

Green recovery of silver as crystalline Nano-particles from corresponding waste solutions by Lime Juice as compared with Ascorbic acid and Citric acid

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Received: January 2, 2017, Accepted: March 17, 2017, Published: March 17, 2017.

ABSTRACT

Different biological methods are gaining recognition for the production of silver nanoparticles (Ag-NPs), However, none of them have concerned to do recovery, removal and separation as a goal. In this study silver nanoparticles (Ag-NPs) were recovered from fixer effluent solution as waste solution of silver by interacting with Lime juice as a bio-reducing and bio-capping agent. The best conditions for obtaining Ag NPs were determined by UV-Visible, FT-IR spectroscopy, DLS technique, SEM and XRD. Finally, the recovery process was assessed with pure citric and ascorbic acids with the same concentration in the applied Lime juice.

Keywords: *silver nanoparticle, bio-separation, waste photography solution, green-recovery, plant extract*

1. INTRODUCTION

The waste X-ray photographic films containing metallic silver to enhance its sensitivity to transmitted X-rays are a good source for silver recovery. It has been reported that 25% of the world's silver needs are provided by recycling and more than 70% of this, is obtained from photographic fixer solution [1]. Metallic silver was formed on photographic films by photo reduction of silver halides. During the development and fixing of film, silver-halide crystals that are not exposed to light are leached by fixer solution [2]. The fixer solution is a photographic waste solution of ammonium or sodium thiosulphate that applied for conversion of the silver chloride or bromide into water soluble silver thiosulphate. Then, this water soluble silver salt transfer from the film into the fixing bath [3]. Another photographic waste solution that contains silver is the spent stabilizer solution. Wastewaters containing free silver ion is very toxic to aquatic organism even at trace concentrations [4,5]. Hence, the removal of silver from these wastes solution is of both economic and environmental benefit.

Various methods have been examined to recover the bulk silver from its waste solutions. Electrolysis, metallic replacement, ion-exchange, chemical precipitation, reverse osmosis and membrane processes are commonly applied to the treatment of industrial effluents [6,7].

In the last decade, there is a trend to switch from the use of bulk materials towards nano-size particles (NPs). Nano metallic particles show unique feature. They considerably changed physical, chemical and biological properties compared to corresponding bulk material, due to their high surface to volume ratio, quantum confinement and other effects [8]. They are currently attracting attention for the wide range from catalysts, sensing and optics to medical application and data storage [9,10].

In recent years, Silver nano particles (AgNPs) are gaining in popularity for their strong antimicrobial activity [11,12] and its relatively low toxicity towards humans [13]. For these reasons, nanosilver is used as an antimicrobial agent in textiles, water treatment systems, cosmetics, electronics and medical devices [14,15]. Besides their antimicrobial features, nanosilvers also exhibits strong optical features making them suitable for biological sensing and imaging [16]. Silver nanoparticles are applied in

conductive inks, adhesives and pastes for electronic devices, due to their high conductivity [17]. Moreover, silver nanoparticles are also used as catalysts in several chemical reactions [16,18].

Silver nanoparticles can be prepared by two major routes [8], the first one is physical approach such as evaporation and laser ablation. The second one is chemical approach in which [19-21]. The reduction of Ag⁺ ions lead to the formation of silver atoms (Ag⁰), as colloidal dispersions in solvents. It is important to use protective or capping agent that can be absorbed on or bind onto the nanoparticle surface and avoiding their agglomeration [19,22].

Plant extracts are often environmentally and economically friendly materials. In the last decade, the use of all parts of plants for reducing silver ions to nanoparticles has attracted attention of both nonscientists and phytochemists [23,24]. They can be used in the synthesis of silver nanoparticles (Ag NPs), replacing potentially hazardous chemicals. The reason plant extracts work so well in the synthesis of nanoparticles is because they act as reducing agents as well as capping agents [25]. Although there are several synthetic routes to make silver nanoparticles as mentioned above, However, none of them have been concerned to do recovery as a goal. They have used standard solution of silver nitrate as primary source of silver ions, while there is substantial difference between the chemical composition of photography waste solution with many interferences and standard solution of AgNO₃ [26]. Consequently, there is a need for method of silver nanoparticles recovery from photographic waste solution that is efficient, selective, and use environmentally benign materials or processes. Recently, new approach is currently being explored, including synthesis of crystalline silver nanowires from AgNO₃ in water. In this method silver nitrate is reduced to silver nanowire at 100 °C by sodium citrate and in the presence of NaOH [27]. Later, Prathna and coworkers have reported lemon juice containing citric acid and ascorbic acid can be reduced Ag⁺ in standard solution of AgNO₃ to Ag NPs in the absence of any synthetic capping agent. In this examination the average size for silver particles, 50-60 nm, has been reported [28]. In recent years, Rao research group have Examined Lemon extract for biosynthesis of silver nanoparticles from standard solution of silver nitrate successfully [29].

