

An environmentally friendly method for extraction of Cobalt and Molybdenum from spent catalysts using deep eutectic solvents (DESs)

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Abstract

There has been a substantially increasing demand for Energy Critical Elements (ECEs) in recent years as energy-related technology has advanced rapidly. Spent catalysts are known as potential sources of ECCs such as Ni, Co, Mo, W, V, and rare earth elements. This study developed an environmentally friendly process for recovering cobalt and molybdenum from spent hydroprocessing catalysts using deep eutectic solvents (DESs). High metal extraction of 93% and 87% were respectively achieved for cobalt and molybdenum at optimum conditions (100°C, pulp density of 20 g/L, and 48 hours) using p-toluenesulfonic acid based DESs. FT-IR and H-NMR analyses were conducted to determine whether hydrogen bonds form between p-toluenesulfonic acid-based DES components. Leaching kinetic models were also developed for DES systems. It was found that shrinking core models fit well with the experimental results. The kinetic studies proved that the diffusion through the product layer was the leaching controlling step of DES-1 (PEG-400:PTSA) with an activation energy of 22.56, and 29.34 kJ/mol for Co and Mo, respectively. On the other hand, DES-2 (ChCl:PTSA) correlates well with the activation energies of 38.09 (cobalt) and 31.48 kJ/mol (molybdenum), indicating that reaction appears to be limited by the mixed control reaction model. This study provides an effective new approach for planning and running ionometallurgical processes in the recycling sector while paying attention to concerns for sustainable development.

Research Highlights

- 93% cobalt and 87% molybdenum were recovered from spent catalysts with Deep Eutectic solvent.
- The formation of hydrogen bonds between DESs components was investigated.
- PTSA:PEG-400 and ChCl: PTSA was the most efficient DES.
- Kinetic models were also developed to evaluate the leaching rate.
- Optimum leaching conditions were solid/liquid ratio of 20 g/L, 100 °C, and 48 hours.

1. Introduction

Global population expansion, more comfortable lifestyles, technological advancements, and political decisions have changed the patterns of supply and demand for raw materials. From the beginning of the 20th century the demand for Energy Critical Elements (ECEs) has increased due to development in modern energy-related technologies (Nuss and Blengini 2018). Spent catalysts known as a potential source of ECCs such as Ni, Co, Mo, W, V, and rare earth elements (Akcil et al. 2015). Co and Mo are the active metal in hydroprocessing catalysts, which is encouraged by other metals on alumina support (Kim et al. 2009). The catalyst's life cycle will expire when its activity decreases below acceptable levels. After extended usage, activity reduction is typically attributed to catalyst sintering, poisoning, fouling, or mechanical damage (Lim et al. 2021). Once deactivated, catalysts are either regenerated or treated to recover usable components. Otherwise, the deactivated catalyst is discarded as waste, producing such waste in large amounts (Stanislaus et al. 1993). Spent catalysts are hazardous pollutants that create

significant environmental problems, and The Environmental Protection Agency (EPA) of the United States categorized spent petroleum catalysts as hazardous waste regularly disposed of in landfills and can contaminate the environment (Le and Lee 2021). Metal recovery from secondary resources is receiving attention due to economic and environmental concerns (Rezaee et al. 2022).

Many studies have been conducted on metal recovery from spent catalysts by hydrometallurgy, pyrometallurgy, or a combination of the two methods (Le and Lee 2020; Meshram and Abhilash 2020). Nevertheless, using traditional techniques still faced real challenges. The pyrometallurgical route consumes high energy (Medvedev and Malochkina 2007; Chauhan et al. 2013). The hydrometallurgy route using inorganic acidic and alkaline solutions have low selectivity and lead to contaminated leachates (Binnemans and Jones 2017). Bioleaching was also used to recycle spent catalysts (Beolchini et al. 2010; Amiri et al. 2011; Tayar et al. 2020), but the rate of bioleaching is slower than other methods, and it takes longer for the metal to dissolve into the leach solution (Abdollahi et al. 2021). Furthermore, due to the participation of many leaching agents and separation phases, metal recovery in hydrometallurgical operations frequently creates a substantial volume of wastewater (Tran et al. 2021).

Finding alternative techniques that would meet both efficient metal recovery and decrease environmental consequences is essential. Traditional techniques can recycle hazardous wastes, but they come with concerns for the environment. Therefore, green chemistry has received a lot of attention in an effort to reduce the negative effects that conventional solvents have on the environment. Deep Eutectic Solvents (DESs), a novel class of green solvents, were first introduced by Abbott et al. at the start of the twenty-first century (Abbott et al. 2003, 2004). DESs are basically mixtures of at least two components, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), with a freezing point significantly lower than either component alone. DESs are green solvents with dipolar nature, non-flammability, and thermal stability, among other qualities (Abbott et al. 2003; Santana-Mayor et al. 2021). Several studies have shown promising results from the application of DESs in metal recovery from secondary resources (Abbott et al. 2009; Bakkar 2014; Bakkar and Neubert 2019). Lithium and cobalt were recovered from spent lithium-ion batteries via DES (Tran et al. 2019). Liu et al. obtained significant leaching rates by using DES to extract REEs from end-of-life NdFeB magnets (Liu et al. 2020). DESs with suitable properties can be designed by using various HBA and HBD components. Jiang et al. designed another class of Poly Ethylene Glycol (PEG) based eutectic solvents with great physical properties such as low viscosity, small volatility, intrinsic conductivity, and low cost, which showed great ability to recover transition metals from metal oxides (Jiang et al. 2019). Chen et al. also used PEG-based eutectic solvents to recover Co and Li from spent lithium-ion batteries and showed significant improvement in leaching efficiency (Chen et al. 2021).

