer than +75–30 μm. For this reason, further experiments were carried out at a particle size of +75–30 μm.

2.6. Effect of liquid/solid ratio

Fig. 8 shows the experimental data performed at L/S ratios ranging from 5 mL/g to 20 mL/g. Based on the results, the dissolution efficiencies were increased for all metals with the increase of L/S ratio, the metal extraction yields increased gradually to 12.5 mL/g and no significant

increase was observed until liquid/solid ratio of 20 mL/g and maximum extraction values of Co (85.4%), Mo (81.0%), Ni (81.7%) and Al (18.2%) were reached at 20 L/S ratio. This is due to the fact that there is no sufficient amount of leaching agent in the medium, therefore the dissolution efficiencies of metals to the solution is limited. Therefore, the next experiments were continued at 12.5 mL/g.

2.7. Effect of sodium persulfate concentration

A series of experiments were performed at different $Na_2S_2O_8$ concentrations and the results were presented in Fig. 9. According to Fig. 9, it is seen that raising $Na_2S_2O_8$ concentration increases the leaching yields of all metals. The extraction values of all metals increased significantly when the $Na_2S_2O_8$ concentration increased from 0.05 mol/l to 0.4 mol/l. A raise in $Na_2S_2O_8$ concentration will increase
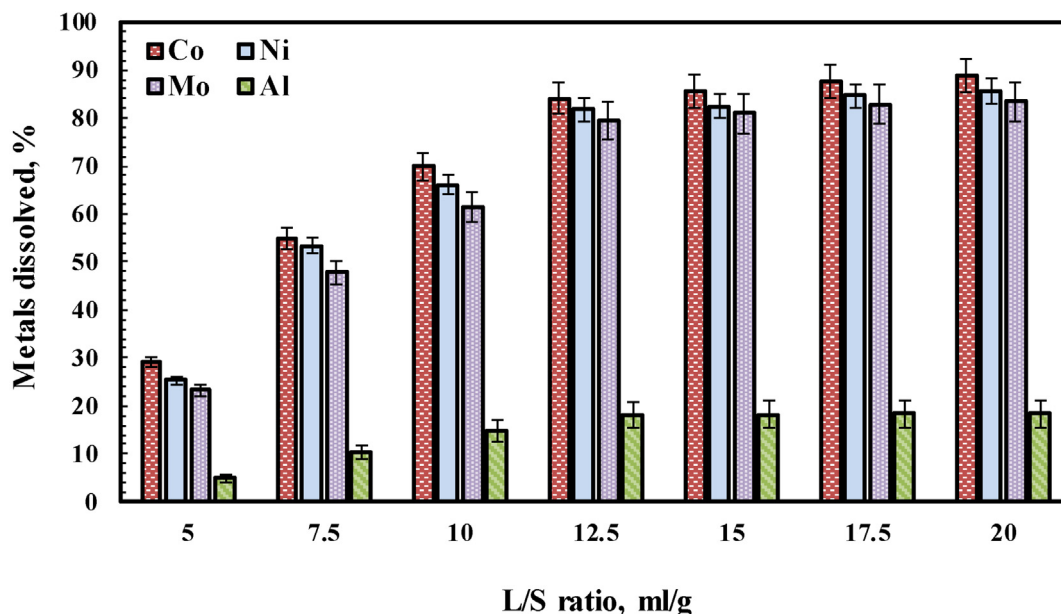

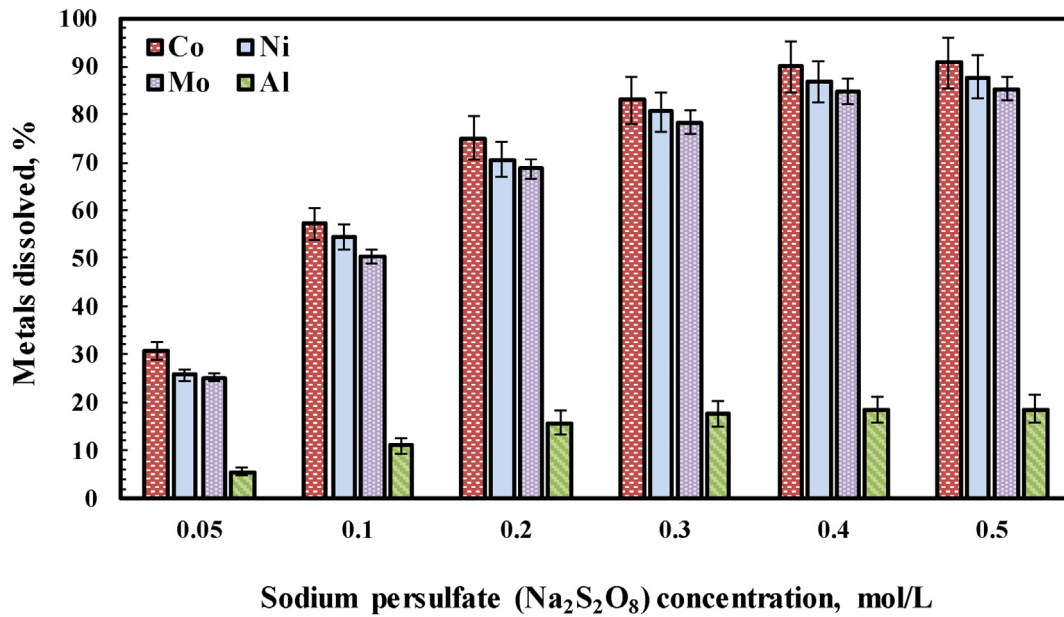**Fig. 8.** Effect of L/S ratio on percentage dissolution of metals.

