

A review on the recovery of high-grade critical metals from spent petroleum catalysts for meeting the demands of Industry 5.0

Dilara Taz, Safak Ozsarac, Sait Kursunoglu, Nilufer Kursunoglu, Soner Top & Mahmut Altiner

To cite this article: Dilara Taz, Safak Ozsarac, Sait Kursunoglu, Nilufer Kursunoglu, Soner Top & Mahmut Altiner (2024) A review on the recovery of high-grade critical metals from spent petroleum catalysts for meeting the demands of Industry 5.0, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 46:1, 4593-4607, DOI: [10.1080/15567036.2024.2332465](https://doi.org/10.1080/15567036.2024.2332465)

To link to this article: <https://doi.org/10.1080/15567036.2024.2332465>



Published online: 22 Mar 2024.



Submit your article to this journal [↗](#)



Article views: 339



View related articles [↗](#)



View Crossmark data [↗](#)



A review on the recovery of high-grade critical metals from spent petroleum catalysts for meeting the demands of Industry 5.0

Dilara Taz^a, Safak Ozsarac^b, Sait Kursunoglu^c, Nilufer Kursunoglu^a, Soner Top^c, and Mahmut Altiner^d

^aDepartment of Petroleum and Natural Gas Engineering, Batman University, Batman, Turkey; ^bDepartment of Geological Engineering, Batman University, Batman, Turkey; ^cDepartment of Nanotechnology Engineering, Abdullah Gul University, Kayseri, Turkey; ^dDepartment of Mining Engineering, Cukurova University, Adana, Turkey

ABSTRACT

In solvent extraction studies, various extractants, including TOPO, Alamine 308, TBP, TOA, LIX 841, LIX 63, and Aliquat 336, were employed for the extraction and separation of vanadium, molybdenum, and cobalt from aqueous solutions of spent petroleum catalysts. Results indicated efficient metal recovery using these extractants. Furthermore, a combination of techniques, such as roasting, chemical or bioleaching, solvent extraction (SX), and precipitation, exhibited promising results in achieving comprehensive metal extraction and separation. Important discoveries have been made in the study of recovering important metals from wasted petroleum catalysts, especially with regard to attaining high metal recovery efficiencies. It is found that the recovery efficiency for manganese is 85%, cobalt is 87%, and nickel is 93%. Furthermore, it shows that this procedure may be carried out with high efficiency, with vanadium recovery surpassing 90% and molybdenum recovery efficiency above 95%. These outcomes signify a significant advancement in the field of metal extraction and separation, aligning with the principles of Industry 5.0 while emphasizing sustainability and efficiency in the production of high-tech materials for the modern era.

ARTICLE HISTORY

Received 1 December 2023
Revised 13 March 2024
Accepted 14 March 2024

KEYWORDS

Critical metals; spent petroleum catalyst; leaching; solvent extraction; Industry 5.0

Introduction

Catalysts are crucial in the petroleum refining process, upgrading and purifying petroleum products (Rocchetti et al. 2013). They have significantly boosted the growth of the refining and petrochemical sectors in the second half of the 20th century. Refineries use catalysts in various operations, including petrochemical, coal chemical, car exhaust purification, and flue gas de-nitration (Sahu, Agrawal, and Mishra 2013). However, many catalysts lose effectiveness over time due to structural changes or material contamination of active surfaces (Chu et al. 2021).

In order to successfully recover molybdenum, vanadium, and other valuable metals from waste catalysts, previous studies combined a variety of technologies, including ionic liquids (Tran, Liu, and Lee 2021), oxidizing agents (Tran, Liu, and Lee 2021), bioleaching (Asghari et al. 2013), and pyrohydro-metallurgical processes (Al-Sheeha et al. 2013; Nagar, Garg, and Gahan 2019; Khaferaj and Ferella 2022). However, the current study addresses the drawbacks of traditional hydro- and pyro-metallurgical techniques by introducing bioleaching as an alternative method for metal recovery from spent petroleum catalysts. It offers a wider perspective and handles multiple waste catalysts, addressing energy costs, safety risks, and secondary contamination (Le and Lee 2019; Xiong, Ji, and Ma 2020). The use of ferric iron as an oxidizing agent in bioleaching addresses environmental restrictions and offers a more eco-friendly approach (Chabhadiya, Srivastava, and Pathak 2021). The research focuses on the

selective separation and recovery of essential critical metals like molybdenum, vanadium, and cobalt from petroleum refining catalysts. It proposes extraction techniques like precipitation, solvent extraction, and ion exchange, aiming to optimize processes for Industry 5.0 applications. The review paper discusses recent research on optimizing metal extraction and separation from spent catalysts, highlighting the use of TOPO, Alamine 308, and TEHA. It emphasizes the importance of staying updated with cutting-edge techniques and methodologies, aligning with Industry 5.0 applications. This approach sets the paper apart from other research that focuses on metal recovery. The recycling techniques outlined in the article have been effectively utilized within industrial settings, demonstrating commercial viability and achieving notable success.

The review emphasizes the need to recover high-grade critical metals from spent petroleum catalysts, crucial for Industry 5.0 applications. With technology advancements and high-tech materials, optimizing extraction and separation processes is essential. Innovative methods, including leaching, solvent extraction, bioleaching, and hydrometallurgical and pyrometallurgical approaches, offer promising avenues for recovering valuable metals from spent catalysts, reducing environmental concerns and resource depletion. The integration of hydrometallurgical and pyrometallurgical processes can offer efficient and sustainable solutions for recovering critical metals from spent catalysts. Hydrometallurgy extracts metals using aqueous solutions, while pyrometallurgy uses high temperatures to separate metals from complex feed materials. This approach supports Industry 5.0 applications, resource conservation, and environmental protection, requiring a multifaceted approach involving innovation, efficiency, and sustainability across various industrial sectors. Optimizing the recovery of high-grade critical metals from spent petroleum catalysts is crucial for manufacturing advanced materials like electronic components and sensors in Industry 5.0 technologies. Using advanced extraction and separation techniques ensures a sustainable and efficient supply chain of these metals.

The current research landscape surrounding the recovery of high-grade critical metals from spent petroleum catalysts underscores the pivotal role these metals play in advancing Industry 5.0 applications. Specifically, there is a need for research to elucidate the critical factors driving the demand for recovered metals, such as the increasing scarcity of natural resources, rising energy costs, and stringent environmental regulations. Moreover, there is a lack of clarity regarding the optimal methods for selectively recovering metals like molybdenum, vanadium, and cobalt, which are essential for various high-tech applications in Industry 5.0. Furthermore, the research gap extends to the identification of innovative technologies and processes that can mitigate the drawbacks associated with traditional extraction methods, including energy-intensive pyrometallurgical techniques and environmentally hazardous chemical agents. By clearly articulating the specific challenges and opportunities in metal recovery from spent catalysts, future research endeavors can be better positioned to devise targeted and sustainable solutions that align with the principles of Industry 5.0 and contribute to the advancement of materials science and engineering.