Although there have been numerous research on the metal recovery from wastes or secondary sources by DES, nevertheless, the recovery of cobalt and molybdenum from spent catalysts has rarely been reported in the literature. For the first time, the present study employs various classes of deep eutectic solvents as leaching agents to recover cobalt and molybdenum from spent catalysts with excellent efficiency at mild conditions. The effect of different parameters on the leaching process was also examined in addition to

the dissolution mechanism. Additionally, a kinetic study was carried out in order to evaluate the rate of leaching in a system containing DESs. In this study, a novel green approach based on DES is introduced for the recovery of cobalt and molybdenum from spent catalysts, without the need for roasting or any addition of oxidative agents.

2. Materials And Methods

2.1. Chemicals and Materials

Choline chloride (ChCl, C₄H₁₂ClNO, 99%), Polyethylene glycol 400 (PEG-400, C_{2n}H_{4n+2}O_{n+1}, 98%), p-Toluene sulfonic acid (PTSA, C₇H₈O₃S, 99%), were purchased from Sigma-Aldrich and used in the experiments.

Spent catalysts were provided by Iran Petroleum Industry Research Institute. Organic contaminants were removed by washing with acetone and drying overnight at 80°C. The catalysts were crushed by a laboratory jaw crusher and ground by a laboratory rod mill for size reduction to d₈₀ of 75 μm. A chemical assay of the spent catalysts was made by X-ray Fluorescence spectroscopy (XRF) by a Philips PW 2404 apparatus (Table 1). The cobalt and molybdenum grade in the spent catalyst samples was 2.65% and 6.04%, respectively (Table 1).

Table 1
Catalysts chemical analysis by XRF

Elements	Al ₂ O ₃	CoO	CaO	SiO ₂	K ₂ O	MoO ₃	SO ₂
(%) in sample	52.64	2.65	0.16	0.31	0.06	6.04	0.09

2.2. Preparation of deep eutectic solvents

A 250 ml conical flask containing the HBD and HBA (Table 2) was used to synthesis DESs, placed on a water bath with temperature control, and continuously stirred with a magnetic stirrer until a homogenous colorless liquid was produced. The synthesis method used was the same as that by Abbot et al. (Abbott et al. 2006). After synthesis, the formed liquid was cooled to room temperature.

Table 2
List of deep eutectic solvents, their components, molar ratio, and viscosity at 298.15 K

DES	Hydrogen Bond Acceptor (HBA)	Hydrogen Bond Donor (HBD)	The molar ratio (HBA: HBD)
1	PEG-400	PTSA	1:1
2	ChCl	PTSA	2:1

2.3. Leaching Experiments

The typical hydrometallurgical approach was used for the leaching experiments; a certain amount of catalyst samples was poured into glass vials containing 5 mL of each DES with initial mixing and continuous temperature control. Then, the solutions were filtered at 25°C using PVDF syringe filters (pore size 0.45µm). The pregnant leach solution was diluted with 0.1 M HCl solution before being analyzed by Inductively Coupled Plasma (ICP). The leaching efficiency was computed as follows:

$$\text{Leaching efficiency} = \frac{c \times V(\text{DES})}{m} \times 100$$

Where *c* is the final concentration of the metal (mg/l) in the solution, *V* (DES) is the volume of the initial leaching solution, and *m* is the mass of the metal in the solid feed (mg).

2.5. Characterizations

The X-ray diffraction (XRD) spectra of spent catalysts were analyzed by Bruker D8-Advance with a CuKα beam. The surface morphology of spent catalysts and leach residues was studied by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscope (EDAX). The Fourier transform infrared (FTIR) spectrometry with KBr (potassium bromide) windows daubing samples was applied to obtain FTIR spectra of selected DESs and leachate by a couple of the attenuated total reflection (ATR-IR) equipment in the range of 600 to 1500 cm⁻¹. Solution ¹H Nuclear magnetic resonance (NMR) spectra (NMR, Varian - INOVA 500MHz, USA) of DESs and their components were measured with deuterium oxide were analyzed using deuterium oxide (D₂O) as the external standard.

2.6. Kinetic modeling

The kinetic leaching process spent catalyst in DES was investigated under various conditions (50–100°C, 0.5–48 h) to analyze the superior overall reaction kinetics of DES (Table S1). contains the kinetic model equations employed in this investigation (Levenspiel 1998; Fogler 2016). In order to calculate the DES leaching rate, it is important to evaluate every possible kinetic mechanism because it is impossible to determine what would be the dominating mechanism beforehand. The rate-controlling step is the mechanism whose equation best fits the results of experiments.

3. Results And Discussion

3.1. Catalyst samples characterization

The catalyst sample was a pyrolysis gasoline hydrogenation spent catalyst. X-ray diffraction was used to investigate the structure of the spent catalyst (Fig. 1). The XRD pattern of the spent catalyst sample indicated that it was an amorphous sample and the major phases detected were, alumina (Al₂O₃), cobalt oxide and molybdenum oxide.

