



Recovery of molybdenum from leach solution using polyelectrolyte extraction



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ABSTRACT

In this research, extraction and purification of molybdenum from a leach solution of molybdenite dissolution was performed. Cationic polyelectrolytes were used for the first time in this study for selective recovery of molybdenum. For this purpose, some water-soluble coagulants of KlarAid PC products were employed and the experimental results in terms of recovery percentages, optimum value of needed polyelectrolyte and their performance were investigated. In order to evaluate the extraction and purification process, the precipitated molybdenum compounds were studied by ICP-OES, XRD, FTIR, and SEM. The results showed that about 88% of molybdenum could be recovered in one step with a final estimated purity of 100%. Afterward, a relatively pure MoO₃ product with a layered-structure was successfully synthesized by a simple heat treatment. Finally, the results showed that the proposed novel method, polyelectrolyte extraction (PX), could be an efficient alternative to other processes (i.e. ion exchange resins and solvent extraction) for selective recovery of metals from acid solution.

1. Introduction

Molybdenum is a strategic metal which is widely used in industrial processes. It is an important alloying element especially in steels, producing corrosion resistance and excellent toughness and strength at high temperatures which makes it suitable for use in aircraft engines. It is also used in pigments, lubricants, and catalysts. Molybdenum compounds are important components of catalysts in a variety of industries such as oil and petroleum refining, polymers, plastics and resins making and alcohol synthesis (Ghiasvand et al., 2005; Park et al., 2010; Sebenik et al., 2002; Valdés et al., 2009).

Molybdenum is extracted usually from molybdenite, the most common mineral of molybdenum in nature which is associated with copper porphyry ores (Basualto et al., 2003). Selective flotation is a prevalent way to separate molybdenite from copper and iron sulfides. However, as Cu and Fe are always present as impurities in the final concentrate, it is very difficult to further use molybdenum product. Therefore, such impurities must be removed from molybdenum. There are some procedures to reduce impurity contents of molybdenum compounds. A major and primary way of molybdenite processing is roasting the sulfide concentrate to produce molybdenum trioxide, the most common precursor for other molybdenum compounds production. In the roasting process, all the impurities are also oxidized. Impure molybdenum trioxide can be treated by evaporation purification or by

acid washing to remove most of these impurities. In the latter case, some of molybdenum is also dissolved in acidic solution which should be separated. It should be noted that roasting is a high-temperature process, consuming a high amount of energy and producing environmentally harmful sulfur oxides. Hence, many researchers have tried to treat molybdenite concentrate through a hydrometallurgical route (Abdollahi et al., 2013; Antonijević and Pacović, 1992; Ashraf, 2011; Cao et al., 2009; Jiang et al., 2012; Jianrong et al., 2007; Kholmogorov et al., 2002; Khoshnevisan et al., 2012; Mirvaliev and Inoue, 2001; Olson and Clark, 2008; Vizsolyi and Peters, 1980). The leaching process brings molybdenum and impurities to the solution (leach liquor). Hence, as in the case of acid washing liquor of molybdenum trioxide, a separation and purification treatment is required.

There are many routine separation methods in hydrometallurgy. These methods have also been employed for molybdenum recovery from solutions, including chemical precipitation usually with pH adjustment and cementation (Li et al., 2012a; Park et al., 2006b; Van den Berg et al., 2002; Warren and Reid, 1982; Zhao et al., 2011), metal ion adsorption on activated carbon surface (Juneja et al., 1996; Kar et al., 2004; Pagnanelli et al., 2011; Park et al., 2006a; Seo et al., 2012), ion-exchange by resins (Fu et al., 2018; Kononova et al., 2003; Nguyen and Lee, 2013; Orrego et al., 2019; Padh et al., 2019; Zhao et al., 2010), supported liquid membrane separation (Basualto et al., 2003; Chaudry et al., 1990; Marchese et al., 2004) and solvent extraction by organic

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Table 1

A comparison of already existing processes on Mo recovery and the novel method proposed in this study (Polyelectrolyte extraction).

Method	Main advantages	Main disadvantages
Chemical precipitation (Li et al., 2012a; Park et al., 2006b; Van den Berg et al., 2002; Warren and Reid, 1982; Zhao et al., 2011)	<ul style="list-style-type: none"> ● Very simple process ● Inexpensive ● Without any special equipment requirement ● Relatively fast method 	<ul style="list-style-type: none"> ● Impure final product ● Needs more purification processes ● Needs different chemical agents for pH adjustment or reductive/oxidative treatment
Metal ion adsorption on activated carbon surface (Juneja et al., 1996; Kar et al., 2004; Pagnanelli et al., 2011; Park et al., 2006a; Seo et al., 2012)	<ul style="list-style-type: none"> ● Relatively inexpensive process ● Relatively simple equipment 	<ul style="list-style-type: none"> ● Small capacity ● Low selectivity ● Time consuming process ● Relatively complex process
Ion-exchange by resins (Fu et al., 2018; Kononova et al., 2003; Nguyen and Lee, 2013; Orrego et al., 2019; Padh et al., 2019; Zhao et al., 2010)	<ul style="list-style-type: none"> ● More selective than the carbon adsorption process ● Relatively simple operation and equipment ● Recyclable component 	<ul style="list-style-type: none"> ● Relatively expensive ● Small capacity ● Time consuming process
Solvent extraction by organic solvents (Alamdari et al., 2012; An et al., 2009; Gerhardt et al., 2001; Imam and El-Nadi, 2018; Li et al., 2012b; Noronha et al., 2013; Park et al., 2010; Sato et al., 1990; Wang et al., 2014; Wu et al., 2012; Zhu et al., 2015)	<ul style="list-style-type: none"> ● More effective ● More applicable ● Selective ● Relatively simple operation and equipment ● Recyclable component ● More production capacity ● High purity final product 	<ul style="list-style-type: none"> ● Expensive solvents with huge inventories ● Large volume of solvents ● Different kinds of chemical compounds (diluting solvents, organic extractants, modifiers and stripping agents) ● High operation costs ● Large equipment (several mixer-settler system) ● High residence time ● Possible formation of emulsions ● Crud formation at interphase ● Sometimes inapplicable economically, for waste leach solutions with low content of molybdenum
Supported liquid membrane separation (Basualto et al., 2003; Chaudry et al., 1990; Malik et al., 2011; Marchese et al., 2004; Parhi, 2012)	<ul style="list-style-type: none"> ● High selectivity ● Combine extraction and stripping into one single stage ● No limitation by the conditions of equilibrium (Uphill Transport Characteristic) ● More efficient process due to high Interfacial area per unit volume ● Smaller equipment than classical solvent extraction systems 	<ul style="list-style-type: none"> ● Rare industrial application due to membrane instability (leads to the reduction of solute flux and membrane selectivity) ● Membrane resistance to mass transfer (more operation time) ● Lack of research
Polyelectrolyte extraction	<ul style="list-style-type: none"> ● Very simple process ● Inexpensive ● Without any special equipment requirement ● Relatively fast method ● High purity final product ● Simple phase separation ● No need to inorganic materials and different chemicals ● Very low operation cost ● Applicable even for solutions with low content of molybdenum 	<ul style="list-style-type: none"> ● Only applicable for recovery and purification purposes in the solutions containing target element as anion and impurities as cations and vice versa (using cationic or anionic polyelectrolytes)

solvents (Alamdari et al., 2012; An et al., 2009; Gerhardt et al., 2001; Imam and El-Nadi, 2018; Noronha et al., 2013; Park et al., 2010; Sato et al., 1990; Wang et al., 2014; Wu et al., 2012; Zhu et al., 2015). Precipitation is considered as being the simplest (it does not require special equipment), most inexpensive and relatively fast process. However, the final product is impure and needs further purification steps. Carbon adsorption is not effective due to its small capacity, low selectivity, time-consuming and more complex procedure. The ion exchange method is the same as the carbon adsorption process, but it is more selective and more expensive. Hence, these two methods are rarely employed in practice (Alamdari et al., 2012; Wu et al., 2012). Supported liquid membrane separation is more effective but has rare applications in industrial scale due to its disadvantages such as capital cost and membrane instability in terms of long time performance (Malik et al., 2011; Parhi, 2012). Solvent extraction is a more effective and applicable technique for separation and purification in industrial practices and many types of research have been conducted in this field (Alamdari et al., 2012; An et al., 2009; Gerhardt et al., 2001; Imam and El-Nadi, 2018; Noronha et al., 2013; Park et al., 2010; Sato et al., 1990; Wang et al., 2014; Wu et al., 2012; Zhu et al., 2015). As in the case of other technologies, this method presents advantages and disadvantages.

