GNP assisted hydrolysis of Methyl Parathion and catalytic reduction of its hydrolysed product

Gadadhar Barman, Swarnali Maiti and J. Konar Laha*

Department of Chemistry, Midnapore College, Midnapore-721101, W.B, India

Abstract: We report a method for the synthesis of gold nanoparticles (GNP) using the aqueous extract of Andrographis Paniculata. In the synthesis of GNP, the aqueous extract of Andrographis Paniculata acts as reducing agent and neutral surfactant Triton® X100 as stabilizing agent. This bio-synthesized GNP has been used as colorimetric sensor for detection and estimation of pesticide (methyl parathion) present in water. One of the hydrolysis products of methyl parathion is p-nitrophenolate is easily reduced by NaBH4 in the presence of the bio-synthesized GNP. The reduction of p-nitrophenolate to p-aminophenolate is evidenced by a decrease in absorbance at 400 nm and simultaneous growing of a new peak at 295 nm associated with formation of p-aminophenolate. The reduction progress was observed for a period of 300 S. The plot of natural log of the absorbance at 400 nm (ln A400nm) versus time produced a straight line. As the reduction reaction is pseudo-first-order in the presence of excess NaBH4 and catalyst, the slope of the plot, yields the apparent reaction rate, kapp (3.13×10-3 s-1). Thus, this is found to be an easy method for determining reaction rate by UV−Visible spectroscopy.

Index Term: Gold nanoparticle; Triton® X100; Pesticide estimation; p-nitrophenolate; p-aminophenolate; Catalytic reduction

1. Introduction

Coinage metal particles in the nanometer size range show characteristic size- and shape-dependent physical, chemical and biological properties compared to their bulk or macro scaled structures. Noble metal nanoparticles have been found useful in areas such as photography, catalysis, biological labeling, photonics, optoelectronics, pesticide detection, heavy metal ion detection etc. Catalysis at the nanoscale level has gained significant attention in the past two decades due to the unique properties of materials at that level [1]. Metal nanocatalysts have found a wide range of applications in various field like carbon nanotube nucleation [2], alcohol dehydrogenation [3], oxidation of aromatic alcohol [4], formation of hydrogen peroxide from H_2 and O_2 [5], formic acid electro-oxidation [6], reduction of oxygen [7] etc. Gold, in particular, has become the basis for novel catalysts due to its special activity at the nanoscale [8].

In this work, we report a noble method for the synthesis of gold nanoparticles (GNP) using the aqueous extract of *Andrographis Paniculata*. In the synthesis of GNP, the aqueous extract of *Andrographis Paniculata* acts as reducing agent and neutral surfactant Triton® X100 as stabilizing agent. This bio-synthesized GNP has been used as colorimetric sensor for detection and estimation of pesticide (methyl parathion) present in water. The

sensor properties were examined from the UV-Vis spectral changes occurred due to the addition of methyl parathion in ppm level. One of the hydrolysis products of methyl parathion is p-nitrophenolate [9-11]. The p-nitrophenolate is easily reduced by $NaBH_4$ in the presence of metals in solution [12,13]. Coinage metal, in particular gold, has been demonstrated to be excellent catalysts for p-nitrophenolate reduction at the nanoscale level [14]. In the present work we have employed bio-synthesized GNP to verify the catalytic activity of it by reducing p-nitrophenolate to p-aminophenolate and the effect was visible from the appearance of a new peak at 295 nm due to the reducing product p-aminophenolate.

2. Materials and method

2.1. Materials

Chloroauric acid of A R grade was purchased from Sigma-Aldrich Chemical Ltd.; Triton® X100 and methyl parathion were purchased from Merck. Double distilled de-ionized water was used in all experiments.

2.2. Preparation of kalmegh (*Andrographis Paniculata*) extract

Kalmegh (Andrographis Paniculata) plant was collected from local forest, washed with water and dried under sunlight for one week. It was then crushed into small pieces using mortar pestle. 5 gm of these were taken in a beaker and 100 ml double distilled de-ionized water was poured into it. Then it was kept standing for 6 hours and was filtered to get aqueous extract of *Andrographis Paniculata.*

2.3. Synthesis of Gold Nanoparticles by aqueous Andrographis Paniculata extract

GNP was produced by reduction of chloroauric acid solution using *Andrographis Paniculata* aqueous extract. 10 ml of aqueous *Andrographis Paniculata* extract was added to an equal volume of 3×10^{-3}(M) Triton® X100 solution and 5 ml of 3×10^{-3}(M) aqueous chloroauric acid was added drop wise in the mixture with continuous stirring. The pH of the reaction mixture was maintained at 9 to 9.5 by monitoring the amount of NaOH solution (0.15 M). The mixture was then cooled for 10 minutes and finally it was heated for 30 minutes at 80^0C. The colour of the solution gradually changed from yellow to violet. The violet colour indicated the formation of gold nanoparticles (GNP).