3.2. Fourier transform infrared (FTIR)

The formation of hydrogen bonds between the HBAs and HBDs is the key factor in the creation of DES (Jiang et al. 2019). The forming of hydrogen bonds and determination of functional groups in the DESs was characterized by the Fourier transform infrared (FTIR) spectra (Fig. 2 (a) and (b)). The absorption peaks of the main functional groups, including oxyalkylene -C-O-C- (1100 cm^{-1}), the hydroxyl groups -OH (3384 cm^{-1}), and the alkyl C-H (2873 cm^{-1}) stretching vibration were observed in the DES-1. As the results are shown in Fig. 2 (a), both the increasing band width and the slight shifts of (-OH), (-C-O-C), and (-C = O) stretching vibration peaks proved the existence of interactions between HBA and HBDs in DES-1. According to the FT-IR spectra of DES-2 shown in Fig. 2 (b), the broad band at 3322 cm^{-1} is related to the stretching vibration of the -OH hydroxyl groups in DES-2. An additional characteristic band at 953 cm^{-1} originating from ChCl was recognized for the C-N + stretching. These results indicated the successful formation of hydrogen bonds based on interactions between HBA and HBD in both DESs.

3.3. ^1H Nuclear magnetic resonance (^1H NMR)

The formation of hydrogen bonds between DES components is the main reason for the temperature-limited phase transition of DESs (Tang et al. 2022). The H-NMR spectra of DES-1, DES-2, and their components are shown in Fig. 3 (a) and (b), demonstrating that the chemical shifts of both DESs are pushed downfield, giving strong evidence of hydrogen bond formation in both DESs. The increased electronegativity of the oxygen atoms from O-H and (COOH) in HBA may draw and reduce the electron cloud densities around the hydrogen atoms of OH in PEG, affecting the chemical shifts values in DESs and the creation of hydrogen bond (Chen et al. 2020).

3.4. Effect of leaching parameters on cobalt/molybdenum Recovery

The effect of leaching parameters such as solid-liquid ratio, leaching duration, and temperature on cobalt and molybdenum leaching efficiency was investigated.

3.4.1. Solid-liquid ratio

The effects of the solid-liquid ratio on cobalt/molybdenum dissolution are depicted in Fig. 4 (a). The response time and temperature were set at 48 hours and 100°C , respectively. The value of cobalt/molybdenum extraction declined as the solid-liquid ratio grew, and all samples demonstrated a similar trend. A larger solid-liquid ratio also resulted in a high metal content in the DESs, resulting in increased viscosity, which hampered the practical process. At solid-liquid ratios of 50 to 100 g/L, there was no notable decline in cobalt/molybdenum dissolution. The best solid-liquid ratio was found to be 20 g/L, which resulted in the most cobalt/molybdenum dissolution for all samples.

3.4.2. Time

The effects of leaching time on cobalt/molybdenum dissolution are shown in Fig. 4 (b). At the start of the reaction, the cobalt/molybdenum dissolution increased with time in the case of DES-1. After 8 hours, the

dissolution of cobalt/molybdenum increased with a linear slope in the second phase, then increased with a slight slope in the third step to the end of the reaction. Although DES-2 was compared to DES-1, cobalt/molybdenum dissolution increased with a slight slope. Although extremely high cobalt/molybdenum recovery rates were obtained with a shorter reaction duration in DES-1, 48-hour reaction durations for both DES may be appropriate.

3.4.3. Temperature

The effect of leaching temperature on cobalt/molybdenum extraction is examined by varying the temperatures from 50 to 100°C while maintaining a constant S/L ratio of 20 g/L and a leaching period of 48 hours. cobalt/molybdenum dissolving increases as the leaching temperature rises. The findings are displayed in Fig. 4. (c). This phenomenon might arise for two reasons: First, the viscosity of DESs lowers with increasing temperature, and reduced viscosity improves ion mobility and mass transfer in the leaching system. falls and reduced viscosity improves ion mobility and mass transfer in the leaching system (Tang et al. 2022). As a result, the chance of a solid fraction colliding with DES components increased, enhancing the cobalt/molybdenum dissolving rate. Furthermore, increasing the leaching temperature enhanced the dissolution rates of the cobalt/molybdenum, allowing it to achieve dissolution equilibrium more quickly. The leaching temperature of 100°C was chosen as the best leaching temperature based on the study's findings.

3.5. SEM and EDAX analysis

Figure 5 shows SEM micrographs of the sample's surface morphology before and after leaching. The EDAX results for residues are shown in Fig. 5 (b) and (c). The absence of a clear peak of elemental cobalt and molybdenum in the leach residues indicates that the cobalt and molybdenum have been extensively dissolved in the DES-1 and DES-2. The results also revealed the presence of Al and Si in the leach residues. This diagram shows that during the DES leaching procedure, an inert layer of alumina covered the surface of the catalyst. This alumina layer limits solvent transport to the catalyst surface, so controlling the dissolution rate.

3.6. Kinetic modeling of cobalt and molybdenum leaching

Typically, heterogeneous reactions occur in several steps, only with the slowest controlling the total reaction rate. The following stages are commonly involved in the dissolution of cobalt/molybdenum spent catalyst in DES as a solid-liquid heterogeneous reaction. The reactant diffuses from the liquid phase's bulk to the interface between the liquid and solid phases. Inert or insoluble substrates, such as alumina, are present in the catalyst samples, forming a product layer around the reacting core. To reach the unreacted core, the reactants must diffuse across this product layer. The porosity and thickness of the inert layer, as well as the diffusion coefficients of the ions created during the reaction, are the key parameters influencing diffusion through the product layer. The reactant then diffuses from the interface to the cobalt and molybdenum major bodies. Furthermore, chemical interactions occur between the reactants and the elements on the surface of the reacting core. Finally, at the interface of inert material,

the products diffuse into the bulk of the liquid phase. The reaction can then proceed topochemical, with the inner core of the sample progressively transforming into the unreacted particle (alumina) (Oza R and Patel S 2011).

