

Producing gold nanoparticles from loaded activated carbon and its separation with carbon fiber film formation at the oil/water interface in the acetone-water-sodium chloride system

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Abstract

Due to the wide spread applications of gold in medicine, electronic computational industries, catalysts, and its special application in biological researches and more over by attention to high cost and complicated production of gold nanoparticles (AuNPs) and in the other hand, the importance of substituting the environmental pollutants such as cyanide compounds in most commonly processes of gold recovery from ores and concentrates, finding a simple, economic and environmental way to achieve AuNPs has to be considered. Because of its large surface area, activated carbon (AC) is used in extracting gold. In this research work a new way has been mentioned for production and separation of AuNPs from loaded AC. By heating loaded AC in the air at 300°C for 30 min, gold metal nanoparticles were produced on the surfaces of AC with reducing the gold cyanide complex. The detachment of the AuNPs from AC surfaces was done by two ways: 1. Abrasion of AC by NaCl 2. Using ultrasound; the separation of the detached AuNPs from AC granules abraded by NaCl was done based on the difference between AC and gold density and using water and oil mixture. Effect of abrasion time, salt to carbon weight ratio and pre-washed loaded AC conditions on the amount of gold recovered from loaded AC was evaluated in abrasion method. In a novel approach, separation of carbon from gold-containing aqueous solution was done by addition of acetone in mixture and forming carbon microfibers film at the oil/water interface. Acid washing was done to remove impurities after separating carbon from gold-containing solution. As a result, relatively pure AuNPs were obtained after acid washing.

Keywords: *gold nanoparticles, loaded activated carbon, gold separation from carbon, carbon separation from aqueous solution, abrasion.*

Introduction

The electronic, optical, thermal and catalytic properties of the gold nanoparticles (AuNPs) has made it more popular in the fields of physics, chemistry, biology, medicine, material science and some interdisciplinary fields. Because of the unique physical and chemical properties of AuNPs, these materials

have many uses in sensors, catalysts, electronic devices, medicine and biological researches [1].

Generally, nanoparticles (NPs) can be made with bottom-up and top-down approaches. In the case of bottom-up approach, the procedures such as: 1) redox synthetic methods notably Turkevich-Frens method, Brust method, and Martin method, 2) electrochemical, 3) photochemical, 4) microwave, 5) template, 6) seed-growth, 7) sonochemical, 8) microemulsion (reversed micelles) [2-4]; and in the top-down approach: 1) laser ablation [5], 2) lithography [6], can be involved.

Generally in the bottom-up approach NPs can be produced based on the chemical methods. It is common to use chlorauric acid (HAuCl₄) as initiator in producing AuNPs [7]. Reducing agent can be minerals such as sodium/potassium borohydrate and hydrazine or organic solvents like sodium citrate and ascorbic acid, and stabilizing agents are consisting of polymers such as different polyethylene glycol, polyvinyl alcohol and surfactant like sodium dodecyl sulfate, tween 80, triton [8].

Although the mentioned chemical methods can produce NPs, but reducing agents remain in solution and their removal is very hard. Also, in many cases, the reducing agents are toxic and thus, complicate the use of NPs in medicine applications [9]. On the other hand, the cost of the top-down methods is a bit high and the production of NPs process is usually slow [2].

The main objective of this project is to find a simple and economic way with environmental considerations in order to produce AuNPs by using loaded AC with extraction methods. The metal gold dissolution in cyanide solution beside the oxygen results in dicyanoaurate(I) salts forming. This process is used in the most of gold recoveries. After leaching the gold ores and concentrates with cyanide, AC is used in gold recovery [10]. AC can adsorb the molecular and ionic species because of AC's large surface area.

Gold loaded adsorbent in Lin et al. [11] method has been combusted after its separation from solution. AuNPs have been separated from solution after acid washing and dissolving the impurities in the ash, by using centrifuge. This process involves AC combustion which has several important drawbacks including:

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I) high economic loss,
 II) the necessity of long-term exposure of AC to high temperatures which itself uses lots of energy and
 III) the incomplete separation of carbon from gold due to the imperfect combustion of AC.

In 2010, Vorob'ev-Desyatovskii et al. [12] reduced the metallic AuNPs on the AC surfaces with considering the thermal behavior of the gold(I) cyanide complex. The adsorption and thermal reduction of the $[\text{Au}(\text{CN})_2]^-$ center happen on the special AC surfaces that are energetically very suitable places. Fig. 1 shows the SEM image from loaded AC, heated in the air at 300°C for 30 min.

