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Synthesis Silver Nanoparticles by Recovery Silver from Anode Slime of Kerman Sarcheshmeh Cooper Complex

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ABSTRACT

According to circumstance of kerman sarcheshmeh cooper complex that its anode slime is mainly consisted of Cu, Ag, Au, Pb and Se. In this work, recovery of silver from anode slime and subsequent synthesis of silver nanoparticles from leaching solution was made. Silver was separated from anode slime by using of HNO_3 and HCl. X-Ray fluorescence spectroscopy (XRF) was used to characterize anode slime components. Silver nanoparticles (SNPs) with average size of 25 nm were obtained through sonication aqueous solution of silver nitrate in the presence of dextrose and polyvinyl pyrrolidone (PVP) as reduction and stabilizing agent respectively. SNPs were characterized by surface plasmon resonance (SPR) and Ultraviolet-Visible (UV-Vis) spectrum. X-Ray diffraction (XRD) pattern confirmed the cubic morphology of metallic SNPs and energy dispersive X-Ray spectroscopy (EDS) spectrum showed peaks of silver free of impurity. Size and distribution of SNPs were determined by dynamic light scattering analysis (DLS) and scanning electron microscopy (SEM).

Keyword: Silver Nanoparticles, Sonification, Kerman Sarcheshmeh Cooper Complex, Anode Slime; Leaching; Nanotechnology.

1. INTRODUCTION

Nanotechnology has had an immense impact on nearly all existing scientific disciplines. Nanoparticles have unique physiochemical and optical properties due to surface and finite-size effect. Metal nanoparticles are at the top of the rapidly increasing list of materials being investigated in the nanostructured [1]. In recent years, researchers in the field of nanotechnology are finding that there is an expanding research in the synthesis of SNPs due to the potential application for the development of novel technologies [1, 2] Silver nanoparticles (SNPs) have been paid enormous attention in various areas, such as, catalysts [2], because of their morphology play important role in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials [3]. In this work, copper anode slime of Kerman Sarcheshmeh cooper complex that

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is in south east of Iran was under analyzing. Anode Slime is characterized by higher amount of Ag, Se, Pb and Cu compared to other metals with very low amount of Au. There is interest in studying methods for recovery of these metals from anode slime. Impurities must also be removed from anode slime before recovery of valuable metals like Ag [4, 5]. Using of chemical route, since discovered, has been studied for yielding kinds of nanomaterials, especially noble metal nanoparticles, such as silver, gold and platinum [6, 7]. Among these researches, chemical method under sonication has been applied widely due to the relatively high reductive ability of it [8, 9].

2. EXPERIMENTAL

Materials used in the synthesis of SNPs involved nitric acid 65%, hydrochloric acid 37%, ammonia, dextrose, sodium hydroxide and polyvinyl pyrrolidone were obtained from Merck.

All glassware were washed with deionized water and dried before use. An aliqute of 40 g anode slime was used in experiment. 400 mL nitric acid was added to 40 g anode slime. After filtering, 2 mL HCl was added and AgCl was obtained from the leach solution. Silver chloride was collected and dissolved in ammonia solution (0.5 M) and this solution and 1:1 wt% pvp was mixed in room temperature and NaOH was added drop by drop for obtain pH 12. In this time solution colour change to yellow. After 10 min, solution of dextrose 0.4 M rapidly was added and colour changed from yellow to dark brown. This solution immediately was transferred to ultrasonic bath and sonicated for 120 min at 70°C. The obtained silver colloids were separated from the solution by vigorous centrifugation at 14000 rpm for 15 min to remove any excess protecting agent and then re-dispersed in distilled water. In order to obtain SNPs powder the silver colloids were set in oven at 120°C for 8 hours to solvent evaporation.

An ultrasonic bath ELMA 60 Hz, Ultraviolet-Visible (UV-Vis) T80, X-Ray flourcence spectroscopy ARL 8410 (XRF), X-Ray powder diffraction (XRD) PW 1800 and energy dispersive X-Ray spectroscopy (EDX) XGT 7200 were used to preparation and confirmation the morphology and purity of metallic SNPs. Size and distribution of SNPs were determined by dynamic light scattering analysis (DLS) ZEN 3600 and scanning electron microscopy (SEM) SBC12.

3. RESULTS AND DISCUSSION

In order to characterize silver percent in anode slime, XRF analysis was applied and the obtained result showed that about 3/8% anode slime is Ag_2O.