In continuing of our general interest to synthesis of biological active compounds [30] we herein report an efficient bio-recovery of silver nanoparticles from photography waste solution by environmental benign process. In the present study, fruits of Citrus Limon were used as a bio-reductant for the recovery of silver nanoparticles from photography waste solution. To the best of our knowledge, no such process for green recovery of silver nanoparticles from silver waste solution has been reported to date. The reason behind selecting this particular plant is because lemons are a rich source of citric acid and ascorbic acid [31]. Moreover, it is commercially economic and abundantly available. It is also principally employed in cooking as a condiment and flavoring material and being largely used in the preparation of some desserts. In medicine, it was once used as a cure for colds. Due to the numerous applications of Citrus Limon, thus commercial productivity of the same is quite high and thereby has promising availability for the commercial recovery of nano-scale silver.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1. Materials

Fresh lemons (*C. limon*) were bought from local market in Jahrom, Fars province, Iran. Reagents were purchased from Merck, Fluka or Aldrich and they were used as-received without further pre-treatments. The industrial effluent used in the recovery process of silver nano-particles were fixing bath from the Shiraz central hospital (MRI) and School of dentistry, shiraz university of medical science photographic west solution. Silver concentration of these baths were 8 gL⁻¹ and 1 gL⁻¹, respectively.

2.2. Experimental procedure

2.2.1. Preparation of extract

Fresh Lime that grew in Jahrom was washed and squeezed for obtaining fresh lime juice. Separation of suspended particles was done by passing obtained Lime juice through the whatman filter paper, No. 42. The filtrate was centrifuged at 6000 rpm for 10 min to remove any undesired impurities and filtered again with whatman #42. This juice was stored at 4°C for further experiments.

2.2.2. Determination of citric acid and L-ascorbic acid in obtained Lime juice

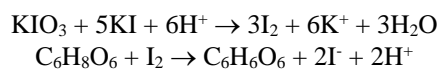
2.2.2.1. Determination of citric acid

The concentration of citric acid in our Lime juice was determined by titration with sodium hydroxide in the presence of phenolphthalein as indicator. The end point of the titration was reached when the color of solution changes from colorless to pale pink color. The concentration of citric acid in our fruit juice sample was obtained 0.356 mol L⁻¹.

2.2.2.2. Determination of L-ascorbic acid

The amount of ascorbic acid can be determined by well-known determination method of vitamin C through a redox titration with iodine. The iodine is produced in situ by the reaction of potassium iodate and potassium iodide in the presence of hydrochloric acid (scheme 1). Then, the iodine is reduced by the ascorbic acid to form iodide. The titration end point is appearance the blue color using starch as an indicator. The concentration of ascorbic acid in our Lime juice samples was obtained 0.23 mol L⁻¹.

2.2.3. Determination of silver concentration in photography waste solution



Scheme 1 chemical equations for determination of concentration of L-ascorbic acid in our juice samples

The concentration of silver in west solution of silver was measured via the method that have been reported by Murphy, previously [32]. For this measurement fixer effluent solution (25 mL) was transferred to a 250 mL beaker. Then distilled water (100 mL), sodium acetate (20 mL; 50 g L⁻¹) and EDTA (20 mL; 50 g L⁻¹) were added to the beaker. Adjust the pH of the solution between 6-7 using ammonia hydroxide and acetic acid. Afterwards, hexaammincobalt (III) chloride solution (30 mL; 30 g L⁻¹) was added. The color of the solution was changed to amethystine. Then, stirred the suspension solution until a quantitative precipitate was formed. Then the suspension solution was filtrated, washed with distilled water and dried at 95 °C until a constant weight was obtained. The conversion factor to silver is 0.2187.

2.2.4. Recovery of silver nanoparticles

In order to determine the optimum parameters of the bio-recovery process, the Factorial Design of Experiments were that the one factor was varied at a time keeping the other factors constant. Different concentrations of fixer effluent solution (Dental; 1 gL⁻¹ and Hospital; 8 gL⁻¹) were interacted with the prepared lime juice in four different mixing ratios of fixer effluent and lime juice (4:0.1, 4:0.2, 4:6 and 4:16) in 70 °C within 15 min time period with vigorous stirring. Moreover, the size, shape and dispersity of Ag NPs were investigated under various temperature, time of reaction and pH. The pH was adjusting with 0.5N NaOH. The formation of nanoparticles if any were used for the subsequent characterization studies. All experiments were performed three times and the result reported represents the average of the values obtained for each reaction.

Citric acid and ascorbic acid were prepared and explored in the recovery process at the optimal conditions separately. The concentrations that were used were based on the maximum concentrations of citric acid and ascorbic acid in the lime juice used for this study.