Methodology

For this study, we methodically selected the most recent publications by taking into account both the quality of the journals in which they were published and the research findings they presented. We conducted a thorough literature search using relevant search terms such as “battery-grade,” “critical metals” “spent petroleum catalysts (SPCs),” and “purification,” “Industry 5.0” to identify the latest advancements in hydrometallurgical processes for the extraction and separation of critical metals from SPCs. To ensure the accuracy and relevance of the chosen articles pertaining to SPCs, we focused on investigating the following major themes:

- Included are recent research papers on chemical and bioleaching techniques for recovering critical metals from SPCs.

- Included articles that were just released and outlined the ideal settings for experimental chemical and bioleaching. These publications were comprised of the study.
- Included in the study were recently released articles that illustrated solvent extraction methods developed for the separation and purification of critical metals from pregnant leach solutions (PLS).
- The current research was divided into two sections: chemical and bioleaching of critical metals from SPCs and solvent extraction purification of metals from aqueous solutions for the achieving of battery-grade critical metals for high-tech materials production.

Chemical and bioleaching of critical metals from petroleum catalysts

Metal recovery is achieved through hydrometallurgy, a chemical reaction process involving leaching, solution concentration and purification, and metal recovery. Studies have shown the recovery of molybdenum and vanadium from SPC ammonia leaching residue (Chen et al. 2006), dissolution of precious metals from waste hydrotreating catalysts (Valverde Jr, Paulino, and Afonso 2008), and recovery of metals from used hydrodesulfurization catalysts using fluidized bed electrolysis and acid-leaching approaches (Jadhav and Hocheng 2012; Lai et al. 2008). Figure 1 illustrates the experimental setup.

Shahrabi-Farahani et al. (2014) tested *Acidithiobacillus thiooxidans* in a bioreactor for recovering heavy metals from hydrocracking waste catalyst, evaluating particle size, pulp density, and aeration rate. Glass bubble column bioreactor was used to conduct the research (Figure 2).

The study used HCl and NaCl for leaching and H_2O_2 for platinum oxidation, with HCl concentration having the most significant impact on leaching effectiveness. The reduction of iron powder improved Pt purity to over 90% (Ding et al. 2019). The fundamental hydrometallurgical process diagram for reclaiming platinum group metals (PGMs) is depicted in Figure 3 (Dong et al. 2015).

Recycling fluid catalytic cracking catalysts (SFCCCs) for metal and rare earth elements (REEs) is a viable recycling approach. Experiments have been conducted using various acids to extract V, Ni, Al, Fe, and Sb (Aung and Ting 2005). Additionally, the recovery of REEs from SFCCCs was

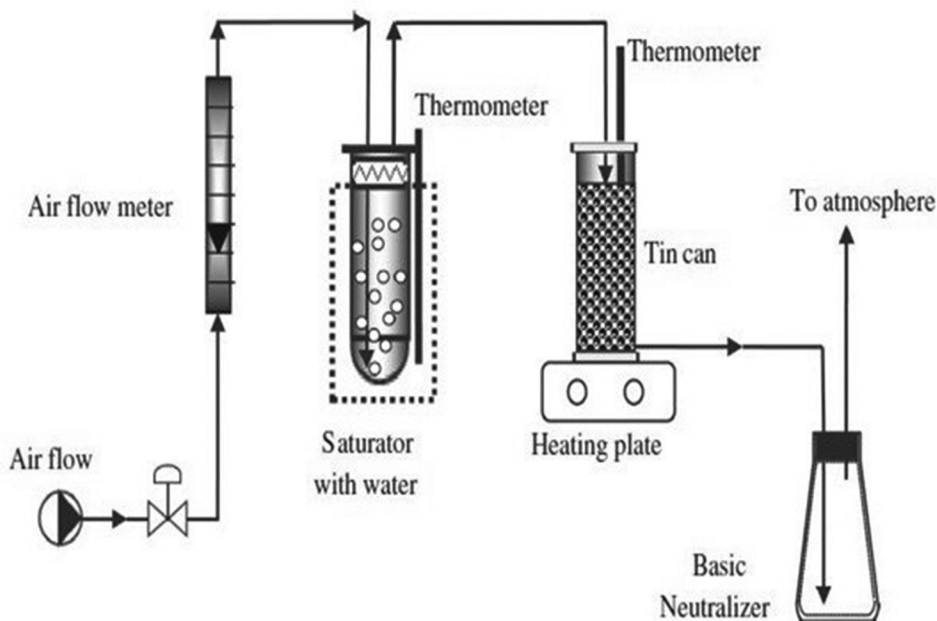


Figure 1. The experimental set-up used for the leaching process (Ramírez et al. 2013).

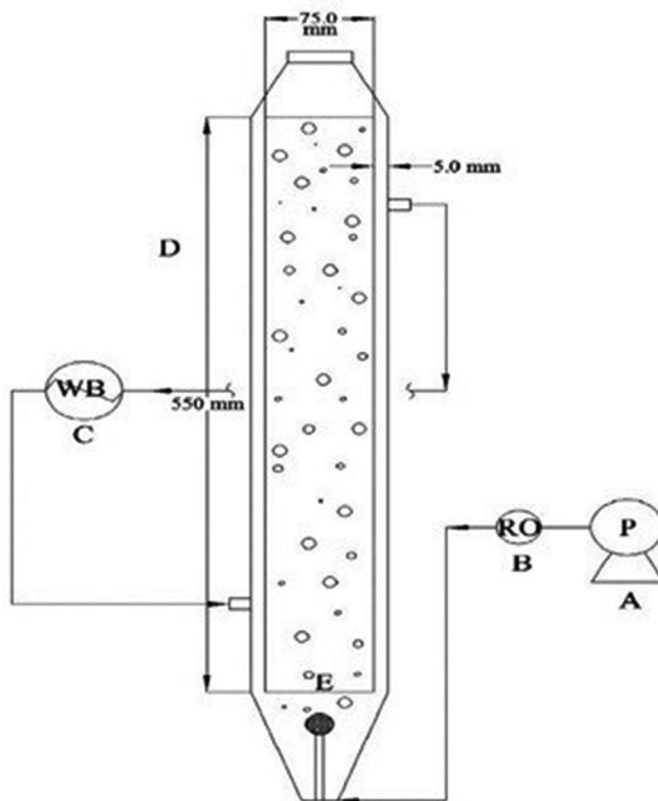


Figure 2. Designed bioreactor (A: aeration pump, B: rotameter, C: water bath, D: jacket, E: sparger (Asghari et al. 2013; Shahrabi-Farahani et al. 2014).

explored using sulfuric, hydrochloric, and nitric acids (Ferella, Innocenzi, and Maggiore 2016; Innocenzi et al. 2015). A patented method for extracting and precipitating REEs from SFCCCs was proposed. Nagar, Garg, and Gahan (2019) reported a three-step bio-pyro-hydrometallurgical process for recovering Ni and Mo from SPC, yielding high leaching yields. The bioleaching method, combined with roasting and alkaline leaching, significantly enhanced the recovery of Mo from discarded catalysts, reducing hazardous SO₂ emissions by 64.95% and releasing residual Mo by 23% from the aluminum silicate matrix. Figure 4 presented a comparison of bioleaching and alkaline leaching of metals.

The study examined the leaching ability of precious metals from petroleum catalysts using a mixture of extractants in kerosene, including D2EHPA, Alamine 336, Aliquat 336, or ALi-D2, and H₂O₂ solution. The ALi-D2 system demonstrated more effective and selective leaching of vanadium and molybdenum. The leaching process involves dissolved ions generation within the aqueous phase and metal ionic species migration from the aqueous phase to the organic phase. Figure 5 demonstrates that ALi-D2 and Aliquat336 have a higher metal leaching ability than D2EHPA and Alamine 336 (Tran, Liu, and Lee 2021).