The operation and equipment are relatively simple and components are recyclable, production capacity is larger than the one achieved by carbon adsorption or ion exchange with resins, and the process leads to high purity final product (Li et al., 2012b). Solvent extraction is considered as a more versatile method for removal of metallic ion impurities. However, it presents serious limitations including expensive solvents, large volume of solvents, different kinds of chemical compounds such as diluting solvents, organic extractants, modifiers and stripping agents, high operation costs, large equipment (several mixer-settler system), high residence time, possible formation of emulsions, crud formation at interphase and phase entrainment difficulties and sometimes due to its low content of molybdenum in waste leach solutions, the SX process in conventional mixer-settler reactors becomes economically inapplicable (Basualto et al., 2003; Valdés et al., 2009).

In the present study, the results of a new process for separation and recovery of molybdenum from solution is present. It involves the use of soluble polymers (polyelectrolytes) that have found applications for solid-liquid separation in a variety of industries such as papermaking, water treatment and mineral processing. They also have some applications in drug delivery, food sciences, cosmetics and fabrication of nanofilms and nanostructures (Frueh et al., 2014; Liu et al., 2017;

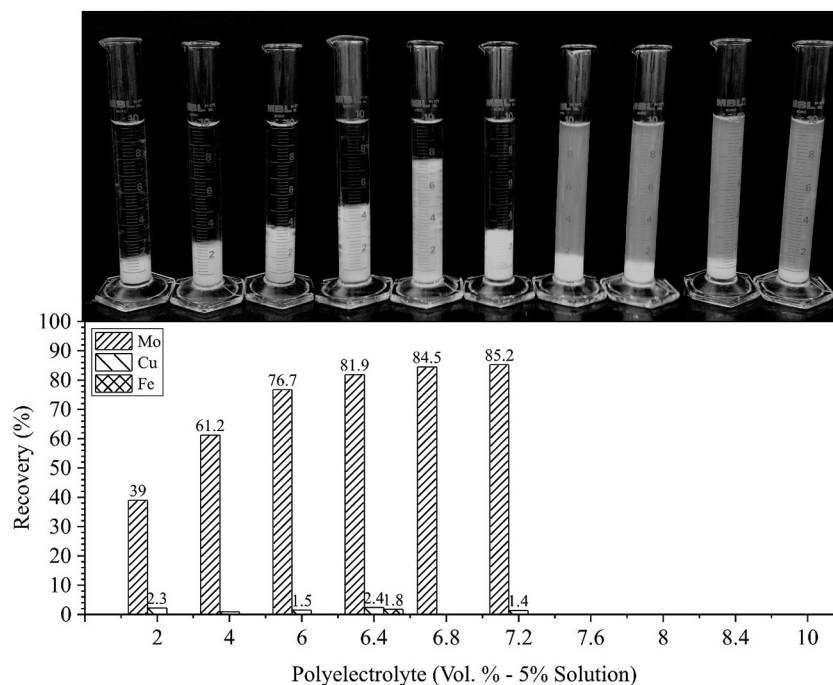


Fig. 1. Coagulation of Mo ions in measuring cylinders by adding different values of KlarAid PC 1192 to the leach liquor for determining the maximum allowed concentration of CPE, with corresponding recovery percentages of Mo, Cu, and Fe.

Petzold and Schwarz, 2013). Surface charge neutralization of solid particles by using these polymers can produce large flocs that can be easily separated/recovered. Polyelectrolytes are polymers whose monomer groups bear a charge that can dissociate into a charged macro-ion and small counter-ion when it is dissolved in a polar solvent and make the solvent electrically neutral but conductive (Frueh et al., 2014). There are two kinds of polyelectrolytes based on the charge of macroions which can be positive or negative and called polycations and polyanions, respectively. In fact, the monomer macro-ions (positive or negative) can interact with the surface of charged particles (negative or positive) in polar solvents and produce flocs to make an efficient solid-liquid separation.

As mentioned above, these polyelectrolytes are mainly used in sedimentation of solid particles, but they have never been used in molybdenum hydrometallurgy. According to the results of this study, when this water soluble extractant is used, high purity solid product containing metal ion can be precipitated. Then, the high purity solid particles are easily separated by filtration. The method is similar to general precipitation but does not need pH adjustment or addition of inorganic materials that can considerably affect the purity of precipitated particles. This will be an ideal process to metal ion recovery from the leaching solution due to very simple equipment. The only needed equipment is a mixing and filtration system, instead of a large number of devices required for solvent extraction process (i.e. mixer-settler systems and columns for countercurrent extraction. In addition, the stripping stage from pregnant phase will be completely omitted.

It should be noted that polyelectrolytes have also been used to remove heavy metal ions from aqueous solutions of wastewaters. In these cases, heavy metal binding with a chemical agent was initially allowed to occur and then the polyelectrolyte was added to initiate the complex precipitation (Hankins et al., 2006; Navarro et al., 2005). The laboratory results of the present study demonstrates for the first time that molybdenum can be selectively precipitated from leach liquor by using a cationic polyelectrolyte (CPE) without any additive or auxiliary agent for the complex formation or even pH adjustment.

So, this paper reports a novel method for simultaneous selective recovery and purification of molybdenum from leach liquor in one step.

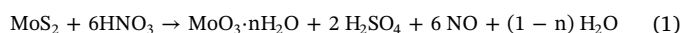
A comparison of main advantages and disadvantages of already existing processes on Mo recovery and the polyelectrolyte extraction is shown in Table 1.

2. Materials and methods

The initial solution for purification experiments was prepared by dissolving some molybdenite (MoS_2) concentrate in nitric acid media. Molybdenite concentrate (55.6% Mo, 0.58% Cu and 0.96% Fe) was supplied by Sarcheshmeh Copper Complex (Iran). The residual superficial organic compound of the concentrate was removed based on a process that has been reported elsewhere (Shalchian et al., 2018; Shalchian et al., 2017). Mechanical activation was performed for 4 h before leaching to improve dissolution efficiency of molybdenite concentrate (Shalchian et al., 2018).

The leaching experiment was performed for 3 h in a 0.2 M nitric acid solution using a cylindrical water jacketed vessel (borosilicate glass, 1 l) under magnetic stirring (500 rpm). A digital bath with a circulating pump (CRIOTERM 10–80 Thermostat) was used to control the temperature at 78 °C (Shalchian et al., 2018).

The most probable reaction for nitric acid leaching of molybdenite is as follows (Vizolyi and Peters, 1980):



Solid to liquid ratio of 1.3 g/l was selected to prevent saturation of molybdenum in solution (Shalchian et al., 2018; Vizolyi and Peters, 1980). The separation of solid and liquid phases was performed using a vacuum filter and the concentration of Mo, Cu and Fe in the final solution was determined by ICP-OES.

For molybdenum extraction, several CPE water-soluble coagulants of KlarAid products (KlarAid PC 1182, KlarAid PC 1192, KlarAid PC 1194, KlarAid PC 1195, KlarAid PC 1196 and KlarAid PC 2712) were employed. The purification experiments have been performed by adding specified amounts of CPE to the initial solution. Their addition have determined the coagulation/precipitation of molybdenum ions. A vacuum filter was used after each experiment to separate the solid from the liquid phase. Filter cake underwent a washing step using distilled water and finally, it was dried at 105 °C for 6 h. Molybdenum, copper

