



Reuse of Spent Hydrotreating Catalyst of the Middle Petroleum Fractions

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Abstract

Reuse of spent hydrodesulphurization (HDS) of middle petroleum fractions catalyst $\text{CoMo}/\gamma\text{Al}_2\text{O}_3$ was accomplished via removal of coke and contaminants such as vanadium, Iron, Nickel, and sulfur. Three processes were adopted; extraction, leaching, decoking. Soluble and insoluble coke was removed. Leaching step used three different solvents (oxalic acid, ammonium peroxydisulfate and oxalic acid + H_2O_2) in separate in order to remove contaminant metals (V, S, Ni and Fe).

The effect of soluble coke removal on leaching step was studied. It was found that the removal of soluble coke significantly enhances the leaching of contaminants and barely affected the removal of active metals (Co and Mo). It was found that the best route (sequence) was soluble coke extraction followed by contaminants leaching then decoking process and the best leaching solvent was oxalic acid. According to this determination, the removed contaminants were 79.9 % for sulfur, 13.69% for vanadium, 82.27 % for iron, and 76.34 % for nickel. The active components loss accompanied with this process were 5.08 % for cobalt and 6.88% for molybdenum. Leaching process conditions (leaching solvent concentration, temperature and leaching time) were studied to determine the best-operating conditions. The rejuvenated catalyst activity was examined by a pilot scale HDS unit of naphtha. Sulfur content removal of naphtha was found to be 85.56 % for single pass operation under typical operating conditions of refinery HDS unit of naphtha which are 1 ml/min feed flow rate, 200 H_2/HC ratio, 32 bar operating pressure and 320 °C operating temperature.

Keywords: Catalyst rejuvenation, spent catalyst, Hydrodesulphurization, Extraction, Leaching, Catalyst activity.

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1- Introduction

Clean fuels are mainly produced via catalytic hydrotreating processes [1]. The catalyst used in these processes consists of an active metal (Mo), carriers (alumina) and promoters (Co or Ni). Hydrotreating processes include hydrodemetallization, hydrodenitrogenation, and hydrodesulphurization, these reactions remove the presented metals, nitrogen, and sulfur in the feed streams.

These processes produce the major amount of hazardous solid wastes (spent catalyst)[2].

However, these catalysts lose activity with time due to fouling resulting from the formation of deposited carbonaceous on the catalyst active sites and deposition of heavy metals (such as nickel and vanadium) from the feedstock.

Poisoning and sintering are other causes of catalyst deactivation[3], [4], [5]. Poisoning is caused by the accumulation of impurities attracted to the catalyst active sites by strong chemisorption. Sintering results from decreasing of catalyst surface area and porosity which is usually associated with high temperature. High temperature may also lead to phase transformation of catalytic components and support [6].

Hydroprocessing spent catalyst represents a dangerous environmental issue. Metals present in the catalyst (Co, Mo, Ni, and V) could be leached when the spent catalyst is disposed and brought into contact with water and this, in turn, brings harmful pollutants. Some reports recorded the liberation of generated hazardous gases as a result of the contact between water and disposed of spent catalyst [7].

Hydroprocessing catalyst has different lifetimes depending on the process in which it is applied. The half-life time values are 1-2 years for atmospheric or vacuum gas oils processing, 0.5-1 years for residue processing, and 5 plus years for naphtha processing [5].

Mainly, there are two sources for contaminants brought to the catalyst during hydroprocessing operations: the feed which is the source for V, Ni, Na and arsenic, and the additives used during processing which are the source for silicon and lead [4].

The amount of produced spent catalyst (with 5-20 wt% C and 7-15% S) depends on the fresh hydrotreating catalyst used. This amount is 120,000 ton based on a dry basis and 150,000 ton based on total weight (includes coke, sulfur, and water),[5].

Therefore, attention has been focused worldwide on developing different methods of handling spent catalysts.

A comprehensive review of the literature on the subject revealed that the following options are available to resolve the problem.

The most common options are disposal as landfill, recovery of metals, reactivation/rejuvenation and reuse of spent catalysts, and production of valuable products starting from the spent catalyst as a raw material. Selection of an option depends upon its technical and economic feasibility.

For disposal as landfill, this treatment method is, however, highly energy intensive and very expensive and they do not offer a profitable solution to the waste disposal problem [6], [7].