These results show that metallic AuNPs are reduced, regarding the thermal stability of the adsorbed gold cyanide complex on loaded AC and controlling the other conditions. In the previewed studies for complete reduction of AuNPs, AC is pre-washed with sulfamic acid primarily, and then process of gold adsorption is conducted on it. So, it also can be concluded that it can be tried to reduce AuNPs on AC surface without combusting AC considering the thermal stability of gold cyanide complex on the surface of industrial loaded AC. This procedure leads to achieving pure AuNPs by developing a method to separate AuNPs from loaded AC. In this process, heating time and temperature of cyanide complex reduction are less than loaded AC combusting method for AuNPs production which was time and cost consuming.

The detachment of the AuNPs from AC surface was done in two ways: 1. Abrasion of AC by NaCl 2. Using ultrasound (US); the separation of the detached AuNPs from AC granules abraded by NaCl was done with density separation. The gold and graphite density are, respectively, 19.30 and 2.09-2.23 g/cm^3 ; but in attention to AC amorphousness, it should have lower density relative to graphite. So it can be said that AC density is about or less than 2 (without considering pores volume). Thus, a liquid with a density larger than 2 g/cm^3 can be an ideal choice for separating the materials.

There are liquids that are used for separation such as bromoform (CHBr_3), 1,6-diiodohexane, diiodomethane, thallium malonate formate, sodium poly tungstate (SPT) and lithium heteropolytungstate (LST). There are two factors limiting the use of these liquids in separation. First, most of these liquids are halogenated organic liquids which have health hazards. Liquids that are based on tungstate are safer, but also expensive. Second, in some cases that density difference or grain size is small; the duration of separation will be longer.

In this experiment, AC density is 0.47 g/cm^3 . If the water entrance into AC pores can be prevented, AC will be floating on the water because of the low density and the gold separates from AC. Regarding the above discussion, it seems that oil is a suitable choice and therefore oil-water (O/W) mixture can separate gold and AC from each other.

In simple and effective way of AC abrasion with NaCl, after AuNPs separation from AC by using the O/W mixture and the dissolution of salt in the water,

the complete separation of carbon from AuNPs-containing salt-water mixture do not occur. As a new approach for carbon atoms separation, acetone is used in order to cause phase separation in ternary $\text{NaCl}-\text{H}_2\text{O}-\text{ACT}$ system (ACT stands for acetone as component). By addition of the acetone to the system, carbons combine together at the O/W interface and separate from salt water mixture. The bottom phase in phase separation contains AuNPs plus salt-water solution and impurities, which will result in pure AuNPs after acid washing.

Experimental procedure

Materials

Coal-based loaded AC was obtained from the Mouth Gold Plant of Iran. The characteristics of AC are listed in Table 1. The vegetable oil used in this research work was prepared from a local market and edible quality that contains mixture of several types of fatty acids. The vegetable oil comprised of 5.11-9.5 saturated fatty acid, 24-32 oleic acid, and 56.3-62.6 linoleic acid. Other chemical reagents used in this experiment were of analytical grade.

Table 1: Activated carbon characteristics

M.B.D	0.47 g/cm^3	P.S.D	
C.T.C	55%	MESH	6×12
Moisture	1.4%	+6	3.8%
Ash	3.0%	6×8	56.1%
Hardness	98.7%	8×12	38.6%
pH	9.8	-12	1.5%
	SE.NO	CSS	61255

Determination of the Au content in samples

For determination of the Au concentration in ash or powder was used aqua regia (3 parts concentrated HCl and 1 part concentrated HNO_3) for digestion the powder in it. The ashes or powdered sample heated twice on a hot plate with aqua regia evaporating each time to moist residue. The residue was then digested twice with concentrated HCl and evaporated each time to moist residue. The solution was filtered when it was cooled.

For the analysis, 50±0.01 g amount of loaded AC was taken in silica crucible, and were heated in the air at 650±1°C for 5 h to burn off the carbon, and the mineral residue was digested in hot aqua regia.