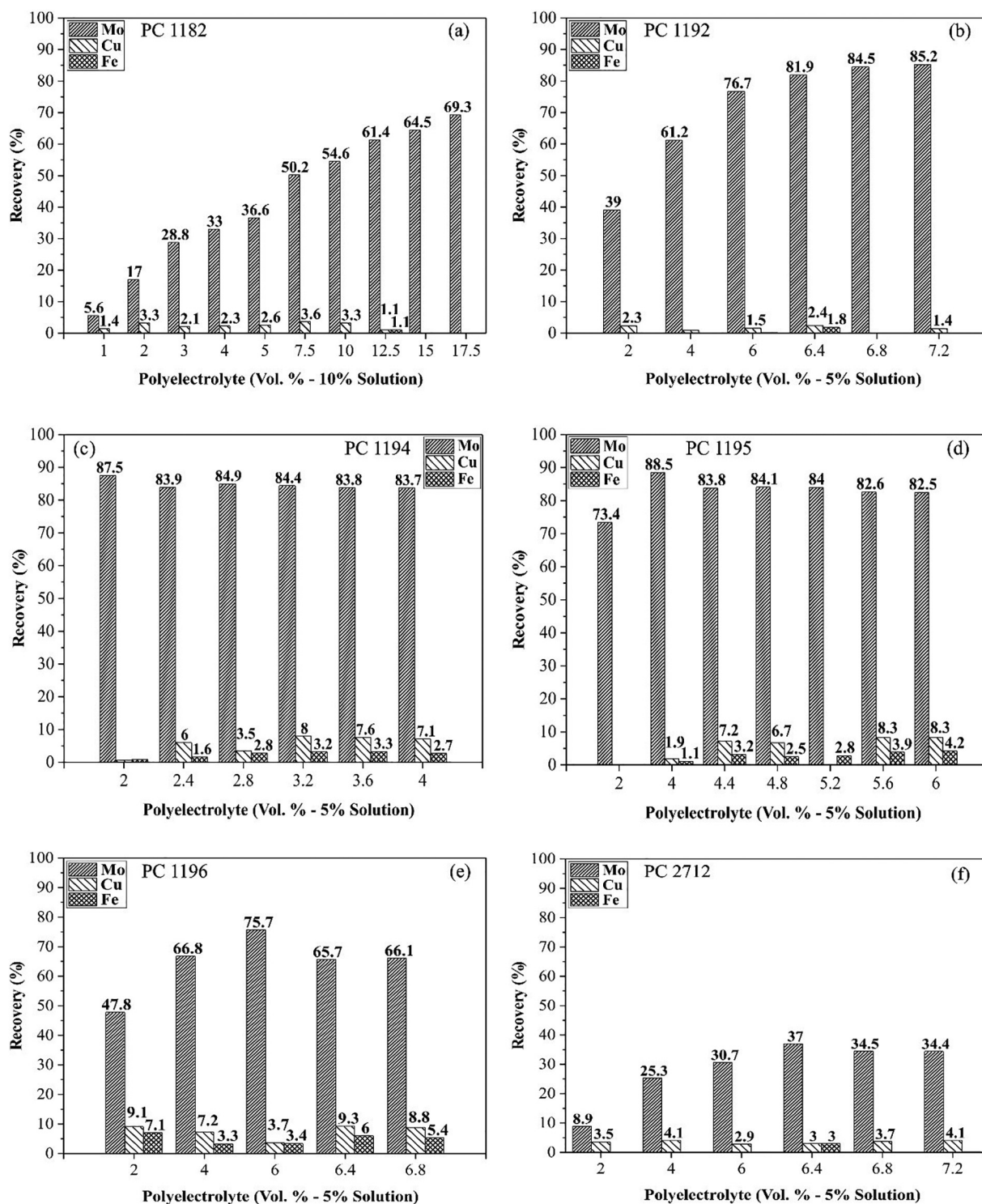


Fig. 2. Recovery percentages of Mo, Cu, and Fe from leach liquor using different CLPE: (a) KlarAid PC 1182, (b) KlarAid PC 1192, (c) KlarAid PC 1194, (d) KlarAid PC 1195, (e) KlarAid PC 1196 and (f) KlarAid PC 2712.

and iron content of the solutions were analyzed by an Inductively Coupled Plasma spectrophotometer (ICP-OES 5100 Agilent Technologies) and recovery efficiency was calculated by mass balance. The dried precipitates were analyzed by a Fourier transform infrared spectrometer (FT-IR, Thermo Nicolet) with KBr pellet technique in the range of 400–4000 cm⁻¹. Thermal treatment and analysis were performed using a LINSEIS STA PT 1600 instrument at a heating rate of 10 °C/min from ambient temperature to 750 °C. Furthermore, the achieved powders (before and after thermal treatment) were

characterized by XRD analysis using a Philips Panalytical instrument with Cu anode material and K-Alpha radiation ($\lambda = 0.154060$ nm). The X-ray diffraction patterns were measured in 2 θ range of 10–90°. Scanning electron microscopy (SEM) observations were performed using a Philips microscope operating at 20 kV. It should be noted that Origin (OriginLab, Northampton, MA) was used for graph drawing and ChemDraw was employed for schematic drawing.

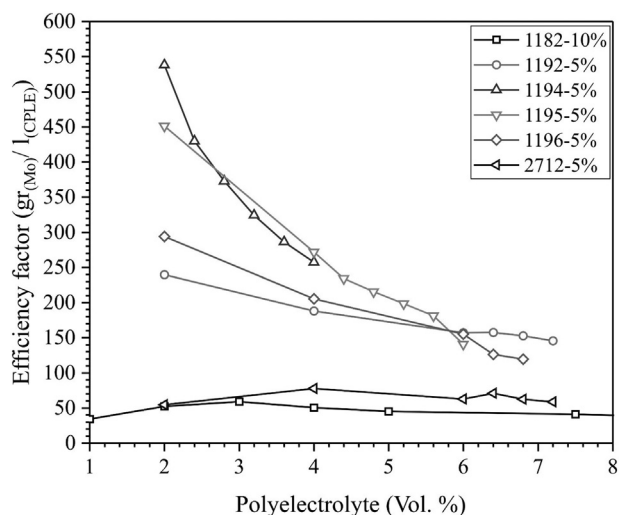


Fig. 3. Calculated Efficiency factor versus CPE values using data in Fig. 2 for KlarAid PC 1182, KlarAid PC 1192, KlarAid PC 1194, KlarAid PC 1195, KlarAid PC 1196 and KlarAid PC 2712.

3. Results and discussion

3.1. Precipitation experiments

ICP analysis showed that Mo, Cu and Fe content of as-received leach liquor is 615.3, 7.4 and 15.7 mg/L, respectively. Hence, molybdenum content is 96.4 wt%, considering the three elements concentration. Iron and copper sulfides dissolve as cations while molybdenite dissolution in nitric acid resulted in the formation of molybdic acid producing MoO_4^{2-} anions (Vizsolyi and Peters, 1980).

In order to investigate the effect of CPE on the extraction and purification of molybdenum ions from solution, some experiments were performed at different values of CPE. For instance, Fig. 1 shows the effect of KlarAid PC 1192 vol% on the precipitation behavior and recovery of Mo, Fe, and Cu. In these experiments, a 5% solution was prepared by dissolving CPE in distilled water. The diluted solution was added to the leach liquor in 2–10 vol% of the total volume. As can be seen, at the early stages, the precipitate volume and recovery percentage of molybdenum increases simultaneously with increasing the CPE value (Fig. 1). By exceeding the 7.2 vol%, phase separation encounters a problem. In fact, the sharp solid/liquid interface is destroyed and some of the solid particles are not precipitated which makes some difficulties in subsequent filtration step.

According to the results of Fig. 1, it is obvious that from one hand there is a threshold for the concentration of CPE in solution in which, phase separation is not possible at higher values of coagulant. On the other hand, the recovery percentage of molybdenum is low at lower values of CPE. Therefore, the maximum usable value of CPE should be determined in experiments. So, it is necessary to specify the allowable range of coagulants concentration at the first step, which was obtained

Table 2

Extracted Mo values from the solutions and removal percentage of Cu and Fe, before and after the washing treatment.

KlarAid PC	Polyelectrolyte value (Vol %)	Before washing of precipitates			After washing of precipitates			Estimated purity of final product (%)
		Mo extraction (%)	Cu removal (%)	Fe removal (%)	Mo extraction (%)	Cu removal (%)	Fe removal (%)	
1182	12.5	61.4	98.9	98.9	60.2	100	100	100
1192	6.4	81.9	97.6	98.2	81.5	98.6	99.2	99.95
1194	2	87.5	99.3	99.2	86.9	100	100	100
1195	4	88.5	98.1	98.9	88.1	100	100	100
1196	6	75.7	96.3	96.6	75.2	97.7	97.9	99.89
2712	6.4	37	97	97	35.7	98.4	98.3	99.83

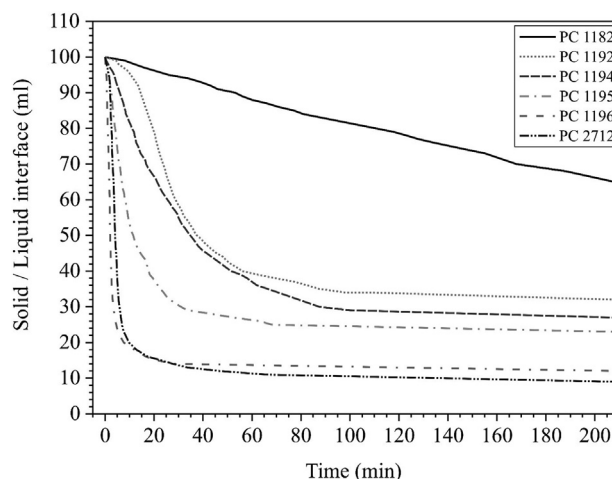


Fig. 4. Effect of type of cationic polyelectrolyte on the rate of precipitation and phase separation, considering interface movement.

by some experiments. Subsequently, the effect of CPE values on the recovery of Mo, Cu, and Fe was investigated and the results are shown in Fig. 2. As can be seen, the recovery of Fe and Cu is very low for all CPEs, indicating a selective separation of Mo from solution (Fig. 2). It should be noted that the recovery percentages of Mo, Cu, and Fe presented in Fig. 2 are calculated by the mass balance between the content of all three elements within the initial solution, depleted solution after filtration and wash water of the filter cake at one step of extraction.