Metal recovery is technically viable, but the fluctuation in prices for the recovered materials sometimes renders the process uneconomical.

Moreover, the current technologies available for this option are themselves a potential source of chemical pollution arising from the chemicals used to leach the metals; hence the application of this option is limited.

Despite the conventional methods using nitrogen/air mixture remove coke completely, complete reactivation could not be attained since the metallic contaminants will not be removed from catalyst surface by these methods which in turn resist the diffusion of reactants [7].

The regeneration/rejuvenation option is considered to be the most attractive approach and has potential advantages from both economic and environmental points of view. In this process, both contaminants (coke and metals deposits) are removed from the spent catalyst and it can be reused.

In recent studies, attention was focused on the hydroprocessing spent catalysts regeneration. A few processes for removal of metals and coke deposits have been reported in patents literature but information on selective removal of the contaminant metal was relatively scarce. Selective leaching of contaminant metals using different organic acids was compared by Sadeek, 2014 [8].

He founded that oxalic acid was the optimum leachate for the remaining contaminants on the surface of the catalyst.

Kinetics and mechanism of leaching metal sulfides from spent catalyst were also investigated by Marafi, 1989. He founded that 0.33-0.1 M oxalic acid had a small effect on metal leaching rate.

The main goal of the present work is to study the rejuvenation of spent hydrodesulphurization catalyst (CoMo/ γ -Al₂O₃). Different rejuvenation stages such as extraction of soluble coke, leaching of contaminants and decoking have to be investigated.

Attention will be focused on the leaching efficiency of solvents, the preferred leaching route for selective leaching of the deposited metal contaminants, the effect of leaching treatment on the concentration and distribution of catalytically active catalyst metals (Co and Mo) originally present in the catalyst and also on the morphology of alumina support.

2- Experimental Work

The present work includes three routes to reactivate the spent hydrodesulphurization catalyst. Each route consists of three stages: extraction of soluble coke using n-hexane as a solvent, leaching of contaminants (undesired metals) from the catalyst using different solvents and removing of insoluble coke.

2.1. Raw Materials

a. Hydrodesulphurization Spent Catalyst

A sample of spent HDS catalysts (CoMo/ γ -Al₂O₃) was brought from the kerosene hydrodesulphurization unit at Baiji Refinery plant. The catalyst pellets had a cylindrical shape with approximate dimensions of 5.5 x 2 mm. The composition of the spent catalyst was determined using XRF spectrometer in Iraqi-German Geological Laboratory at Geological Department / College of Science / University of Baghdad. Table 1 shows the chemical analysis of the spent HDS catalyst.

Table 1. Characteristics of spent HDS catalyst

Property	Value
Co %	3.915
Mo %	8.57
Ni %	0.04674
Fe %	0.4476
S %	1.026
V %	0.0038
Surface area	216.96 m ² /g
Pore volume	0.348

b. Solvents

The solvents were n-hexane, oxalic acid, hydrogen peroxide, and ammonium peroxydisulfate, [9], [8], [10], [11], [4]

2.2. Apparatus

Three processes were adopted in this work: soluble coke removal, leaching of metals and removal of insoluble coke. Apparatus used for these processes were.

a. Catalyst Washing

Reciprocating shaker was used for catalyst washing using sweet heavy naphtha to remove dust and rust accumulated on the spent catalyst. 30 g of the catalyst was mixed with 300 ml of sweet heavy naphtha at room temperature for 90 min, and then the catalyst pellets were filtered and dried at 100 °C for 24 h.

b. Soluble Coke Removal

Fig. 1 shows Soxhlet apparatus [12] used for soluble coke removal step. This apparatus consists of a still pot, Thimble, distillation path, catalyst, siphon top, siphon exit, and condenser. The extraction step was conducted by putting 30 g of deoiled catalyst in the thimble with 150 ml of n-hexane in the still pot at 69 °C (boiling point of n-hexane) for 6 hours in order to extract the soluble coke. Then the catalyst was dried at 100 °C for 24 hours.