Based on the results in Tables S2-S5, it was observed that spherical geometry models give a more appropriate approximation for kinetic processes than all other models studied. Diffusion control (Eq. 2), chemical reaction control (Eq. 3), and mixed control models (surface reaction control; and diffusion via product layer) (Eq. 4) are commonly proposed as methods for managing the rate of leaching reactions by reducing core models (Meshram et al. 2015).

$$kt = 1 - 3(1 - X)^{2/3} + 2(1 - X) \text{ (Eq. 2)}$$

$$kt = 1 - (1 - X)^{1/3} \text{ (Eq. 3)}$$

$$kt = -\ln(1 - X) \text{ (Eq. 4)}$$

Where X is the cobalt/molybdenum leaching efficiency (%), k is the apparent rate constant (h^{-1}); and t is the leaching time (h). The rate-controlling step is thought to be the mechanism with high correlation coefficients (R^2), and its model shows the best matches with experimental data.

Figure S1 and S2 show the well-fitted graphs for (DES-1). According to the correlation coefficients shown in Table S2 (DES-1, Cobalt), the diffusion through the product layer was well-matched with the experimental data. A perfect linear relationship $1 - 3(1 - X)^{2/3} + 2(1 - X)$ and t was observed in the case of (DES-1), indicating that the leaching kinetic mechanism for DES-1 was diffusion control through the product layer. Based on correlation coefficients presented in Table S3 and Fig. S2-S3, the mixed control model well matched (DES-2) during the reaction (about 12 hrs).

The apparent activation energy (E_a) of cobalt/molybdenum leaching reaction in different DESs, was determined by the Arrhenius equation using the apparent reaction rate constants k obtained from the slopes of the kinetics models at various temperatures:

$$\ln k = -\frac{E_a}{RT} + \ln A \text{ (Eq. 5)}$$

Where k is the apparent reaction rate constant; t is the leaching time, h; E_a is the apparent activation energy, kJ/mol; R is the universal gas constant, 8.314 J/K.mol; T is the temperature, K; and A is the pre-exponential factor.

The activation energy provides important insights into the kinetics and thermodynamics of chemical processes. The greater the activation energy, the greater the influence of temperature on the rate. Activation energies can also be used to assess the kinetics control step. Mass transit plays a significant role in the overall rate of many responses. Diffusion is one example of a low-activation-energy mass transport method. The activation energy of surface chemical reactions is substantially larger than that of

diffusion control (Levenspiel 1998; Fogler 2016). As a result, the temperature has less effect on diffusion-controlled processes than it does on chemical-controlled processes. The activation energy is often used to estimate mass transport and response control in processes (L. Free 2022).

The plot of $\ln k$ against $1/T$ for all samples presented in Fig. 6 shows a straight line with an intercept of $\ln k$ and a slope of E_a/R . According to (Anand et al. 1988), A diffusion-controlled process has an activation energy that varies between 3 and 6 kcal/mol (12.55–25.08 kJ/mol). The activation energy of a chemically regulated process is often greater than 10 kcal/mol (41.84 kJ/mol) (Habashi 2017). A mixed control has an activation energy in the range of 20.92–33.44 kJ/mol or 5–8 kcal/mol (Habashi 1999). According to Fig. 6 (a,b), the calculated activation energies were 22.56, and 29.34 kJ/mol for Co and Mo in the (DES-1), respectively. Therefore, it is evident that the (DES-1) leaching controlling step was the diffusion through the product layer. Based on Fig. 6 (c,d), the calculated activation energies were 38.09, and 31.48 kJ/mol for Co and Mo in the (DES-2), respectively. Therefore, the mixed control reaction may control the kinetic mechanism of the spent catalyst in (DES-2).

4. Concluding Remarks

This study is a potential opening step toward developing a cleaner approach for the recycling of spent catalysts via Deep Eutectic Solvents (DESs). The potential of two DESs as leaching agents to recover cobalt/molybdenum from spent hydroprocessing catalysts was evaluated for the first time in this study. DES-1 (PEG-400:PTSA) and DES-2 (ChCl:PTSA) as leaching agents showed strong leaching ability. The pulp density of 20 g/L, the temperature of 100°C, and the leaching time of 48 hrs were found to be the optimum leaching conditions for all samples. The kinetic studies proved that the diffusion through the product layer was the leaching controlling step for DES-1 with an activation energy of 22.56, and 29.34 kJ/mol for Co and Mo, respectively. On the other hand, DES-2 (ChCl:PTSA) correlates well with the activation energies of 38.09 (cobalt) and 31.48 kJ/mol (molybdenum), indicating that reaction appears to be limited by the mixed control reaction model.

Declarations

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review and editing, Funding acquisition. **Ali Rezaei:** Resources, Equipment. **Hadi Abdollahi:** Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Validation, Resources.

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Ethics declarations

Ethics approval: I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously.

Consent to participate: All the authors listed consent to participate.