Fig. 9. Effect of sodium persulfate concentration on percentage dissolution of metals.

its concentration gradient around particle surface and will increase the leaching rates of metals as a result of contacting the particle with sufficient amount of leaching agent [26]. However, a raising in acid concentration from 5 to 6 did not cause an obvious increase in leaching ratios of all metals. The maximum dissolution yields of Co, Mo, Ni and Al are 89.9%, 84.8%, 86.7% and 18.4% in $Na_2S_2O_8$ concentration of 0.4 M, respectively. Consequently, $Na_2S_2O_8$ concentration was selected is to be 0.4 M for further studies.

2.8. Effect of reaction temperature and time

The effects of the reaction temperature and time on the metal extraction yields at $Na_2S_2O_8$ concentration of 0.4 M was examined in the range of 10-60 °C and 15–180 min, while other experimental conditions are constant. According to Fig. 10, it is seen that a raise of the reaction temperature significantly affects the metal extraction efficiency and the dissolution percentage exhibits an increasing trend with the temperature increasing from 10 °C to 50 °C. It means that the leaching process from the spent catalyst is an endothermic reaction. However, no significant change was observed in the dissolution rates for all metals at 60 °C. In addition, the maximum dissolution values of Co (92.2%), Mo (85.1%), Ni (89.9%) and Al (19.8%) were obtained under 50 °C for 90 min and the metal extractions were found to remain stable after 90 min as shown Fig. 11. Therefore, follow up-experiments were performed at 50 °C and 90 min.

2.9. Effect of stirring speed

The effect of stirring speed on the extraction of Co, Mo, Ni and Al for leaching time of 90 min is given in the Fig. 12. The experimental
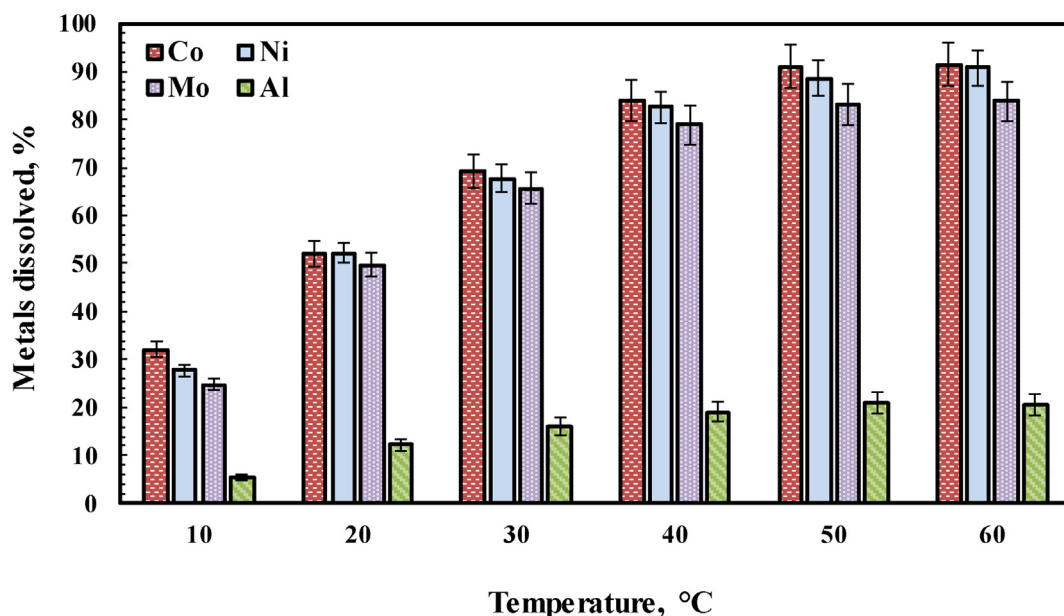

