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Pol. J. Environ. Stud. Vol. 30, No. 2 (2021), 1-5
DOI: *10.15244/pjoes/124113* ONLINE PUBLICATION DATE:

Original Research

A Green Approach for Extraction of Ammonium Molybdate from Molybdenite Using Indigenous Resources

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Received: 13 May 2020
Accepted: 17 June 2020

Abstract

Present work reports on the microwave assisted extraction of molybdenum in the form of ammonium molybdate from molybdenum concentrate. In this processing, the ore was heated in air at 750ºC. The process converted the molybdenum sulphides to its oxides and evolved SO_2. Molybdenum oxides were then converted into sodium molybdate which was further changed into calcium molybdate and finally ammonium molybdate using different processes. Hence, the process proved to be efficient and economical for the extraction of high quantity of molybdenum as ammonium molybdate from molybdenum ore. The spectroscopic analysis data revealed that the molybdenite contains 31.2% molybdenum from which 26 % have been extracted in the form of ammonium molybdate. The project is also very valuable because the extraction process is very simple and cost effective as compared to the previously reported processes.

Keywords: molybdenite ore, microwave, UV/Vis spectroscopy, extraction

Introduction

Molybdenum is a strategic metal which is widely used in thermocouples, fabrication of radios, and in anticathode of X-rays. It is also used to produce special steel alloys. Molybdenum is an element having industrial importance due to their applications in many technological fields [1-4]. There is a huge demand for molybdenum due to its various applications.

Molybdenum and sulphur combine to form of a mineral commonly known as molybdenite (MoS_2) that is the main commercial source to produce molybdenum. Molybdenite is found in the igneous rocks present deep under the earth crust near the hot magma. Molybdenum is also found in some other minerals such as wulfenite ($PbMoO_4$) which is yellow-red to yellow orange

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in color and powellite ($CaMoO_4$); greenish brown, yellow and sometimes grey in color. It is estimated that more than 90% of molybdenum, produced now a day is from mineral molybdenite [5-7]. The commercial route for molybdenum extraction involves the roasting, purification and reduction of molybdenite, but this route is associated with the production of large amount of SO_2 that poses a serious environmental threat**.**

Moreover, pyrochemical processes needs high grade concentrate and they are not useful for the extraction of molybdenum from low grade molybdenite because it forms molybdates of impure elements which renders the processing difficult [8-11]. Extraction of molybdenum from low grade molybdenite concentrates without the emission of SO_2 has therefore received much attention in recent years. From low grade concentrates, selective extraction of molybdenum has been carried out by leaching with HNO_3, NaOCl solution, NaOH and using chlorination in the presence of oxygen [12-16]. Leaching with cyanide containing solution or by $FeCl_3$ solution has been used especially for the removal of impurities from low grade concentrates. The roasting process has also been modified for low grade molybdenite concentrate and is carried out in the presence of soda ash or lime. High quantity of various metals like Ni, Al, U, W, V, Re, Co and Cu are also present in molybdenum resources [17-21].

Due to strict environmental regulations, electro oxidation has become one of the best routes or an alternative method for the roasting process. In electro oxidation method, MoS_2 is oxidized in the electrolysis bath with solution of NaOCl to yield aqueous solution containing molybdenum. Several researchers have studied the extraction of molybdenum from this aqueous solution using several methods, including ion exchange, supported liquid membrane**,** solvent extraction and precipitation [22-24].

Herein, we report on the development/modification of a process for the extraction of pure molybdenum salt from MoS_2 that is more economical and efficient. Moreover, this method yielded 99% of molybdenum in the form of molybdate of different metals that were present in MoS_2.