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Figures

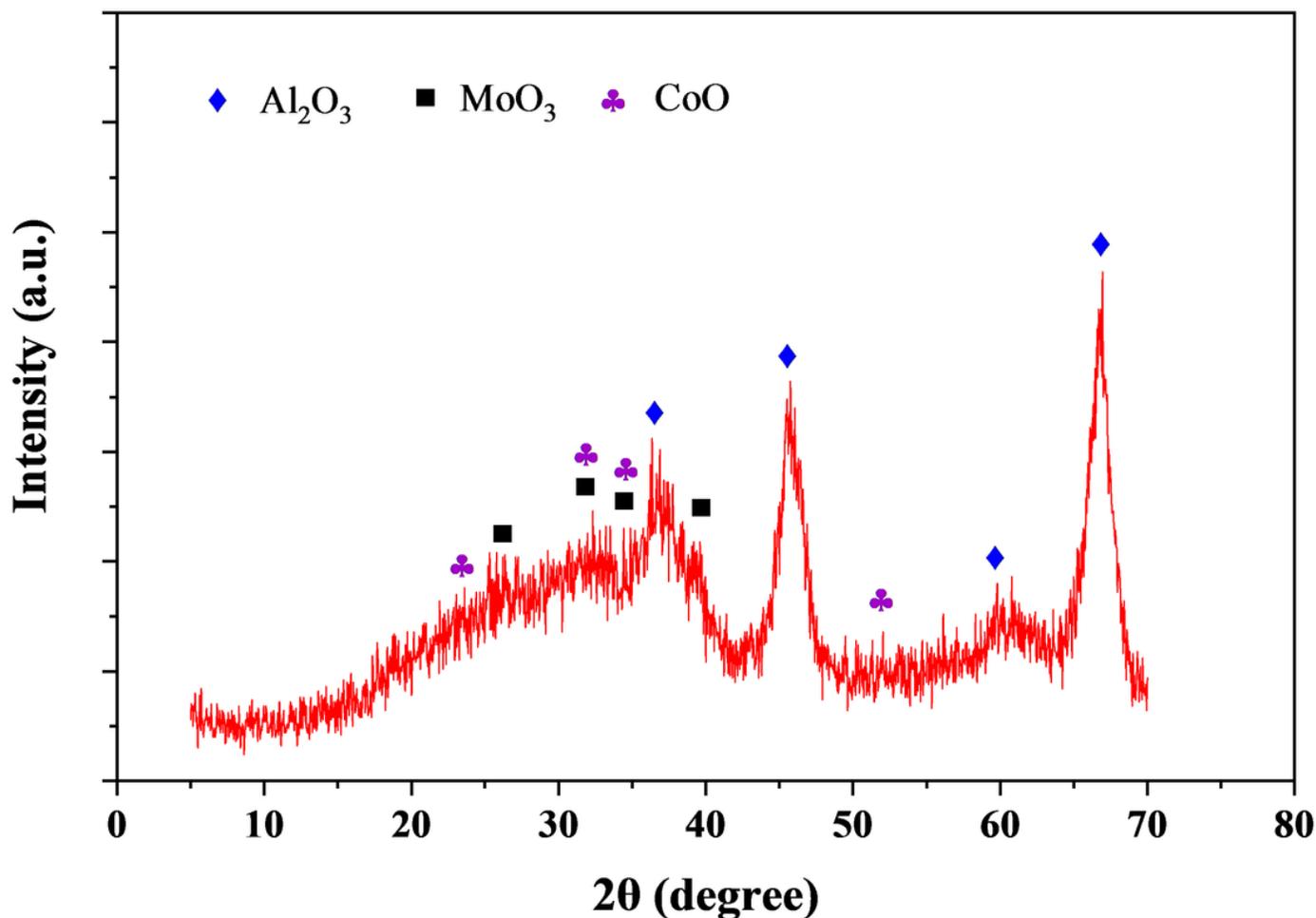


Figure 1

X-ray diffraction (XRD) patterns of spent catalyst

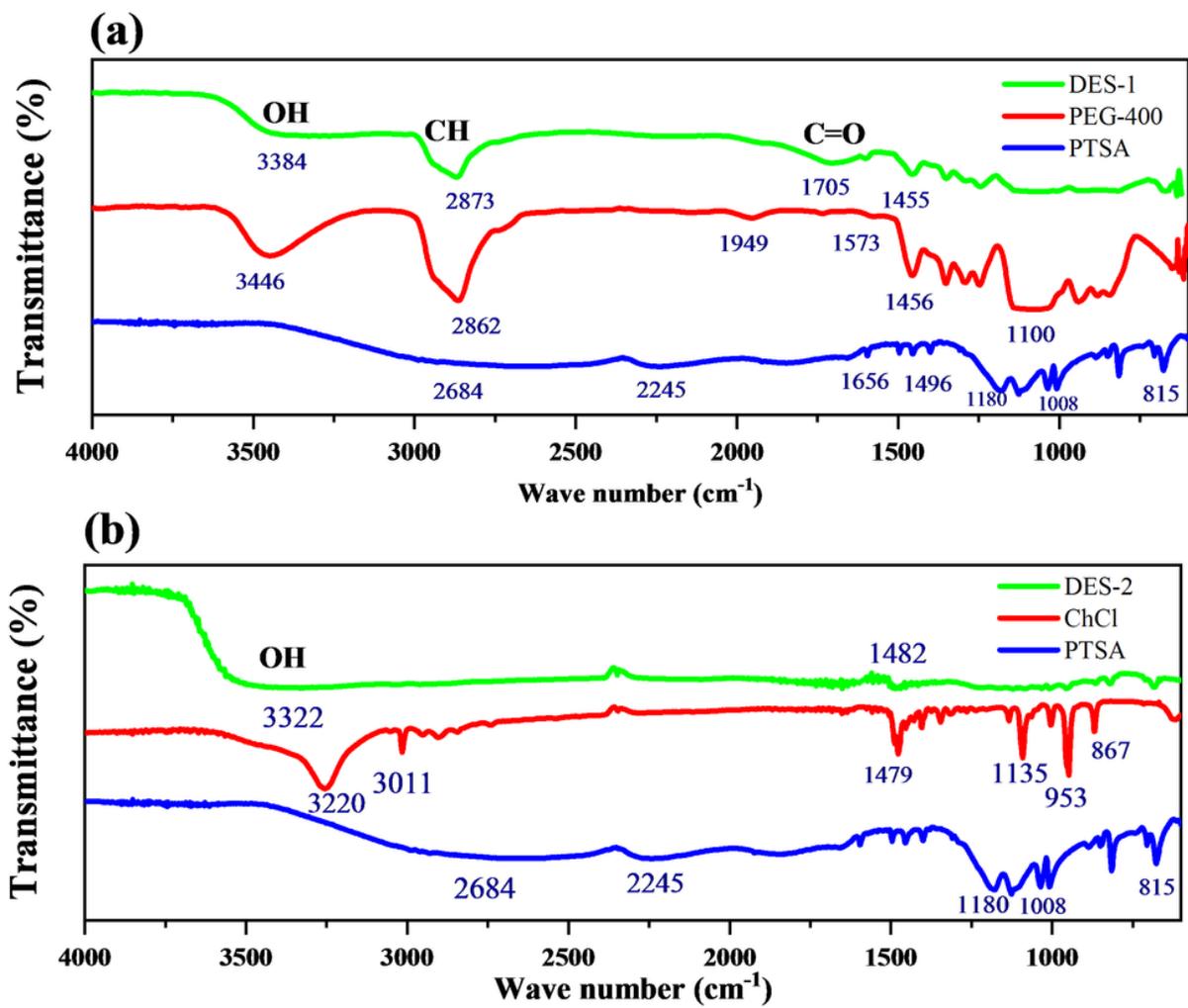


