

## Catalytic reduction of 4-nitrophenol using magnetic biostabilised silver nanoparticles

Salsadhila Bt. Jusoh and Mustafa Shamsuddin\*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

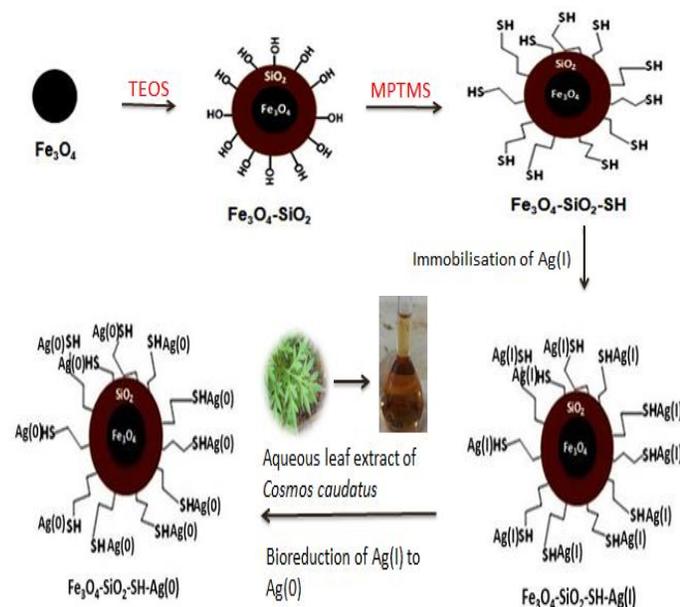
Corresponding Author: mustaffa@kimia.fs.utm.my

### Article history :

Received 20 June 2017

Accepted 21 July 2017

### GRAPHICAL ABSTRACT



### ABSTRACT

Due to their high surface area to volume ratio, silver nanoparticles (AgNPs) have higher reactivity and made them a powerful tool for removal of contaminant in aqueous system. Green synthesis of AgNPs utilizing plant extract has been suggested as possible eco-friendly alternatives to chemical and physical methods. Due to their higher reactivity, AgNPs have tendency to agglomerate resulting in large particle size. Ligand assisted method employing functionalized ligands will covalently anchor the AgNPs onto the solid support thus controlling the AgNPs particle size and preventing agglomeration. In this research, the AgNPs biosynthesised using *Cosmos caudatus* leaf extract were successfully immobilised onto 3-mercaptopropyltrimethoxysilane (MPTMS) functionalised silica-coated magnetite. The magnetic biostabilised AgNPs were characterised using FTIR, XRF, XRD and AAS analyses. FTIR spectroscopy confirmed that the biomolecules present in the *Cosmos caudatus* leaf extract act as reducing and capping agents. The amount of sulphur as determined by XRF was  $3.52 \text{ mmol g}^{-1}$ . The XRD diffractogram showed that the crystalline AgNPs have been immobilised on the thiol-functionalised silica-coated magnetite. The average crystallite size of AgNPs calculated using Debye Scherrer equation is  $27.52 \text{ nm}$ . The Ag loading in the magnetic biostabilised AgNPs determined by AAS is  $0.42 \text{ mmol g}^{-1}$ . The catalytic performance of AgNPs in the reduction of 4-nitrophenol to 4-aminophenol was investigated. The magnetite supported biostabilised AgNPs show good catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess  $\text{NaBH}_4$ . The magnetic catalyst can be efficiently separated from the reaction mixture using an external magnet.

**Keywords:** Silver nanoparticles, 3-mercaptopropyltrimethoxysilane, *Cosmos caudatus* leaf extract, catalytic reduction of 4-nitrophenol.

© 2017 Dept. of Chemistry, UTM. All rights reserved

## 1. INTRODUCTION

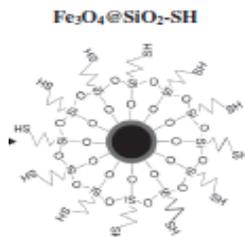
Nanotechnology or nanoscience has become a great trend nowadays especially in catalysis. It becomes one of the major breakthroughs of modern science, enabling materials of distinctive size, structure and composition to be formed. Such materials in nanodimension exhibit a variety of unique chemical, physical and electronic properties than their bulk counterparts [1]. Precious noble metal such as silver has gain a lot of attention as a useful catalyst in homogeneous and heterogeneous system.