Materials and Method

The mineral molybdenite was obtained from Azad Kashmir. The chemical constituents of the mineral are molybdenum (31.21%), Sulphur (23.24%), copper (0.31%), iron (1.60%), nickel (0.16%), rhenium (0.02%) and silicon (7.40%). Distilled water, hydrochloric acid, sulphuric acid, magnesium chloride, barium chloride, ferrous chloride, nitric acid, sodium nitrate, sodium carbonate, sodium hypochlorite, isobutyl alcohol, ammonium thiocyanate, sodium thiocyanate, potassium thiocyanate, diethyl ether, yellow ammonium sulphide were purchased from Sigma-Aldrich (USA). All the chemicals were of analytical grade and used as such without further purification. FTIR spectroscopy of the products was carried out on a Frontier Optica FTIR instrument (Perkin Elmer, USA) in the spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The extraction process for the extraction of ammonium molybdate and other salts of molybdenum from the mineral molybdenite involves the following steps.

Crushing of the Ore

The treatment of molybdenum ore such as molybdenite with sodium compounds, the sulphur present in the ore was converted in to insoluble sulphur which form a layer or envelop on the surface of molybdenite ore. This covering retarded or completely prevented the reaction. To overcome, it was necessary to grind and crush the molybdenite to a fine powder. The molybdenite ore was crushed in the mortar and pestle to a mesh size of about 80-100. The fine crushing leads to better results. Finely grounded ore leads to better fusion with sodium compounds (like sodium carbonate, sodium hydroxide). The finely divided powder has large surface area and so there are greater chances for molybdenum to have fusion with sodium compounds.

Roasting

The finely powdered molybdenite ore was then roasted, prior to roasting the pulverized ore was mixed with certain sodium compounds e.g. sodium carbonate, sodium hydroxide, sodium nitrate etc. After thorough mixing of pulverized molybdenite and sodium compounds, it was placed in a furnace for about two hours. In each case the temperature range should be such that is necessary to promote the reaction. In the case of sodium nitrate the temperature was above the melting point of sodium nitrate similarly for sodium hydroxide and sodium carbonate the temperature was above the melting points of these salts. The charge was intermittently agitated as to expose it to fresh supply of oxygen during the roasting process, which was very essential for the reaction [25]. The start of the reaction was indicated by the red glow, because the reaction was highly exothermic. After roasting the mass was cooled down for further processing.

Hydrometallurgical Treatment

The mass that was roasted after cooling was subjected to hydrometallurgical treatment that involves leaching with water for about two hours under stirring conditions at high temperature. During roasting the molybdenum sulphide was converted into molybdenum oxide (oxidation of molybdenum) and in the presence of certain sodium compound, it was converted into sodium molybdate ($NaMoO_4$). Sodium molybdate is a water-soluble compound, in this way during leaching it goes in the water leaving behind the solid matter.

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Table 1. Characteristic IR absorption frequencies of Ammonium Molybdate.

Compound	Types of vibration	Observed value (cm^{-1}) for NH	Observed value (cm^{-1}) for OH
$(NH_4)_2MoO_4$	Bending	1600	1400
	Stretching	3395	3600

After leaching this molybdenum solution is filtered off leaving behind the solid impurities [26].

Neutralization with Magnesium Chloride

Magnesium chloride in aqueous solution was added to the solution of molybdenum (sodium molybdate solution), along with constant stirring and heating until the molybdenum solution became almost neutral. Alternatively, magnesium chloride can be replaced with other neutralizing agents such as nitric acid. Magnesium chloride is preferably used as a neutralizing agent because one of its main functions is the formation of insoluble magnesium compounds of phosphorous and arsenic. Then these insoluble compounds can be filtered off. So, in this way we can eliminate impurities from the molybdenum solution. In this way we obtained the pure molybdenum solution in the form of sodium molybdate.

Calcium, iron and other water-soluble chloride are added to the molybdenum solution that was free from the precipitates of magnesium. The molybdenum solution was heated up to the boiling temperature and constantly stirred until all the molybdenum that was present in the solution was precipitated as iron, calcium and other molybdates. The molybdates that were formed were filtered out. The collected precipitate was then washed with warm water to eliminate impurities.

Formation of Calcium Molybdate

Calcium chloride was added to the molybdenum solution that was free from the precipitates of magnesium. The molybdenum solution was heated up to the boiling temperature and constantly stirred until all the molybdenum that was present in the solution was precipitated calcium molybdate. The calcium molybdate that was formed filtered out. The collected precipitate was then washed with warm water to eliminate impurities.