To separate silver from anode slime, acid leaching was used. The anode slime was leached with nitric acid at 90°C. In this condition, Cu, Pb, Se is leached as well as Ag. In order to Ag separation from other component, HCl was added and silver was precipitated as AgCl and $PbCl_2$ that both of them were white solid. $PbCl_2$ was removed by washing hot water.

$$\text{Anode slime} + HNO_3 \rightarrow AgNO_3 + Cu(NO_3)_2 + Pb(NO_3)_2 + Se(NO_3)_4 + \text{Other solid} \quad (1)$$

$$Ag_2O + 2HNO_3 \rightarrow 2AgNO_3 + 2H_2O \quad (2)$$

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O \quad (3)$$

Table 1: *XRF analysis of anode slime.*

Composition	Weight (%)	Composition	Weight (%)	Composition	Weight (%)
Al_2O_3	0.24	As_2O_3	0.24	Fe_2O_3	0.21
TeO_2	0.52	SiO_2	2.6	SeO_2	13.7
Ag_2O	3.8	Sb_2O_3	4.4	SnO_2	0.4
Au	0.2	LaO	1	Cl	0.2
CuO	7.2	SrO	1.5	CaO	0.17
PbO	3.6	BaO	37.32	SO_2	22.7

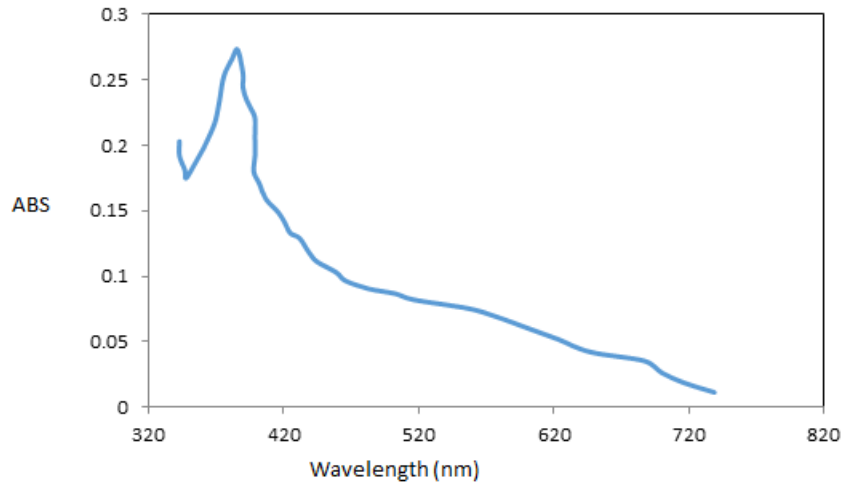


Figure 1: *UV-Vis absorption spectra for SNPs powder without sonication and after sonication with 2 hours.*

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O \quad (4)$$

$$SeO_2 + 4HNO_3 \rightarrow Se(NO_3)_4 + 2H_2O \quad (5)$$

$$\text{Nitrate solution} + HCl \rightarrow AgCl + PbCl_2 \quad (6)$$

$$AgCl + PbCl_2 + \text{Washing with hot water} \rightarrow \text{Only } AgCl\downarrow \quad (7)$$

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl \quad (8)$$

$$Ag(NH_3)_2^+ + PVP \rightarrow Ag(PVP)^+ + 2NH_3 \quad (9)$$

$$CH_2OH-(CHOH)_4-CHO + 2Ag(PVP)^+ + 2OH^- \rightarrow CHOH-(CHOH)_4-COOH + 2Ag + 2PVP + H_2O \quad (10)$$

$$CH_2OH-(CHOH)_4-CHO + 2Ag^+ + 2OH^- \rightarrow CHOH-(CHOH)_4-COOH + 2Ag + H_2O \quad (11)$$

According to previous study alkaline solution for synthesis of SNPs is more effective than pure solution [10-12]. As OH^- injected to solution makes accelerate the reaction and help dextrose and pvp to converted Ag^+ to Ag° more and better.

Table 2: *Band Gap Energy.*

h = Planks constant	6.62 x 10 $^{-34}$ Joules
C = Speed of light	3.0 x 10^8 meter/sec
λ = Cut of wavelength	385 x 10^{-9} meter
E = h C / λ	5.1584 x 10^{-19} Joules
1 eV = 1.6 x 10^{-19}	3.21 eV

To study the absorbance of SNPs in UV-Vis spectrum (DRS) is applied. There is a band around 385 nm that is related to SNPs.