Nevertheless, there are many conventional methods in synthesizing AgNPs such as evaporation – condensation, laser ablation and reduction reaction using toxic reducing agents such as hydrazine and sodium borohydride. However, these methods usually lead to the undesirable small clusters of particles and aggregation [2]. Thus, eco-friendly methods such as biological methods using plant extract has been applied for a safer and economical synthesis. [3]

Biosynthesis of AgNPs employing *Cosmos caudatus* leaf extract has been successfully grafted onto 3-mercaptopropyltrimethoxysilane (MPTMS) functionalised silica-coated magnetite. The ease of separation of silver nanoparticles from reaction mixture is due to the presence of superparamagnetic magnetite ( $\text{Fe}_3\text{O}_4$ ) using only external magnet.

4-nitrophenol is one of the common organic waste water pollutants which is widely used in the preparation of pesticides, explosives and pharmaceuticals industries. This compound poses significant health risks due to its carcinogenic activities. On the other hand, 4-aminophenol is an important intermediate for the production of pharmaceuticals substances, photographic materials and rubber materials. Since the reduction of the nitro group into an amine is an important process,

this present study focusing on the application of biosynthesized AuNPs for the reduction of 4-nitrophenol to 4-aminophenol with the presence of excess  $\text{NaBH}_4$  as reductant [4].



**Figure 1** MPTMS modified silica-coated magnetite nanoparticles

This research will focus on synthesising and characterisation of magnetite supported biostabilised silver nanoparticles as well as the catalytic performance of the as-prepared nanocatalyst in the reduction of 4-nitrophenol.

## 2. EXPERIMENTAL

The experiment involved a few stages, starting from the preparation of magnetite until the reduction of 4-nitrophenol using silver (Ag) nanocatalyst.

### 2.1 Preparation of magnetite ( $\text{Fe}_3\text{O}_4$ )

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is prepared via co-precipitation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions.

### 2.2 Preparation of silica-coated magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2$ )

Dried magnetite ( $\text{Fe}_3\text{O}_4$ ) from previous reaction is added with 125 mL deionized water and poured into the round-bottomed flask containing 300 mL of ethanol. While stirring under  $\text{N}_2$  atmosphere, a mixture of 200 mL ethanol with 4 mL concentrated  $\text{NH}_3$  is added into the flask. The mixture is left stirred (850 rpm) at room temperature for 15 minutes. 10 mL of tetraethylorthosilicate (TEOS) is then added dropwise within 2 minutes and the solution mixture is vigorously stirred (850 rpm) for 16 hours at room temperature.

### 2.3 Preparation of 3-MPTMS functionalised silica-coated magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH}$ )

The synthesised silica-coated magnetite nanoparticles,  $\text{Fe}_3\text{O}_4\text{-SiO}_2$  (500mg) are dispersed in dry toluene (100 mL) by immersing the round-bottomed flask in an ultrasonic bath for 15 minutes. The solvent is then removed by using external magnet. Dry toluene (100 mL) is added to the round-bottomed flask and 3-MPTMS (1 mL) is added dropwise. The solution is stirred (200 rpm) under  $\text{N}_2$  atmosphere for 24 hours.

### 2.4 Immobilisation of Ag(I) ions on 3-MPTMS functionalised silica-coated magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH}$ )

Two batches of 3-MPTMS functionalised silica-coated magnetite (100 mg) are prepared. Silver nitrate solution (45.7198 mL; 1 mmol) is added to each batch and are shake for 24 hours. The final product is recovered by using external magnet and washed twice with deionized water.

### 2.5 Preparation of *Cosmos caudatus* leaf extracts

The cleaned and dried *Cosmos Caudatus* leaves are ground using an electrical blender and sieved by using a 20 mesh sieve. 4 g of finely ground dried leaves are extracted with 200 mL of deionized water using Soxhlet extraction method.