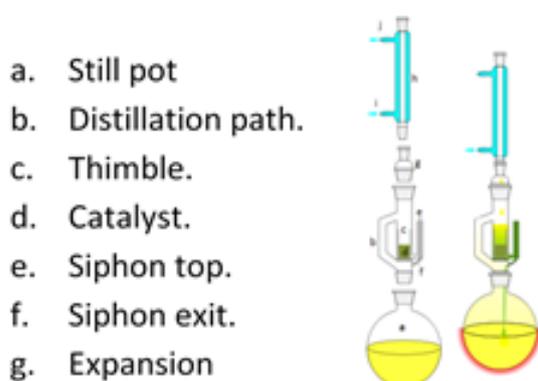


Fig. 1. Schematic diagram of the Soxhlet apparatus

2.3. Leaching of Metals

Three necks round flask with a thermometer and magnetic stirrer were used for metals leaching. Three leachates in separate were used for leaching. The ratio of catalyst to leachate solution ratio was 1/10 g at various temperatures of 25, 50, 70, and 90 °C. The time of leaching were 15, 30, 60, 90 and 120 min and the concentrations were 0.04, 0.06, 0.01, 0.12 and 0.16 M. Stirring was fixed at 200 rpm (Excessive stirring tends to break catalyst extrudes, and a slow stirring decreases leaching yield). After each leaching process, the leached catalyst pH was adjusted to 7 by filtration and washing with water, then dried at 150 °C for 2 h.

2.4. Removing of Insoluble Coke

Muffle – furnace was used for insoluble coke removal. The catalyst was heated to 500 °C for 4 h at a heating rate of 1 °C/min.

3- Results and Discussion

3.1. Removal of Soluble Coke

Removal of soluble coke played an important role in the catalyst rejuvenation as a result of enhancement in porosity and surface area, and this, in turn, will promote the removal of contaminants step.

Effect of soluble coke removal on the catalyst characteristics is shown in **Table 2** which shows the difference between leached metals percentage with and without soluble coke extraction stage.

The enhancement percent between the two parts was 27.9% for Fe and the smallest leaching percent was 0.62% for Mo. The leaching percentage was different for different metals according to their solubility in the used leachate.

Table 2. Effect of soluble coke removal on metals leaching with oxalic acid (0.08 M, 30 min, 25 °C and 200 rpm)

Element	Wt. % leached without soluble coke extraction	Wt.% leached with soluble coke extraction
S	60.59	70.79
V	3.39	13.69
Fe	54.37	82.27
Co	3.93	5.08
Ni	63.78	76.34
Mo	6.26	6.88

3.2. Removal of Insoluble Coke Process

Careful control of decoking conditions is essential to avoid permanent damage to the catalyst as a result of sintering and phase transformation. The removal of insoluble coke was carried out in a furnace at 500 °C for 4 hours with a heating rate of 1 °C/min. the slow heating rate was selected in order to increase the activity of the recovered catalyst. The catalyst was weighted before and after the decoking process in order to estimate the percent of the volatile matter which was found to be 12 wt% of the spent catalyst sample.

3.3. Leaching of Metals

Catalyst active surface area obviously reduced as a result of pores entrance plugging via the contaminants accumulating at the catalyst pellet. To reactivate the catalyst, both the coke and metal deposits have to be removed from the catalyst surface. In order to rejuvenate the catalyst efficiently, diffusion resistance represented by contaminant metals should be removed and attention should be paid for keeping the original physical and chemical properties of the catalyst.

Mechanism of contaminants leaching from spent catalyst could be explained as follow; the solvent diffuses through the interface to the solid surface of the catalyst, then the diffused solvent reacts with presented solute (contaminants) in the solid phase to form the products those, in turn, diffuse back to the solvent bulk. **Table 3** compares the characteristics of the spent catalyst before rejuvenation with those of fresh catalyst.

Table 3. Physical and chemical properties of spent and fresh CoMo/γAl₂O₃ catalyst

Property	Value in the fresh catalyst	Value in the spent catalyst
Co %	4.048	3.915
Mo %	10.28	8.57
Ni %	0.03413	0.04674
Fe %	0.1896	0.4476
S %	0.5632	1.026
V %	0.0032	0.0038
Surface area	314.79	216.96
Pore volume	0.410158	0.348

This table shows that considerable amounts of metals (V, Ni, Fe, and S) had been accumulated on the spent catalyst. The presence of contaminant metals along with the catalytic metals (Co and Mo) is confirmed by X-ray Fluorescence. The surface area of the spent catalyst is about 31.08 % and the pore volume is about 15.15 % lower than those of the fresh catalyst. It can be seen that vanadium has concentrated in a high amount near the interior surface of the catalyst. Nickel penetrated further into the interior of the catalyst pellet due to its smaller molecule size. The active catalyst metals (Co and Mo) are uniformly distributed within the pellet [9]

3.4. Comparative Study of the Sequence of Reactivation Stages

In the present work, three routes with three solutions were used as shown in Fig. 2 to reactivate the spent HDS catalyst. The primary aims of the study were to compare the effectiveness of these routes (route A, route B, and route C) for selective leaching the deposited metals from spent catalyst and to recommend the preferred leaching route.