Characterization instruments

The concentration of Au was analyzed with atomic absorption spectrophotometer (GBC Avanta PM, Australia). The morphology and composition of the carbon fiber film was determined using a scanning electron microscope VEGAI SEM (TESCAN a.s., Czech Republic) coupled with an EDX system QUANTAX QX2 (RONTEC, Germany). The particle size was determined by dynamic light scattering (DLS) method using Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK).

Procedure

Thermal stability of $[\text{Au}(\text{CN})_2]^-$ on the AC

The study of thermal stability of $[\text{Au}(\text{CN})_2]^-$ on the AC and selection of the best process for AuNPs production, loaded AC were contacted with acidic and neutral solutions. Three batches of 50 ± 0.01 g amount of loaded AC were each taken in beakers (1L volume), contacted with 500 ± 1 ml of: 1) 0.01 M HCl; 2) 0.1 M NaCl; 3) distilled water for 24 h. Portions of the washed, loaded AC samples were dried in an oven at a temperature of $105 \pm 1^\circ\text{C}$ for 8 h. Then samples were transferred into Pyrex container ($28\text{cm} \times 12\text{cm}$) and heated in the air at 300°C for 30 min.

Detachment of AuNPs by abrasion of AC

In this method, the AC and NaCl were taken in a plastic container. Then the container was swirled in a planetary mill (56 rpm). This operation can do handy, but planetary mill was used to keep the conditions constant. The time of abrasion was equal 0.5, 1 and 2 h. After the predetermined time period, the AC abraded and salt were transferred in a beaker (1L volume) containing oil/water (O/W) mixture. At first water, and then oil was poured onto beaker, followed by the AC and salt poured into O/W mixture. The amount of the water was changed proportional to the amount of salt. The salt was dissolved in water. AC granules, floating on the oil, were collected. After separating of AC granules and oil, AuNPs-containing solution that was oily yet, was transferred to a separating funnel. Density separation between AC and Au was occurred in this step. Then the bottom phase was poured out and evaporated. The Au content in powder was measured by its digestion with aqua regia.

Detachment of AuNPs from AC via US

In the second method, 50 ± 0.01 g pre-soaked AC with distilled water was heated at $300 \pm 1^\circ\text{C}$. After drying, it was poured in a beaker and then distilled water was added to the beaker. The beaker was shaken by sonication at 50 Hz for 4 h. Then the beaker was transferred to a separating funnel. The separating funnel prevents from the entrance of AC granules to the beaker. The bottom phase was poured out, evaporated and the Au content was measured by its digestion with aqua regia.

Carbon separation from water-salt mixture with formation of carbon fiber film at the O/W interface

After the dissolution of salt in the water and the collection of AC granules, the oil-water-salt mixture transferred to a separating funnel. Then the bottom phase was poured out and the AuNPs-containing oil-water-salt mixture was shaken by US for 1 h. After sonication, the suspension was transferred to a separating funnel and acetone was added to the system. By controlling the amount of the acetone and water/salt solution, the separation of the carbons from the solution was occurred. Carbons were combined together at the O/W interface, simultaneously. The combination of the carbons was visible to the naked

eye. Then the bottom phase containing AuNPs was poured out and dissolved in dilute HCl, HNO_3 and HF acids. Acid washing was used to remove impurities such as oxides of calcium, potassium, sodium and silicon, and then pure AuNPs are obtained. If the Au content in the loaded AC was higher, AuNPs could be separated from solution by centrifuge.

Results and discussion

AuNPs recovery from loaded AC via abrasion

The measurements showed that the average of content of Au in a 50 ± 0.01 g loaded AC was 35.2×10^{-6} g. The Au recovery values from AC abraded by NaCl followed by separating with O/W mixture are shown in Table 2.

Table 2: AuNPs recovery from loaded AC by means of abrasion with different conditions (amount of AC: 50 g, volume of solution: 500 ml, time of contact: 24 h)

Sample	Pre-washed conditions	Abrasion time (h)	Salt to AC weight ratio	Quantity recovered Au ($\text{g} \times 10^{-6}$)
1	Water	2	2	20.8
2	0.1 M NaCl	2	2	20.8
3	0.01 M HCl	0.5	2	3.24
4	0.01 M HCl	1	2	4.32
5	0.01 M HCl	2	2	28.8
6	0.01 M HCl	2	0	0
7	0.01 M HCl	2	1	22.4
8	0.01 M HCl	2	3	35.2

Effect of abrasion time on the quantity of AuNPs recovered from loaded AC

According to Table 2, the AuNPs recovery value is increased by increasing the abrasion time. Comparing these results and Au content in loaded AC, it can be observed that about 81% and 100% of the gold was recovered under condition 5 and 8, respectively. Also, the effectiveness of pre-soaked conditions on the gold recovery values was negligible. In Zadra process and Elution with Organic Solvents, 2 days and 6 h are required for elution, respectively [10]. However, in this experiment, about 100% of the Au from loaded AC was recovered by means of abrasion by NaCl. In fact, the gold from loaded AC is recovered by using of simple and quick method based on density separation that was not used toxic cyanide.