## 2.6 Bioreduction of Immobilised Ag(I) ions on MPTMS-Functionalised Silica-Coated Magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH-Ag(I)}$ )

A calculated amount of  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH-Ag(I)}$  is treated with a known volume of aqueous *Cosmos Caudatus* leaf extract. The mixture is stirred at room temperature for 24 hours. The bioreduced  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH-Ag(0)}$  nanoparticles is magnetically collected from the solution, washed with deionized water three times and allowed to dry in a vacuum desiccator.

## 2.7 Reduction of 4-nitrophenol

The reduction of 4-Nitrophenol by the synthesised  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH-Ag(0)}$  nanocatalyst is done in the presence of excess amount of  $\text{NaBH}_4$  and monitored by UV-Vis spectrophotometer in the range of 200 – 500 nm. 4-Nitrophenol (2.5 mL; 0.1 mM) is mixed with freshly prepared  $\text{NaBH}_4$  (2.5 mL; 20 mM). Subsequently, a known amount of nanocatalyst is added to the solution and UV-Vis spectra are recorded every 5 minutes.

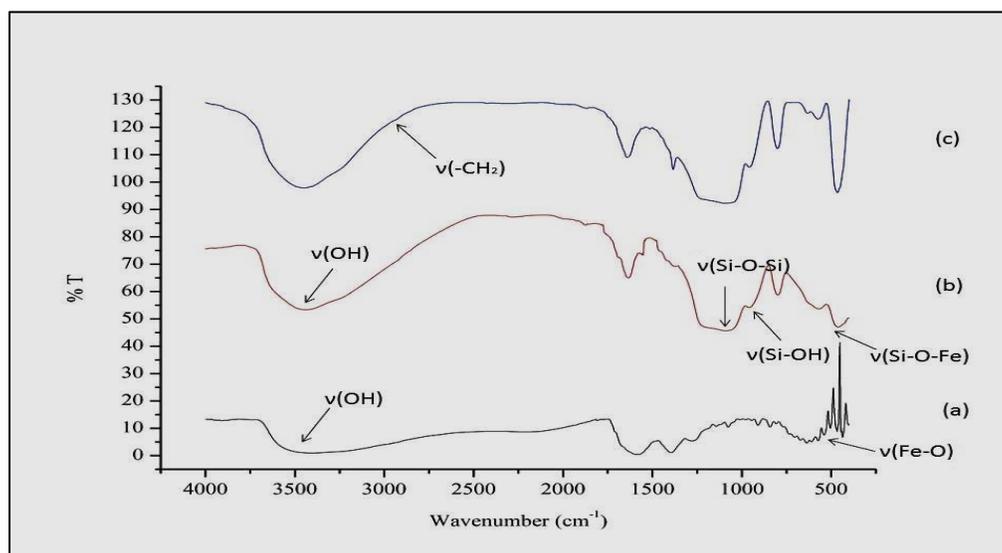
## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis and characterisation of catalyst support

Synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ), silica-coated magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2$ ) and MPTMS-functionalised silica-coated magnetite ( $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH}$ ) is verified by FTIR and XRF analyses.

From the FTIR analysis, the absorption band at  $572\text{ cm}^{-1}$  appeared to be  $\text{Fe}_3\text{O}_4$ . There was a broad absorption band at  $3400\text{ cm}^{-1}$  due to the O-H stretching vibration, which corresponds to hydroxyl groups on the surface of iron oxide which can be assigned to the adsorbed water molecules [5]. A broad peak observed at  $1114\text{ cm}^{-1}$  was attributed to the stretching band of Si-O-Si whereas the peak at  $463\text{ cm}^{-1}$  is an indication of the presence of Si-O-Fe [6]. A broad absorption band can be seen at  $3432\text{ cm}^{-1}$  due to O-H stretching vibration from the silanol groups on the surface of silica.

A band which appeared at  $2898\text{ cm}^{-1}$  was attributed to the stretching of  $-\text{CH}_2-$  of alkyl chain, indicating that MPTMS were successfully functionalised onto the surface of  $\text{Fe}_3\text{O}_4\text{-SiO}_2$ . Due to relative small amount of thiol and poor sensitivity of infrared (IR) to the thiol group, the peak indicating the (SH) group cannot be observed. Thus, XRF analysis was done showing an amount of 3.52 mmol of MPTMS molecules present in every 1 gram of  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH}$  sample.