Figure 2

FTIR spectra of (a) DES-1 and (b) DES-2 with their pure HBA and HBD components

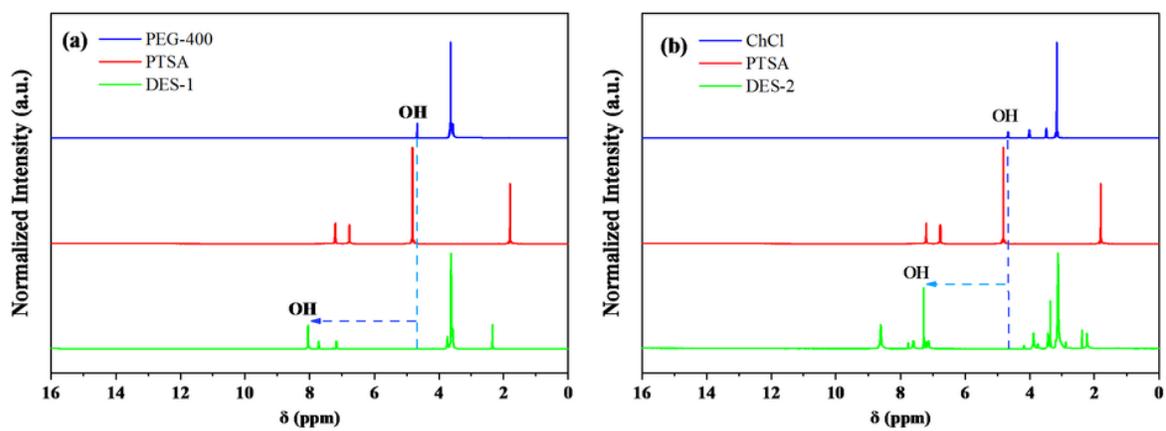


Figure 3

^1H NMR spectra (a) DES-1, (b) DES-2 and their components

