

Preparation of nano silver powder from acid leaching tail in gold room

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Abstract

According to the unique properties and many applications of nano silver powder, it was prepared from acid leaching tail solution. The low value residual gold and silver ions were occurred with fellow heavy metals as pollutants (Fe^{2+} , Cu^{2+} and Zn^{2+}) in acid leaching tail solution in Mouteh gold mine in Iran. Preparation of nano silver particles was achieved in two steps: first, by addition of ammonia as a separation step and second by using different reagents as precipitation and extraction steps. Different controlled parameters were including pH, residence time and temperature, mixing time, and reducing reagents to metals molar ratio. Acid leaching process was carried out with sulphuric and nitric acid via suitable reductants. In order to remove copper, zinc, and silver ions from solution, all of the conditions were controlled. The optimum conditions for preparation of nano silver powder with less than 90 nm were pH 10.5, hydrazine/methanol to silver molar ratio of 3 to 4, and reduction time of 5 min in 45°C. The results were evaluated via SEM, A.A and UV- Vis spectroscopy analytical methods.

Keywords: *Nano silver powder, Acid leaching tail solution, Hydrazine, Methanol*

1. Introduction

In the recent years investigators have applied a number of chemical approaches to control size and shape of particles and to produce the powder of metals with advanced morphology. In this regard numerous factors are considerable. Technology of Synthesis and assembly of valuable Nanoparticles such as silver with less than 50 micron dimensions is an important base of industry. Silver particles having fine or ultra fine size are of considerable current use in electronics chemical industry, medicine and engineering materials due to unique properties such as high electric and thermal conductivity, high resistance to oxidation, bacterial action, etc.[1-5].

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So the price of the nano metal powders is 20% percent more than their bar. Respect to capacity and potential of moteh mine this project can be a valuable process. Hydrometallurgical methods for separating elements from an industrial waste are dividing to four processes: 1- solvent extraction. 2- Electrolysis. 3- Ion exchange. 4- Precipitation & washing [4]. The purpose of this project which is based on the fourth method was extracting silver in nano shape from acid leaching process of moteh mine. In this way for the first step through adding ammonia and separating the sediment, hydrazinium sulphate salt was added to mother liquor to reduce silver ions to silver ions. The second step was washing the resulted deposited with sulphuric acid 1 molar. Third was producing silver nitrate in aqueous phase by using nitric acid 8 molar, finally by adding hydrazinium sulphate with stoichiometry ratio of hydrazine to silver was 3:4 at pH 10.5 and temperature of 45 °C (in 20 percent ethanol) in 5 minutes the silver nano particles were gained.

2. Materials and methods

When one litre of industrial solution was filtered and its pH was demonstrated 0.177, then pH increased due to adding Ammonia to this solution and in this condition a brown precipitate was appeared. Using ammonia was stopped at pH=10.5. And the resulted mother liquor was blue. Silver with zero oxidation valent was gained by using hydrazinium sulphate in a stoichiometrical ratio and after drying precipitate for removing impurities it was washed with sulphuric acid. And resulted deposit was washed with water and it was dried again. By dissolving this sediment in nitric acid while stirring silver nitrate was achieved at which ammonia was added until pH= 10.5. In this condition the brown silver oxide was disappeared and $[\text{Ag}(\text{NH}_3)_2]^+$ was produced in the medium. Via gradual adding hydrazinium sulphate salt ammoniacal complex of silver with (molar ratio 3:4) in the presence of 20% methanol at 45 °C in 5 minutes, the silver nano powder was prepared and then these particles were investigated by UV-Vis. Spectroscopy and Scanning electron microscopy (SEM)/EDAX.

3. Results and discussion

The amounts of Ag, Au, Cu, Zn, and Fe in the industrial solution were determined as follow 25 ppm, 86 ppm, 2536 ppm, 169 ppm and 16731 ppm.