Lesser concentrations of silver ion (Dental fixer effluent; 1 gL⁻¹) did not yield significant results in this recovery process.

2.3. Characterization

The silver nanoparticles were preliminary characterized by UV-Visible spectroscopy. The spectra were recorded on HACH UV-Vis Spectrophotometer DR 5000 single beam spectrophotometer from 300 to 800 nm after dilution with distilled water. The solids of suspension were then subjected to FTIR spectroscopy measurements. The measurements were carried out on a PerkinElmer Spectrum RXI.

The particle size distribution of the nanoparticles was determined using dynamic light scattering (DLS) HORIBA Light Scattering Particle Size Analyzer LB-550. Particle size along with its poly-dispersity were assessment based on measuring the time dependent fluctuation of laser light scattering undergoing Brownian motion. Scanning Electron Microscope of nanoparticles were performed by KYKY-EM3200 Digital Scanning Electron Microscope. SEM

images were carried out by drop coating the dispersion containing the particles onto a glass slide after required reaction time. Afterwards, the obtained coating was scanned at a rate of 100 mV s^{-1} in the range $50\mu\text{m}\times 50\mu\text{m}$. The obtained nano-powders was subjected to X-ray diffraction analysis, Philips PW-180, Netherlands. The target was Cu K_{α} with wavelength of 1.5406 \AA and the scanning range was selected between 10° and 100° under the 40 kV generator power and 30mA current.

3. RESULTS AND DISCUSSION

3.1. Optimization of conditions

3.1.1. Optimization of mixing ratio

Preliminary, the formation of silver nanoparticles was monitored through visual assessment. The reaction mixture turned to dark brown color from yellow color within 15 min indicated the synthesis of silver nanoparticles (Fig. 1).

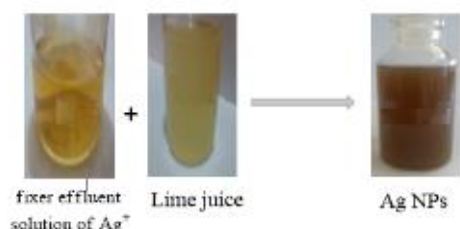


Fig 1 bio-recovery of Ag-NPs from fixer effluent solution of Ag^+ interacted with the prepared lime juice

For obtaining the best conditions the fixer effluent solution (Hospital; 8 gL^{-1} , 4mL) was heated to 70°C . Then, prepared lime juice was interacted with it in four separate experiments with different volume of Lime juice (0.1 [28], 0.2, 6 and 16mL). Afterwards, the temperature was kept 70°C within 15 min time periods with vigorous stirring. Determination of particle size of obtained metallic silver could be the key factor for efficiency evaluation of each experiment. Particle size of obtained Ag-NPs were determined by measuring the random changes in the intensity of light scattered from a suspension of them (Fig. 2). This technique is commonly known as dynamic light scattering (DLS). The particle size determined by dynamic light scattering is the hydrodynamic size. That is, the determined particle size is the size of a sphere that diffuses the same way as target particle. (Fig. 2)

We found that down to 49 nm particles size of metallic Ag were obtained when 0.2mL of Lime juice was interacted with 4mL of fixer effluent (Fig. 2-b). This particles size increased by reducing the amount of Lime juice down to 0.1 mL (Fig. 2-a). 0.2 mL of Lime juice was sufficient, and an excess did not decrease the particles size (Fig. 2-c, d). Moreover, Fig 2-b shows the distribution of particle size is narrow. It is worth to mention that homogeneity of these particles is important in many applications [33].

3.1.2. Optimization of pH, temperature and time period of reaction

As mentioned above the formation of silver nanoparticles was accomplished with browning the color of mixing solution (Fig. 1). So, UV-Visible spectroscopy is a good, cheap and reliable method for evaluation of formation nanoparticles of metals.

Light wavelengths in the 300-800 nm are generally used for characterizing various metal nanoparticles [34].

Spectrophotometric absorption measurements in the wavelength ranges of 400-500 nm [35] are used in characterizing the silver nanoparticles. This characteristic peak is due to the oscillation of conduction band electrons of Ag-NPs known as the surface plasmon resonance (SPR) [36]. UV-Vis spectroscopy was ascertained to check the formation of Ag-NPs at pH 6.

For assessment of the formation of Ag-NPs in the upper pH near to neutral condition, the reaction was done under optimized ratio of fixer effluent solution to lime juice (20:1) at pH 6 by addition of NaOH (0.8mL, 0.5N) to 4mL pre heated fixer solution at mentioned temperature (70°C) for 5 min time period with stirring. Then, the reaction was followed with the addition of Lime juice (0.2mL) and stirring the mixture for additional 15 min. During this time the color of the mixture was changed from pale yellow to dark brown. The UV-Vis spectrum of result solution is shown in Fig 3a.