Fig. 2 reveals that there are three behaviors based on used CPE values and Mo extraction. In type 1, Mo extraction increases linearly proportional to increment of CPE vol% up to the threshold limit. KlarAid PC 1182 is an example of this type. For the second type, Mo extraction improves by increasing coagulant value, but it reduces gradually. CPE of KlarAid PC 1192, KlarAid PC 1196 and KlarAid PC 2712 are categorized in type 2. Finally, the Mo extraction is independent of CPE value in type 3. The recovery percentage of Mo ions using KlarAid PC 1194 is almost the same at different vol% of CPE solution (Fig. 2). Therefore, it belongs to type 3. Considering the above explanations, KlarAid PC 1195 can be categorized either in type 2 and type 3.

The suitable value of CPE is the lowest level which leads to Mo recovery as high as possible in one step of extraction. Therefore, considering the linear relation of Mo recovery versus CPE value (17.5 vol% for KlarAid PC 1182 in Fig. 2) in type 1, the maximum vol% of CPE before the threshold limit of phase separation can be chosen. On the other hand, in type 2, the optimum value of CPE is somewhere between initial and threshold limit, in which the recovery rate of molybdenum decreases. It is obviously that the lowest value of CPE is acceptable in type 3, due to the independence of Mo recovery by CPE vol% (Fig. 2).

As claimed by Fig. 2, the highest value of Mo recovery in one step is obtained using KlarAid PC 1192, KlarAid PC 1194 and KlarAid PC 1195. The lowest value of Mo recovery belongs to KlarAid PC 2712 which is a type 2 member. In addition, the Fig. 2 shows that the highest

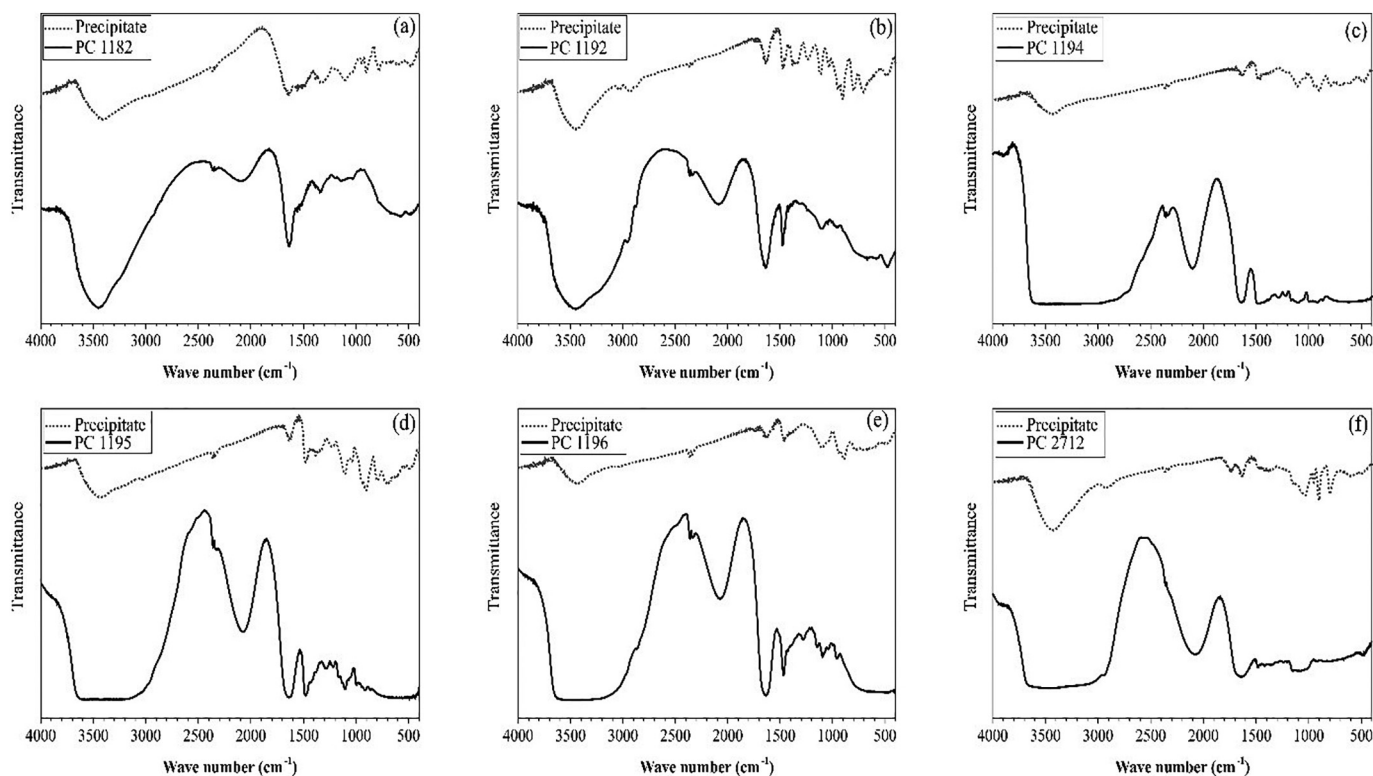


Fig. 5. FTIR analysis of cationic polyelectrolytes and relevant precipitates after drying.

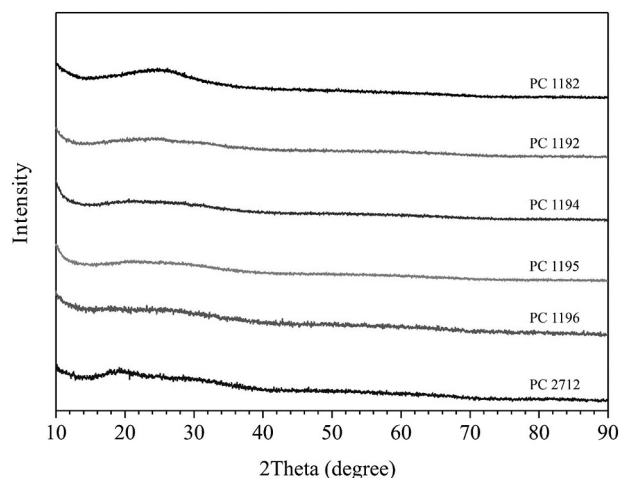


Fig. 6. XRD patterns of precipitates after drying.

usage of CPE is related to KlarAid PC 1182. 17.5 vol% of a 10% solution is used to recover only 69% of molybdenum ions, while similar recovery degrees of Mo have been achieved with lower volumes of 5% of the others 5 CPEs.

In order to investigate the performance of CPEs, the efficiency factor is quantitatively defined. The aforementioned parameter is obtained by dividing molybdenum recovery to the used value of CPE. In fact, the efficiency factor expresses the recovered Mo (grams) per unit volume of CPE (liter) as follows:

$$\text{Efficiency factor}_{(M_{Mo}/l_{CPE})} = \frac{C \times R}{P \times D} \times \frac{1}{1000} \quad (2)$$

where C is Mo concentration of leach liquor in mg/L, R represents the recovery percentage of molybdenum, P is equal to CPE quantity (vol%), and D is dilution percentage of CPE solution (%) which is considered 5% and 10% in this study.

Fig. 3 shows the calculated efficiency factor for 6 used CPEs according to the data of Fig. 2. It is clear that the efficiency factor for KlarAid PC 1182 and KlarAid PC 2712 has the lowest value (less than 100 g per liter of CPE). Fig. 3 reveals also that the efficiency factor decreases by increasing CPE quantity. In other words, the increment rate of Mo extraction is less than the increasing rate of CPE quantity. In the case of an equality of two of the aforementioned rates, it is expected that the slope of the graph tends to zero value and at a reverse situation, when the rate of Mo extraction is higher than the increasing rate of CPE quantity, efficiency factor increases.

Concerning Fig. 3, the maximum value of efficiency factor belongs to KlarAid PC 1194 which decreases by the addition of more CPE up to 4 vol%. Based on the above explanations, KlarAid PC 1194 is a member of type 3 with the independence of recovery percentage to CPE quantity and Mo recovery is almost constant in the whole range of studied CPE values. So, regarding to Eq. (2), efficiency factor decreases by a constant numerator and increasing denominator.

Fig. 3 also disclosure another point about the behavior of CPEs. As discussed earlier, KlarAid PC 1195 could be categorized either in type 2 and type 3, but Fig. 3 shows its similar trend to KlarAid PC 1194. Therefore, it can be said KlarAid PC 1195 belongs to type 3 of CPEs.

The obtained precipitates after coagulation and filtration were washed using distilled water which improved the purity of the product by removing more Cu and Fe ions. Table 2 represents the recovery percentages of Mo, Cu, and Fe before and after washing step. The estimated purity of the final product was also calculated by mass balance.

It is evident that the purity increased, especially for KlarAid PC 1182, KlarAid PC 1194 and KlarAid PC 1195 with complete removal of Cu and Fe impurities (Table 2). It seems that the low values of undesirable elements in precipitates before washing are trapped during coagulation and can easily be removed by washing. Therefore, the results have shown that CPE is an efficient extraction and purification agent for molybdenum.