3.1. The Effect of pH of silver extraction efficiency via adding ammonia

According to UV analysis results at pH= 10.5, there were ammoniac complexes of copper, zinc, and silver in the aqueous environment and no gold and iron were presented. Corresponding to atomic spectroscopy results iron and gold didn't exist in the mother liquid (or they were less than detection limit) and the other metals had approximately their initial quantities.

As shown in [Figure 1](#) by adding ammonia (0.18 cc corresponding to pH= 9.32) pH suddenly increased and it found amount of 10.33 when 0.2 cc ammonia was used. This phenomenon illustrates that in pH= 9.32 adding ammonia leads to producing brown sediment of silver oxide and as the following producing $[\text{Ag}(\text{NH}_3)_2]^+$ and in this stage (producing $[\text{Ag}(\text{NH}_3)_2]^+$) releasing OH^- makes the gap of pH diagram. At least pH=10 was known as a suitable point for transferring all of the silver ions to colourless ammonias solution.

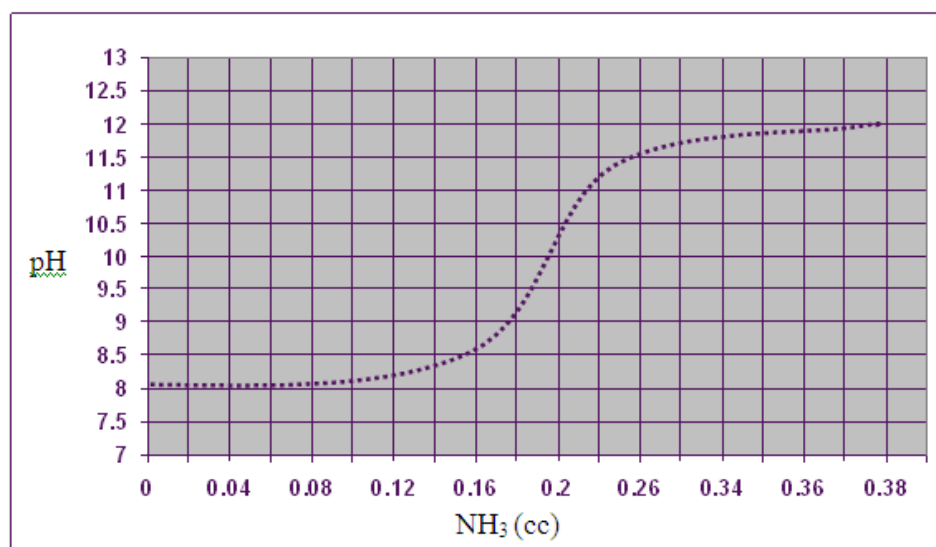
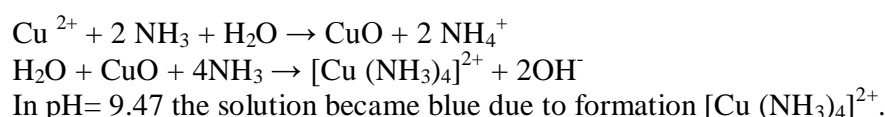
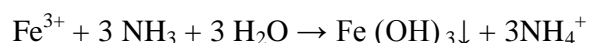


Fig.1. pH variations above the adding of ammonia 1.335 M to silver nitrate 0.00023 M solution

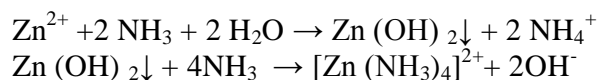
Respecting to ammonia and cyanide separating methods in Mouteh mine for refining gold and silver from acidic waste ammonia was used which not only is available and cheap but also is able to form stable complexes with silver and gold (due to the ligand field theory, ligand power: $\text{CN}^- > \text{NH}_3 > \text{OH}^-$). In this investigation at first ammonia was added to the solution until $\text{pH}=10.5$ and the reactions which occurred were as below, although all of Copper ions didn't form ammonia complex so copper ions still exist in medium.