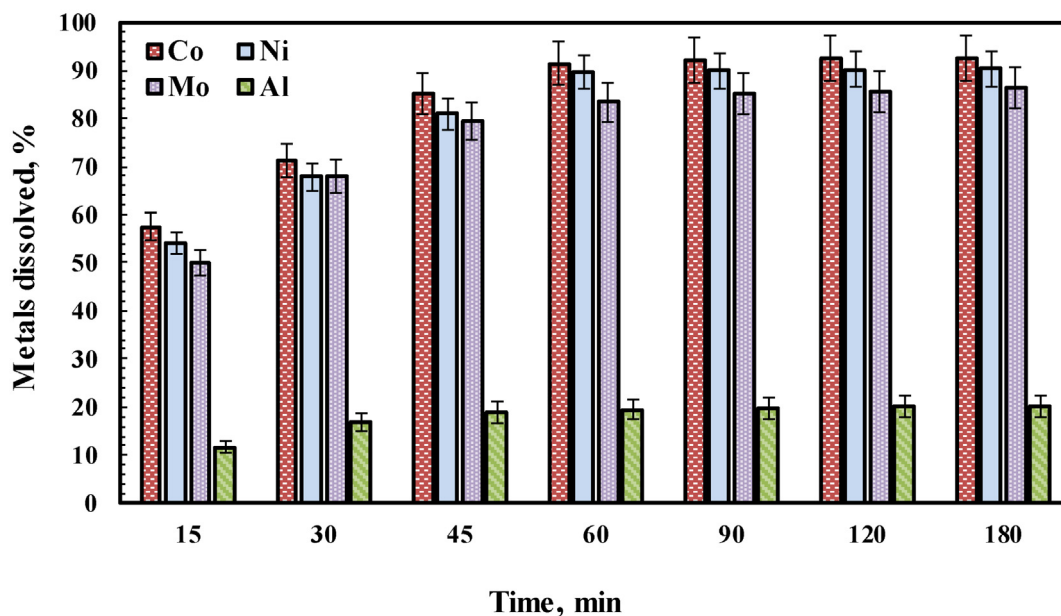**Fig. 10.** Effect of leaching temperature on percentage dissolution of metals.

Fig. 11. Effect of leaching time on percentage dissolution of metals.

data clearly indicates that the stirring speed has a remarkable influence on metal extraction. It is attributed to the raising in stirring speed to improve mass transfer and thus to accelerate the dissolution rate of metals [27]. On the other hand, it is clear that has no effect on the leaching efficiency of a raise in the stirring speed from 400 rpm to 600 rpm. This indicates that the process is controlled by the surface chemical reaction [28]. In addition, it is sufficient to study at a stirring speed of 300 to eliminate the effect of liquid film diffusion on leaching efficiency [29].

Consequently, the highest extraction yields of Co (98.5%), Mo (92.6%), Ni (95.3%) and Al (21.3%) were achieved under optimum experimental conditions; roasting temperature, 500 °C; roasting time, 120 min.; particle size, +75–30 μm; liquid/solid ratio, 12.5 mL/g; $Na_2S_2O_8$ concentration, 0.4 M; leaching temperature, 50 °C; leaching

time, 90 min and stirring speed, 400 r/min. For further the precipitation processes performed at different pH values, Mo (89.8%), Ni (81.2%) and Co (86.5%) from leach solutions were recovered as $(NH_4)_2MoO_4$, $Ni((CH_3C(NOH)C(NO)CH_3))_2$, $Co(OH)_2$, respectively. Finally, the average purity of the extracted metals is 95%.