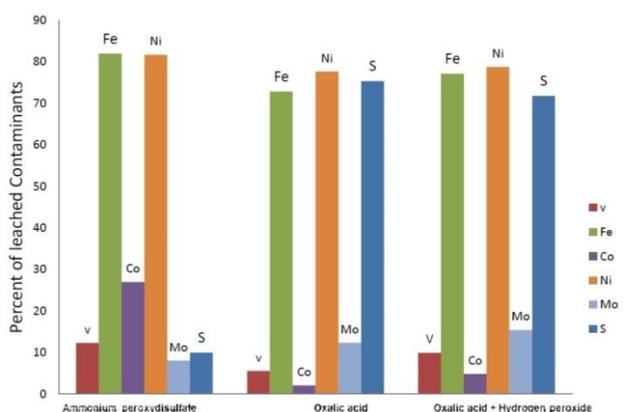


Fig. 2. Percent of leached metals in route A (Extraction of soluble coke Decoking Leaching of metals)

a. Effect Of Solvent Type

The sequence of stages in route A was as follows; the deoiled spent catalyst was extracted by n-hexane to remove soluble coke then it was decoked at a controlled temperature, and the last step was the leaching of the catalyst. Three different solvents were used in the leaching step in order to find out which solvent is suitable for the leaching step, these solvents are; oxalic acid, ammonium peroxydisulfate, and (oxalic acid + hydrogen peroxide) under the same conditions of 30 °C, 30 min, 200 rpm. Oxalic acid and ammonium peroxydisulfate with 0.1 M for each were prepared. The pH of the prepared oxalic acid solution was 1.46 while for ammonium peroxydisulfate, pH was 1.54. One ml of hydrogen peroxide was added to 50 ml of oxalic acid the resulted pH was 1.41. Figure 2 shows the comparison between the three used solvents results for route A.

It is obvious that removal of Ni, Fe, and V shows a slight response to the type of solvent used, while sulfur removal was strongly affected by the solvent.

This can be attributed to the effect of pH of the solution (between 1.54 and 1.46).

The addition of oxidizing agent (H_2O_2) has only a slight effect on the removal of sulfur. In the case of molybdenum, it was found that leaching percentage was increased when using different solvents in the order ammonium peroxydisulfate > oxalic acid > oxalic acid + hydrogen peroxide.

So, it can be concluded that oxalic acid is the most suitable solvent for leaching since it is characterized with high ability to remove contaminants (S, V, Fe, and Ni) and low ability to remove active metals (Co and Mo).

In route B, the deoiled spent catalyst was leached with the same three solutions in route A (oxalic acid, ammonium peroxydisulfate, and oxalic acid + Hydrogen peroxide), and then the soluble coke was extracted by n-hexane.

The last stage in this route was the insoluble coke removal by muffle-furnace under controlled temperature. The operating conditions of the leaching stage were the same as those used in route A.

The results of this route were presented in Fig. 3.

The contaminants (S, V, Ni, and Fe) and active catalyst metals (Co and Mo) showed similar behavior to that shown in route A. So, the optimum solution is oxalic acid.

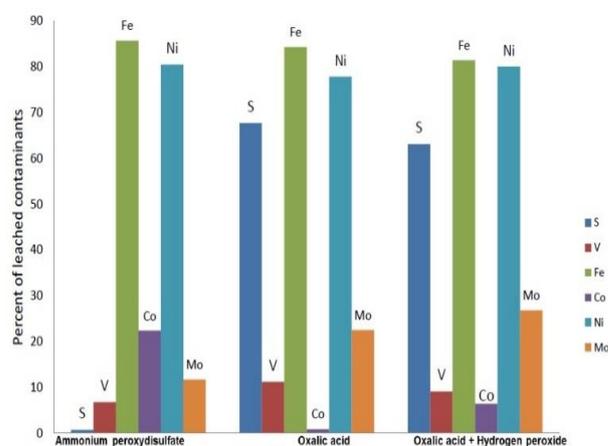


Fig. 3. Percentage of leached metals in route B

The sequence of stages in route C was the soluble coke was extracted from the spent catalyst after deoiling step.