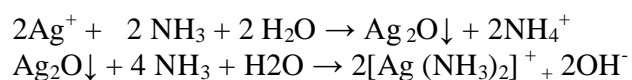
Feric ions came to an end in solution and remained as brown sediment on surface of solution and this sediment didn't dissolve in the extra ammonia reactant.



Just like copper, zinc transferred to mother liquid but all of Zinc ions didn't form ammoniacal complexes so a part of zinc ions were still in the solution.



With extra amount of ammonia silver was found in mother liquor and appeared as the colourless ammoniac complex, $[\text{Ag}(\text{NH}_3)_2]^+$ [7].



In the present of ammonia, gold remained on the filter paper as $[\text{Au}(\text{NH}_3)_2(\text{OH})_2] \text{OH}$.

3.2. The Effect of adding hydrazine sulphate salt as reducing agent to ammonia industrial solution

Corresponding to UV results after adding hydrazinium sulphate salt (with stoichiometrical ratio to silver) and separating the resulted sediments, $[\text{Ag}(\text{NH}_3)_2]^+$ didn't exist in the environmental solution. In Figure 2 EDAX (SEM) illustrates the effect of applying hydrazinium sulphate salt as reducing agent in the ammoniac industrial solution.

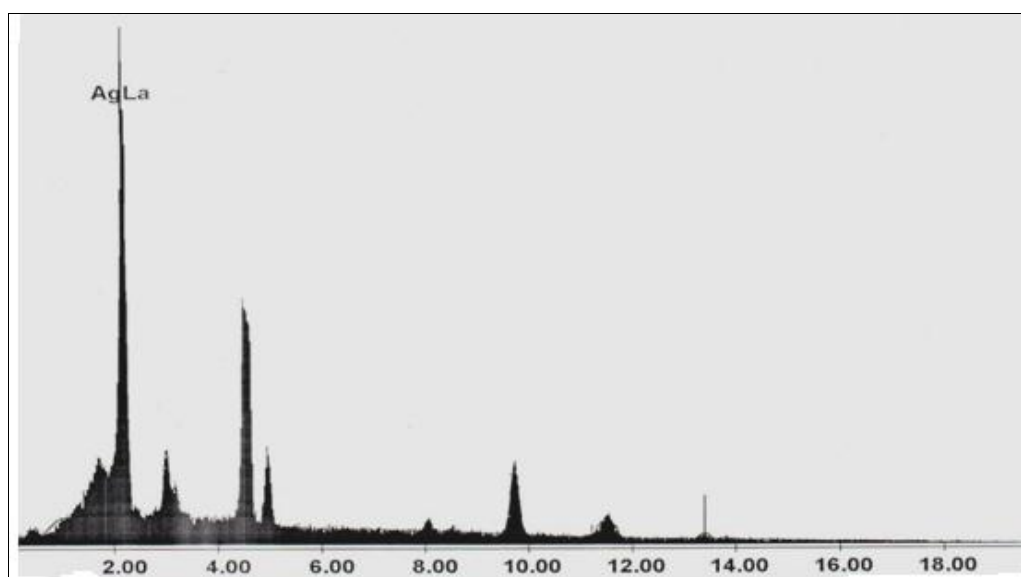
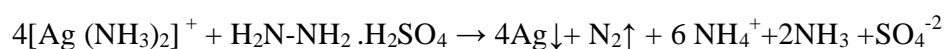


Fig.2. EDAX (SEM) analysis results after adding hydrazine sulphate to ammoniac industrial solution

By applying stoichiometrical amount of hydrazine sulphate silver ions precipitated as silver with zero valence. Respected Figure 2, this precipitate included 86.99% silver, although there were copper and zinc impurities in precipitate [6-7].



3.3. The Effect of sulphuric acid on purification of silver

In Figure 3 the effect of sulphuric acid on purification of silver is distinguished by EDAX (SEM) analysis.