2.4. Colorimetric sensor property of methyl parathion in presence of GNP

500 µl of solution containing different concentrations of methyl parathion (10 to 200 ppm) was added to 5 ml of GNP and mixture was heated for 5 minutes with continuous stirring at 80^0C. The violet color sol gradually changed into greenish. The intensity of the colour gradually increased with the increase of pesticide concentration. This colour

change may be responsible for sensing property of bio-synthesized GNP.

2.5. GNP catalyzed reduction of p-nitrophenolate

The catalytic reduction of p-nitrophenolate to p-aminophenolate has been carried out in presence of GNP. A freshly prepared aqueous solution of sodium borohydride 3 ml of 15 mM was added in the reaction mixture (4ml) containing bio-synthesized GNP and the hydrolyzed product p-nitrophenolate from 50 ppm methyl parathion. The colour of the solution changed gradually from greenish to colourless as the reduction proceeded. The peak at 295 nm in UV–Vis spectrum is expected to be due to the p-aminophenolate was monitored at a time interval of 60 s to examine the order of the reaction.

2.6 Characterization

The absorbance spectra of the GNPs were analyzed by using a 'SHIMADZU' UV 1800 spectrophotometer and TEM images were taken using JEOL-JEM 2100 high resolution transmission electron microscope (HR-TEM). Samples for the TEM studies were prepared by placing a drop of the aqueous suspension of particles on carbon-coated copper grids followed by solvent evaporation under vacuum. The crystalline nature of the GNPs was examined using X' Pert Pro X-ray diffractometer operated at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. The FT-IR measurements are done using PerkinElmer Spectrum Version 02 spectrometer.

3. Result and discussion

3.1. UV-Visible study

The bio-synthesis of metal nanoparticles using plant extract is in vogue now-a-days. The use of varied biological systems for the synthesis of nanoparticles is evolving different kind of important branches of nanotechnology. The present study deals with the synthesis of Gold nanoparticles using aqueous extract of *Andrographis Paniculata*. Probably the water soluble andrographolide present in the extract acts as reducing agent and neutral surfactant Triton® X100 as stabilizing agent for bio-synthesis of GNP. This bio-synthesized GNP exhibits violet color in water and a smooth, narrow absorption band was observed at 527 nm (Fig. 1A). The color appears due to the excitation of the Localized Surface Plasmon vibrations of the metal nanoparticles.

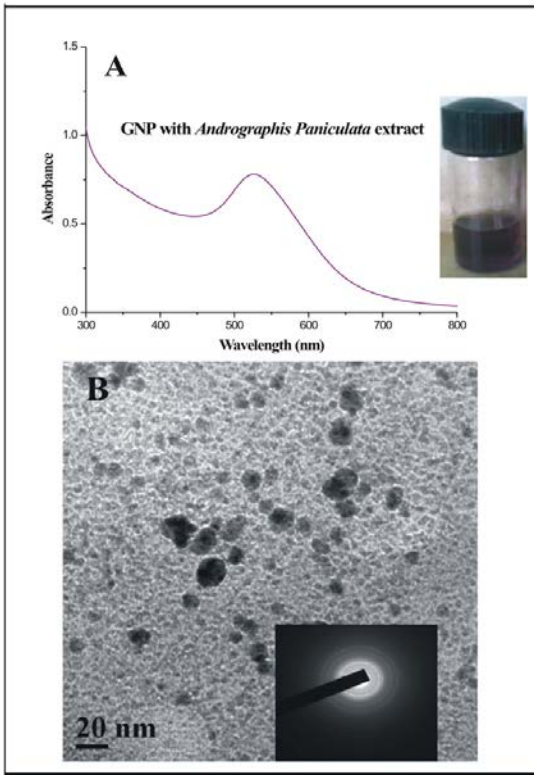


Fig. 1. UV-Vis spectra of (A) GNP synthesized from *Andrographis Paniculata* extract in presence of Triton® X100 (Inset: digital photographic images) and (B) TEM micrograph (Inset: SAED image).