The UV-Vis spectrum was shown there is no any absorption between 400-500 nm. It means that the Ag-NPs was not formed at pH 6. So, the reaction is not needed to adjust pH. In fact, increasing the pH not only did not improve the particle size but also increased it. This experiment was shown that this bio-recovery is a green method for production of Ag-NPs without needs to artificial chemical compounds such as NaOH. Although, the source of Ag^+ in our experiment is effluent fixer solution which there are difference with AgNO_3 solution in terms of constituent, interferences and nature, but the result in compliance with previous reported works [28]. According to Murphy [27], in these reactions the citrate is performing dual tasks. It strongly complexes the silver ion and also responsible for the reduction of silver ion and acts as a capping agent to the silver metal resulted nanoparticles of Ag. Alternatively, solutions with NaOH shows products that form larger metallic silver particles.

Considering the above mentioned the reaction in the present of NaOH, although nearly all of the citrate would be deprotonated and thus available for capping the silver, there may be competition from the hydroxide ion for the silver ion. Hydroxide is weakly complexing agent for silver ion and could interfere with the capping ability of citrate, consequently lead to the agglomeration of metallic silver particles.

In another try to evaluate feasibility of the reaction in milder condition we did the reaction at 35°C . The color was changed to dark brown after 48h. Then for assessment of resulted mixture UV-Visible spectra was taken (Fig 3b). On the basis of Fig 3b the UV-Vis spectrum was shown there is no any absorption between 400-500 nm. So, as mentioned before this showed at this temperature Ag-NPs was not formed. Thus, 70°C was chosen for our bio-recovery of Ag-NPs as optimal temperature.

In order to determine minimum time of interaction for obtaining best results the reaction was carried out for different time periods under optimized conditions. The UV-Vis spectrum of resulted suspension solutions are shown Ag^+ completely reduced to form silver nanoparticles within 15 min. It can be confirmed by the fact that there is no further change of UV-Vis spectra after elongation time of interaction or addition of NaBH_4 . It is worthwhile mentioning that NaBH_4 is introduced to the as-prepared colloidal solution.

3.2. Characterization of Ag NPs

The recovery of silver as nanoparticles under optimized conditions

	a	b	c	d
mixing ratios fixer effluent : Lime Juice	40:1	20:1	2:3	1:4
Mean value of Ag particle size	160	99	2885	3551

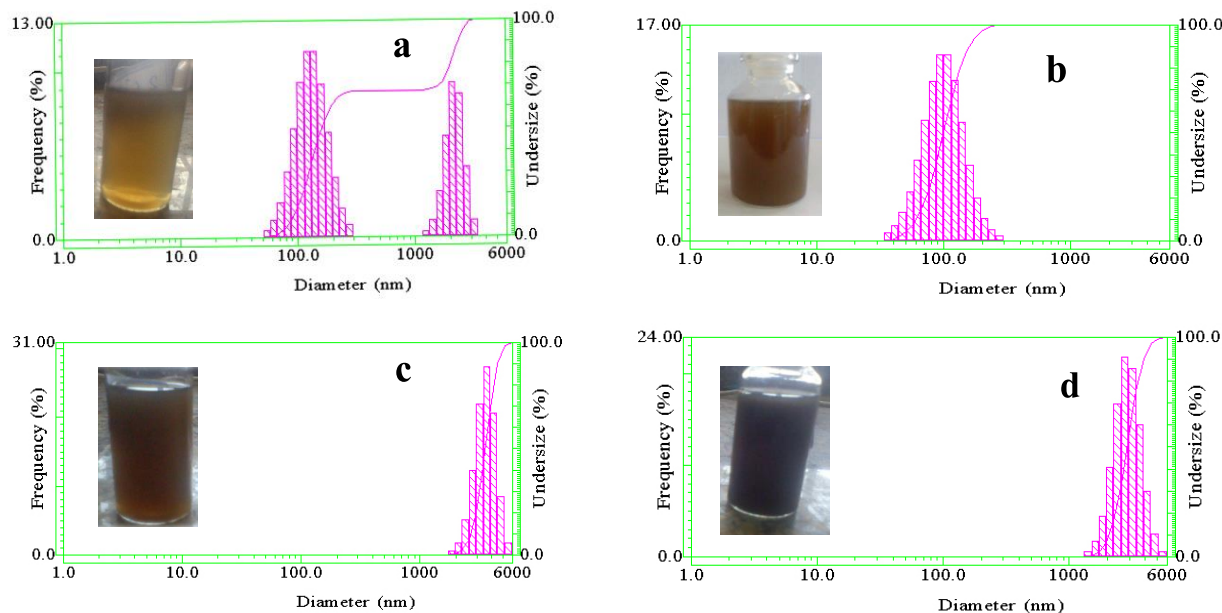


Fig 2 DLS results for interaction of different mixing volume ratios of fixer effluent:Lime juice at 70 °C within 15 min time period a) 4:0.1, b) 4:0.2, c) 4:6, d) 4:16