It draws attention to the following; Al is the metal with the largest proportion in the spent HDS catalyst and also has the lowest extraction efficiency among metals. As is known, Al production is carried through from bauxite mineral with high alumina content under rigid process conditions; high temperature and pressure, high-alkaline medium (concentrated NaOH) [30]. On the contrary, this study was conducted at low temperature and atmospheric pressure, low $Na_2S_2O_8$ concentration. Therefore, the amount of aluminum leached (about 20%) is limited even under optimum experimental conditions.
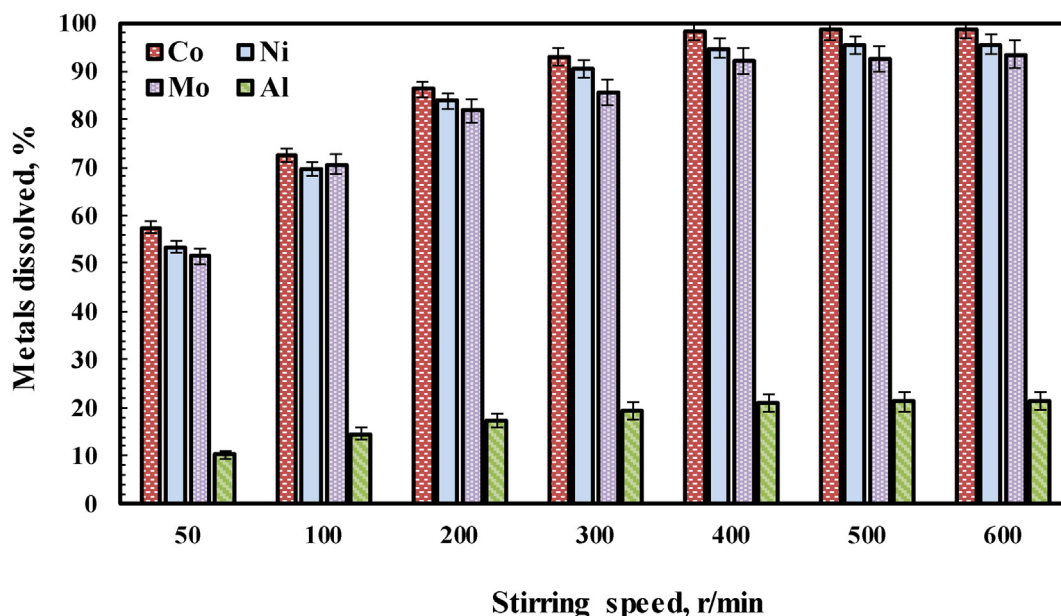

Fig. 12. Effect of strring speed on percentage dissolution of metals.

2.10. Kinetic studies

The leaching of Co, Mo, Ni and Al from the spent catalyst is a heterogeneous reaction between the solid and liquid phases. The metal oxides contained in the solid spent catalyst are dissolved and passed to the solution during the leaching process. The shrinking core model is one of the models used to evaluate the kinetic data of the leaching process. In this reaction model, when the reactant in the core is shrinking during reaction time, the porosity layer is formed around the unreacted solid or reaction products over time. This situation is confirmed by the results of BET surface areas of solid samples before and after leaching. Thus, there are two resistances for mass transfer between solid and liquid phase; the resistance to the diffusion of fluid along the outer layer and the resistance to the reaction between the fluid and the solid. The slowest step in all leaching reactions controls the reaction rate [31,32]. In our study, the optimum experimental parameters will be determined to overcome these two resistances and to obtain the maximum yield of metals from the spent HDS catalyst. According to the shrinking core model, any leaching process is controlled by either the liquid film diffusion (eq. 1), film diffusion through product layer (eq. 2) or surface chemical reaction (eq. 3) mechanism. The equations of the above-mentioned reaction mechanisms are as follows;

$$t = k[1-(1-x)] \tag{10}$$

$$t = k\left[1-3(1-x)^{2/3} + 2(1-x)\right] \tag{11}$$

$$t = k\left[1-(1-x)^{1/3}\right] \tag{12}$$

x is the amount of metal passing into solution, t is the reaction time (min) and k is the reaction rate constant (min^{-1}). For each equation above, the correlation coefficients (R^2) values at different temperatures for all metals were calculated separately. In the light of the findings, it is clearly seen that leaching kinetics of all metals are very compatible with liquid phase diffusion mechanism due to the highest R^2 (0.99) value at all temperatures as presented Fig. 13.

The activation energy (E_a) values for each metals in the leaching process were calculated using Arrhenius equation (eq. 4).