Scanning electron microscopy (SEM) image in Figure 2, confirmed the morphology of SNPs nanostructure. SEM images showed that the size of SNPs in nanosize and their spherical morphology that was prepared by this method.

DLS plot showed the distribution of SNPs for sample in Figure 3. Result showed that SNPs in range of 20-40 nm.

DLS plot for size distribution of SNPs by volume in Figure 4 was shown that the relation between number of particles and volume of particles that was occupied. This relation was directly, due to our SNPs was spherical and the formula of spherical volume that is V= 4/3 π r^3, so as particles in a space or volume be more

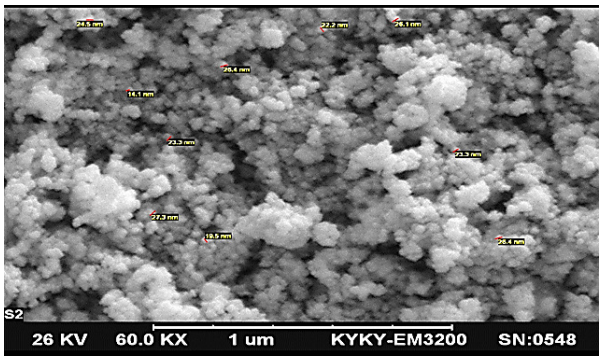
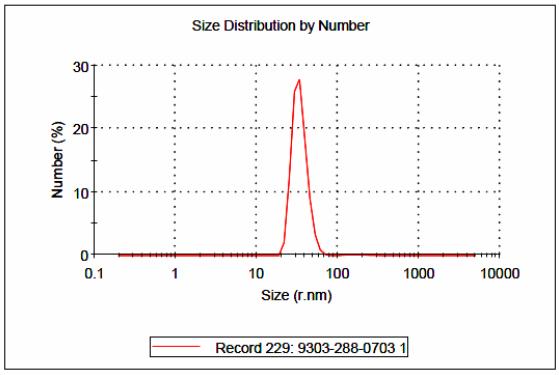
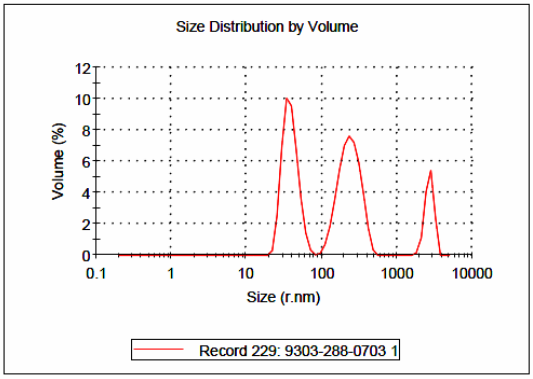


Figure 2: *SEM image of SNPs after 2 hours sonicating.*



Size r.nm	Number %	Size r.nm	Number %
0.2000	0.0	34.03	27.8
0.2316	0.0	39.41	18.4
0.2682	0.0	45.64	8.9
0.3106	0.0	52.85	3.2
0.3597	0.0	61.21	0.9
0.4166	0.0	70.89	0.2
0.4825	0.0	82.09	0.0
0.5587	0.0	95.07	0.0
0.6470	0.0	110.1	0.0
0.7493	0.0	127.5	0.1
0.8678	0.0	147.7	0.1
1.005	0.0	171.0	0.1
1.164	0.0	198.0	0.1
1.348	0.0	229.3	0.1
1.561	0.0	265.6	0.0
1.808	0.0	307.6	0.0
2.093	0.0	356.2	0.0
2.424	0.0	412.5	0.0
2.807	0.0	477.7	0.0
3.251	0.0	553.2	0.0
3.765	0.0	640.7	0.0
4.360	0.0	741.9	0.0
5.050	0.0	859.2	0.0
5.848	0.0	995.1	0.0
6.772	0.0	1152	0.0
7.843	0.0	1335	0.0
9.083	0.0	1545	0.0
10.52	0.0	1790	0.0
12.18	0.0	2073	0.0
14.11	0.0	2400	0.0
16.34	0.0	2780	0.0
18.92	0.0	3219	0.0
21.91	2.0	3728	0.0
25.37	12.2	4317	0.0
29.39	25.9	5000	0.0