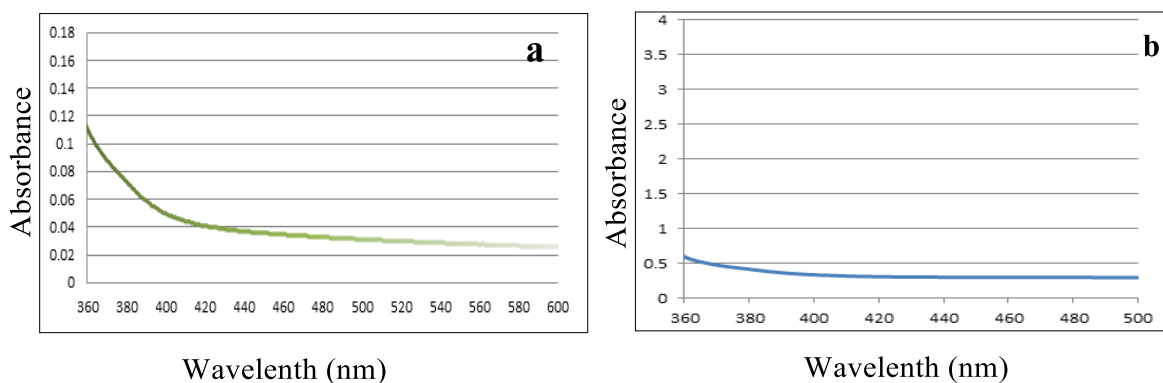


Fig 3 UV-Vis spectrum correspond to interaction of effluent fixer solution and Lime juice under optimized ratio (a) at pH 6 (b) at 35°C

was done. We also examined the process with pure citric acid and ascorbic acid separately instead of Lime juice as reducing and capping agent. In these assessments the reactions were examined with same amount of citric acid and ascorbic acid in optimized volume of Lime juice separately, at 70 °C and pH 6 within 15 min time period. The obtained solutions were characterized by instrumental analysis.

3. 2. 1. UV-Visible spectra

As mentioned above UV-Visible spectroscopy is used for

monitoring the signature of silver nanoparticles due to strong surface plasmon resonance absorption in the visible region. The UV-Vis spectrum of Lime juice before and after interacting with waste photography solution at optimized conditions was shown in Fig 4a. Fortunately, there is no interference absorption between Lime juice and Ag NPs.

In order to determine the stability of bio-recovered of silver in the form of Ag-NPs, the obtained solution of nanoparticles was stored at 4 °C under air condition for 28 days. After this time, without

any shaking or stirring, stability of synthesized Ag-NPs was evaluated by UV-Visible spectroscopy (Fig 4b). Absorption peak at 410 nm in UV-Visible spectrum was confirmed the stability of nanoparticles even after 28 days which can be attributed to surrounding of nanoparticles by citrate or other organic constituent that born with Lime juice.

In another try for evaluation of pure solution of citric and L-ascorbic acids efficiency, 1.368 g of citric acid and 0.8 g of L-ascorbic acid were dissolved in 20 mL deionized water, separately. Then, 2 mL of obtained solutions was added to effluent fixer solution (40 mL) independently, at 70 °C and 15 min. (Fig 5). Based on the obtained results, pure solution of citric acid could be produce Ag NPs (Fig 5b). In contrast, although ascorbic acid has been used for the synthesis of gold nanoparticles [37] but in our experiment, pure solution of ascorbic acid did not give desirable

So, for determination of particles size, dynamic light scattering and SEM image are powerful techniques for the measurement of particles size. It also able to assess dispersion size of particles. For this purpose, particle size analysis data was taken. (Fig 2b & 6) With compression of particle size resulted from interaction of effluent fixer solution with Lime juice and same concentration of obtained from citric acid smaller than interacting with Lime juice. It can be attributed to the capability of citrate for capping the nano pure citric acid solution (Fig 2b & 6) were found the particles size of silver. In the Lime juice maybe other chemical compounds such as ascorbic acid compete with citrate for surrounding particles that have lower capability for capping Ag particles than citrate.