$$k = A.e^{-E_a/RT} \tag{13}$$

k is the reaction constant (min^{-1}), A is the frequency factor, E_a is the activation energy (J/mol) and t is the leaching temperature (K). From
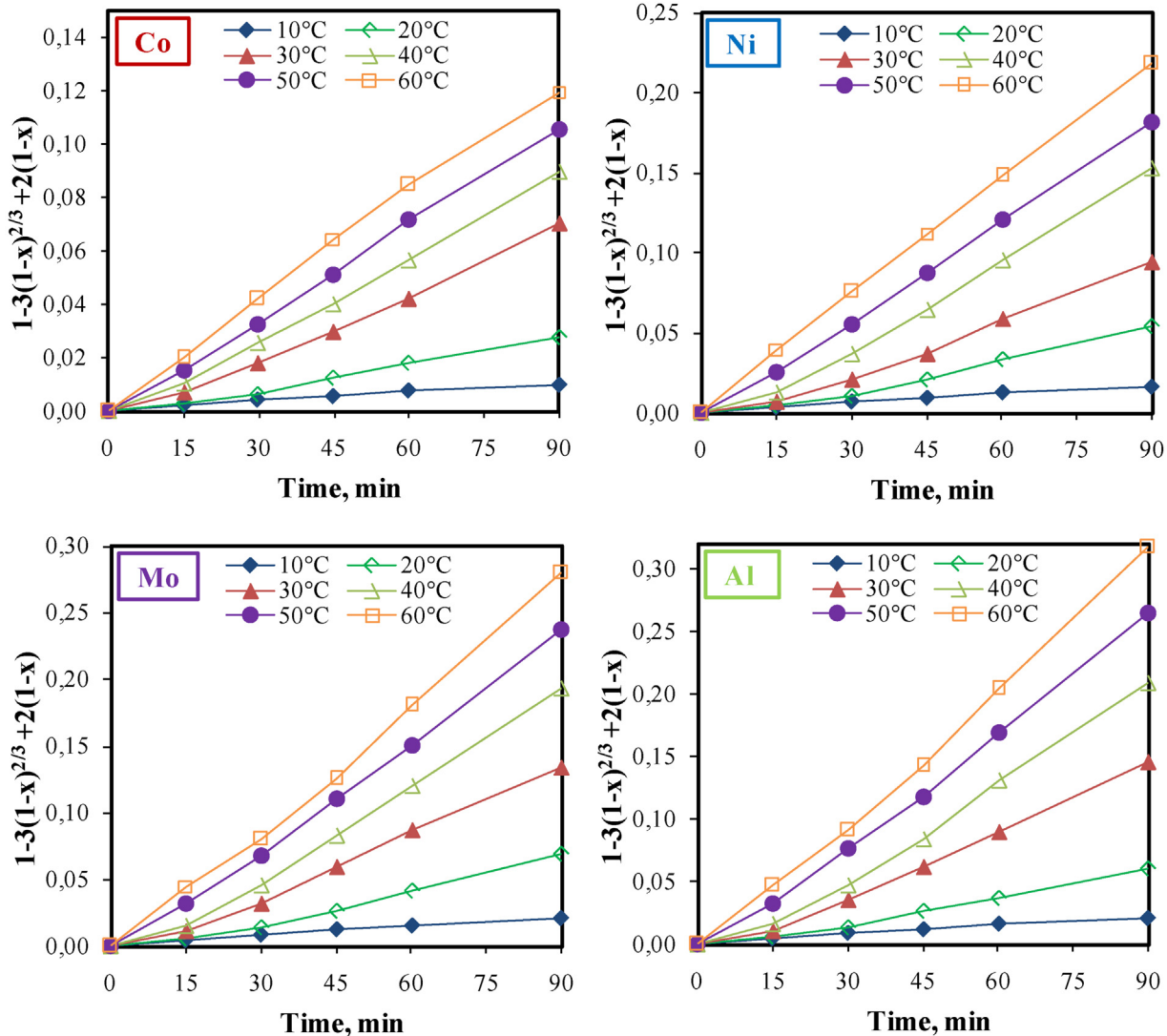

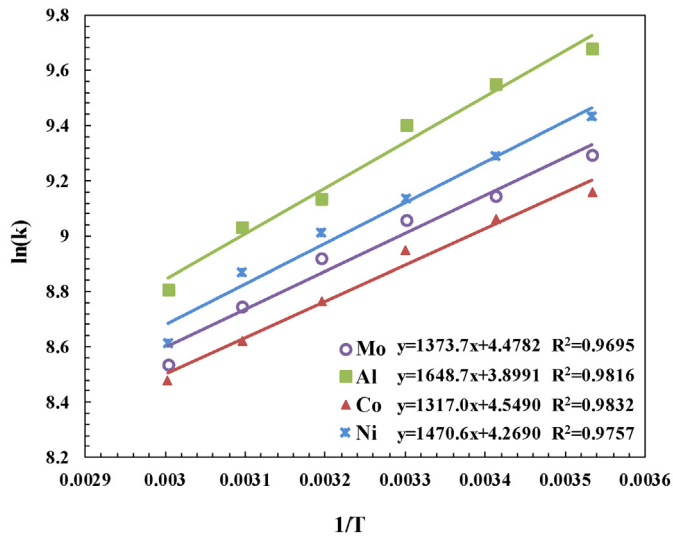**Fig. 13.** Liquid film diffusion model of each leached metals at different temperatures.

Fig. 14. Arrhenius plot for leaching of spent Mo-Co-Ni/Al$_2$O$_3$ catalyst by Na$_2$S$_2$O$_8$.

Fig. 14 data, E$_a$ values were found to be Mo, Co, Ni and Al 12.23 kJ/mol, 10.95 kJ/mol, 11.42 kJ/mol and 13.71 kJ/mol, respectively. Its magnitude indicates that the leaching process was controlled by the Liquid film diffusion control mechanism [33].