Then, the metals were leached by the following solutions (Ammonium peroxydisulfate, oxalic acid, and oxalic acid + hydrogen peroxide) the conditions were the same as those used in route A.

The last step in this route was the removal of insoluble coke by muffle-furnace. The percentage of removed metals was shown in Fig. 4.

This figure shows that the same behavior followed by route A and B. Again oxalic acid was the suitable leaching solvent.

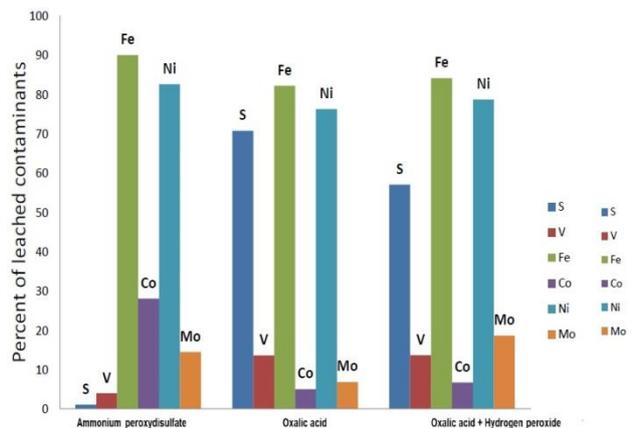


Fig. 4. Percentage of leached metals in route C

3.5. Best Leaching Conditions

From the above discussion, the best leaching solvent was oxalic acid (Figs. 2 – 4). These results confirm the result reached by Sadeek, 2014 [8] who examined three solvents for leaching of contaminants using NiMo/ γ -Al₂O₃.

These solvents were oxalic acid, benzoic acid and boric acid at different concentrations.

He concluded that oxalic acid is the optimum solvent for leaching from spent catalyst.

Fig. 5 represents the removal of each contaminant by oxalic acid for route A, B, and C. It is clear that the optimal route is route C since the removal of contaminants (S, V, Fe, and Ni) is relatively large while the loss of active metals (Co and Mo) is relatively small. Pereira et al 2011 [9] adopted the same sequence of stages in route C (extraction of soluble coke → leaching of metals → removal of insoluble coke).

After the determination of best solvent for optimum route, the favorable leaching conditions were determined experimentally by studying temperature, leachate concentration and leaching time in order to attain suitable conditions for catalyst rejuvenation. Stirring rate was fixed at 200 rpm.

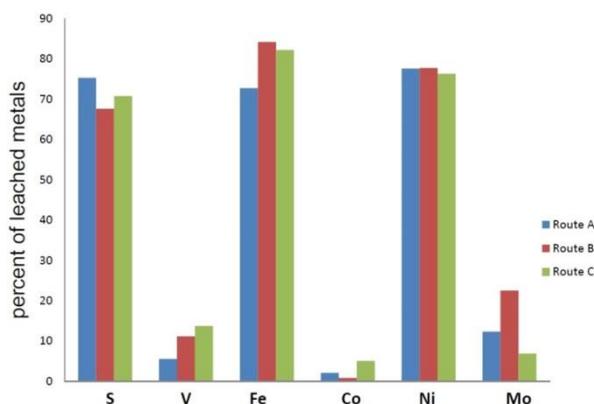


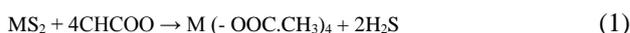
Fig. 5. Comparison among routes A, B, and C for metal removal

a. Effect of Oxalic Acid Concentration

Internal active surface area inside the pores significantly reduced via the pore entrance plugging caused by the contaminants accumulated at the catalyst surface.

Effect of oxalic acid concentration on metals leaching was studied at 30°C for 30 min and 200 rpm stirring speed, for different concentrations of oxalic acid (0.04, 0.06, 0.08, 0.12 and 0.16 M).