Effect of NaCl on the quantity of AuNPs recovered from loaded AC via abrasion

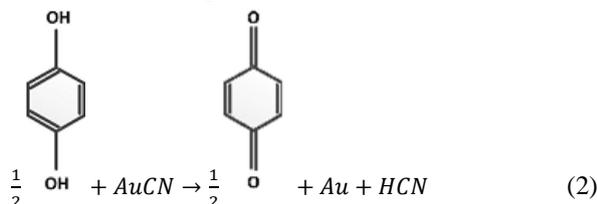
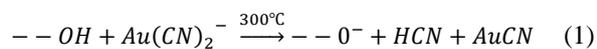
The results, as shown in Table 2, indicate that in the absence of salt, the Au is not recovered at all. By increasing the salt to AC weight ratio, the quantity of AuNPs recovered is increased. According to AC characteristics that have large specific surface area, a larger amount of salt is required to abrade the AC surfaces.

Effect of pre-washed loaded AC on the quantity of AuNPs recovered via abrasion

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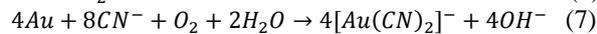
The decomposition of gold(I) cyanide complex adsorbed on the AC surface begin after 240°C and the complete reduction of Au occurs on 300°C. The reduction of Au(I) on AC happens in two steps. In the first, according to Eq. (1), anion reacts with the proton of the acid group of the carbon in AC and results in HCN. Then, as the second step AuCN is reduced by hydroquinone like centers that in this case results in HCN with metallic gold [12, 13].



According to reactions 1 and 2, in acidic conditions, the availability of H^+ is responsible of the formation of HCN and also the reduction of $\text{Au}(\text{CN})_2^-$. So, the quantity of AuNPs recovered from the loaded AC is increased. In the neutral conditions (water and 0.1 M NaCl) the AuNPs recovery values remain unchanged. This result indicates that in equal pH, ionic strength difference in solutions has no effect on the quantity of AuNPs recovered.

Effect of US on the quantity of AuNPs recovered from heat-treated loaded AC

The amount of 1.25×10^{-6} g AuNPs is recovered from a 50 ± 0.01 g amount of heat-treated loaded AC by sonication at 50 Hz for 4 h, which is considered to be a very small quantity. Already, in gold stripping processes, US was used to enhance the desorption of Au from the AC. Feng et al. [14] have suggested two reasons as the explanation of the improvement of the elution of Au from AC via US. First, the generation of H^* radicals from the following reactions:



causes the reduction of the dissolved oxygen according to Eq. (6). So, desorption of Au from the AC could increase by decreasing the dissolved oxygen, as shown in Eq. (7). Second, the eluent pH increased by using US and thus Au desorption increases, as shown in Eq. (7).

In their study, AC was eluted by pre-soaking in 1% w/v NaOH and 0.1% w/v KCN. Then gold elution from AC was investigated by sonication at 40 kHz. The frequency used in the present experiment is 50 Hz which is lower than 40 kHz. Thus, it can be concluded that this quantity of Au recovered from AC, can also be related to metallic Au which has not chemical bonding with the AC surface. So, based on the data (Table 2), the complete reduction of gold compounds to metallic Au is not reachable in all examined conditions; this means that US was effective in gold recovery for both metallic and gold cyanide complex

state. These results show that the abrasion method is better in comparison with the US method regarding both the time and the quantity AuNPs recovered.

Carbon separation from water-salt mixture

For further understanding of this process, the phase diagram of the ternary NaCl-H₂O-ACT system was theoretically studied at standard conditions. The NaCl-H₂O-ACT phase diagram is shown in Fig. 2. The phase diagram of this system has been taken from [15]. The black region indicates the favored region for phase separation. In this separation, the bottom phase and the top phase were the water-based solution and the organic-based solution, respectively. Acetone is found to be efficient extractive agent in this experiment.