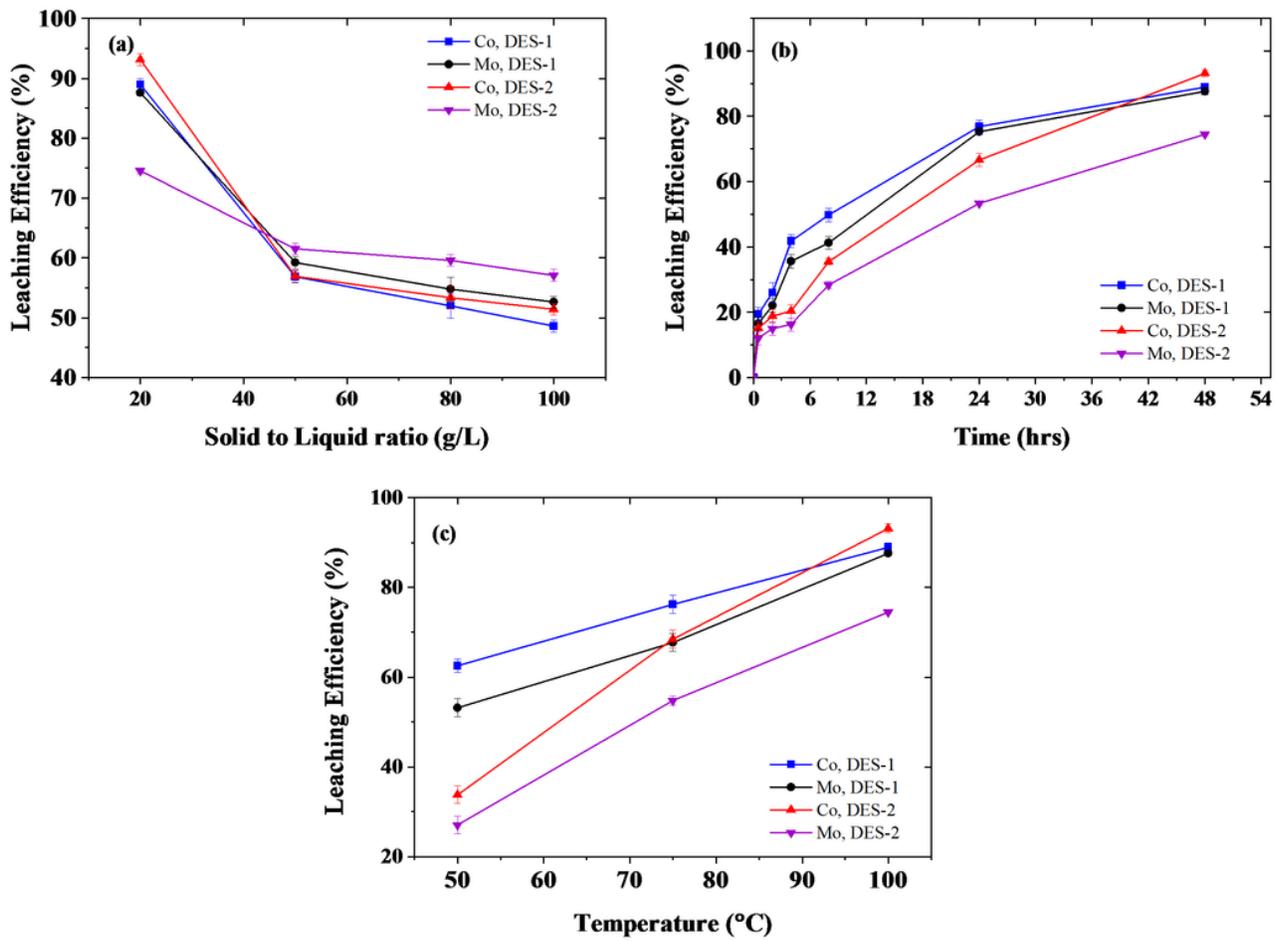


Figure 4

Effect leaching parameters of (a) Solid to liquid ratio, (b) Time, (c) Temperature on cobalt/molybdenum extraction