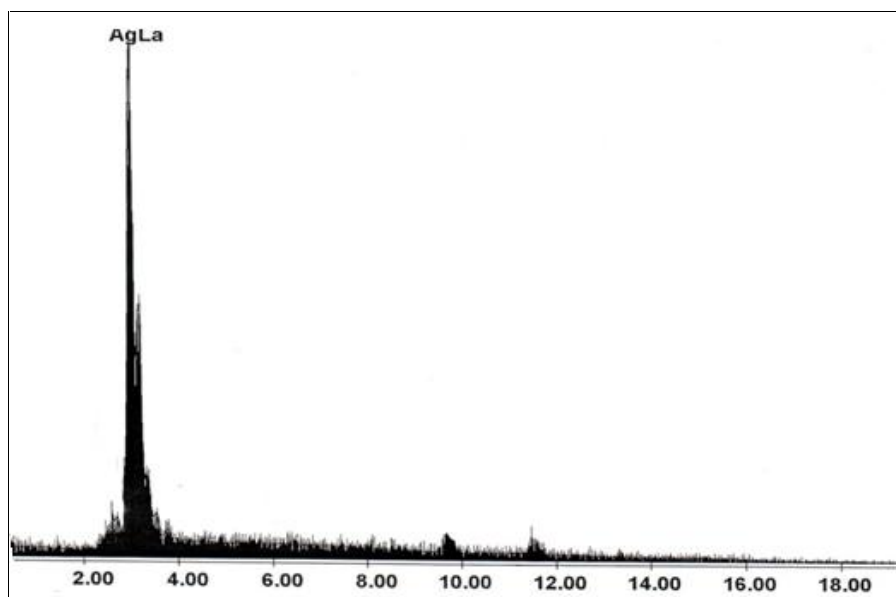
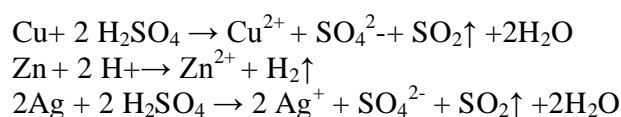


Fig.3. Analysis EDAX (SEM). Effect of sulphuric acid in purification of silver

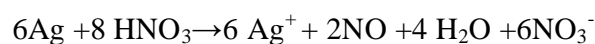
By adding sulphuric acid the silver with zero valence resulted from reduction of silver ammonical complex by hydrazinium sulphate, pure silver remained in precipitate and as you see this precipitate includes 100% silver.

After washing the silver (which was resulted from reduction stage) by sulphuric acid the amount of silver, copper and zinc in the mother liquid were distinguished as follow 0 ppm 12.05ppm, 0.03 ppm (corresponding to industrial solution) by atomic absorption spectroscopy. It means that for purification process, silver was dissolved in dilute sulphuric acid to remove impurities. If hot and concentrate sulphuric acid was applied silver would be dissolved according this reaction too:



3.4. The effect of various parameters on dimensions of Ag nano particles by UV- VIS spectroscopy

According to bear Lambert low the UV Visible absorption is depend on the size and concentration of particles. Nano silver particles also absorb this ray and this absorption band shows the size of particles [8,9].



For these tests the silver resulted from washing with sulphuric acid was dissolved in nitric acid and silver nitrate was appeared in medium. In all off experiences pH controlled by using ammonia.

Figure 4 shows the absorption of nano silver particles in pH=10.5 when molar ratio of hydrazinium sulphate and silver was 3:4 in present of 20% methanol in alternative times of reduction.