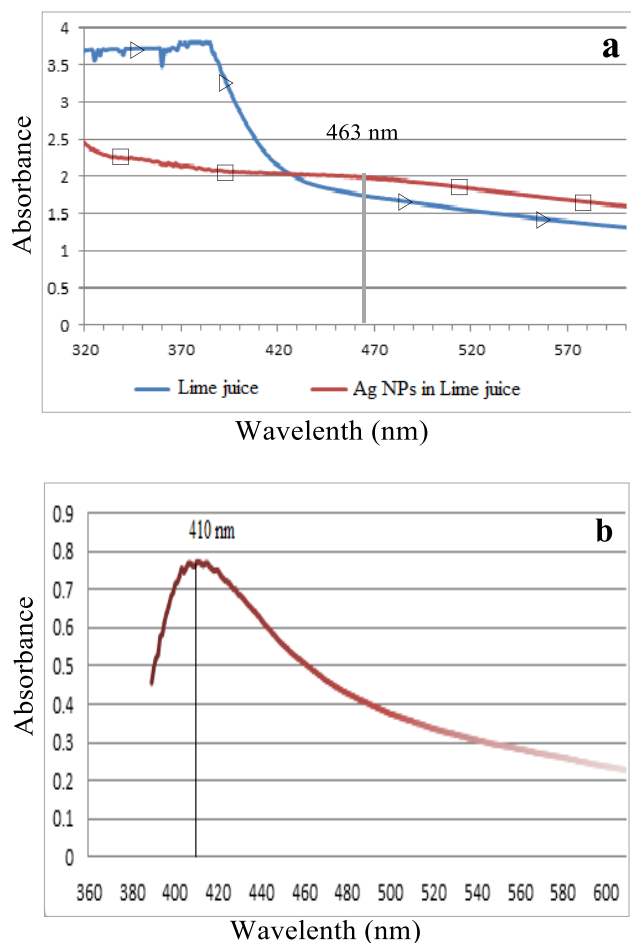


Fig 4 UV-Vis spectrum of Lime juice (a) before (blue) and right after (red) interacting with effluent fixer solution under optimized conditions (b) after 28 days

result (Fig 5a). It may be due to the low concentration of Ag^+ in effluent fixer solution, influence of interferences or weaker reducing capability of it compared with citric acid. This experiment shows the citric acid is responsible for reducing of silver ions.

3. 2. 2. Particle size analysis

Fig 4 and 5b showed the AgNPs were formed in both mixtures.

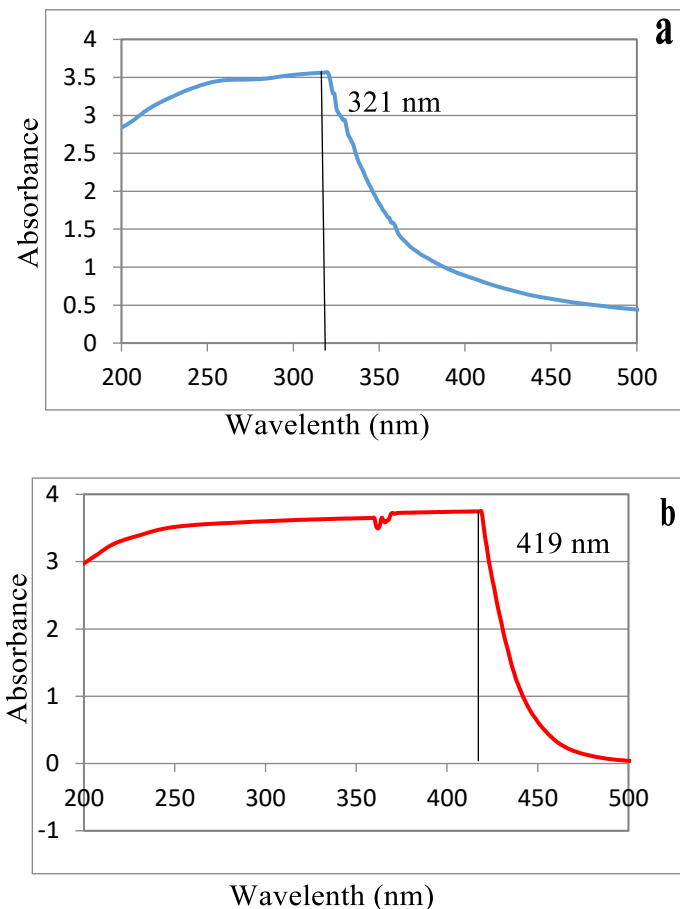


Fig 5 UV-Vis spectrum of (a) L-ascorbic acid and (b) Citric acid after interacting with waste solution with same concentration in the lime juice used for this study

3. 2. 3. FT-IR studies

FT-IR analysis was used for the characterization of the extract and the synthesized nanoparticles (Fig 7). The FT-IR spectra were recorded to identify the possible biomolecules responsible for the reduction of the Ag^+ ions and capping of the bio-reduced Ag-NPs recovered by the Lime juice. The FT-IR spectra of the Lime juice before (Fig 7a) and after (Fig 7b) interaction with effluent fixer solution have showed significant changes. In Fig 10b, marked peak in 1075.78 cm^{-1} can be allocated to the stretching vibration of the C-OH bond from citrate in the Lime juice. Distinct peaks in the region 1272.92 cm^{-1} and 1389 cm^{-1} may be attributed to the presence of stretching vibrations of alcohols, esters and carboxylic

acids. Two segregated peaks in 2921.73 cm^{-1} and 3279 cm^{-1} respectively, related to the stretching vibrations of C-H bonds and the O-H bonds in carboxylic acids and hydroxyl functional groups. Change the position of the clear pick in 1646 cm^{-1} in Lime juice. spectrum related to C=O stretching corresponding to carboxylic acid to 1579 cm^{-1} in Fig 7b shows there is some interaction between carboxyl group and metallic silver. This is confirmed the role of citrate as capping agent. Furthermore, absence of specific picks at $1618, 2143, 3429$ and 3439 cm^{-1} related to thiosulfate group in b spectrum are shown after bio-reduction there is no any interaction between thiosulfate and Ag.