The metals in spent HDS catalyst are presented as sulfides. Leaching occurred with the chemical reaction between the metal sulfide and solvent as shown in reaction (1) [13]



Where M refers to the metal in the catalyst

The influence of the oxalic acid concentration on the contaminants leaching is presented in Fig. 6. For vanadium, the leached contaminants percentage increases with increase in oxalic acid concentration, the removal was raised from 13.16% at acid concentration of 0.04 M to 21.05% at acid concentration of 0.16 M.

The leached percentage of iron showed a slight increase with increasing in oxalic acid concentration; this was from 82.46% to 85.84%.

On the other hand, as oxalic acid concentration increased, the leached percentage of cobalt was nearly unaffected around and remained at 40%. Similar to cobalt, the leached percentage of nickel and molybdenum was nearly constant with oxalic acid concentration to be around 82% for nickel and 26% for molybdenum. This behavior is consistent with literature [9].

In spite of increasing removal of contaminants of spent catalyst (S and V) by increasing acid concentration, increasing in acid concentration may enhance the removal of active catalyst metals (Co and Mo).

So, the best concentration was 0.08 M of oxalic acid which leached as large as possible of the contaminants and leached as small amount as possible of the active metals.

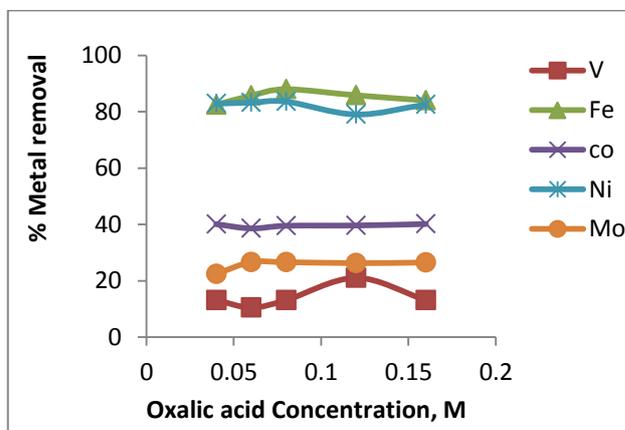


Fig. 6. Metal removal at 30 °C and 30 min

b. Effect of Leaching Temperature

Effect of temperature on the leaching process is presented in Fig. 7. This effect was examined for different temperatures (30, 50, 70 and 90 °C) at 0.08 M of oxalic acid for 30 min and 200 rpm stirring speed. From figure 7, the leached percentage of V increased with temperature, while the removal of Fe, Co, Ni, and Mo showed a slight response to temperature. The best leaching temperature was 50 °C since it removed a high percentage of contaminants and a low percentage of active metals. This value is consistent with the literature [6]. The increasing in leaching rate with temperature is due to the direct proportion of reaction rate and temperature according to Arrhenius equation [14].

$$k = A \cdot e^{-E/RT} \quad (2)$$

Where: k is the reaction rate constant.

The temperature may also affect the leaching rate by enhancing diffusion of solvent into catalyst pores since the viscosity decreases as temperature increases and this, in turn, promote the leaching rate.

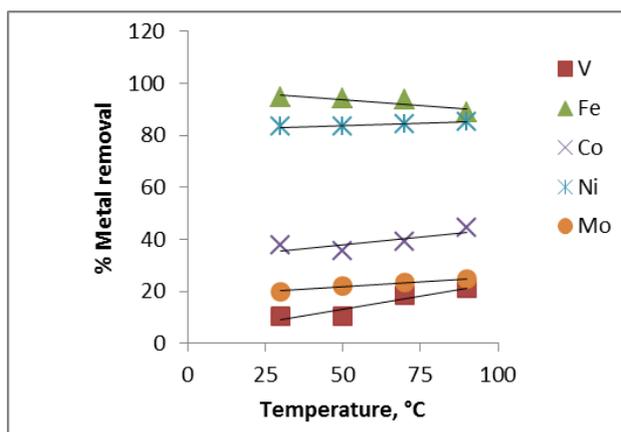


Fig. 7. Metal removal at 0.08 M and 30 min

c. Effect of Leaching Time

Effect of leaching time on the contaminants removal was examined at 30 °C and 0.08 M oxalic acid concentration for different periods of time (15, 30, 60 and 120 min).

Effect of time is presented in figure 8. This figure showed that the leaching percentage increased with time since longer contact time between contaminants and solution resulted in the increasing movement of contaminant toward oxalic acid.