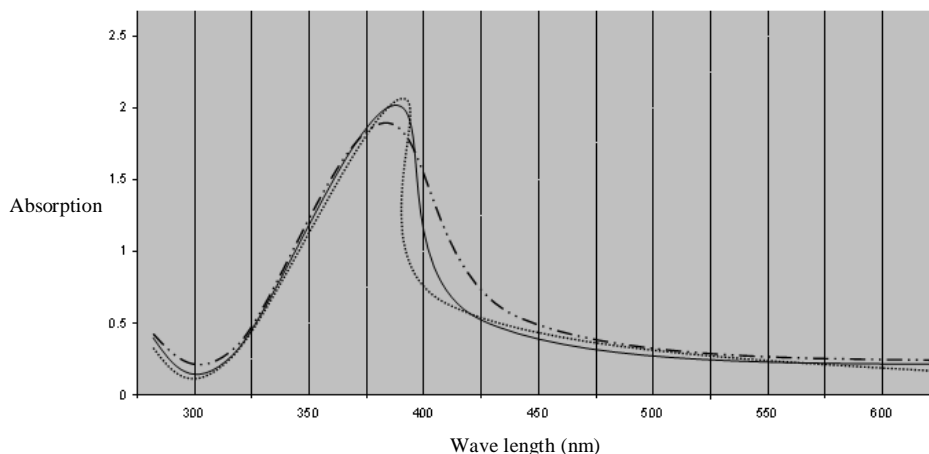


Fig.4. the absorption curves of nano silver particles in pH=10.5 while molar ratio of hydrazinium sulphate and silver was 3:4 in present of 20% methanol at 45°C and alternative times of reduction

If time of reduction be longer, red shift will be seen in the absorption peak and there is more absorption too due to the propagation of particles which relates to the longer times of reaction[10].

According Grijalva's reports if the reduction time be longer the surface absorption of ions will be more [11, 12].

3.4.2. The effect of molar ratio of oxidant and reduction on the size of nano particles

Figure 5 shows the absorption curves of nano silver particles in pH=10.5 and in present of 20% methanol at 45°C with alternative molar ratio of Hydrazinium sulphate and silver(3:4, 1:4 & 2:4).

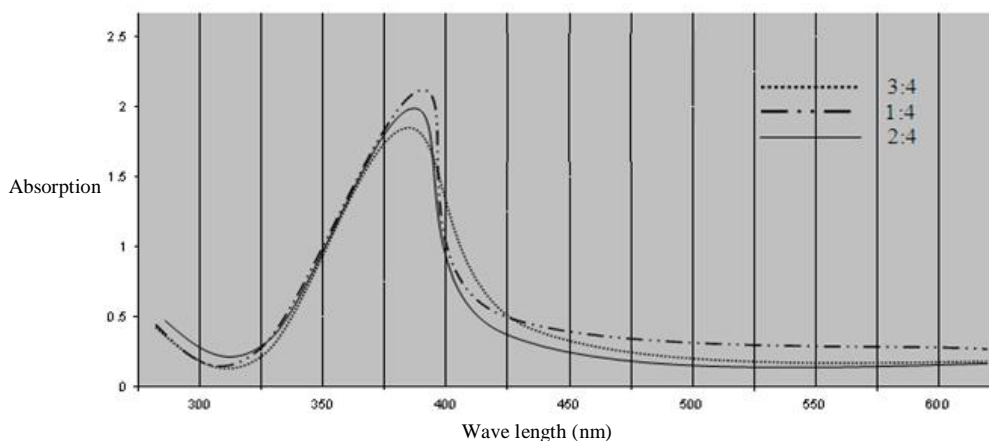


Fig. 5. Absorption curves of nano silver particles in pH=10.5 and in present of 20% methanol at 45°C with alternative molar ratio of Hydrazoinium sulphat and silver (3:4, 1:4 & 2:4)

If amount of reducing agent be more than silver the particles will have a more little size and a blue shift will be seen in the absorption peak [13, 14].

3.4.3. The effect of pH in the size of silver nano particles

Figure 6 shows the absorption curves of nano silver particles in pH=10.5 and in present of 20% methanol and molar ratio of Hydrazoinium sulphate and silver 3:4 at alternative temperatures.