3.2. TEM study

Fig. 1(B) illustrates the transmission electron microscopic (TEM) images of the nearly monodispersed gold nanoparticles synthesized in this method. This monodispersity can be explained from the fact that Triton® X100 being a strong capping agent stabilizes the GNP as soon as nucleation happens and there by restricts the nanoparticles to a finite size. As a result we received nearly monodispersed gold nanoparticles of size 5-13 nm as supported by TEM data and we can conclude that Triton® X100 capped GNP has much better colloidal stability. The crystalline natures of gold nanoparticles are shown in SAED images (Fig. 1B inset).

3.3. Estimation of methyl parathion in presence of GNP

The bio-synthesized GNP was used to study the sensor property and catalytic property. Methyl parathion was added in GNP by varying concentration of pesticide from 10 to 200 ppm and corresponding changes of absorption coefficients were observed. As soon as methyl parathion was added we observed a new peak at around 400 nm in addition to the peak found at 527nm. The increase in the absorbance of that peak was observed when the concentration of methyl parathion varied from 10 to 200 ppm (Fig. 2). Most probably, the newly found peak is due to the 4-nitrophenolate which might have produced by hydrolysis of methyl parathion in presence of GNP. The catalytic hydrolysis reaction of methyl parathion produces 4-nitrophenolate [15] and sodium di-O-methyl thiophosphonate (scheme 1). The literature confirms that 4-nitrophenolate has a characteristic absorption peak at 400 nm [16]. The increase in the concentration of methyl parathion in the mixture quantitatively increased the amount of the 4-nitrophenolate ions in the medium which are reflected in the absorption spectra shown in Fig. 2A.

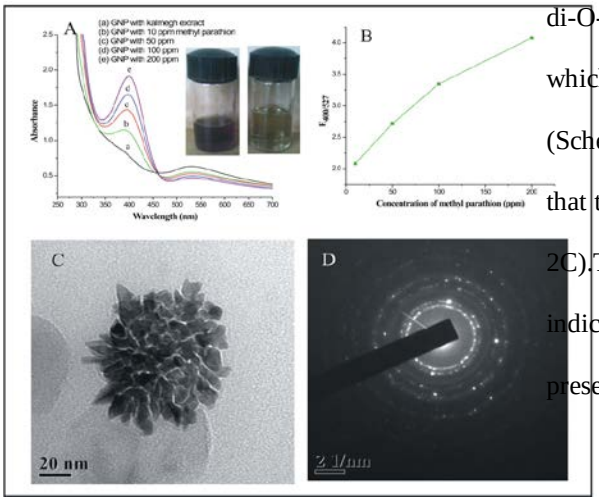
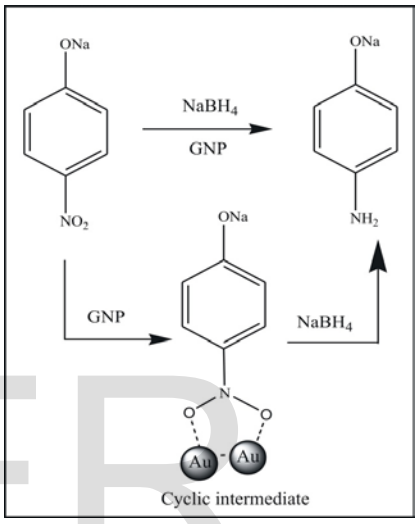
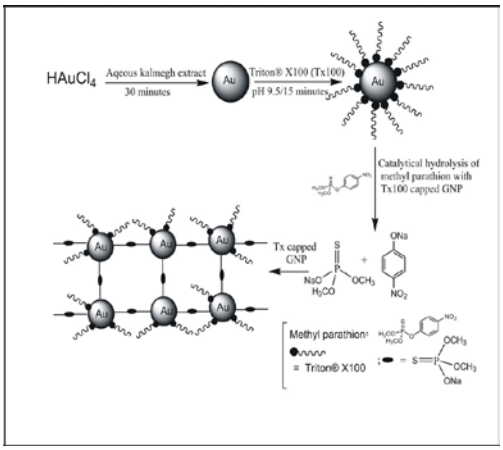


Fig.2. UV-Vis spectra of Triton® X100 capped GNP produced from *Andrographis Paniculata* extract at different concentration of methyl parathion (A) 10 to 200 ppm and (B) the corresponding calibration curve between absorption coefficients ($Ex_{400/527}$) versus concentration of methyl parathion, (C) TEM micrograph of GNP in presence of methyl parathion and (D) the corresponding SAED pattern.