Formation of Ammonium Molybdate

The precipitates of calcium molybdate were then dried and refluxed for two hours with aqueous solution of ammonia to get ammonium molybdate. After that, the precipitates of molybdenum were collected, dried, and identified by FT-IR and UV/Vis spectrophotometer.

Results and Discussion

The IR spectra were recorded in the range of 4000-400 cm^{-1} as KBr pallets. The IR spectra of ammonium molybdate exhibited the bending vibrations due to NH and OH groups at 1600 cm^{-1} and 1400 cm^{-1} respectively. Similarly, the stretching vibrations of O-H and N-H groups were observed at 3600 cm^{-1} and 3395 cm^{-1} correspondingly. The broad bands for N-H stretch and O-H stretch indicate the presence of hydrogen bonding. Otherwise, the sharp bands would have appeared. Table shows the FTIR results for stretching and bending vibrations.

In the presence of HCl colored complex (orange-yellow) was formed by adding thiocyanate in the solution of molybdenum. Isobutyl alcohol was added to the molybdenum solution in a separating funnel and shaken for some time. This solution was allowed to stand for some time, the colored complex formed was moved to the organic phase and no trace of color was left into the aqueous phase. The organic phase was separated out and passed through a small filter paper to remove any suspended water droplet. Then the absorption spectrum was measured by using 1 cm cell with reference to a blank solution containing all the reagents except molybdenum. This complex shows maximum absorption at 470 nm (λmax)

Different dilutions of the standard were prepared by weighing the respective quantities of the said compound. The dilutions used were 0%, 10%, 20%, 30%,40% and 50% which gave absorbance 0.066, 0.158, 0.251, 0.344, 0.445 and 0.55 respectively. The ore sample was prepared for spectrophotometric determination of molybdenum using the standard procedure. The

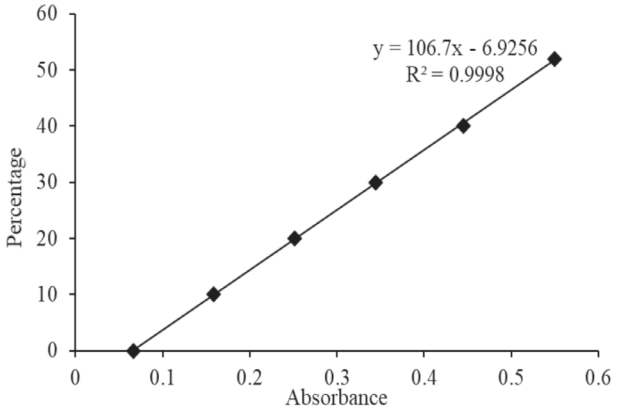

Fig. 1. UV analysis for percentage of Molybdenum.

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assignment was made based on the earlier reported work [12, 27-33].

The absorption spectra of ore complex were recorded at 470 nm which was found to be 0.370. This absorbance value was computed with the factor value 106.7x - 6.9256 (Fig. 1). After computing, the percentage of molybdenum in the ore sample was calculated which was found to be 31.2%. The sample was prepared for spectrophotometric determination of percentage of molybdenum by using the standard procedure. The absorption of extracted ammonium molybdate was recorded at 470 nm which was found to be 0.315. This absorbance value was computed with the factor value = 106.7x – 6.9256 (obtained from Fig 1). After computing, the percentage of molybdenum in the extracted sample was calculated which was found to be 26%.

Conclusions

It has been concluded that mineral chemistry is one of the most important and useful tools for the extraction of different types of minerals. In this project, the molybdenum has been recovered to its useful form as ammonium molybdate using heat energy. The project is also very valuable because the extraction process is very simple and cost effective as compared to the previously reported. The spectroscopic analysis data revealed that the extraction yield was more than 83%. This is manifested by 26% extraction in the form of ammonium molybdate from molybdenite containing 31.2 % molybdenum.

Conflict of Interest

The authors declare no conflicts of interest.

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