In the coagulation process, the rate of phase separation and sedimentation is different for various kinds of CPEs. Naturally, at a faster

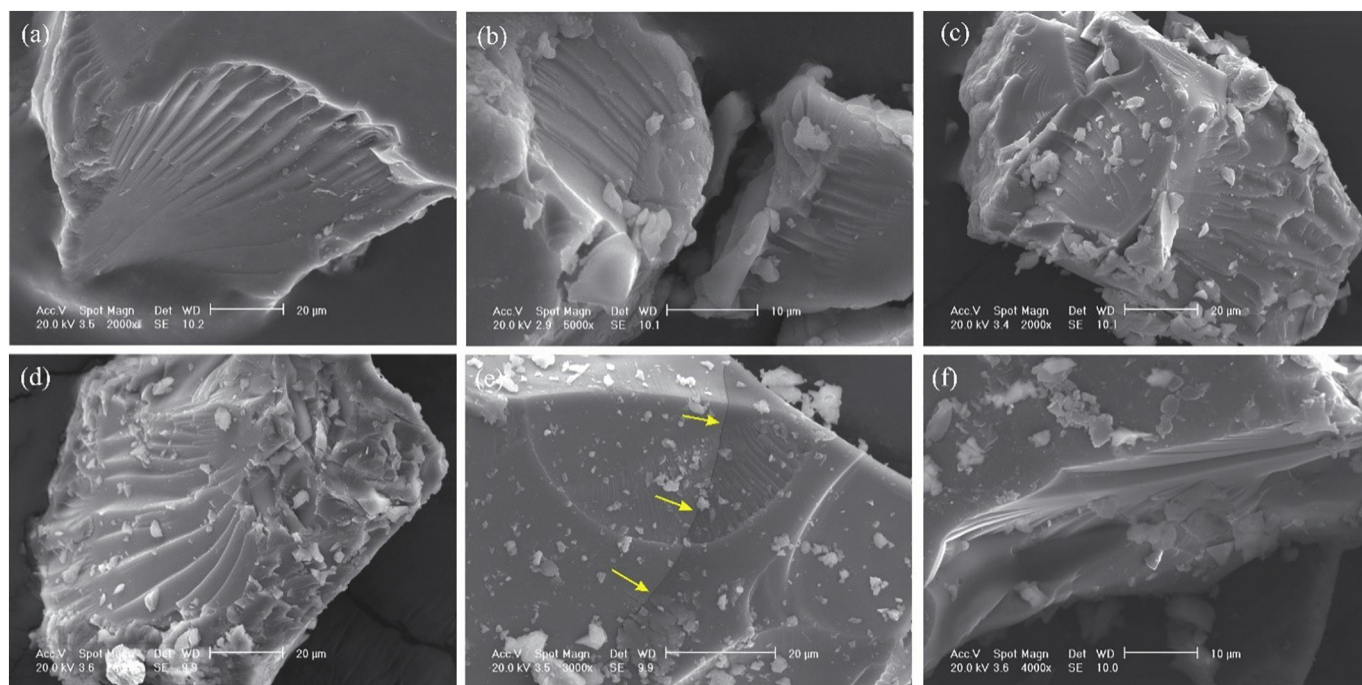


Fig. 7. Scanning electron microscopy images of obtained precipitates by using cationic polyelectrolytes: (a) KlarAid PC 1182, (b) KlarAid PC 1192, (c) KlarAid PC 1194, (d) KlarAid PC 1195, (e) KlarAid PC 1196, (f) KlarAid PC 2712.

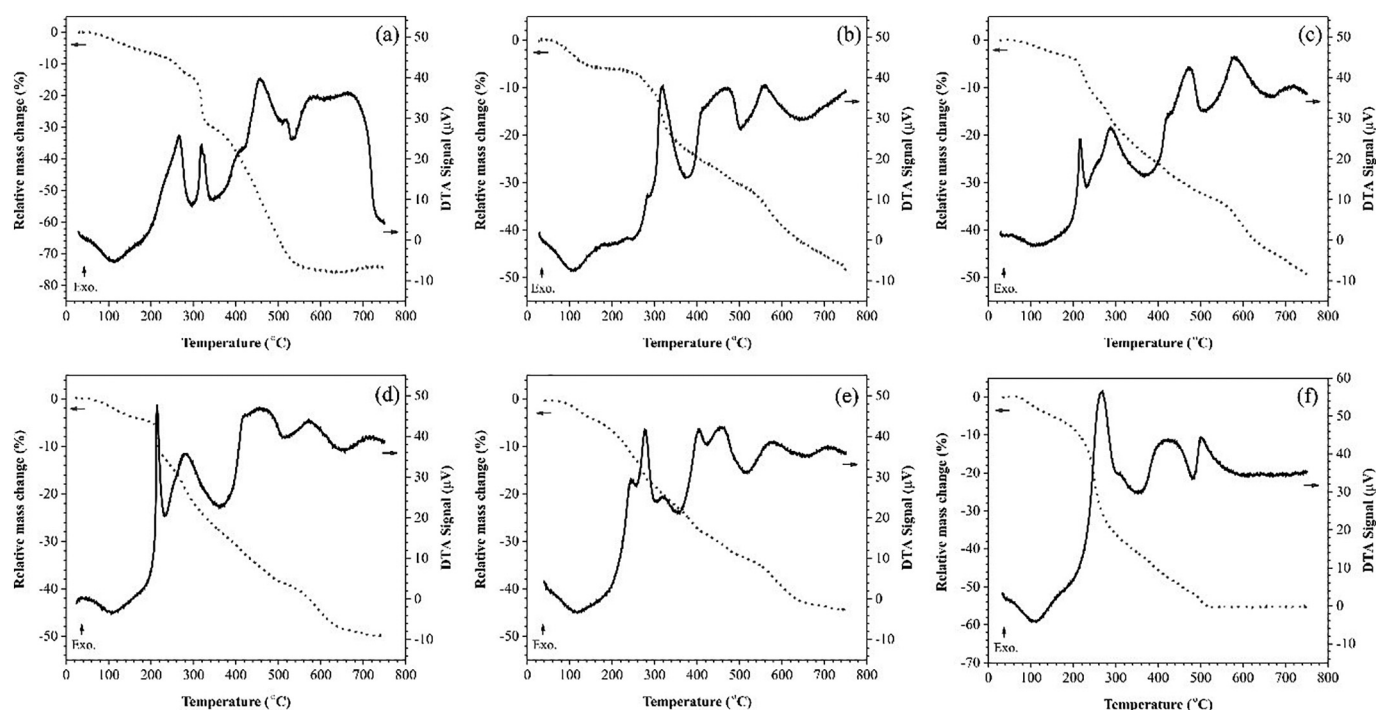


Fig. 8. TGA-DTA graph of obtained dried precipitates by using cationic polyelectrolytes: (a) KlarAid PC 1182, (b) KlarAid PC 1192, (c) KlarAid PC 1194, (d) KlarAid PC 1195, (e) KlarAid PC 1196, (f) KlarAid PC 2712.

rate of solid/liquid phase separation, the process is simpler, time-saving and consequently more economic. Therefore, the aforementioned parameter was studied for different CPEs (Fig. 4). The rate of phase separation was plotted by measuring the movement of solid/liquid interface versus time in cylinder. As it can be seen, the interface reaches to 30 ml in 90 min in the case of KlarAid PC 1194. Fig. 4 also shows that the lowest rate of precipitation belongs to KlarAid PC 1182 and the highest one is related to KlarAid PC 1196 and KlarAid PC 2712.

3.2. Characterization of precipitates

Fig. 5 illustrates FTIR spectrums of different CPEs and related precipitates after the coagulation process. As can be seen, there is a wide absorption between 3000 and 4000 cm^{-1} in all cases corresponding to $-\text{OH}$ bonds of water molecules of as-received CPEs solutions. Considering FTIR analysis of CPEs before adding to leach liquors and after precipitation, relatively complex spectra are obtained after the coagulation process for 6 kinds of CPEs. So, almost all of the added

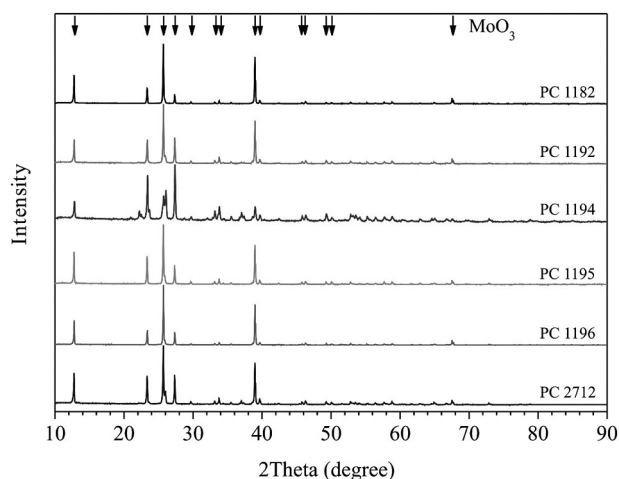


Fig. 9. XRD patterns of precipitates after thermal treatment.

absorptions before 2000 cm^{-1} are related to extracted Mo ions by polyelectrolytes. For example, related bands of Mo–O bonding present at the range of $700\text{--}950\text{ (cm}^{-1}\text{)}$ (Carrazan et al., 1996) reveals the absorption of $[\text{MoO}_4]^{2-}$ by CPEs.