A calibration curve between absorption coefficients of 400 nm peaks versus concentration of pesticide enable one to estimate quantitatively the presence of methyl parathion in a sample at ppm level by estimating the 4-nitrophenolate which is produced by hydrolysis of methyl parathion in the medium (Fig. 2B). With the increase in the concentration of methyl parathion, the decrease in the absorption peak at 527 nm suggests that gold nanoparticle capped with Triton® X100 becomes unstable. This instability might be due to the presence of the other hydrolyzed product sodium di-O-methyl thiophosphonate containing sulphur which may accelerate the agglomeration of GNP (Scheme 1). It is observed from the TEM image that the particles agglomerate to form clusters (Fig. 2C).The formation of agglomeration of GNP is indicated by the broadening of the 527 nm peak in presence of methyl parathion.



Scheme 2. Schematic diagram for reduction of p-nitrophenolate to p-aminophenolate in presence of $NaBH_4$ and GNP through cyclic intermediate.



Scheme 1. Strategy of the formation of GNP, catalytic hydrolysis of methyl parathion and aggregation of GNP.

3.4. GNP Catalyzed reduction of p-nitrophenolate

We have employed bio-synthesized GNP to verify the catalytic activity of it by reducing the hydrolyzed product of methyl parathion i.e. p-nitrophenolate. The reduction of p-nitrophenolate in the presence of $NaBH_4$ and bio-synthesized GNP is fast. From literature it is confirmed that the role of the metallic catalyst is to bind the p-nitrophenolate molecule through the two oxygen of the nitro group [17-21]. The reduction pathway are shown in Scheme 2, where a single nitro group of p-nitrophenolate binds two atoms of Au surface and creates a pentagonal Au−O−N−O−Au cyclic intermediate.

p-nitrophenolate absorbs strongly in the visible range with a maximum absorbance at 400 nm [9]. The reduction of p-nitrophenolate to p-aminophenolate is evidenced by a decrease in absorbance at 400 nm and simultaneous growing of a new peak at 295 nm associated with formation of p-aminophenolate (Fig. 3). The reduction progress was observed for a period of 300 S (Fig. 3).

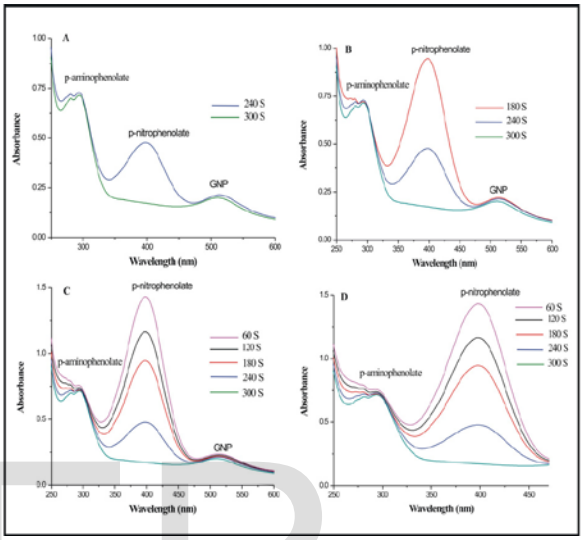


Fig. 3. UV−Visible spectra (A-D) show the reduction progress of p-nitrophenolate with time interval of 60 S.

The plot of natural log of the absorbance at 400 nm (ln A_{400nm}) versus time produced straight lines. As the reduction reaction is pseudo-first-order in the presence of excess $NaBH_4$ and catalyst, the slope of the plot mentioned above, yields the apparent reaction rate, kapp (Fig, 4). Thus, this is found to be an easy method for determining reaction rate by ultraviolet−visible (UV−vis) spectroscopy [22].

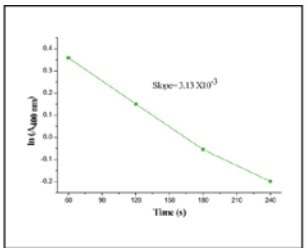


Fig. 4. Reduction of p-nitropenolate in presence of NaBH4 and bio-synthesized GNP. The plot of the natural log of the absorbance at 400 nm versus time; data points are separated by 60 s intervals. The slope yields the apparent rate constant k_{app} = 3.13×10^{-3} (s^{-1}) for this trial.