A bioleaching technique using chemo-lithotrophic sulfur-oxidizing bacteria was used to recover vital metals from vanadium-rich used refinery catalysts (Mishra et al. 2007). The efficiency of this method was compared, showing lower yields for molybdenum compared to nickel and vanadium. Filtration of the leach liquor impeded metal extraction, with nickel and vanadium showing faster dissolution kinetics (Beolchini et al. 2010). *Aspergillus niger* was used to explore the bio-recovery of heavy metals from spent hydrocracking catalysts (Gholami, Mousavi, and Borghei 2012). The study

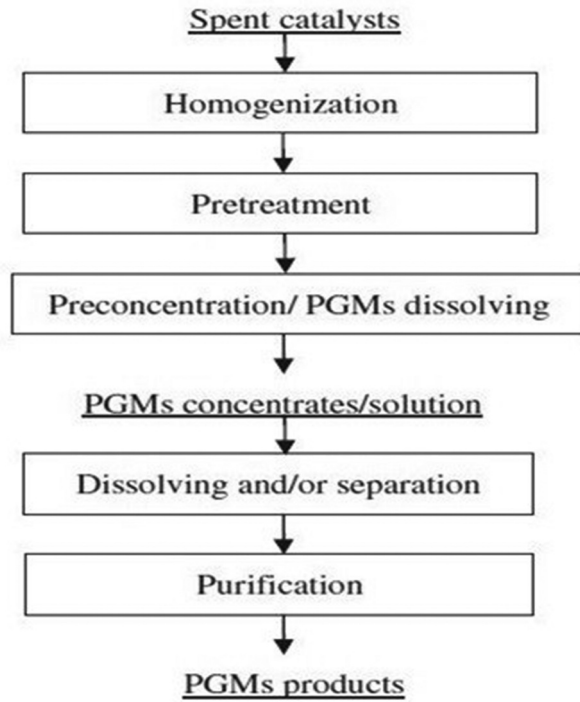


Figure 3. The basic hydrometallurgical flow sheet for the PGMs (Dong et al. 2015).

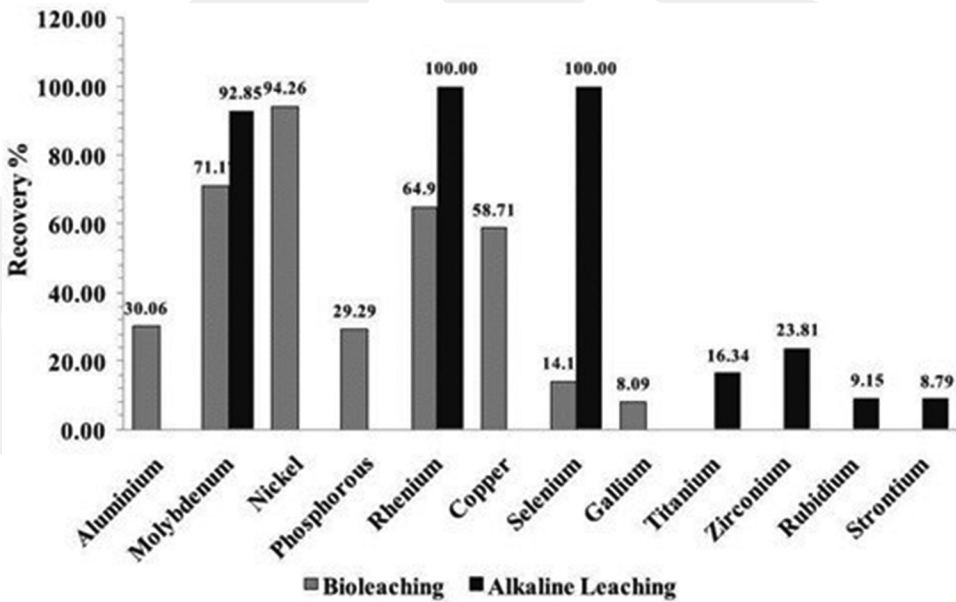


Figure 4. Comparison of bioleaching and alkaline leaching of metals (Nagar, Garg, and Gahan 2019).

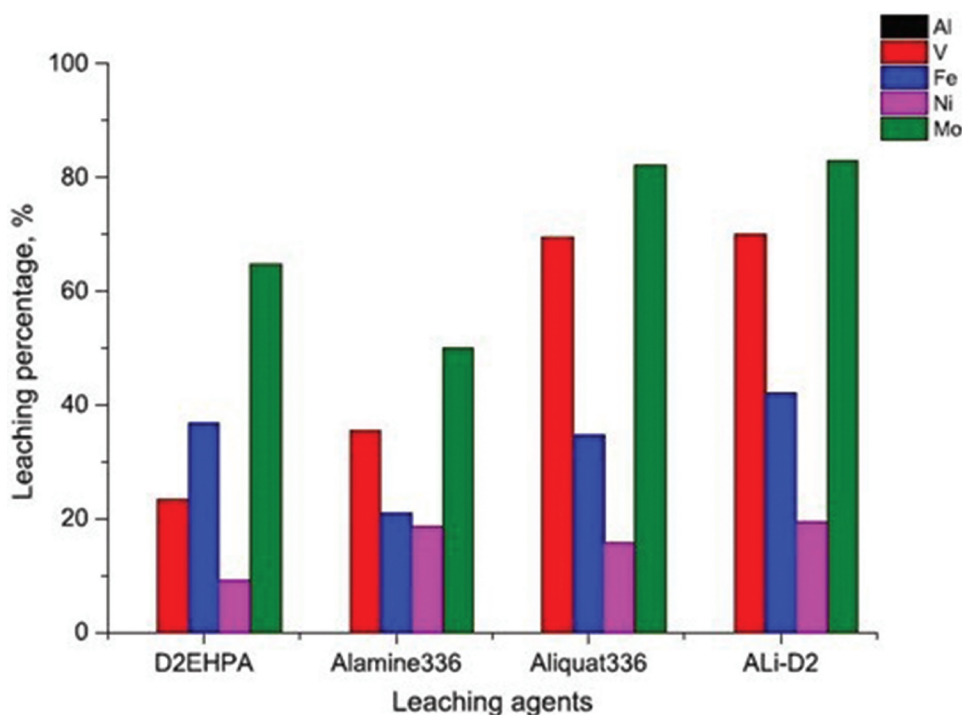
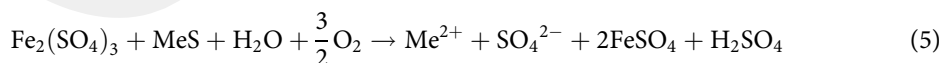
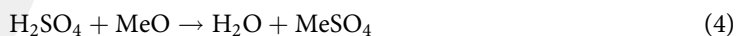
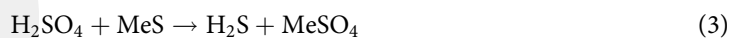
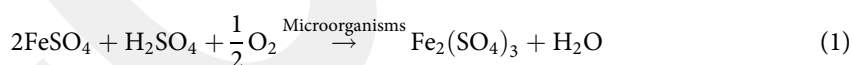
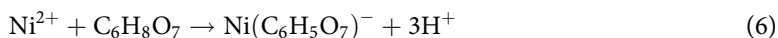


Figure 5. Leaching of metals from SPCs (conditions: reagent con.: 0.1M, 1/5:H₂O₂/leach solution, 60°C temperature, 700 rpm, 120 min) (Tran, Liu, and Lee 2021).