XRD patterns of dried precipitates after the coagulation process are shown in Fig. 6. There is the same pattern for all 6 kinds of CPEs, showing the same crystallographic nature for all samples. It is clear that there is not any specific peak of crystalline phases. In other words, the obtained product after drying is a non-crystalline material with glassy characteristics. It should be noted the appearance of the dried filter cake of precipitates has also a glassy shape (not shown here), which is in accordance with XRD patterns.

In order to get more details, all samples were evaluated by scanning electron microscopy. Fig. 7 shows SEM images of obtained precipitates by adding 6 different kinds of CPEs to the leach liquor after drying. Can be seen that the particles in all images are similar in shape. A notable point of Fig. 7 is a seashell-like fracture pattern of particles which is

evident especially in Fig. 7 (a), (b) and (d). The aforementioned pattern is a consequence of brittle fracture of particles. It should be mentioned that, in order to obtain a fine powder, the coarse dried and glassy particles of precipitates were ground before XRD and SEM analysis. So, it seems that the grinding process resulted in such a fracture. XRD analysis, on the other hand, revealed that the obtained precipitates consist of an amorphous and glassy phase (Fig. 6). Therefore, the seashell-like pattern is observed during fracture phenomena of the brittle glassy particles. Fig. 7 (e) shows a crack without plastic deformation also illustrating somewhat the brittle nature of the particles.

3.3. Synthesis of MoO_3

Fig. 8 shows the results of thermal analysis for 6 dried precipitates using various CPEs. The organic constituents of cationic polyelectrolytes are dissociated during heating. Negative mass changes and related peaks in DTA analysis correspond to outgoing of materials in different temperatures leaving behind inorganics. The aforementioned phenomena resulted in about 50% mass reduction in different samples. Most of the mass reduction and related DTA peaks occurred at the range of $200\text{--}600\text{ }^\circ\text{C}$ for all the dried precipitates. It should be noted the highest value of mass reduction belongs to KlarAid PC 1182, which is in accordance with the highest value of used polyelectrolyte in the coagulation process (Fig. 2).

The residual constituents after thermal treatment using DTA-TGA analysis were evaluated by X-ray diffraction. Fig. 9 shows XRD patterns of obtained precipitates. It is clear that amorphous phases before thermal analysis (Fig. 6) are crystallized during heating up to $750\text{ }^\circ\text{C}$ leading to the formation of MoO_3 crystals (Fig. 9). For KlarAid PC 1194, it seems that the transformation is not completed yet, needing more temperatures. So, it can be said that thermal treatment is useful to evaporate organic components and formation of relatively pure Molybdenum trioxide (Table 2). The pure MoO_3 crystals in Fig. 9 are also in accordance with the estimated purity of the final product in Table 2.

The obtained MoO_3 particles were further investigated using SEM. Fig. 10 illustrates electron microscopy images of the final products of 6 precipitates after thermal treatment. Crystalline nature of particles is

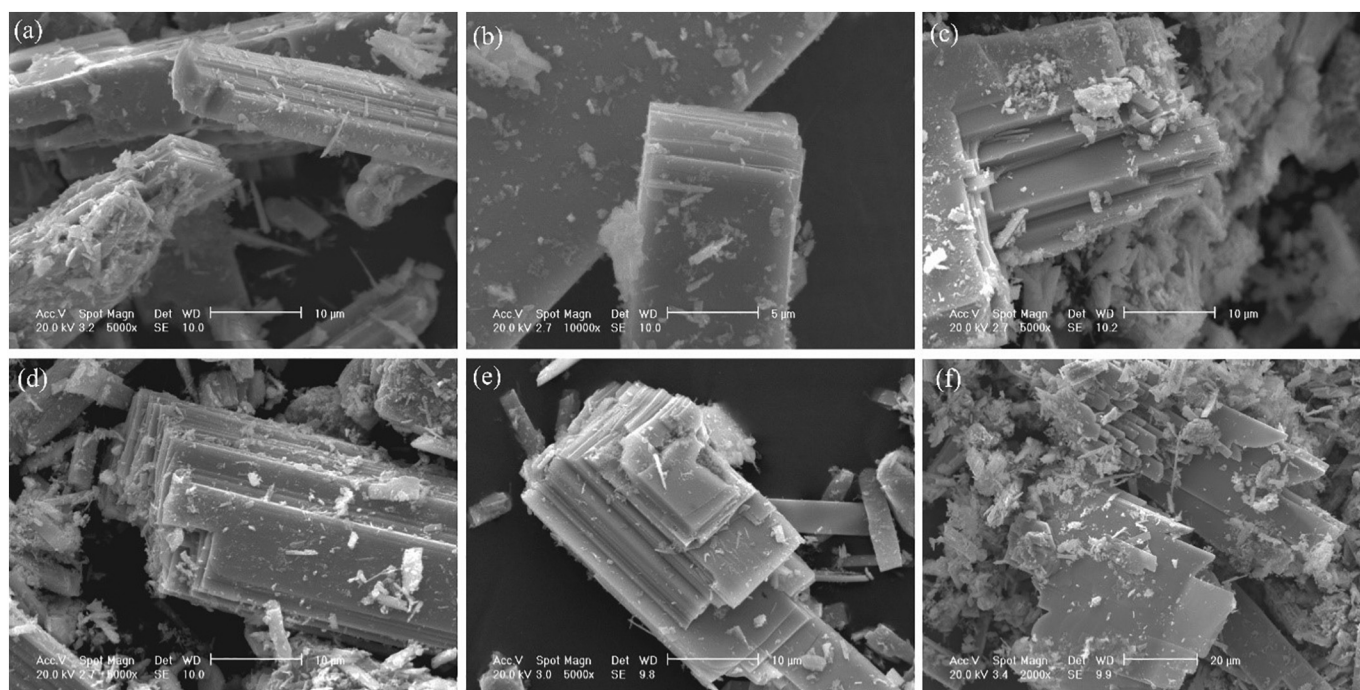


Fig. 10. Scanning electron microscopy images of precipitates after thermal treatment by using cationic polyelectrolytes: (a) KlarAid PC 1182, (b) KlarAid PC 1192, (c) KlarAid PC 1194, (d) KlarAid PC 1195, (e) KlarAid PC 1196, (f) KlarAid PC 2712.

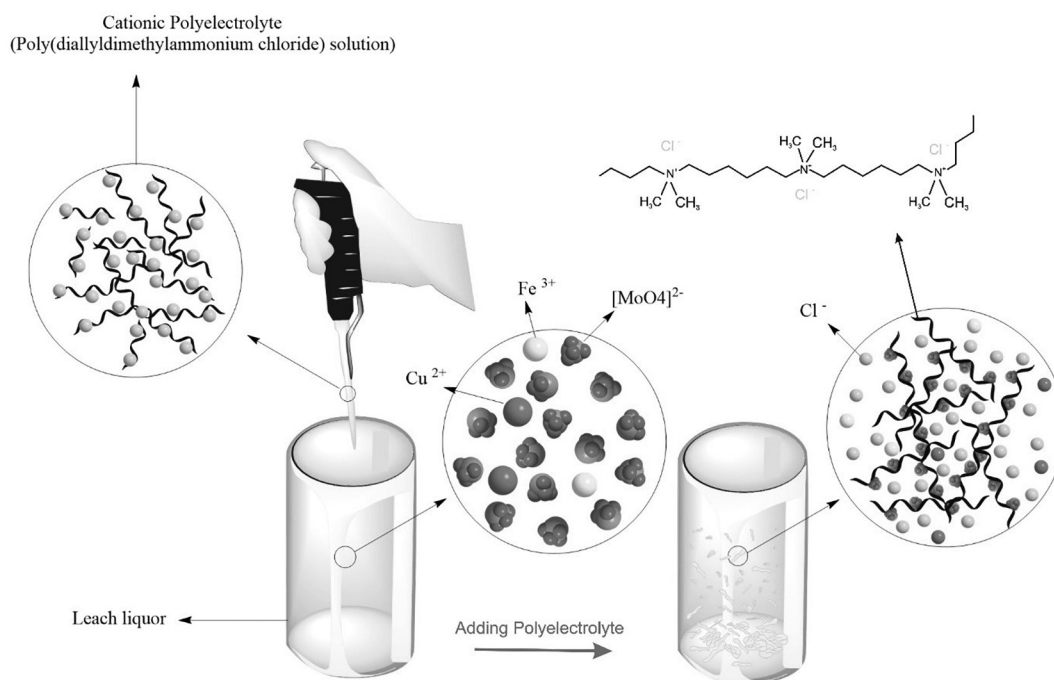


Fig. 11. A schematic of molybdenum recovery and purification from leach liquor using a cationic polyelectrolyte.