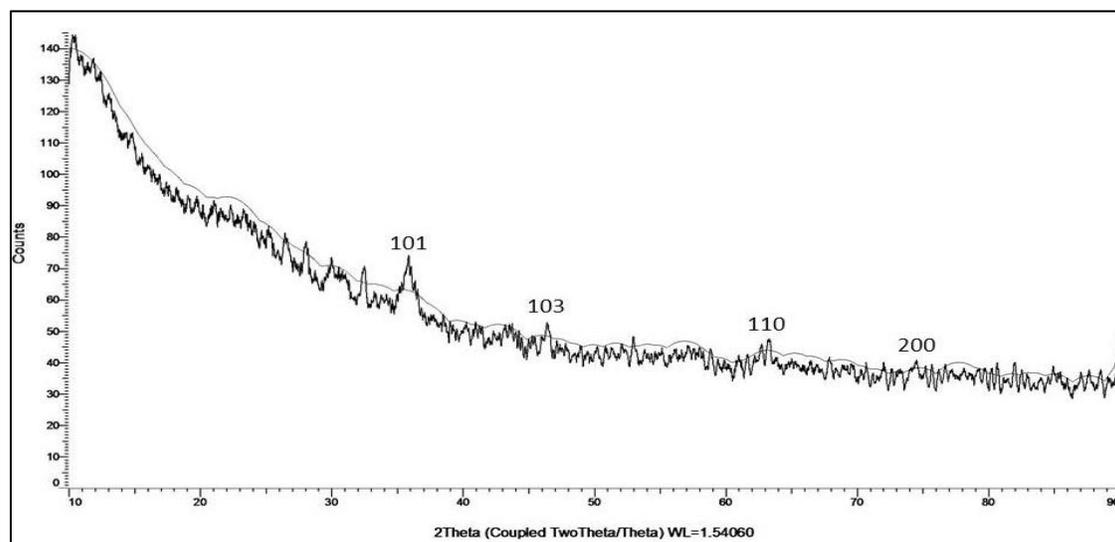


**Figure 2** The FTIR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4\text{-SiO}_2$  and (c)  $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-SH}$ .

### 3.2 Synthesis and Characterization of Silver Nanoparticles (AgNPs)

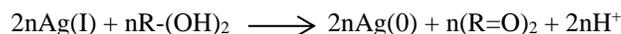
The crystalline structure of biostabilised AgNPs deposited onto Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-SH was verified using X-ray diffraction analysis. The diffractogram of AgNPs are shown in the given figure 3. The Bragg reflection peaks at 2θ of 37.04°, 45.31°, 64.52° and 76.01° are corresponding to the (101), (103), (110) and (200) lattice planes of hexagonal AgNPs, respectively. The peak assigned to the (101) plane is more intense than others, suggesting that it is the predominant orientation [7]. The average crystallite size of AgNPs calculated using Debye Scherrer equation (Eq. 1) was 27.52 nm, whereby D is the crystallite size, K is the dimensionless shape factor (1.0), λ is the X-ray wavelength (1.54060 Å), β is the line broadening at half the maximum intensity (FWHM) in radian and θ is the Bragg angle in degrees.

$$D = K\lambda/\beta \cos \theta \quad (\text{Eq. 1})$$



**Figure 4.3** XRD pattern of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-SH-Ag

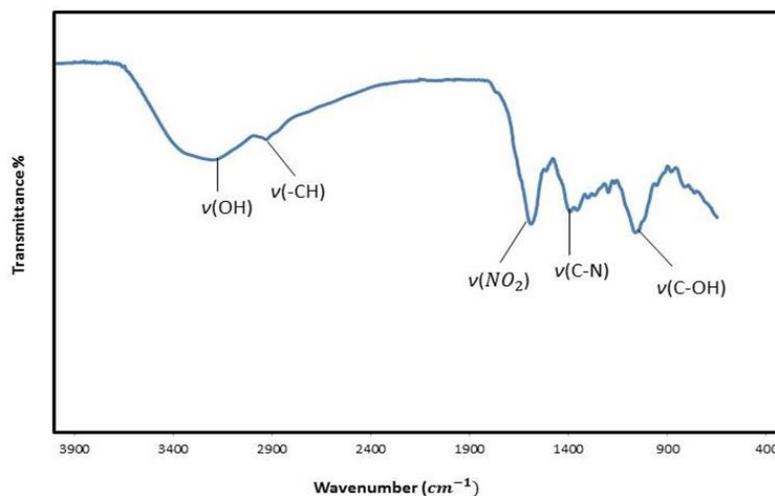
Biomolecules in plant extract (*Cosmos Caudatus*) can act as reducing agents and are believed to play a part in the bioreduction of Ag(I) ions to Ag(0). The bioreduction might occur according to the equation below:



All the vibration bands are functional groups of plant extracts which are responsible for both bioreduction and stabilising agents of nanoparticles. The figure 4 showed the absorption spectra for *Cosmos caudatus* leaf extract.

The spectra of *Cosmos caudatus* leaf extract showed a few strong and broad bands at 3218, 2933, 1590, 1393 and 1059 cm<sup>-1</sup> which contribute to the potential biomolecules present. A broad band at 3218 cm<sup>-1</sup> revealed to be the OH stretching vibration, while a weak peak at 2933 cm<sup>-1</sup> indicated the asymmetric stretching of CH groups. A strong peak at 1590 cm<sup>-1</sup> was due to the asymmetric stretching of aliphatic nitro (NO<sub>2</sub>) compound and the peak at 1393 cm<sup>-1</sup> was for C-N stretching vibrations of amines. An absorption band at 1059 cm<sup>-1</sup> was indicated for C-OH stretching of secondary alcohols.

From AAS analysis, the data obtained showed that the amount of Ag metal present in the supported Ag catalyst (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-SH-Ag(0)) was 4.54 wt%. From this data, it was calculated that 0.42 mmol of Ag present in every 1 gram sample of supported Ag catalyst (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-SH-Ag(0)), indicating that only 12% of thiol groups have covalently bonded to the Ag metal.



**Figure 4** Absorption spectra of *Cosmos caudatus* leaf extract

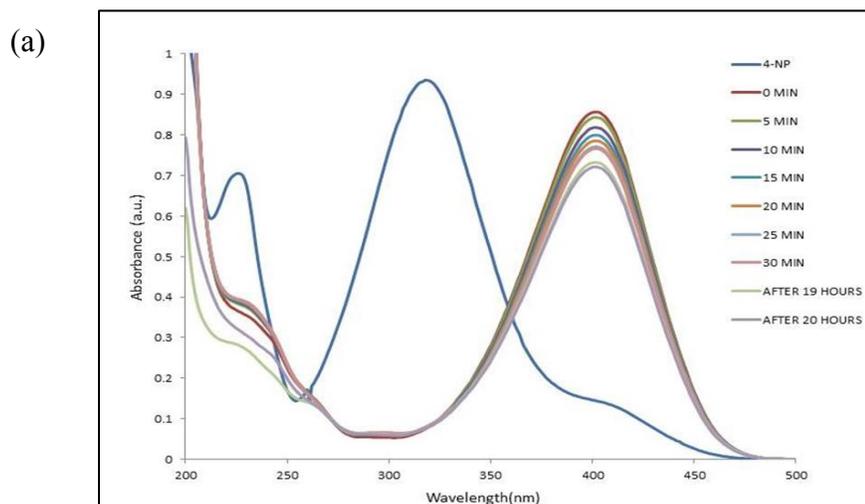
### 3.3 Catalytic study

The ability of AgNPs acting as a nanocatalyst was tested in the reduction of 4-nitrophenol (4-NP) to its derivative, 4-aminophenol in the presence of excess NaBH<sub>4</sub>. The extent of reaction is monitored by the change in UV-Vis absorbance in the range of 200 to 500 nm. 4-nitrophenol showed absorption at 317 nm. After adding the freshly prepared excess NaBH<sub>4</sub>, the light yellow of 4-nitrophenol changed to bright yellow and the maximum peak shifted to 400 nm. This was due to the presence of 4-nitrophenolate ion in alkaline condition by NaBH<sub>4</sub> [8].

The control experiment for 4-NP reduction with excess NaBH<sub>4</sub> without the catalyst was done within 20 hours. The result showed that the reaction proceeds very slowly and it may not proceed only with the presence of NaBH<sub>4</sub>.