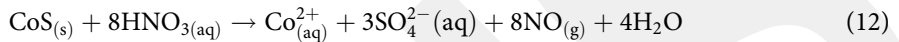
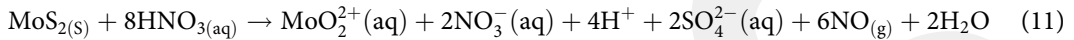
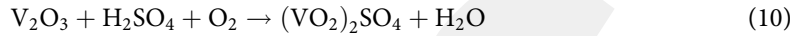
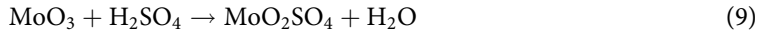
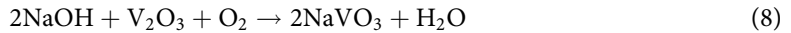
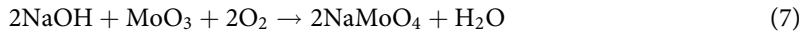
discusses the efficacy of a two-stage sequential integrated bioleaching process to enhance metal recovery from decoked, used petroleum catalysts (Srichandan et al. 2015). *A. ferrooxidans* can exclusively convert ferrous iron and elemental sulfur into ferric iron and sulfuric acid, respectively. As can be seen from Equations 1–5, these metabolites can then indirectly act as reactive species facilitating the solubilization of metal sulfides and oxides during the bioleaching process (Liang et al. 2022; Wen et al. 2023).



Complexes occur on metal surfaces due to ligand exchange, which polarizes crucial bonds and allows metal species to detach from the surface. The following is an example of a complexolysis process that could occur to create nickel citrate (Equation 6).



Alkaline and acidic leaching also facilitated the extraction of Mo and V. Leaching's chemical reactions are given in (Equations 7–12).



Arslandoğlu and Yaraş (2019) studied the leaching kinetics of a Mo-Co-Ni/Al₂O₃ catalyst with formic acid. Pathak et al. (2022) introduced a novel octadentate chelating agent (OCA) to extract harmful metals from industrial spent atmospheric residue desulfurization catalysts. OCA's chelating capacity explained its reactivity with different metals and its leaching efficiency. The abundance of metal-complexing groups formed metal-enclosed chelate rings (Figure 6).

Chen et al. (2022) developed a sulfuric acid leaching-stepwise extraction method for recovering critical metals from spent hydroprocessing catalysts. After roasting at 400°C, effective leaching was achieved using 1 M sulfuric acid at 75°C within 20 minutes. The study analyzed the impact of roasting, leaching temperature, duration, and sulfuric acid concentration (Figure 7).

Aslan, Aslan, and Ilhan (2023) investigated the hydrometallurgical recovery of critical metals from Ni-Mo HDS catalysts. They found that particle size, stirring speed, acid concentration, and temperature significantly influenced the leaching of MoO₃, NiMoO₄, Al₂O₃, and AlPO₄, with HCl concentration affecting NiMoO₄ and Al₂O₃ leaching rates at low and high temperatures. Table 1 summarizes the leaching of critical metals from SPCs using different chemical solutions.

The recycling methods discussed in the article have been successfully employed in industrial applications and have achieved commercial success. For instance, Chabhadiya, Srivastava, and Pathak (2021) investigated a two-stage leaching process and its kinetics for the environmentally friendly recovery of critical metals from waste Li-ion batteries. This research focused on making the recycling process more sustainable by demonstrating the practical implications of minimizing the environmental impact of critical metals extracted from waste Li-ion batteries. Furthermore, a study

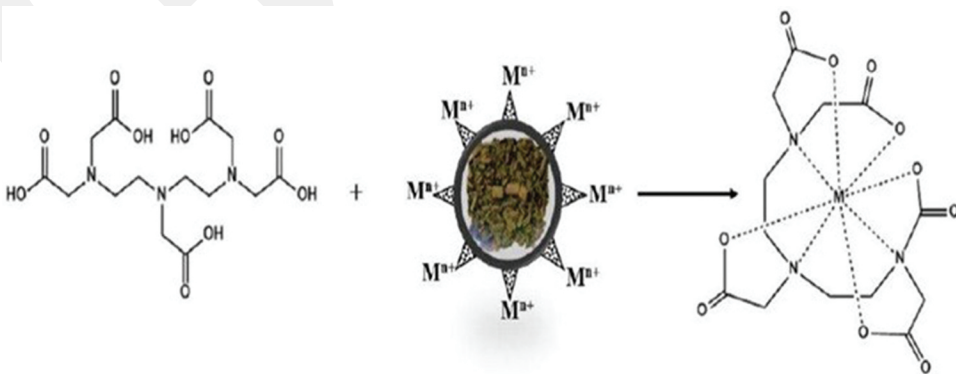


Figure 6. OCA reaction mechanism with metal ions (Pathak et al. 2022).

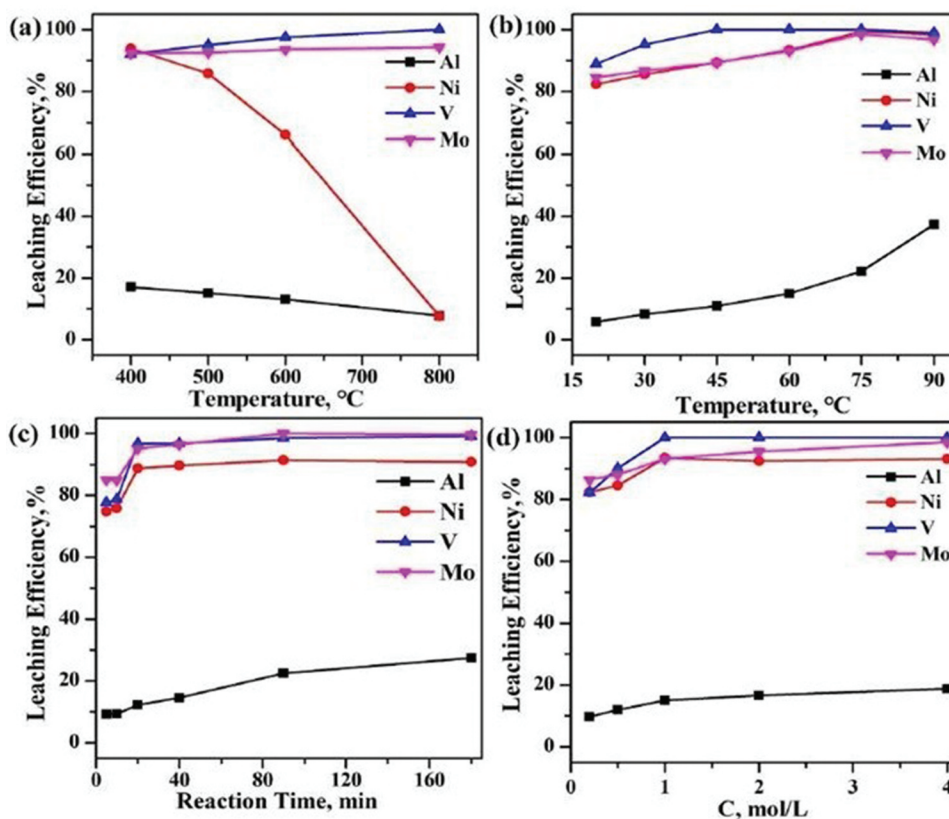


Figure 7. Effects of roasting and leaching temperature (a–b), leaching time (c), sulphuric acid concentration on the leaching efficiency (d) (Chen et al. 2022).