Figure 3: *DLS analysis for SNPs size distribution by number.*



Size r.nm	Volume %	Size r.nm	Volume %
0.2000	0.0	34.03	10.0
0.2316	0.0	39.41	9.5
0.2682	0.0	45.64	6.7
0.3106	0.0	52.85	3.6
0.3597	0.0	61.21	1.4
0.4166	0.0	70.89	0.3
0.4825	0.0	82.09	0.0
0.5587	0.0	95.07	0.1
0.6470	0.0	110.1	0.7
0.7493	0.0	127.5	1.9
0.8678	0.0	147.7	3.6
1.005	0.0	171.0	5.5
1.164	0.0	198.0	7.0
1.348	0.0	229.3	7.6
1.561	0.0	265.6	7.2
1.808	0.0	307.6	5.9
2.093	0.0	356.2	3.9
2.424	0.0	412.5	1.7
2.807	0.0	477.7	0.4
3.251	0.0	553.2	0.0
3.765	0.0	640.7	0.0
4.360	0.0	741.9	0.0
5.050	0.0	859.2	0.0
5.848	0.0	995.1	0.0
6.772	0.0	1152	0.0
7.843	0.0	1335	0.0
9.083	0.0	1545	0.0
10.52	0.0	1790	0.2
12.18	0.0	2073	1.1
14.11	0.0	2400	4.1
16.34	0.0	2780	5.4
18.92	0.0	3219	2.3
21.91	0.3	3728	0.0
25.37	2.5	4317	0.0
29.39	6.9	5000	0.0

Figure 4: *DLS analysis for SNPs size distribution by volume.*

the plot of these particles is more too. For this reason and the volume in range of 10 till 100 nm is bigger than others, because the number of SNPs in this range is more.

Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition of a material. EDS for SNPs from powder samples shown in Figure 5, the peak of silver in their plot in 3, 23 and 26 KeV. The purity of silver was shown in Table 1 97.3% that was

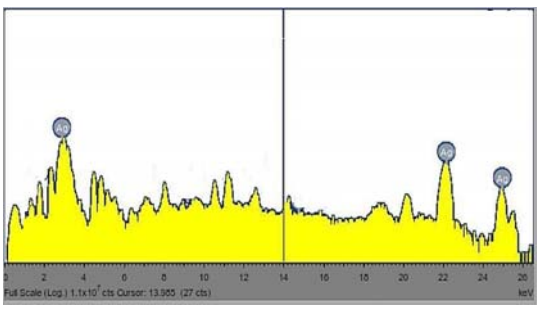


Figure 5: *EDS spectra for SNPs under 2 hours sonicated.*

Table 3: *Output results of EDS analysis of SNPs under 2 hours sonicate.*

Elem.	Line	Mass (%)	Atomic (%)	Intensity	Formula	Mass (%)
16 S	K	0.05	0.12	2.12	S	0.05
22 Ti	K	0.16	0.26	2.57	TiO_2	0.27
26 Fe	K	0.05	0.06	1.77	Fe_2O_3	0.07
29 Cu	K	0.06	0.07	3.31	CuO	0.08
34 Se	K	0.13	0.13	7.83	SeO_2	0.19
47 Ag	K	97.39	95.55	230.63	Ag	99.24
82 Pb	L	0.1	0.04	1.75	Pb	0.1
O		2.06	3.77			

noticeable for synthesize of SNPs.

X-Ray diffraction was used to identify crystalline phases. Figure 6 shows X-Ray diffraction patterns of the powder. Morphology of SNPs were cubic, the exhibited picks correspond to the (111) and (220) in 2Ɵ 38 and 44 of a cubic structure is identified by using of the standard data.

4. CONCLUSIONS

In summary in this work leaching of anode slime showed that almost all of silver could be separated from anode slime by nitric acid. SNPs was yielded with high purity 97/3% at 70°C under sonication with using of dextrose and pvp in the role of reduction and stabilizer. 20-40 nm diameter SNPs were obtained, the concentration of silver cation in proportion to the concentration of pvp was kept constant during all the experiments. OH- has the effects of helping to yield the nucleation sites and acting as surfactant. This combined method to synthesize SNPs have small diameter and better purity of SNPs, it can be applied in fabricating composite because of simple process and condition.

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