As a result, the leaching reagent and roasting pretreatment are also highly effective on the leaching efficiency in hydrometallurgical processes. Table 2 shows the comparison of other studies in the literature with our study in terms of both experimental conditions and metal extraction efficiencies.

According to Table 2, Mo and Co dissolution efficiencies are above 90% and the high amount of Al (>60%) passed into solution [35]. However, a high concentration of sulfuric acid was used as leaching agent in the mentioned paper and the leaching temperature is twice that of our study. In addition, although the process was carried out in the presence of deionized water, the high leaching temperature provided a significant advantage on the metal dissolution [36,37]. On the other hand, for oxidizing leaching processes without roasting pre-treatment, while Mo, Co and Ni dissolution percentages are close to our results, the dissolution efficiency of Al is quite low [21,40,41]. In our study, the dissolution rates of aluminum as well as other metals increased with the roasting process.

Table 2
Comparison of dissolution efficiencies and process conditions of waste catalyst in literature.

Roasting Conditions	Leaching Conditions	Extraction Yield (%)	References
T = 500 °C t = 3 h	Na$_2$CO$_3$ = 30 g/l T = 90 °C t = 1 h L/S = 10	Mo = 98 Al = 2.6	[16]
T = 500 °C t = 2 h	Concentrated NH$_3$ Room temperature L/S = 25	Mo = 83	[34]
T = 500 °C t = 3 h	H$_2$SO$_4$ = 6 mol/l T = 30 °C t = 1 h L/S = 10	Mo = 97 Co = 87 Al = 38	[14]
T = 450 °C t = 2 h	H$_2$SO$_4$ = 10 g/l T = 100 °C t = 2 h L/S = 20	Mo = 96 Co = 91 Al = 68	[35]
T = 500 °C t = 3 h KHSO$_4$ 10 wt%	Deionized water T = 90–100 °C t = 40 min	Mo = 99 Co = 91 Al = 96	[36]
T = 750 °C t = 30 min Na$_2$O nNa$_2$O/nAl$_2$O$_3$ = 1.2	Deionized water T = 80 °C t = 2 h L/S = 10	Mo = 99 Al = 97	[37]
T = 600 °C t = 30 min Na$_2$CO$_3$ 12 wt%	Deionized water T = 80 °C t = 2 h L/S = 10	Mo = 92	[38]
T = 900 °C t = 1 h NaCl 20 wt%	Deionized water T = 70–90 °C t = 1 h L/S = 5	Mo = 99	[39]
No roasting	Na$_2$CO$_3$ = 85 g/l H$_2$O$_2$ = 10 vol% t = 1 h L/S = 5	Mo = 84 Ni = 0.3 Al = 1.5	[21]
No roasting	H$_2$O$_2$ pH =1.3 t = 1 h L/S = 7.5	Mo = 90 Co = 83 Al = 8	[40]
No roasting	Na$_2$CO$_3$ = 40 g/l H$_2$O$_2$ = 6 vol% t = 1 h L/S = 5	Mo = 85 Ni = 65 Al = 3	[41]
T = 500 °C t = 2 h	Na$_2$S$_2$O$_8$ = 0.4 mol/l T = 50 °C t = 90 min L/S = 12.5	Mo = 92.1 Co = 98.4 Ni = 94.7 Al = 20.8	This study

3. Conclusions

The proposed combination of roasting and $Na_2S_2O_8$ leaching process can be used effectively in the recovery of metals from the hydrodesulphurization catalysts containing alumina-based Co, Mo and Ni metals. The optimum process conditions were determined as roasting temperature, 500 °C; roasting time, 120 min.; particle size, +75–30 μm; liquid/solid ratio, 12.5 mL/g; $Na_2S_2O_8$ concentration, 0.4 M; leaching temperature, 50 °C; leaching time, 90 min and stirring speed, 400 r/min. Recovery of Mo (89.8%), Co (86.5%) and Ni (81.2%) from leach solution were achieved by precipitation method. The results find out that a raise in temperature and $Na_2S_2O_8$ concentration positively affect leaching efficiency. The liquid film diffusion control mechanism best represents the proposed leaching process. On the other hand, the magnitude of E_a values (<20 kJ/mol) indicates that the leaching process is controlled by liquid film diffusion.