Table 1. Leaching of critical metals from SPCs using different lixivants.

Chemical/Bacteria	Acid con., M	Time, min	Tem., °C	V ext., %	Mo ext., %	Co ext., %	Ni ext., %	Ref.
Roasting with Na_2CO_3 +water leaching	-	15	80–90	>90	>91	-	-	Chen et al. (2006)
H_2SO_4 + HNO_3	0.5+4	300	50	-	>99	>99	-	Barik et al. (2012)
H_2SO_4	0.05	-	-	>99	<20	-	>99	Rocchetti et al. (2013)
<i>Acidithiobacillus thiooxidans</i>	-	240 h	-	>90	>88	-	>79	Srichandan et al. (2015)
Na_2CO_3 - NaHCO_3	-	100 h	70	-	71	-	94	Nagar, Garg, and Gahan (2019)
ALi-D2 with H_2O_2	0.4	150	60	>69	>83	-	-	Tran, Liu, and Lee (2021)
DTPA (7.5%)	-	300	60	>81	>83	-	>64	Pathak et al. (2022)
Mo-Ni/ Al_2O_3	-	-	60	-	97.8	-	98.1	Gao et al. (2022)

conducted by Khaferaj and Ferella (2022) assessed the overall efficiency of the extraction and recovery process of metals from HDS catalysts. The bioleaching process, developed by Asghari et al. (2013), has shown potential for sustainable metal recovery from waste HDS catalysts. The process can be integrated into industrial operations, providing environmental sustainability and economic advantages. This approach enhances waste management strategies, minimizing the environmental impact of metals from petroleum refinery waste catalysts. The results suggest that this process can be a significant step toward sustainable industrial processes.

Studies explore recovering critical metals from spent petroleum catalysts, considering environmental challenges and Industry 5.0 applications. Techniques include hydro-metallurgical, pyro-

metallurgical, and bioleaching. However, a nuanced evaluation is needed considering cost, extraction efficiency, and economic benefits. Xiong, Ji, and Ma (2020), compares the environmental and economic aspects of remanufacturing lithium-ion batteries and traditional manufacturing, examining energy consumption, greenhouse gas emissions, and resource utilization. Al-Sheeha et al. (2013) highlight the cost-effectiveness of recycling and recovery methods, which can optimize metal recovery and provide long-term economic sustainability. Tran, Liu, and Lee (2021), explored a recovery method for molybdenum and vanadium from spent petroleum catalysts using a mixture of ALi-D₂ solution and hydrogen peroxide as a leaching solution. The leaching conditions, including concentration, volume, temperature, reaction time, and pulp density, were investigated for environmental concerns. Nagar, Garg, and Gahan (2019) explored an integrated bio-pyro-hydro-metallurgical approach for recovering metal values from spent catalysts in petroleum refineries. The study aimed to optimize energy consumption and operational costs, offering a more environmentally friendly alternative to traditional methods. This approach could potentially reduce operational costs and promote environmental sustainability.

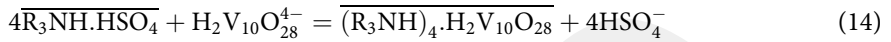
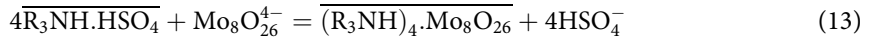
Early studies on metal recovery methods have shown unique approaches, but a deeper analysis is needed to advance the field. Researchers have explored recycling routes for spent hydroprocessing catalyst waste (Al-Sheeha et al. 2013), remanufacturing lithium-ion batteries (Xiong, Ji, and Ma 2020), and recovering molybdenum and vanadium compounds from petroleum catalysts (Tran, Liu, and Lee 2021). Some researchers have adopted integrated bio-pyro-hydro-metallurgical approaches, studied the effects of key parameters in bioleaching processes, proposed a two-step leaching process for recycling critical metals from spent Li-ion batteries, and focused on metal extraction and recovery from spent HDS catalysts. Le and Lee (2019) study the extraction of rare metals from petroleum catalysts using an organic acid solution. The method, which is environmentally friendly and cost-effective, effectively separates target metals. However, challenges like slow leaching rates and selectivity issues in processing complex metal mixtures are highlighted, highlighting the need for more efficient metal recovery processes. To truly innovate, these studies should be synthesized into a cohesive narrative that not only lists the methods but critically evaluates their applicability, efficiency, and environmental impact. The writers ought to provide analysis of the cutting-edge industrial procedures, pointing out their flaws and suggesting possible fixes. Moreover, the articles ought to go beyond a simple comparison of approaches and instead engage in a comprehensive conversation that encompasses the writer's viewpoint about the forthcoming advancement patterns in recycling technologies. This will give readers a thorough grasp of the current state of the art and direct further study and implementation of environmentally friendly waste management techniques. To put it simply, the papers ought to do more than merely report findings; they ought to actively influence the conversation and provide new avenues for research.

Solvent extraction (SX) of critical metals from leach solutions

The method for recovering metal values from SPC selectively combined acid leaching with solvent extraction (Mishra et al. 2010). A SX flow-sheet was created to extract Mo and V from leach liquid with preference. 98% Mo was extracted using 10% LIX-84I, and 40% LIX-84I from Mo-barren raffinate. A solution of NH₄OH-(NH₄)₂CO₃ was used for stripping. Mo⁶⁺ and V⁵⁺ were extracted and separated from other metals at pH 1.5. Alamine 308 produces anionic salts soluble in oil at low pH levels, forming amine salts through reactions with inorganic and organic acids. These salts interact with anions like molybdenum and vanadium, making them effective for selective extraction and separation in kerosene. Sahu, Agrawal, and Mishra (2013) studied the selective extraction of molybdenum and vanadium from PLS leach solution of SPCs using a 10% alamine 308 solution, finding higher affinity for vanadium at lower solvent concentrations.

Banda, Sohn, and Lee (2012) discussed a method for separating molybdenum from cobalt and aluminum in Escald 110 using TOPO (trioctylphosphine oxide). They successfully stripped Mo completely using a mixture of NH₄OH and (NH₄)₂CO₃. Post-molybdenum separation, cobalt can

be selectively recovered using Alamine 308. Additionally, tertiary amines such as alamine 304 (tridodecylamine) and alamine 336, obtained from the processing of used industrial catalysts, were employed to recover molybdenum using solvent extraction. At a pH of approximately 1.8, alamine 304 showed the best performance in molybdenum recovery (Valverde Jr, Paulino, and Afonso 2008). The following is a description of how alamine 336 extracts molybdenum and vanadium (Equations 13,14).