clearly evident in comparison to the initial precipitates before thermal treatment (Fig. 7) which confirms the crystallization of MoO₃ from amorphous and glassy particles. These results are in accordance with the XRD analysis. A noticeable point is the synthesis of MoO₃ crystals with long ordered layered-structure is achieved by this procedure. Considering the increasing importance of two-dimensional materials nowadays, it is easy to achieve nanometric layers of MoO₃ by different known methods of exfoliation, which are very useful in nanoscience and technology (Chen et al., 2018; Etman et al., 2018; Liu et al., 2018; Sharma et al., 2018; Su et al., 2019; Zhong et al., 2018). Therefore, in addition to extraction and purification of Mo in leach liquor, pure MoO₃ crystals with layered-structure were synthesized directly, using cationic polyelectrolytes coagulation followed by a thermal treatment.

4. Concluding remarks

In this research, the effectiveness of cationic polyelectrolytes in selective precipitation and purification of Mo ions from leach liquor containing Fe and Cu was proven. The mechanism of coagulation of Mo ions can be expressed based on the charged nature of ions and polyelectrolytes in solution. From a theoretical point of view, positively-charged molecules would be able to attract anions and repel cations. Cationic polyelectrolytes on the other hands forms positively charged molecules by ionization in water. So, they would be able to selectively attract anions of molybdenum ([MoO₄]²⁻) by counter-ion binding and reduce the barrier against coagulation due to the electroneutrality phenomenon. Therefore, Mo ions are aggregated with positive molecules of polyelectrolytes and Fe and Cu cations are repelled to the solution as impurities. Consequently, purification of Mo ions occurred simultaneously, in addition to molybdenum recovery from leach liquor. A schematic of the process is illustrated in Fig. 11 using poly (diallyldimethylammonium chloride) solution. The results of Table 2 confirmed that cationic polyelectrolytes only coagulate Mo anions. It seems that a few amounts of Fe and Cu cations are trapped during coagulation because a simple water washing reduced their concentration significantly.

A remarkable point is the simplicity of the proposed method. So that coagulation occurs as soon as polyelectrolytes are added to the solution

and molybdenum ions are precipitated in the form of small flakes. Therefore, it is possible to separate the solid phase quickly, by a simple filtration step. A glassy and amorphous phase is obtained by drying the filter cake which is transformed into layered crystals of pure MoO₃ through thermal treatment. Accordingly, synthesis of pure MoO₃ crystals is the other impressive feature of the proposed process which can be used to produce few-layers or even mono-layers of MoO₃ during an appropriate exfoliation process. Therefore, considering the benefits of the proposed method, it would be more effective for processing molybdenum leach liquors than to perform the common extraction methods such as solvent extraction and ion exchange using resins. Finally, it should be said that the aforementioned method could be used for extraction and purification of other metal ions by appropriate selection of cationic or anionic polyelectrolytes for anions and cations, respectively.

5. Summary

In summary, we investigated the extraction and purification of molybdenum from a leach liquor containing iron and copper ions as impurities using some cationic polyelectrolytes for the first time. The outstanding results are as follows:

- recovery and purification of Mo from Fe and Cu ions was performed by using relatively low values of polyelectrolytes concentration in a single step;
- there is an optimum concentration for any polyelectrolytes. The recovery percentage of molybdenum is low at lower values of cationic polyelectrolytes. On the other hands, phase separation is not possible at values higher than the threshold concentration;
- in order to investigate the recovery efficiency of precipitated molybdenum based on used polyelectrolyte, the efficiency factor was defined. The aforementioned parameter was used to evaluate the performance of polyelectrolytes;
- using of various polyelectrolytes led to different rates of coagulation and precipitation, ranging from 10 min to more than 200 min in experimental conditions;
- for cationic polyelectrolytes of KlarAid PC 1194 and KlarAid PC

1195, the best conditions of Mo extraction and purification were obtained. The highest value of the efficiency factor with an estimated purity of 100% and a mid-range rate of precipitation were achieved in both cases;

- XRD and SEM investigations showed that a glassy and amorphous phase is obtained after drying of coagulants. Finally, relatively pure MoO₃ layered-crystals were synthesized by heating the precipitates up to 750 °C.

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Declaration of Competing Interest

None.