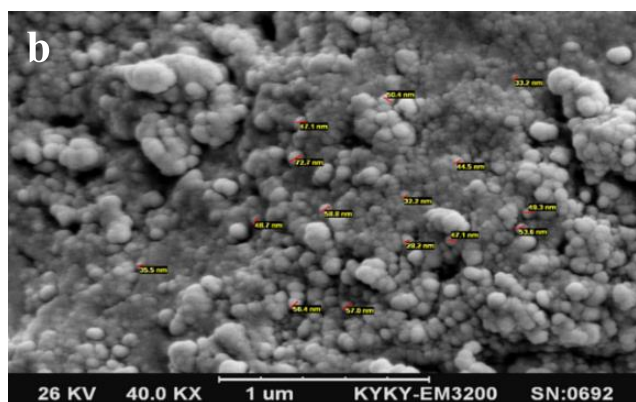
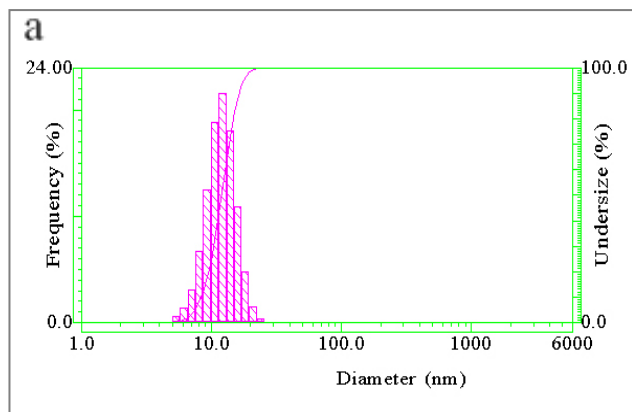


Fig 6 (a) DLS results for citric acid after interacting with waste solution with same concentration in the lime juice used for this study and (b) SEM image

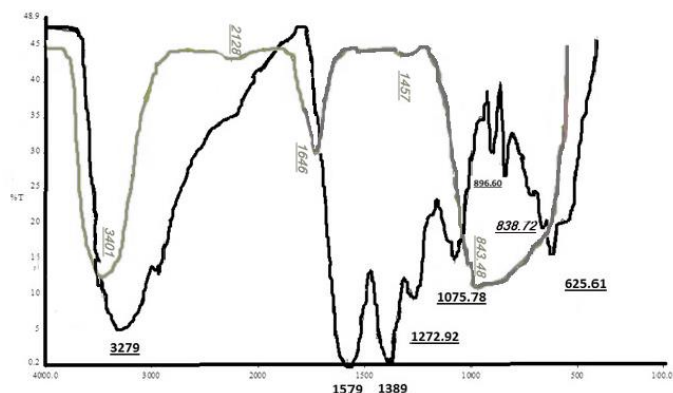


Fig 7 FT-IR spectrum of Lime juice (a) before and (b) after interacting with effluent fixer solution under optimized conditions

3. 2. 4. Morphology studies

In addition of particle size analyzer instrument, scanning electron microscopy (SEM) also able to determine particles size. More than this, SEM images are used for morphological characterization at the nanometer [38]. SEM analysis shows uniform distribution of silver nanoparticles that indicate the nanoparticles are stabilized by capping agents. (Fig 8a, 6b)