Banda et al. (2013) conducted experiments to recover molybdenum and cobalt from SHDSCs using solvent extraction. They loaded TBP with Mo, recovered via SX, and removed Mo. Alamine 308 was used to recover Co from Mo-free raffinate, followed by effective Co stripping using acidified distilled water. TEHA (tri-2-ethylhexylamine) was used for both extraction and stripping. Figure 8 illustrates a developed flow sheet outlining the recovery process of Mo and Co from the HDS catalyst leach liquor.

Chen et al. (2022) used a stepwise extraction separation technique to recover molybdenum, nickel, and vanadium from acidic leachate of spent hydrogenation catalysts. The technique, combining TOA

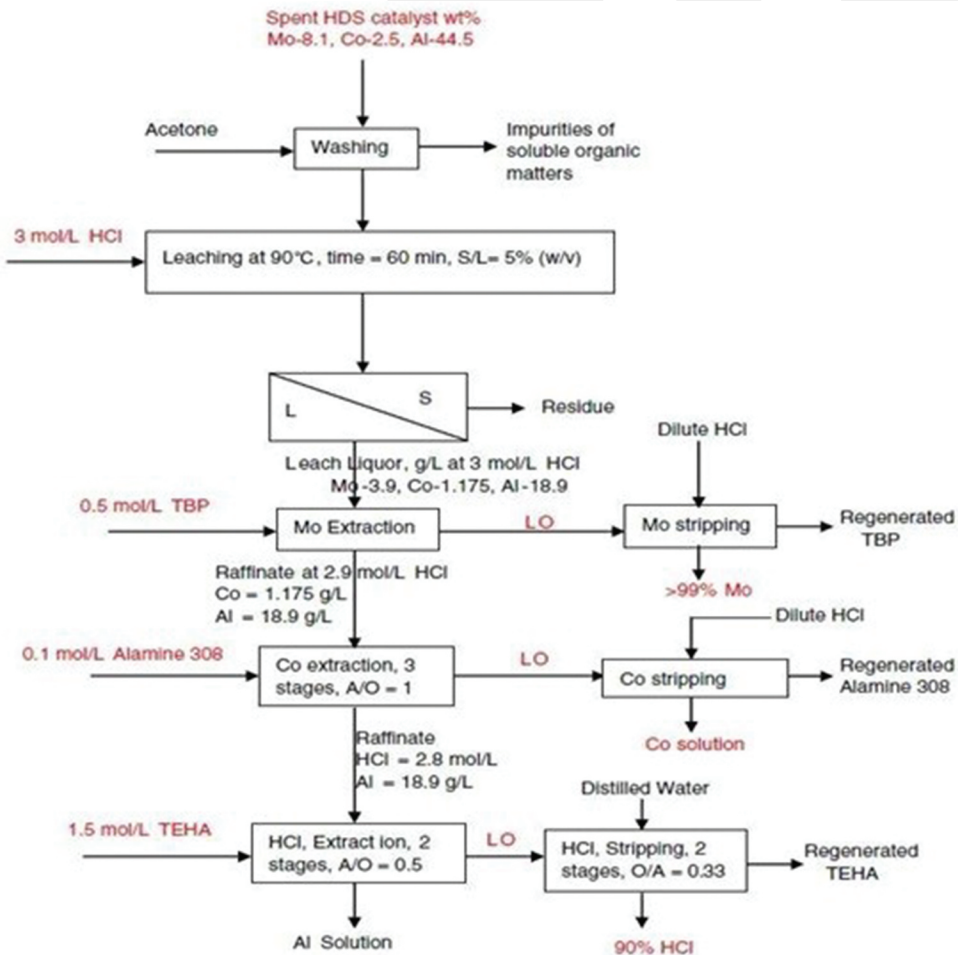


Figure 8. The recovery of Mo and Co from chloride leach liquors of SHDS (Banda et al. 2013).

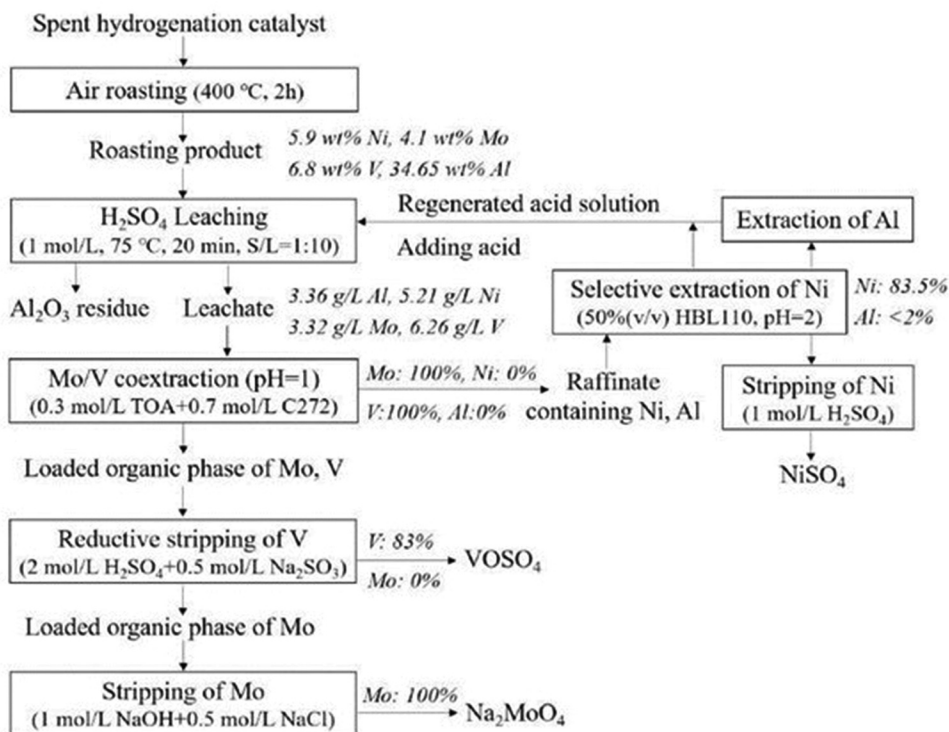


Figure 9. The stepwise recovery of Mo, V, and Ni from SHGCs (Chen et al. 2022).

(trioctylamine) and Cyanex 272, showed high extraction selectivity over Ni and Al. The selective stripping of vanadium was improved, and reductive sodium sulfite was used for enhanced removal. An alkaline solution was also used for efficient removal of remaining molybdenum. Figure 9 serves as an illustrative representation of a stepwise process for the separation and recovery of molybdenum, vanadium, and nickel from SHGCs, as recommended in the study.