In general, the best time was 30 min which leached the contaminants as large as possible maintaining the active catalyst metals (Co and Mo) as low as possible.

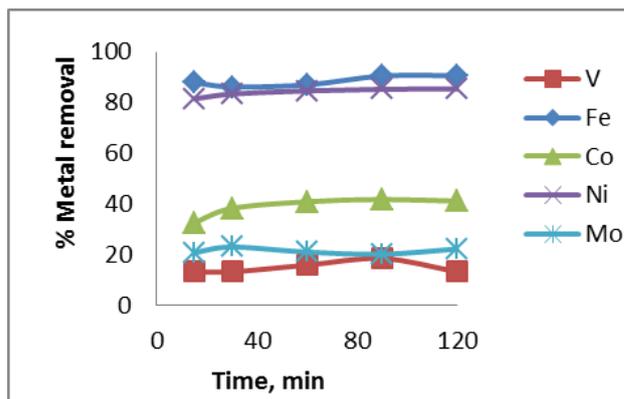


Fig. 8. The percentage of metal removal versus time at 0.08 M and 30 °C

3.7. Test of Activity of Rejuvenated Catalyst

In order to determine the activity of rejuvenated catalyst, reduction in naphtha sulfur content was measured for both spent and rejuvenated catalyst. The test was accomplished in a pilot scale hydrodesulfurization unit in PRDC with 17.5 mm inside diameter and 25.4 mm outside diameter with 300 mm length 361L stainless steel reactor. Fifty grams of spent catalyst were uploaded to the reactor and naphtha was fed at 1 ml/min flow rate. Operating conditions were 320 °C temperature, 200 H₂/HC ratios, and 32 bars. Sulfur content reduced by 75.4 % for one pass hydrodesulphurization. For rejuvenated catalyst test, fifty grams of rejuvenated catalyst were uploaded to the same reactor. Under the same operating conditions, sulfur content of feed naphtha reduced by 85.55 % for one pass hydrodesulphurization. The difference between these values showed that the activity of rejuvenated catalyst enhanced by 10.15 % sulfur content removal under the best rejuvenation conditions.

4- Conclusion

- 1- For spent HDS catalyst rejuvenation, the effective removal of most important contaminants such as S, Fe, and V was enhanced more than 15 % when the soluble coke was removed.
- 2- Oxalic acid is a very suitable solvent in reactivation of spent HDS catalyst.
- 3- The best route for rejuvenation of spent catalyst was the extraction of soluble coke followed by leaching of metals then finally decoking stage.
- 4- The best leaching with oxalic acid conditions was 0.08 M at a temperature of 50 °C and leaching time of 30 min.
- 5- The activity of spent HDS catalyst enhanced to more than 10 %.
- 6- Rejuvenation of spent catalyst can give a catalyst with active metals content only less than 10 % compared with fresh catalyst and the other characteristics remain nearly the same.