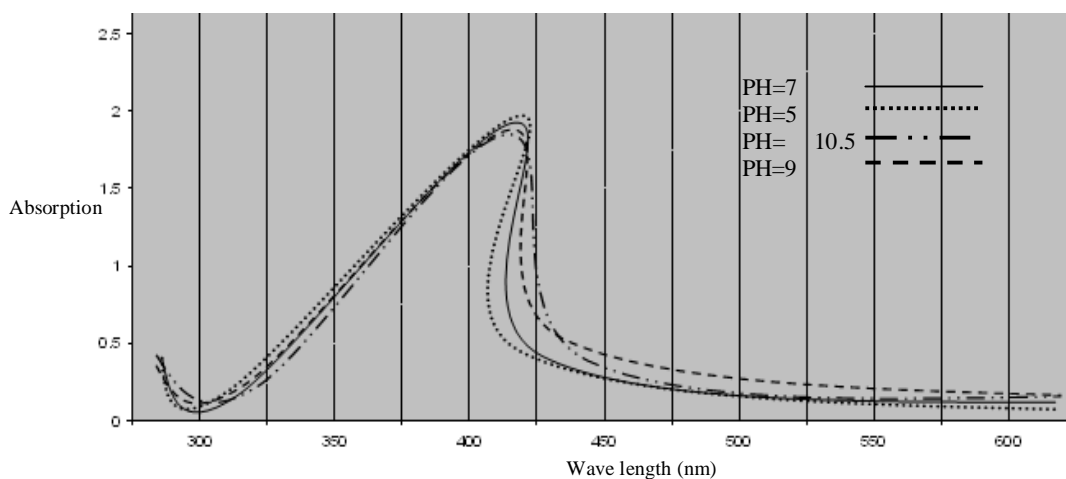


Fig .6. Absorption curves of nano silver particles at 45°C in present of 20% methanol and molar ratio of Hydrazoinium sulphate and silver 3:4 while 5 min reduction in alternative pH.

By increasing pH the particles will have a more little size and a blue shift will be seen in the absorption peak. Otherwise there will be more absorption due to the propagation of particles.

3.5. Canning electronic microscope (SEM) images of produced silver powders

The comparison between Figure 7 and Figure 8 shows if higher temperature maybe used, the size of particles will increase. In Figure 7 the size of particles is less than 90 nm. In comparing of Figure 8 and 9 of silver nano particles produced from industrial solution at 45°C in present of 20% methanol , pH=10.5 and molar ratio of Hydrazoinium sulphate and silver 3:4 in 5 minutes have the more little size. In Figure 9 the size of particles is less than 90 nm and according Figure 10 purity homogeneity of particles is 93.1%.

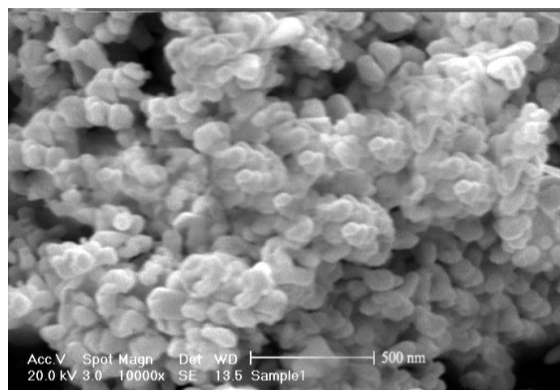


Fig.7. SEM image of silver particles produced from standard solution at 45°C in the presence of 20% methanol, pH=5 and molar ratio of Hydrazoinium sulphate and silver 3:4 in 5 minutes.