A variety of techniques have been explored in the literature to efficiently extract and separate valuable metals such as Mo, V, Ni, and Co from these waste materials. In this context, the study by Gao et al. (2022) presents a novel approach for high-efficiency recycling of Mo and Ni via soda roasting and solvent extraction. The study proposes a two-step process, beginning with soda roasting of the spent catalysts to convert Mo and Ni into water-soluble sodium molybdate and nickel carbonate, respectively. Comparative studies on extractants and process parameters can help determine optimal conditions for Mo and Ni recovery. Economic assessments, considering reagent costs, energy consumption, and waste management, are crucial for evaluating the feasibility and scalability of the proposed recycling method. Singh, Mahandra, and Gupta (2018) investigated the recovery of Mo using Cyphos IL 102, an ionic liquid extractant, for sustainable resource management and environmental stewardship. The study optimizes parameters like extractant concentration, pH, temperature, and contact time to improve Mo extraction efficiency from spent catalyst leachate. Cyphos IL 102, an ionic liquid, offers high selectivity, stability, and lower environmental impact, making it ideal for Mo extraction from complex matrices in petroleum refinery spent catalyst leachates. The sequential steps involved in the metal recovery process and a flow sheet depicting the process for the recovery of Mo and V from spent petroleum catalysts were given in Figure 10.

Spent catalysts from various industries contain critical metals like molybdenum, vanadium, nickel, cobalt, and aluminum. Mo enhances reaction rates and product yields in hydroprocessing catalysts, while vanadium and nickel contribute to stability and activity in catalytic cracking catalysts (Chen

- Research was concentrated on separating two metal ions (Mo and V) from leach solutions, according to the literature review. Hydrometallurgical procedures, however, inevitably involve multicomponent metals like Ni, Co, Mn, and Li in leach liquor. To produce high grade metal values, a new chemical or bioleaching procedure followed by SX must be suggested.
- The combination of roasting, chemical or bioleaching, SX, and precipitation resulted in good extraction and production recoveries. Future efforts must consider the creation of a new flow sheet, which is combined with an artificial intelligence method such as machine or deep learning that predicts production metal values, grade, and recoveries prior, for the critical metal recovery from SPCs.

The research on recovering critical metals from spent petroleum catalysts has yielded significant insights, particularly in achieving high metal recovery efficiencies. The recovery efficiency of nickel is determined to be 93%, cobalt recovery is 87%, and manganese recovery is 85%. Furthermore, with molybdenum recovery efficiency exceeding 95% and vanadium recovery surpassing 90%, it demonstrates that this process can be carried out with high efficiency. These results underscore the importance of recycling waste petroleum catalysts from both environmental and economic standpoints. Bioleaching, an environmentally friendly alternative to traditional chemical methods, offers cost-effective, simpler, and simpler methods for recovering metals from spent catalysts, aligning with the global shift toward environmentally conscious practices. The research focuses on advancing metal extraction and separation methodologies, focusing on sustainability and efficiency. As Industry 5.0 transitions, environmentally conscious practices become crucial. Quantifiable success rates in vanadium and molybdenum recovery demonstrate the potential of these methodologies for a high-tech, environmentally conscious society.

Acknowledgments

The authors thank the Editor-in-Chief and anonymous reviewers for improving the manuscript.

Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Safak Ozsarac  <http://orcid.org/0000-0002-8319-9275>

Sait Kursunoglu  <http://orcid.org/0000-0002-1680-5482>

Soner Top  <http://orcid.org/0000-0003-3486-4184>

Mahmut Altiner  <http://orcid.org/0000-0002-7428-5999>

Credit authorship contribution statement

Dilara Taz: Investigation, Data Curation

Safak Ozsarac: Investigation, Data Curation, Visualization

Sait Kursunoglu: Conceptualization, Methodology, Investigation, Writing-original draft

Nilufer Kursunoglu: Investigation, Writing-original draft, Writing-review&editing

Soner Top: Investigation, Writing-review&editing

Mahmut Altiner: Investigation, Writing-review&editing

References

Al-Sheeha, H., M. Marafi, V. Raghavan, and M. S. Rana. 2013. Recycling and recovery routes for spent hydroprocessing catalyst waste. *Industrial & Engineering Chemistry Research* 52 (36):12794–801. doi:10.1021/ie4019148.

- Arslanoğlu, H., and A. Yaraş. 2019. Recovery of precious metals from spent Mo–Co–Ni/Al₂O₃ catalyst in organic acid medium: Process optimization and kinetic studies. *Petroleum Science and Technology* 37 (19):2081–93. doi:10.1080/10916466.2019.1618867.
- Asghari, I., S. M. Mousavi, F. Amiri, and S. Tavassoli. 2013. Bioleaching of spent refinery catalysts: A review. *Journal of Industrial and Engineering Chemistry* 19 (4):1069–81. doi:10.1016/j.jiec.2012.12.005.
- Aslan, B. G., C. Aslan, and S. İlhan. 2023. Hydrometallurgical recovery of valuable metals from hazardous petrochemical industry waste and kinetic investigation. *Journal of Sustainable Metallurgy* 9 (4):1–15. doi:10.1007/s40831-023-00745-7.
- Aung, K. M. M., and Y. P. Ting. 2005. Bioleaching of spent fluid catalytic cracking catalyst using *Aspergillus niger*. *Journal of Biotechnology* 116 (2):159–70. doi:10.1016/j.jbiotec.2004.10.008.
- Banda, R., T. H. Nguyen, S. H. Sohn, and M. S. Lee. 2013. Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction. *Hydrometallurgy* 133:161–7. doi:10.1016/j.hydromet.2013.01.006.
- Banda, R., S. H. Sohn, and M. S. Lee. 2012. Process development for the separation and recovery of Mo and Co from chloride leach liquors of petroleum refining catalyst by solvent extraction. *Journal of Hazardous Materials* 213:1–6. doi:10.1016/j.jhazmat.2011.12.078.
- Barik, S. P., K. H. Park, P. K. Parhi, J. T. Park, and C. W. Nam. 2012. Extraction of metal values from waste spent petroleum catalyst using acidic solutions. *Separation and Purification Technology* 101:85–90. doi:10.1016/j.seppur.2012.09.020.
- Beolchini, F., V. Fonti, F. Ferella, and F. Vegliò. 2010. Metal recovery from spent refinery catalysts by means of biotechnological strategies. *Journal of Hazardous Materials* 178 (1–3):529–534. doi:10.1016/j.jhazmat.2010.01.114.
- Chabhadiya, K., R. R. Srivastava, and P. Pathak. 2021. Two-step leaching process and kinetics for an eco-friendly recycling of critical metals from spent Li-ion batteries. *Journal of Environmental Chemical Engineering* 9 (3):105232. doi:10.1016/j.jece.2021.105232.
- Chen, Y., Q. Feng, Y. Shao, G. Zhang, L. Ou, and Y. Lu. 2006. Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst. *International Journal of Mineral Processing* 79 (1):42–8. doi:10.1016/j.minpro.2005.11.009.
- Chen, R., C. Feng, J. Tan, C. Zhang, S. Yuan, M. Liu, H. Hu, Q. Li, and J. Hu. 2022. Stepwise separation and recovery of molybdenum, vanadium, and nickel from spent hydrogenation catalyst. *Hydrometallurgy* 213:105910. doi:10.1016/j.hydromet.2022.105910.
- Chu, H., J. Wang, B. Tian, C. Qian, T. Niu, S. Qi, Y. Yang, Y. Ge, X. Dai, and B. Xin. 2021. Generation behavior of extracellular polymeric substances and its correlation with extraction efficiency of valuable metals and change of process parameters during bioleaching of spent petroleum catalyst. *Chemosphere* 275:130006. doi:10.1016/j.chemosphere.2021.130006.
- Ding, Y., H. Zheng, J. Li, S. Zhang, B. Liu, C. Ekberg, and Z. Jian. 2019. Recovery of platinum from spent petroleum catalysts: Optimization using response surface methodology. *Metals* 9 (3):354. doi:10.3390/met9030354.
- Dong, H., J. Zhao, J. Chen, Y. Wu, and B. Li. 2015. Recovery of platinum group metals from spent catalysts: A review. *International Journal of Mineral Processing* 145:108–113. doi:10.1016/j.minpro.2015.06.009.
- Ferella, F., V. Innocenzi, and F. Maggiore. 2016. Oil refining spent catalysts: A review of possible recycling technologies. *Resources, Conservation and Recycling* 108:10–20. doi:10.1016/j.resconrec.2016.01.010.
- Gao, B., H. Jiang, M. Zeng, M. Peng, L. Hu, W. Zhang, and L. Mao. 2022. High-efficiency recycling method for Mo and Ni from spent catalyst via soda roasting and solvent extraction. *Journal of Cleaner Production* 367:132976. doi:10.1016/j.jclepro.2022.132976.
- Gholami, R. M., S. M. Mousavi, and S. M. Borghei. 2012. Process optimization and modeling of heavy metals extraction from a molybdenum rich spent catalyst by *Aspergillus niger* using response surface methodology. *Journal of Industrial and Engineering Chemistry* 18 (1):218–224. doi:10.1016/j.jiec.2011.11.006.
- Innocenzi, V., F. Ferella, I. De Michelis, and F. Vegliò. 2015. Treatment of fluid catalytic cracking spent catalysts to recover lanthanum and cerium: Comparison between selective precipitation and solvent extraction. *Journal of Industrial and Engineering Chemistry* 24:92–97. doi:10.1016/j.jiec.2014.09.014.
- Jadhav, U. U., and H. Hocheng. 2012. A review of recovery of metals from industrial waste. *Journal of Achievements in Materials and Manufacturing Engineering* 54 (2):159–67.
- Lai, Y. C., W. J. Lee, K. L. Huang, and C. M. Wu. 2008. Metal recovery from spent hydrodesulfurization catalysts using a combined acid-leaching and electrolysis process. *Journal of Hazardous Materials* 154 (1–3):588–594. doi:10.1016/j.jhazmat.2007.10.061.
- Le, M. N., and M. S. Lee. 2019. Leaching of rare metals from spent petroleum catalysts by organic acid solution. *Journal of the Korean Institute of Resources Recycling* 28 (6):36–45. doi:10.7844/kirr.2019.28.6.36.
- Liang, X., J. Tang, L. Li, Y. Wu, and Y. Sun. 2022. A review of metallurgical processes and purification techniques for recovering Mo, V, Ni, Co, Al from spent catalysts. *Journal of Cleaner Production* 376:134108. doi:10.1016/j.jclepro.2022.134108.
- Mishra, D., G. R. Chaudhury, D. J. Kim, and J. G. Ahn. 2010. Recovery of metal values from spent petroleum catalyst using leaching-solvent extraction technique. *Hydrometallurgy* 101 (1–2):35–40. doi:10.1016/j.hydromet.2009.11.016.