References

- [1] [L. Wu and Y. Liu, "Environmental impacts of hydrotreating processes for the production of clean fuels based on life cycle assessment," vol. 164, pp. 352–360, 2016.](#)
- [2] [M. Mara and A. Stanislaus, "Waste Catalyst Utilization : Extraction of Valuable Metals from Spent Hydroprocessing Catalysts by Ultrasonic-Assisted Leaching with Acids," *Ind. Eng. Chem. Res.*, pp. 9495–9501, 2011.](#)
- [3] [J. R. Chang, S. L. Chang, and T. B. Lin, "γ-Alumina-supported Pt catalysts for aromatics reduction: A structural investigation of sulfur poisoning catalyst deactivation," *J. Catal.*, vol. 169, no. 1, pp. 338–346, 1997.](#)
- [4] A. Stanislaus, *Handbook of Spent*. 2016.
- [5] [P. Dufresne, "Hydroprocessing catalysts regeneration and recycling," vol. 322, pp. 67–75, 2007.](#)
- [6] [M. Marafi, "studies on deactivation and reactivation of spent hydroprocessing catalyst," 1996.](#)
- [7] [M. Marafi and A. Stanislaus, "Options and processes for spent catalyst handling and utilization," vol. 101, pp. 123–132, 2003.](#)
- [8] [S. A. Sadeek, H. S. Ahmed, E. A. ElShamy, H. A. El Sayed, and A. A. Abd El Rahman, "Hydrotreating of waste lube oil by rejuvenated spent hydrotreating catalyst," *Egypt. J. Pet.*, vol. 23, no. 1, pp. 53–60, 2014.](#)
- [9] C. N. da S. e J. C. A. Alexandre Luiz de Souza Pereira, "Quim. Nova," *Quim. Nova*, vol. 34, no. 10, pp. 1704–1716, 2011.
- [10] [J. S. Yoo, "Metal recovery and rejuvenation of metal-loaded spent catalysts," *Catal. Today*, vol. 44, no. 1–4, pp. 27–46, 1998.](#)
- [11] [W. Wang, S. Wang, Y. Wang, H. Liu, and Z. Wang, "A new approach to deep desulfurization of gasoline by electrochemically catalytic oxidation and extraction," *FUEL Process. Technol.*, vol. 88, pp. 1002–1008, 2007.](#)
- [12] [H. A. Abdullah, A. Hauser, F. A. Ali, and A. Al-Adwani, "Optimal conditions for coke extraction of spent catalyst by accelerated solvent extraction compared to Soxhlet," *Energy and Fuels*, vol. 20, no. 1, pp. 320–323, 2006.](#)
- [13] [E. S. P. B. V, M. Marafi, A. Stanislaus, C. J. Mumford, and M. Fahim, "Regeneration of Spent Hydroprocessing Metals Removal Catalysts :," vol. 47, no. 3989, pp. 85–96, 1989.](#)
- [14] [O. Levenspiel, *Chemical reaction engineering O. Levenspiel Wiley. Third edition*, vol. 19, 1999.](#)

اعادة تدوير العامل المساعد المستهلك والمستخدم في هدرجة المستقطرات الوسطية

الخلاصة

اعادة استخدام العامل المساعد المستخدم في هدرجة المستقطرات الوسطية لازالة الكبريت $CoMo/\gamma Al_2O_3$ انجزت بواسطة ازالة الكاربون والملوثات الاخرى كالفناديوم، الحديد، النيكل والكبريت. تم استخدام ثلاث عمليات في المعالجة وهي : الانتزاع , الاستخلاص، وازالة الكاربون. تمت ازالة كل من الكربون القابل للذوبان والكاربون الغير قابل للذوبان في خطوة الاستخلاص، وتم استخدام ثلاثة مذيبات بصورة منفصلة وهي حامض الاوكزالك، الامونيوم البيروكسي ثنائي السلفات، وحامض الاوكزالك + بيروكسيد الهيدروجين. تمت دراسة تأثير ازالة الكاربون الذائب ووجد ان ازالته مهمة في تعزيز عملية الانتزاع للملوثات وتأثيرها قليل بالنسبة للمعادن الفعالة للعامل المساعد (الكوبلت والمولبدنيوم). وجد ان افضل مسار هو ازالة الكاربون الذائب متنوعة بانتزاع الملوثات وازالة الكاربون الغير ذائب وافضل مذيب كان حامض الاوكزالك. وفقا لهذه العملية كانت نسبة ازالة الملوثات هي 79.9% للكبريت، 13.69% للفناديوم، 82.27% للحديد، و 76.34% للنيكل. كمية الفقدان في المادة الفعالة بسبب هذه العملية كانت 5.08% للكوبلت، و 6.88% للمولبدنيوم.

تمت دراسة ظروف عملية الانتزاع (تركيز المذيب المستخدم في الانتزاع, درجة الحرارة, وقت العملية) من اجل تحديد افضل الظروف.

تم اختبار فعالية العامل المساعد المنشط في وحدة نطاق تجريبي للهدرجة لازالة الكبريت للنفثا. نسبة الكبريت المزال من النفثا كانت 85.56% لعملية تمرير واحدة للنفثا تحت ظروف تشغيلية مثالية لوحدة ازالة الكبريت بالهدرجة للمصافي النفطية والمتمثلة بمعدل جريان 1 مل ادقيقة, نسبة هيدروجن اهدروكاربونات =200, ضغط 32 بار, ورجة حرارة 320 درجة سلييزية.

الكلمات الدالة: اعادة تدوير العامل المساعد, العامل المساعد المستهلك, ازالة الكبريت بالهدرجة, استخلاص, انتزاع, فعالية العامل المساعد