After the carbon separation, carbon fiber film was formed at the O/W interface. Fig. 3 and 4 show the SEM images of carbon fiber precipitation in NaCl-H₂O-ACT mixture after evaporation of H₂O and ACT. The carbon nanospheres were observed also in Fig. 4. The EDS analysis (Table 3) of the area marked by arrow in Fig. 4 shows the presence of carbon and NaCl. Sodium and chlorine have the equal atomic percent (%at) which is because of the precipitated salt under carbon fiber film. The presence of Au in this precipitation was not observed in the EDS (Fig. 5). That is probably because of the low metallic fraction present, small size of the AuNPs and the low sensitivity of the used method. Thus, DLS method was used for detecting the AuNPs.

Table 3: EDS result of the area marked by arrow in Fig. 4

Element	wt.-%	at.-%
Carbon	42.49	64.06
Sodium	23.80	18.75
Sulfur	0.17	0.09
Chlorine	32.75	16.73
Potassium	0.58	0.27
Calcium	0.20	0.09
Gold	0.00	0.00

CMFs were formed by combining the carbon nanographite particles together. AC consists of 3D disordered networks of nanographite (graphene) particles [12]. Self-assembly of nano- or microsized particles at the liquid- liquid interface such as O/W is an approach to fabricate two-dimensional array [16]. The interfacial tension of O/W interface is high, and thus the assembly is highly dynamic [17]. According to [16], the difference in wettability of the carbon by the oil and water was caused the interface to form a meniscus around each carbon, created capillary forces and formed a particle monolayer at the O/W interface. If the surface tensions of the particle-oil, particle-water and oil-water interface are denoted by γ_{po} , γ_{pw} and γ_{ow} , the three phases contact angle as the following Young's equation is:

$$\cos \theta = (\gamma_{po} - \gamma_{pw}) / \gamma_{ow} \quad (8)$$

And the interfacial energy (ΔE) can be given by [17]:

$$\Delta E = -\pi r^2 \gamma_{ow} (1 - \cos \theta) \quad (9)$$

where r represent the equivalent radius of CMFs.

In this experiment, by means of abrasion of the AC and separation of the granular AC from salt-water solution by using the O/W mixture, nanographite particles stayed in the mixture. Then US radiation forced the O and W phases into numerous drops. Thus, by creating a large interfacial area between O and W, carbon particles were preferentially adsorbed at the O/W interface. By addition the acetone, ΔE is reached a minimum, the combination of these particles together occurs at the top-phase according to the procedure given previously, then CMFs film is formed and the carbons separate from the solution.

Size of the AuNPs

The size histogram of AuNPs is illustrated in Fig. 6 mean hydrodynamic size of 191 nm was obtained for AuNPs from DLS measurement.

Conclusion

In this study, a simple and economic method based on the environmental considerations is introduced to produce and separate the AuNPs from the loaded AC. By heating loaded AC in the air at 300°C for 30 min, gold metal nanoparticles were produced on the surfaces of AC with reduction of the gold cyanide complex. The detachment of the AuNPs from AC surfaces was occurred in two ways: 1. Abrasion of AC by NaCl 2. Using US; The influence of thermal stability of $[\text{Au}(\text{CN})_2]$ on the loaded AC were investigated under the acidic and neutral condition. By increasing the weight ratio of salt to AC, the abrasion time and acidic conditions, the amount of AuNPs recovered was increased and about 100% of the Au from loaded AC was recovered via the abrasion when the weight ratio of salt to AC equals 3 and pre-washed with 0.01 M HCl for 2 h. It is also observed that in a constant pH, ionic strength difference in solutions shows no effect on the quantity of AuNPs recovered. The results show that the abrasion method was better in comparison with the US method regarding both the time and the quantity AuNPs recovered.

In a novel approach, the O/W mixture was used for separation of detached metallic gold from AC and carbon fiber film formation at the O/W interface using phase separation in ternary water-acetone-sodium chloride system. Acid washing was done to remove impurities after separating carbon from gold-containing solution. The relativity pure AuNPs are obtained after acid washing.