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References

- Abdollahi, H., Shafaei, S., Noaparast, M., Manafi, Z., Aslan, N., 2013. Bio-dissolution of Cu, Mo and Re from molybdenite concentrate using mix mesophilic microorganism in shake flask. *Trans. Nonferrous Metals Soc. China* 23 (1), 219–230.
- Alamdari, E.K., Darvishi, D., Haghshenas, D., Yousefi, N., Sadrnezhad, S., 2012. Separation of Re and Mo from roasting-dust leach-liquor using solvent extraction technique by TBP. *Sep. Purif. Technol.* 86, 143–148.
- An, J., et al., 2009. Production of high purity molybdenum compounds from a Cu–Mo acid-washed liquor using solvent extraction. Part 1: laboratory studies. *Miner. Eng.* 22 (12), 1020–1025.
- Antonijević, M., Pacović, N., 1992. Investigation of molybdenite oxidation by sodium dichromate. *Miner. Eng.* 5 (2), 223–233.
- Ashraf, M., 2011. Hydrometallurgical recovery of molybdenum from Egyptian Qattar molybdenite concentrate. *Physicochem. Probl. Miner. Process* 47, 105–112.
- Basualto, C., Marchese, J., Valenzuela, F., Acosta, A., 2003. Extraction of molybdenum by a supported liquid membrane method. *Talanta* 59 (5), 999–1007.
- Cao, Z.-f., Zhong, H., Qiu, Z.-h., Liu, G.-y., Zhang, W.-x., 2009. A novel technology for molybdenum extraction from molybdenite concentrate. *Hydrometallurgy* 99 (1), 2–6.
- Carrazan, S., Martin, C., Rives, V., Vidal, R., 1996. An FT-IR spectroscopy study of the adsorption and oxidation of propene on multiphase Bi, Mo and Co catalysts. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 52 (9), 1107–1118.
- Chaudry, M.A., Malik, M.T., Ali, A., 1990. Transport of Mo (VI) ions through tri-n-octylamine-xylene based supported liquid membranes. *Sep. Sci. Technol.* 25 (3), 263–291.
- Chen, Q., et al., 2018. Rapid preparation of large size, few-layered MoO₃ by anisotropic etching. *Mater. Lett.* 229, 305–307.
- Etman, A., Wang, L., Nyholm, L., Edström, K., Sun, J., 2018. One-Pot Synthesis of MoO₃-x Nanosheets for Supercapacitor Applications, the E-MRS 2018 Spring Meeting, June 18 to 22. Strasbourg, France.
- Frueh, J., Gai, M., Halstead, S., He, Q., 2014. Structure and Thermodynamics of Polyelectrolyte Complexes. *Polyelectrolytes*. Springer, pp. 19–86.
- Fu, Y., et al., 2018. Direct extraction of Mo (VI) from acidic leach solution of molybdenite ore by ion exchange resin: batch and column adsorption studies. *Trans. Nonferrous Metals Soc. China* 28 (8), 1660–1669.
- Gerhardt, N.I., Palant, A., Petrova, V., Tagirov, R., 2001. Solvent extraction of molybdenum (VI), tungsten (VI) and rhenium (VII) by diisododecylamine from leach liquors. *Hydrometallurgy* 60 (1), 1–5.
- Ghiasvand, A., Shadabi, S., Mohagheghzadeh, E., Hashemi, P., 2005. Homogeneous liquid–liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum. *Talanta* 66 (4), 912–916.
- Hankins, N.P., Lu, N., Hilal, N., 2006. Enhanced removal of heavy metal ions bound to humic acid by polyelectrolyte flocculation. *Sep. Purif. Technol.* 51 (1), 48–56.
- Imam, D., El-Nadi, Y., 2018. Recovery of molybdenum from alkaline leach solution of spent hydrotreating catalyst by solvent extraction using methyl tricuprammonium hydroxide. *Hydrometallurgy* 180, 172–179.
- Jiang, K., Wang, Y., Zou, X., Zhang, L., Liu, S., 2012. Extraction of molybdenum from molybdenite concentrates with hydrometallurgical processing. *JOM* 64 (11), 1285–1289.
- Jianrong, P., Dajin, Y., Jiayi, C., Jiangfeng, Y., 2007. Experimental study on alkaline leaching of crude Molybdenite under pressure of oxygen. *Chinese J. Rare Metals* 31 (S1), s110–s113.
- Juneja, J., Singh, S., Bose, D., 1996. Investigations on the extraction of molybdenum and rhenium values from low grade molybdenite concentrate. *Hydrometallurgy* 41 (2), 201–209.
- Kar, B., Datta, P., Misra, V., 2004. Spent catalyst: secondary source for molybdenum recovery. *Hydrometallurgy* 72 (1), 87–92.
- Kholmogorov, A., et al., 2002. Molybdenum recovery from mineral raw materials by hydrometallurgical methods. *Eur. J. Miner. Process. Environ. Prot.* 2 (2), 82–93.
- Khoshnevisan, A., Yoozbashizadeh, H., Mozammel, M., Sadrnezhad, S.K., 2012. Kinetics of pressure oxidative leaching of molybdenite concentrate by nitric acid. *Hydrometallurgy* 111, 52–57.
- Kononova, O., Kholmogorov, A., Kachin, S., Kalyakina, O., Sadovskaya, E., 2003. Ion exchange recovery of molybdenum from nitric acidic solutions using macroporous anion exchangers with long-chained cross-linking agents. *Hydrometallurgy* 68 (1), 83–87.
- Li, J., Zhao, Z., Cao, C., Zhang, G., Huo, G., 2012a. Recovery of Mo from Ni–Mo ore leach solution with carrier co-precipitation method. *Int. J. Refract. Met. Hard Mater.* 30 (1), 180–184.
- Li, X., et al., 2012b. Co-extraction and selective stripping of vanadium (IV) and molybdenum (VI) from sulphuric acid solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. *Sep. Purif. Technol.* 86, 64–69.
- Liu, X., Chapel, J.-P., Schatz, C., 2017. Structure, thermodynamic and kinetic signatures of a synthetic polyelectrolyte coacervating system. *Adv. Colloid Interf. Sci.* 239, 178–186.
- Liu, H., et al., 2018. Aqueous and mechanical exfoliation, unique properties, and theoretical understanding of MoO₃ nanosheets made from free-standing α -MoO₃ crystals: Raman mode softening and absorption edge blue shift. *Nano Res.* 11 (3), 1193–1203.
- Malik, M.A., Hashim, M.A., Nabi, F., 2011. Ionic liquids in supported liquid membrane technology. *Chem. Eng. J.* 171 (1), 242–254.
- Marchese, J., Valenzuela, F., Basualto, C., Acosta, A., 2004. Transport of molybdenum with Alamine 336 using supported liquid membrane. *Hydrometallurgy* 72 (3), 309–317.
- Mirvaliev, R., Inoue, K., 2001. Pressure oxidation leaching of Molybdenite in alkaline media-autoclave processing of low-grade molybdenite concentrates (2nd report). *Sigen-to-Sozai* 11, 72–76.
- Navarro, R.R., Wada, S., Tsumi, K., 2005. Heavy metal precipitation by polycation–polyanion complex of PEI and its phosphonomethylated derivative. *J. Hazard. Mater.* 123 (1–3), 203–209.
- Nguyen, T.H., Lee, M.S., 2013. Separation of molybdenum and vanadium from acid solutions by ion exchange. *Hydrometallurgy* 136, 65–70.
- Noronha, L., Kamble, G., Kolekar, S., Anuse, M.A., 2013. Recovery of molybdenum (VI) from hydrochloric acid medium by solvent extraction with 2-n-octylaminopyridine. *Int. J. Chem. Sci. Tech.* 3, 15–24.
- Olson, G.J., Clark, T.R., 2008. Bioleaching of molybdenite. *Hydrometallurgy* 93 (1), 10–15.
- Orrego, P., Hernández, J., Reyes, A., 2019. Uranium and molybdenum recovery from copper leaching solutions using ion exchange. *Hydrometallurgy* 184, 116–122.
- Padh, B., Rout, P., Mishra, G., Suresh, K., Reddy, B.R., 2019. Recovery of nickel and molybdenum from ammoniacal leach liquors of spent HDS catalysts using chelating ion exchange resin. *Hydrometallurgy* 184, 88–94.
- Pagnanelli, F., Ferella, F., De Michelis, I., Vegliò, F., 2011. Adsorption onto activated carbon for molybdenum recovery from leach liquors of exhausted hydrotreating catalysts. *Hydrometallurgy* 110 (1), 67–72.
- Parhi, P., 2012. Supported liquid membrane principle and its practices: a short review. *J. Chem.* 2013.
- Park, K.H., Mohapatra, D., Reddy, B.R., 2006a. Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method. *J. Hazard. Mater.* 138 (2), 311–316.
- Park, K.H., Reddy, B.R., Mohapatra, D., Nam, C.-W., 2006b. Hydrometallurgical processing and recovery of molybdenum trioxide from spent catalyst. *Int. J. Miner. Process.* 80 (2), 261–265.
- Park, K.-H., Kim, H.-I., Parhi, P., 2010. Recovery of molybdenum from spent catalyst leach solutions by solvent extraction with LIX 84-I. *Sep. Purif. Technol.* 74 (3), 294–299.
- Petzold, G., Schwarz, S., 2013. Polyelectrolyte Complexes in Flocculation Applications, Polyelectrolyte Complexes in the Dispersed and Solid State II. Springer, pp. 25–65.
- Sato, T., Watanabe, H., Suzuki, H., 1990. Liquid-liquid extraction of molybdenum (VI) from aqueous acid solutions by TBP and TOPO. *Hydrometallurgy* 23 (2–3), 297–308.
- Sebenik, R.F., et al., 2002. Molybdenum and molybdenum compounds. In: *Ullmann's Encyclopedia of Industrial Chemistry*.
- Seo, S.Y., Choi, W.S., Yang, T.J., Kim, M.J., Tran, T., 2012. Recovery of rhenium and molybdenum from a roaster fume scrubbing liquor by adsorption using activated carbon. *Hydrometallurgy* 129, 145–150.
- Shalchian, H., et al., 2017. On the mechanism of molybdenite exfoliation during mechanical milling. *Ceram. Int.* 43 (15), 12957–12967.
- Shalchian, H., et al., 2018. An enhanced dissolution rate of molybdenite and variable activation energy. *Hydrometallurgy* 175, 52–63.
- Sharma, A.K., et al., 2018. Two dimensional α -MoO₃-x nanoflakes as bare eye probe for hydrogen peroxide in biological fluids. *Anal. Chim. Acta* 1015, 58–65.
- Su, L., et al., 2019. MoO₃ nanosheet-assisted photochemical reduction synthesis of Au nanoparticles for surface-enhanced Raman scattering substrates. *Sensors Actuators B Chem.* 279, 320–326.
- Valdés, H., et al., 2009. Characterization of chemical kinetics in membrane-based liquid–liquid extraction of molybdenum (VI) from aqueous solutions. *Chem. Eng. J.* 151 (1), 333–341.
- Van den Berg, J., Yang, Y., Nauta, H., Van Sandwijk, A., Reuter, M., 2002. Comprehensive processing of low grade sulphidic molybdenum ores. *Miner. Eng.* 15 (11), 879–883.
- Vizsolyi, A., Peters, E., 1980. Nitric acid leaching of molybdenite concentrates.

- Hydrometallurgy 6 (1), 103–119.
- Wang, M.-Y., Wang, X.-W., Jiang, C.-J., Tao, C.-F., 2014. Solvent extraction of molybdenum from acidic leach solution of Ni–Mo ore. *Rare Metals* 33 (1), 107–110.
- Warren, I., Reid, D., 1982. The recovery of molybdenum from leach solutions by reduction. *Metall. Trans. B* 13 (4), 565–570.
- Wu, J., et al., 2012. Selective extraction of Mo using Cyanex-272 and tributyl phosphate from low grade Ni–Mo ore leach liquor. *Sep. Purif. Technol.* 99, 120–126.
- Zhao, Z., et al., 2010. Recovery and purification of molybdenum from Ni–Mo ore by direct air oxidation in alkaline solution. *Hydrometallurgy* 103 (1), 68–73.
- Zhao, Z., Cao, C., Chen, X., Huo, G., 2011. Separation of macro amounts of tungsten and molybdenum by selective precipitation. *Hydrometallurgy* 108 (3), 229–232.
- Zhong, M., et al., 2018. Highly anisotropic solar-blind UV photodetector based on large-size two-dimensional α -MoO₃ atomic crystals. *2D Materials* 5 (3), 035033.
- Zhu, Z., Tulpatowicz, K., Pranolo, Y., Cheng, C.Y., 2015. Solvent extraction of molybdenum and vanadium from sulphate solutions with Cyphos IL 101. *Hydrometallurgy* 154, 72–77.