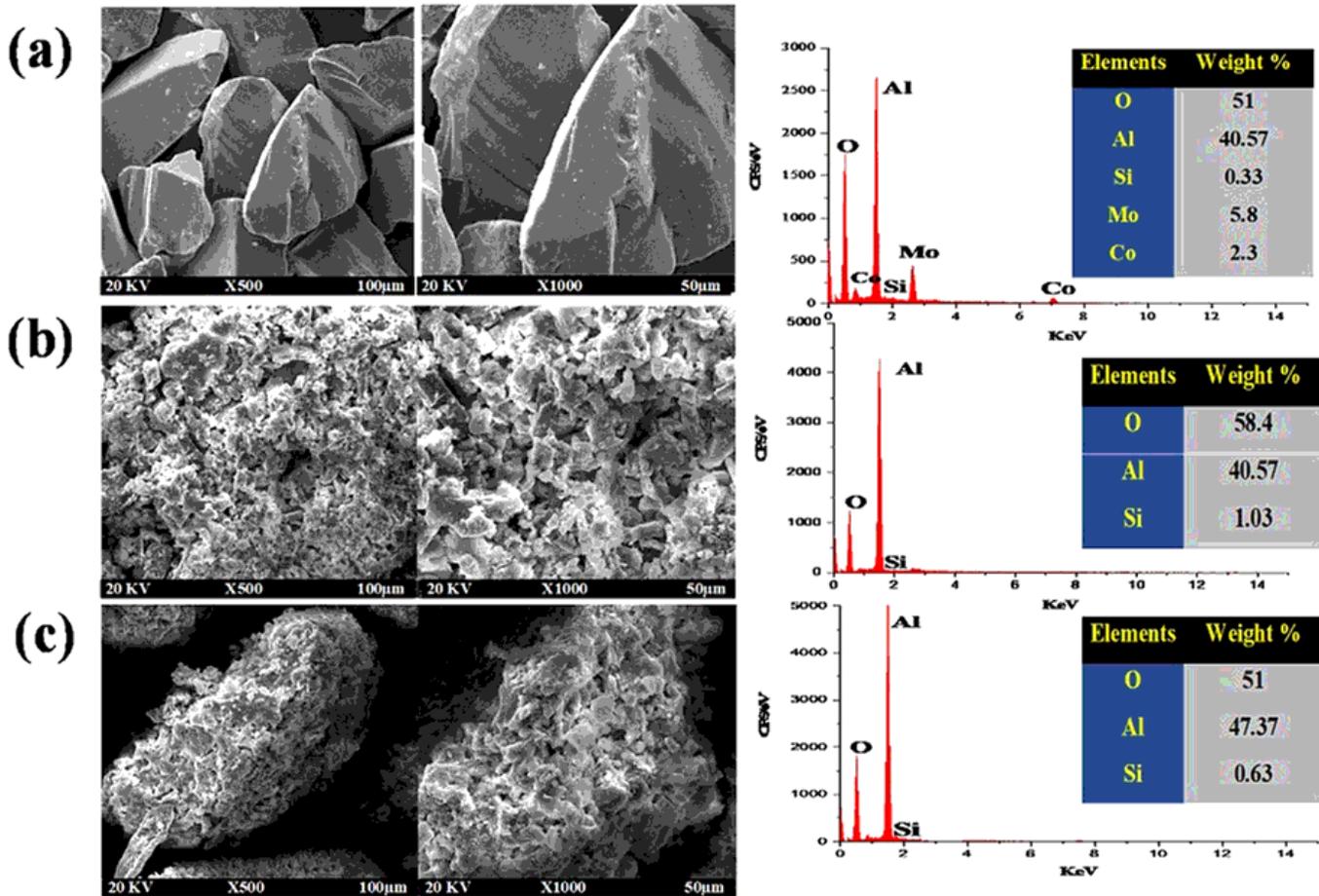


Figure 5

The SEM micrographs and EDAX analysis of samples (a) catalyst, leach residues (b) DES-1, (c) DES-2 (48 hrs leaching time, temperature of 100°C, particle size of 75 µm, S/L ratio of 20 g/L)

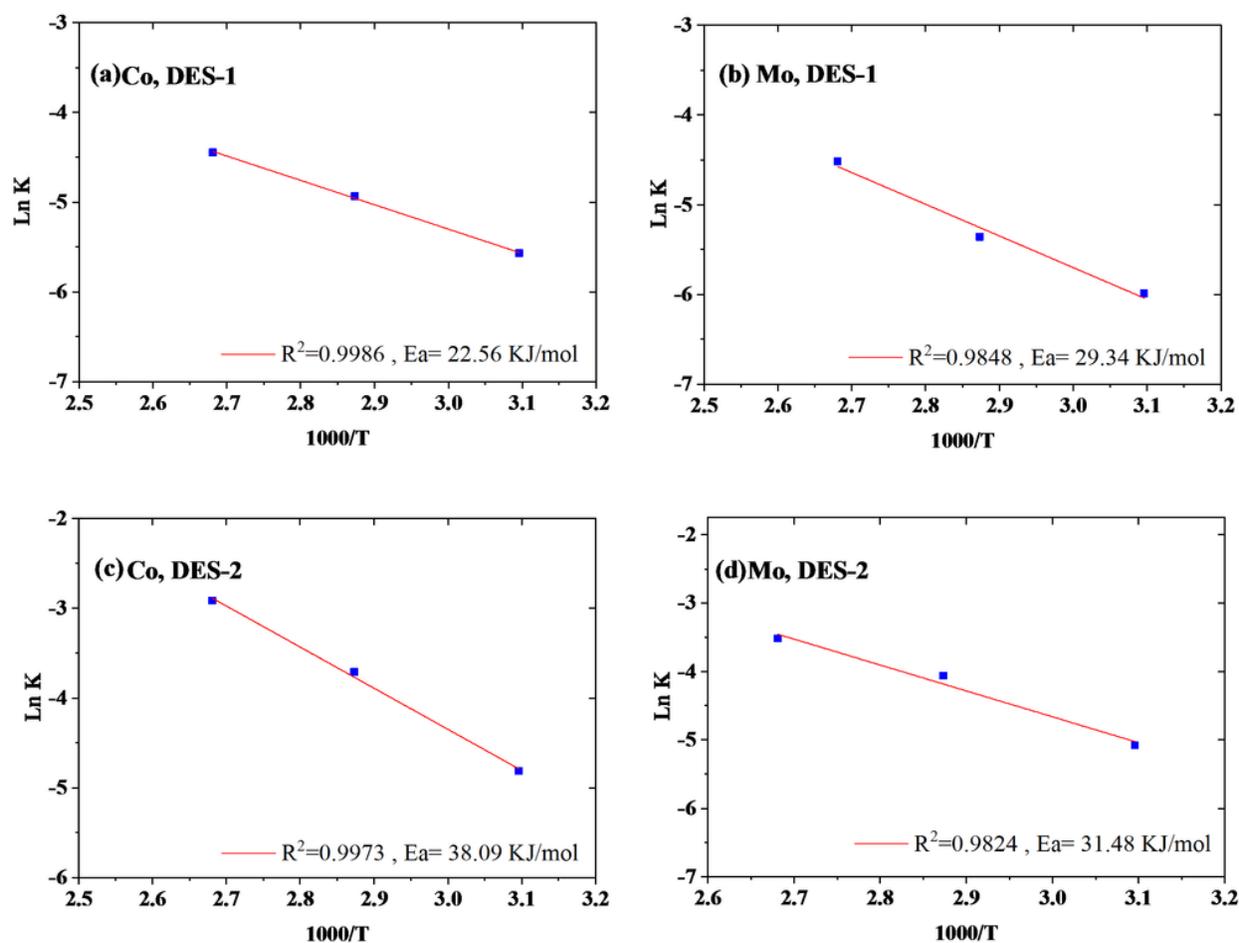


Figure 6

Arrhenius plots of (a) DES-1 Cobalt, (b) DES-1 Molybdenum, (c) DES-2 Cobalt, (d) DES-2 Molybdenum

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