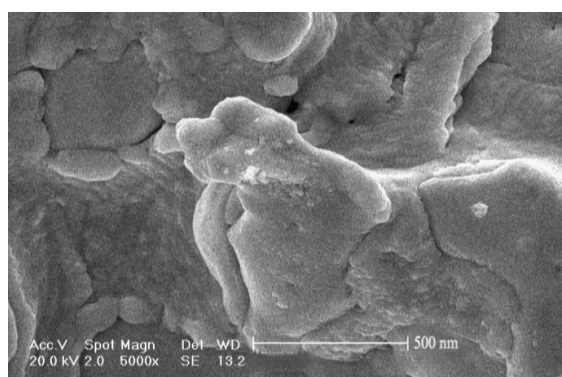


Fig.8. SEM image of silver particles produced from industrial solution at room temperature without methanol, pH=5 and molar ratio of Hydrazoinium sulphate and silver 1:4 in 5 minutes.

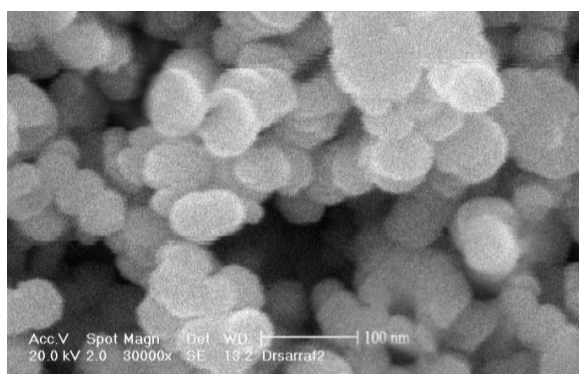


Fig.9. SEM image of silver nano particles produced from industrial solution at 45°C in the presence of 20% methanol, pH=10.5 and molar ratio of Hydrazoinium sulphate and silver 3:4 in 5 minutes.

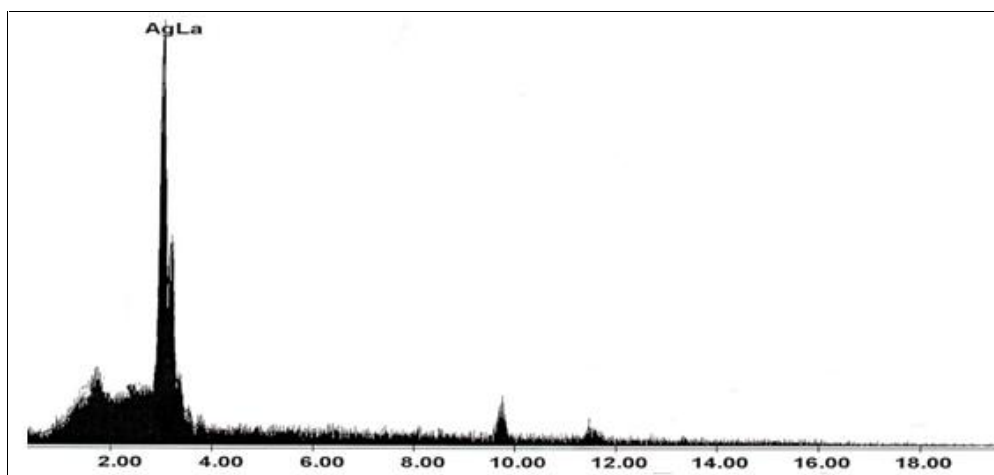


Fig.10. EDAX profile of silver powder prepared from industrial waste

4. Conclusion

This paper presents preliminary experimental test work results for the recovery of silver by extraction of waste acidic tailing solution, containing low level of silver soluble in the waste water with high levels of the other pollutant metals. Silver separation from the other metals in industrial waste in pH variation by addition is possible. Silver nano powder <90 nm from industrial waste solution of chemical reduction by hydrazinum sulfate with methanol, is resulted. In this investigation preparation nano silver particles with lower size and more homogeneity from the industrial waste by control of pH and change of molar ratio hydrazinum sulfate to silver and low reduction time accomplished. From the dissolution, pH changes, combustion reagents, time and molar ratio, preparation of nano silver particles with high efficiency is possible.

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