The recycling of the leaching reagent is extremely critical for the extraction process. In this sense, no studies were found in the literature on the recyclability of acids/bases as leaching agents. However, it is known that EDTA can be recycled following that a series of treatments in chelating extraction processes [42,43]. Therefore, the authors will focus on recovery and re-utilization of the leaching agent for further studies.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

References

[1] A. Akcil, F. Vegliò, F. Ferella, M.D. Okudan, A. Tuncuk, A review of metal recovery from spent petroleum catalysts and ash, Waste Manag. 45 (2015) 420–433.
[2] M. Marafi, A. Stanislaus, Options and processes for spent catalyst handling and utilization, J. Hazard. Mater. 101 (2003) 123–132.
[3] M. Marafi, A. Stanislaus, Spent catalyst waste management: a review: part I—developments in hydroprocessing catalyst waste reduction and use, Resour. Conserv. Recycl. 52 (2008) 859–873.
[4] M. Marafi, A. Stanislaus, Spent hydroprocessing catalyst management: a review: part II. Advances in metal recovery and safe disposal methods, Resour. Conserv. Recycl. 53 (2008) 1–26.
[5] P. Dufresne, Hydroprocessing catalysts regeneration and recycling, Appl. Catal. A Gen. 322 (2007) 67–75.
[6] C. Liu, Y. Yu, H. Zhao, Hydrodenitrogenation of quinoline over Ni–Mo/Al2O3 catalyst modified with fluorine and phosphorus, Fuel Process. Technol. 86 (2005) 449–460.
[7] I. Asghari, S.M. Mousavi, F. Amiri, S. Tavassoli, Bioleaching of spent refinery catalysts: a review, J. Ind. Eng. Chem. 19 (2013) 1069–1081.
[8] L.E. Macaskie, I.P. Mikheenko, P. Yong, K. Deplanche, A.J. Murray, M. Paterson-Beedle, V.S. Coker, C.I. Pearce, R. Cutting, R.A.D. Pattrick, Today's wastes, tomorrow's materials for environmental protection, Hydrometallurgy. 104 (2010) 483–487.
[9] J.K. Pradhan, S. Kumar, Metals bioleaching from electronic waste by Chromobacterium violaceum and pseudomonads sp, Waste Manag. Res. 30 (2012) 1151–1159.
[10] A. Marafi, S. Fukase, M. Al-Marri, A. Stanislaus, A comparative study of the effect of catalyst type on hydrotreating kinetics of Kuwaiti atmospheric residue, Energy Fuel 17 (2003) 661–668.
[11] H. Srichandan, S. Singh, K. Blight, A. Pathak, D.J. Kim, S. Lee, S.W. Lee, An integrated sequential biological leaching process for enhanced recovery of metals from decoked spent petroleum refinery catalyst: a comparative study, Int. J. Miner. Process. 134 (2015) 66–73.
[12] M. Motaghed, S.M. Mousavi, S.O. Rastegar, S.A. Shojaosadati, Platinum and rhenium extraction from a spent refinery catalyst using bacillus megaterium as a cyanogenic bacterium: statistical modeling and process optimization, Bioresour. Technol. 171 (2014) 401–409.
[13] D. Mishra, G.R. Chaudhury, D.J. Kim, J.G. Ahn, Recovery of metal values from spent petroleum catalyst using leaching-solvent extraction technique, Hydrometallurgy. 101 (2010) 35–40.
[14] D. Mohapatra, K.H. Park, Selective recovery of Mo, co and Al from spent co/Mo/γ-Al2O3 catalyst: effect of calcination temperature, J. Environ. Sci. Heal. Part A. 42 (2007) 507–515.
[15] A.J. Chaudhary, J.D. Donaldson, S.C. Boddington, S.M. Grimes, Heavy metals in the environment. Part II: a hydrochloric acid leaching process for the recovery of nickel value from a spent catalyst, Hydrometallurgy 34 (1993) 137–150.
[16] A. Ognyanova, A.T. Ozturk, I. De Michelis, F. Ferella, G. Taglieri, A. Akcil, F. Veglio, Metal extraction from spent sulfuric acid catalyst through alkaline and acidic leaching, Hydrometallurgy. 100 (2009) 20–28.
[17] H.-I. Kim, K.-H. Park, D. Mishra, Influence of sulfuric acid baking on leaching of spent Ni–Mo/Al2O3 hydro-processing catalyst, Hydrometallurgy. 98 (2009) 192–195.
[18] Y.-C. Lai, W.-J. Lee, K.-L. Huang, C.-M. Wu, Metal recovery from spent hydrodesulfurization catalysts using a combined acid-leaching and electrolysis process, J. Hazard. Mater. 154 (2008) 588–594.