Figures

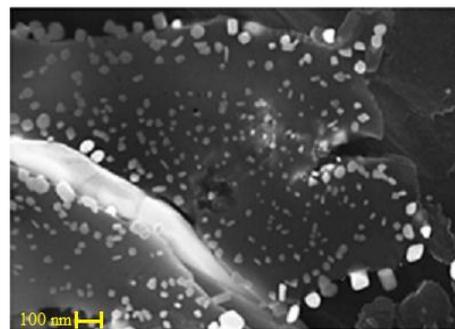


Fig. 1: SEM image of the AuNPs on the AC after heating at 300°C. Scale: 100 nm [12].

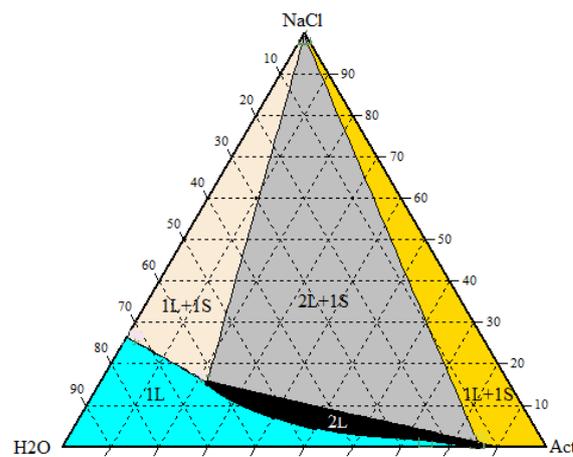


Fig. 2: H₂O-ACT-NACl phase diagram.

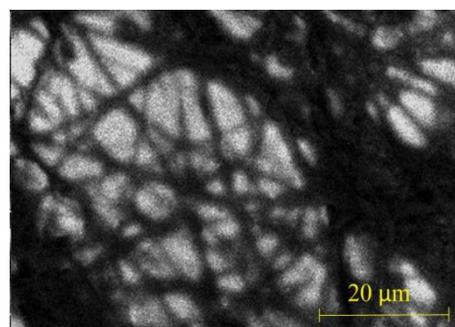


Fig. 3: SEM image of CMFs precipitated in acetone-water-salt mixture.

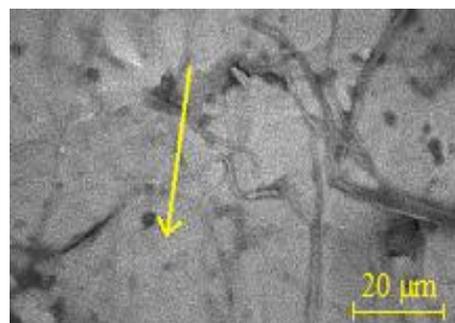


Fig. 4: SEM image of CMFs precipitated in acetone-water-salt mixture.

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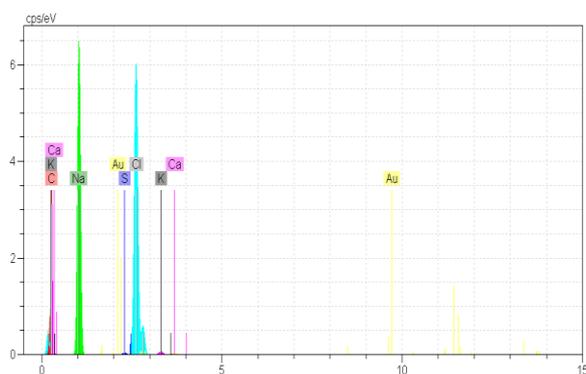


Fig. 5: EDS result of the area marked by arrow in Fig. 4.

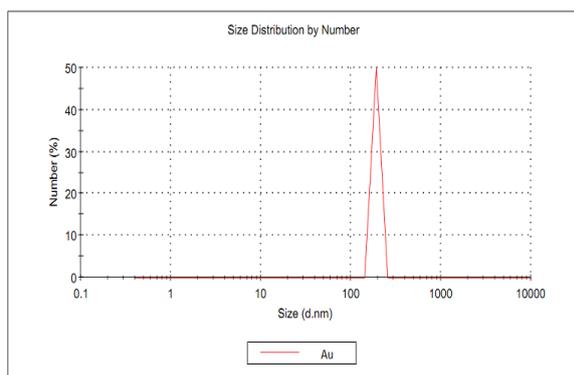


Fig. 6: Size histogram of AuNPs. This data was obtained from DLS measurement.

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