When 7.5 mg of Ag nanocatalyst is added to the reaction solution, it can be observed that the bright yellow turns colourless and the absorption peak at 400 nm decreased within 5 minutes along with appearance of new peak at 300 nm indicating the formation of 4-aminophenol. The reduction reaction happened at a fast rate, almost 100% complete indicating that AgNPs possessed a good catalytic ability in the reduction of 4-nitrophenol.

Figure 5 showed the UV-Vis absorption for both control experiment and reduction of 4-NP with aid of catalyst.



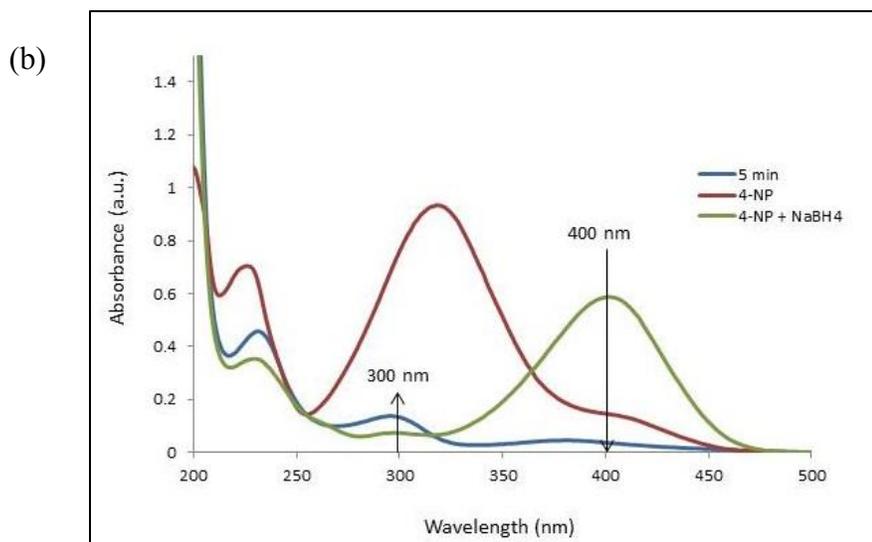


Figure 5 (a) control experiment, (b) reduction of 4-NP using Ag nanocatalyst

#### 4. CONCLUSION

The bioreduction of AgNPs using *Cosmos caudatus* leaf extract had proved to be safer and economical methods compared to physical and chemical methods as the presence of biomolecules that contribute to the reduction of nanoparticles had been characterised by FTIR analysis. Besides, AgNPs shows good catalytic activity in the reduction of 4-nitrophenol as the rate of reaction is fast and almost 100% complete within 5 minutes. The magnetic biostabilised AgNPs can be efficiently separated from reaction mixture using external magnet, thus overcome the limitation in the separation process of catalyst such as filtration and centrifugation.

#### REFERENCES

- [1] Moores, A. and Goettmann, F. (2006). *New J. Chem.*, 30, (8), 1121.
- [2] Khomutov, G., Gubin, S., (2002). *Mater. Sci. Eng. C* 22, 141.
- [3] Irvani, S. (2011). *Green Synthesis Of Metal Nanoparticles Using Plants*. *Green Chem.*, 13, 2638.
- [4] Borhamdin, S., Shamsuddin, M. and Alizadeh, A. (2016). *Biostabilised Icosahedral Gold Nanoparticles: Synthesis, Cyclic Voltammetric Studies and Catalytic Activity Towards 4-Nitrophenol Reduction*, *J Exp Nanosci*, 11, 518-530.
- [5] Hakami, O., Zhang, Y., Banks, C. J. *Water Res.* (2012) 46, 3913.
- [6] Khosroshahi, M. E., Ghazanfari, L. *Mater. Chem. Phys.* (2012) 133, 55.
- [7] Talam, S., Karumuri, S. R. and Gunnam, N. (2012). *Synthesis, Characterization, and Spectroscopic Properties of ZnO Nanoparticles*, *International Scholarly Research Network*, Vol. 2012, 1-6.
- [8] Chang, Y. C. and Chen, D. H. (2009). *Catalytic Reduction of 4-Nitrophenol by Magnetically Recoverable Au Nanocatalyst*, *Journal of Hazardous Materials*, 165, 664-669.