[19] M.A. Rabah, I.F. Hewaidy, F.E. Farghaly, Recovery of molybdenum and cobalt powders from spent hydrogenation catalyst, Powder Metall. 40 (1997) 283–288.
[20] A. Szymczycha-Madeja, Kinetics of Mo, Ni, V and Al leaching from a spent hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide, J. Hazard. Mater. 186 (2011) 2157–2161.
[21] K.H. Park, B.R. Reddy, D. Mohapatra, C.-W. Nam, Hydrometallurgical processing and recovery of molybdenum trioxide from spent catalyst, Int. J. Miner. Process. 80 (2006) 261–265.
[22] M. Marafi, A. Stanislaus, M. Absi-Halabi, Heavy oil hydrotreating catalyst rejuvenation by leaching of foulant metals with ferric nitrate-organic acid mixed reagents, Appl. Catal. B Environ. 4 (1994) 19–27.
[23] F. Ferella, A. Ognyanova, I. De Michelis, G. Taglieri, F. Vegliò, Extraction of metals from spent hydrotreating catalysts: Physico-mechanical pre-treatments and leaching stage, J. Hazard. Mater. 192 (2011) 176–185.
[24] J. Huang, M. Chen, H. Chen, S. Chen, Q. Sun, Leaching behavior of copper from waste printed circuit boards with Brønsted acidic ionic liquid, Waste Manag. 34 (2014) 483–488.
[25] M. Gharabaghi, M. Irannajad, A.R. Azadmehr, Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions, Chem. Eng. Res. Des. 91 (2013) 325–331.
[26] L. Li, Y. Bian, X. Zhang, Y. Guan, E. Fan, F. Wu, R. Chen, Process for recycling mixed-cathode materials from spent lithium-ion batteries and kinetics of leaching, Waste Manag. 71 (2018) 362–371.
[27] S. Hall, Rules of Thumb for Chemical Engineers, Butterworth-Heinemann, 2017.
[28] M.R. Tavakoli, D.B. Dreisinger, The kinetics of oxidative leaching of vanadium trioxide, Hydrometallurgy 147 (2014) 83–89.
[29] E. Kim, M. Kim, J. Lee, J. Jeong, B.D. Pandey, Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution, Hydrometallurgy. 107 (2011) 124–132.
[30] M. Authier-Martin, G. Forte, S. Ostap, J. See, The mineralogy of bauxite for producing smelter-grade alumina, JOM 53 (2001) 36–40.
[31] C.Y. Wen, Noncatalytic heterogeneous solid-fluid reaction models, Ind. Eng. Chem. 60 (1968) 34–54.
[32] O. Levenspiel, Solid catalyzed reactions, Chem. React. Eng. (1999) 376–426.
[33] E.A. Abdel-Aal, Kinetics of sulfuric acid leaching of low-grade zinc silicate ore, Hydrometallurgy. 55 (2000) 247–254.
[34] D.D. Sun, J.H. Tay, H.K. Cheong, D.L.K. Leung, G. Qian, Recovery of heavy metals and stabilization of spent hydrotreating catalyst using a glass–ceramic matrix, J. Hazard. Mater. 87 (2001) 213–223.
[35] T.N. Angelidis, E. Tourasanidis, E. Marinou, G.A. Stalidis, Selective dissolution of critical metals from diesel and naptha spent hydrodesulphurization catalysts, Resour. Conserv. Recycl. 13 (1995) 269–282.
[36] R.G. Busnardo, N.G. Busnardo, G.N. Salvato, J.C. Afonso, Processing of spent NiMo and CoMo/Al2O3 catalysts via fusion with KHSO4, J. Hazard. Mater. 139 (2007) 391–398.
[37] Y. Chen, Q. Feng, Y. Shao, G. Zhang, L. Ou, Y. Lu, Research on the recycling of valuable metals in spent Al2O3-based catalyst, Miner. Eng. 19 (2006) 94–97.
[38] B.B. Kar, P. Datta, V.N. Misra, Spent catalyst: secondary source for molybdenum recovery, Hydrometallurgy. 72 (2004) 87–92.
[39] B.B. Kar, B.V.R. Murthy, V.N. Misra, Extraction of molybdenum from spent catalyst by salt-roasting, Int. J. Miner. Process. 76 (2005) 143–147.
[40] V. Ruiz, E. Meux, M. Schneider, V. Georgeaud, Hydrometallurgical treatment for valuable metals recovery from spent CoMo/Al2O3 catalyst. 2. Oxidative leaching of an unroasted catalyst using H2O2, Ind. Eng. Chem. Res. 50 (2011) 5307–5315.
[41] K.H. Park, D. Mohapatra, B.R. Reddy, Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method, J. Hazard. Mater. 138 (2006) 311–316.
[42] G. Chauhan, K.K. Pant, K.D.P. Nigam, Metal recovery from hydroprocessing spent catalyst: a green chemical engineering approach, Ind. Eng. Chem. Res. 52 (2013) 16724–16736.
[43] K.R. Vuyyuru, K.K. Pant, V.V. Krishnan, K.D.P. Nigam, Recovery of nickel from spent industrial catalysts using chelating agents, Ind. Eng. Chem. Res. 49 (2010) 2014–2024.