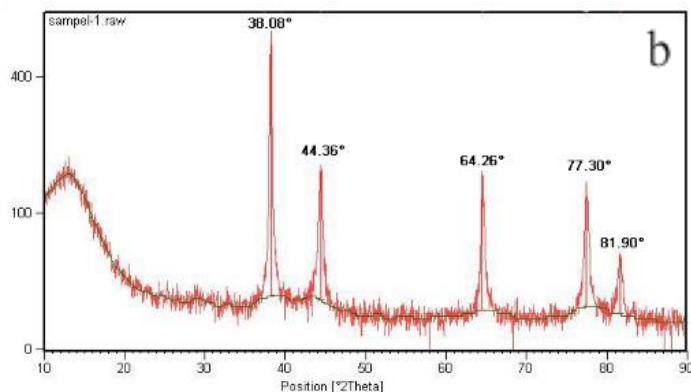
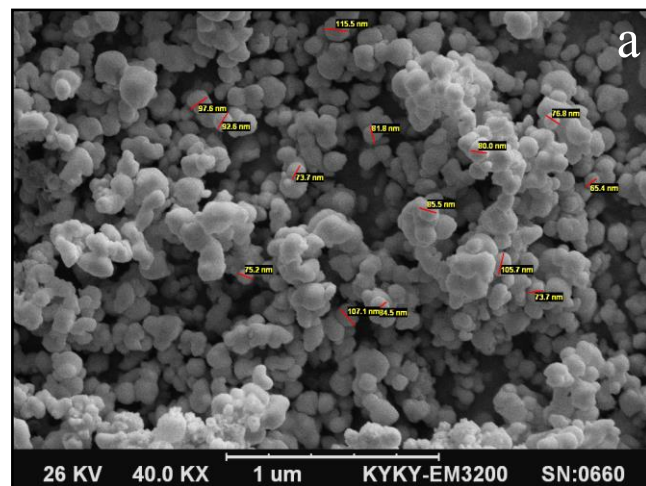


Fig 8 (a) SEM image of Ag NPs obtained from interacted effluent fixer solution with Lime juice and (b) XRD pattern

SEM images of Ag NPs shows AgNPs to be confined within a supporting matrix, likely comprised biomolecules such as citrate acting as a capping agent or stabilizer during synthesis, and thus controlling nanoparticle growth and clustering. Fig 6b corresponds to interacted waste solution with citric acid. The size of nano particles of that is smaller than Ag NPs was obtained from interaction of effluent fixer solution and Lime juice, on the base of SEM images. (Fig 6b & 8a) This is in accordance to particle size analyzer data. Fig 8a was also shown the silver nanoparticles were spherical in shape and dispersity of particle size very close to results were acquired by other techniques in this research and confirmed that.

3. 2. 5. XRD studies

X-ray diffractions used for the phase identification and characterization of the crystal structure of the silver nanoparticles. The crystalline nature of synthesized Ag NPs using Lime juice was confirmed from X-ray diffraction (XRD) patterns. (Fig 8b)

The XRD patterns of obtained nano particles of silver indicated that the structure of Ag NPs is face-centered cubic (fcc) [39]. Furthermore, the silver nanoparticles had a similar diffraction profile and the XRD peaks at 2θ of 38.08° , 44.36° , 64.26° , 77.30° and 81.90° can be indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) Bragg's reflections of the face-centered cubic (fcc) silver crystals, respectively [40]. More over the XRD pattern shows the main crystalline phase was silver and there were no obvious other phases as impurities were found in the XRD patterns (Ag XRD Ref. No. 01-087-0719). The particle size of the Ag-NPs formed were calculated using Debye - Scherrer equation that was almost 84 nm that were good in agreement with SEM and particle size analyzer results.

4. CONCLUSION

An interesting bio-recovery of Silver nano-sized particles as a green recovery method has been developed. This method is a novel, environmental friendly and cost effective method that excludes the use of toxic chemicals as external stabilizing and capping agents and to the best our knowledge this is the first report for producing of silver nano particles from effluent fixer solution. The effects of various process variables like mixing ratio of effluent fixer solution to Lime juice, pH, temperature, interaction time period and concentration were investigated. With mixing ratio of effluent to Lime juice 4:0.2 in 70°C and pH 6 during 15 min of interaction time, nanoparticles below 90nm size with spherical shape and narrow dispersion was produced. The size of nano particles were determined with different techniques and the results of all of them in accordance with each other. FT-IR studies and SEM image showed the presence of bio-organic components which probable acted as a stabilizer for the silver nanoparticles. The effluent solution was interacted with citric and ascorbic acid with same concentration in the lime juice used for optimized mixing ratio, separately. For ascorbic acid nano particles was not formed on the base of UV- Vis spectrum. It presumably can be attributed to the low reducing power of ascorbic acid or weakly capability for capping the particles. The size of nano particles with citric acid was smaller than obtained from Lime juice. It likely due to the strong capability of citrate as reducing and stabilizing of silver nano particles. It is in good agreement with previous work that have been done by other researcher.

5. ACKNOWLEDGMENT

This study was supported by the Iran nanotechnology initiative council and by a grant from Islamic Azad University, Shiraz branch. The authors thank to Shiraz Central Hospital (MRI) and School of dentistry, Shiraz University of medical science for giving us photography waste solution. The authors also declare that they have no conflict of interest.

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Citation: Hamid Reza Safaei *et al.* (2017). Green recovery of silver as crystalline Nano-particles from corresponding waste solutions by Lime Juice as compared with Ascorbic acid and Citric acid, *J. of Physical and Chemical Sciences*.V5I1. DOI: 10.15297/JPCS.V5I1.01

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