- Mishra, D., D. J. Kim, D. E. Ralph, J. G. Ahn, and Y. H. Rhee. 2007. Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs. *Hydrometallurgy* 88 (1–4):202–9. doi:10.1016/j.hydromet.2007.05.007.
- Nagar, N., H. Garg, and C. S. Gahan. 2019. Integrated bio-pyro-hydro-metallurgical approach to recover metal values from petroleum refinery spent catalyst. *Biocatalysis and Agricultural Biotechnology* 20:101252. doi:10.1016/j.bcab.2019.101252.
- Pathak, A., H. Al-Sheeha, A. A. Ali, and M. S. Rana. 2022. Development of a novel chelation-based recycling strategy for the efficient decontamination of hazardous petroleum refinery spent catalysts. *Journal of Environmental Management* 322:116055. doi:10.1016/j.jenvman.2022.116055.
- Ramírez, S., P. Schacht, R. Quintana-Solórzano, and J. Aguilar. 2013. Leaching of heavy metals under ambient resembling conditions from hydrotreating spent catalysts. *Fuel* 110:286–292. doi:10.1016/j.fuel.2012.09.005.
- Rocchetti, L., V. Fonti, F. Vegliò, and F. Beolchini. 2013. An environmentally friendly process for the recovery of valuable metals from spent refinery catalysts. *Waste Management & Research* 31 (6):568–576. doi:10.1177/0734242X13476364.
- Sahu, K. K., A. Agrawal, and D. Mishra. 2013. Hazardous waste to materials: Recovery of molybdenum and vanadium from acidic leach liquor of spent hydroprocessing catalyst using alamine 308. *Journal of Environmental Management* 125:68–73. doi:10.1016/j.jenvman.2013.03.032.
- Shahrabi-Farahani, M., S. Yaghmaei, S. M. Mousavi, and F. Amiri. 2014. Bioleaching of heavy metals from a petroleum spent catalyst using *Acidithiobacillus thiooxidans* in a slurry bubble column bioreactor. *Separation and Purification Technology* 132:41–49. doi:10.1016/j.seppur.2014.04.039.
- Singh, R., H. Mahandra, and B. Gupta. 2018. Optimization of a solvent extraction route for the recovery of Mo from petroleum refinery spent catalyst using cyphos IL 102. *Solvent Extraction and Ion Exchange* 36 (4):401–19. doi:10.1080/07366299.2018.1507797.
- Srichandan, H., S. Singh, K. Blight, A. Pathak, D. J. Kim, S. Lee, and S. W. Lee. 2015. An integrated sequential biological leaching process for enhanced recovery of metals from decoked spent petroleum refinery catalyst: A comparative study. *International Journal of Mineral Processing* 134:66–73. doi:10.1016/j.minpro.2014.11.002.
- Tran, T. T., Y. Liu, and M. S. Lee. 2021. Recovery of pure molybdenum and vanadium compounds from spent petroleum catalysts by treatment with ionic liquid solution in the presence of oxidizing agent. *Separation and Purification Technology* 255:117734. doi:10.1016/j.seppur.2020.117734.
- Valverde Jr, I. M., J. F. Paulino, and J. C. Afonso. 2008. Hydrometallurgical route to recover molybdenum, nickel, cobalt and aluminum from spent hydrotreating catalysts in sulphuric acid medium. *Journal of Hazardous Materials* 160 (2–3):310–317. doi:10.1016/j.jhazmat.2008.03.003.
- Wen, J., X. Wang, F. Yu, M. Tian, C. Wang, G. Huang, and S. Xu. 2023. Recovery and value-added utilization of critical metals from spent catalysts for new energy industry. *Journal of Cleaner Production* 419:138295. doi:10.1016/j.jclepro.2023.138295.
- Xhaferaj, N., and F. Ferella. 2022. Extraction and recovery of metals from spent HDS catalysts: Lab- and pilot-scale results of the overall process. *Metals* 12 (12):2162. doi:10.3390/met12122162.
- Xiong, S., J. Ji, and X. Ma. 2020. Environmental and economic evaluation of remanufacturing lithium-ion batteries from electric vehicles. *Waste Management* 102:579–86. doi:10.1016/j.wasman.2019.11.013.