3.5. XRD analysis

The XRD analysis was performed to confirm the crystalline nature of biologically synthesized GNP. Various Braggs' diffractions pattern were clearly visible (Fig. 5). The face centered cubic (fcc) structure of the bulk gold having sharp peaks at 38.24°, 44.42°, 64.64°, 77.78° and 82.73° indicated the presence of corresponding (111), (200), (220), (311) and (222) planes, respectively. On the basis of these Braggs' diffractions, we can say that the synthesized GNP are fcc and essentially crystalline in nature. The (200), (220), (311) and (222) set of lattice planes were observed to be weak and broadened compared to (111) Bragg's diffraction, which indicated that the biologically synthesized GNP was (111) oriented.

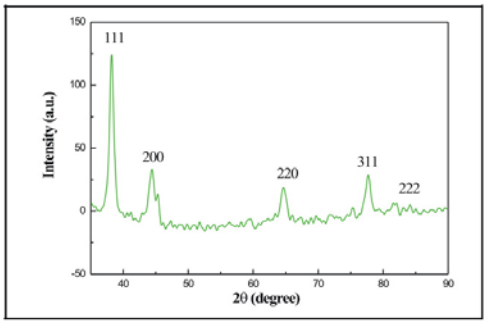


Fig. 5. XRD of (A) GNP and (B) cysteine capped GNP prepared from *Andrographis Paniculata* extract.

3.6. FTIR analysis

FTIR analysis was performed to identify the bio-molecules localized on the surface and responsible for the reduction of gold solution. Representative FTIR spectra of aqueous extract of pure *Andrographis Paniculata* and the synthesized GNP are shown in Fig. 6A and B respectively.

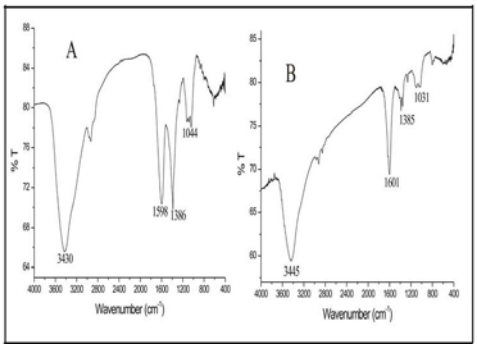
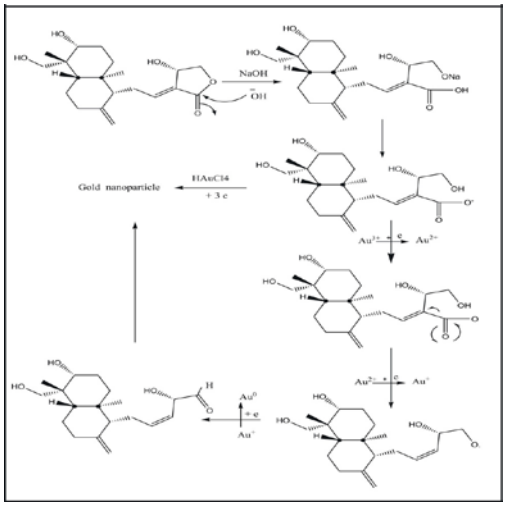


Fig. 6. FT-IR spectra of (A) vacuum-dried powder of *Andrographis Paniculata* and (B) GNP synthesized from aqueous *Andrographis Paniculata* extract.

As the aqueous extract of *Andrographis Paniculata* was used for sol preparation, the only

possibility of finding the compound in aqueous extract might be the andrographolide, other terpenoids present in *Andrographis Paniculata* being insoluble in water should not be involved in reduction. The spectrum of the dried aqueous extract of *Andrographis Paniculata* shows number of frequencies at 3430, 2933, 2848, 1740, 1598, 1386, 1268, 1123, 1083, 1044 and 873 cm^{-1}. Most of these peaks are also found in GNP reduced by *Andrographis Paniculata* but slightly shifted. The peak at 1385 cm^{-1} is found to be most affected which is probably due to the lactones group present in andrographolide [23]. The findings can be understood if we consider that the lactone group is getting hydrolyzed in alkaline medium to produce acid salt. At the same time the decarboxylation of this acid salt produces aldehyde. These two might be responsible for reduction of chloroauric acid. The sugar unit mostly glucose present in *Andrographis Paniculata* extract may also be responsible for reduction of chloroauric acid to gold sol. The probable mechanism for reduction may be represented by the following steps (Scheme 3).



Scheme 3. Schematic diagram of reduction of chloroauric acid with andrographolide through electron transfer pathway.

4. Conclusions

The bio-synthesized GNP was used to study the sensor property and catalytic property. Methyl parathion was added in GNP by varying concentration of pesticide from 10 to 200 ppm and corresponding changes of absorption coefficients were observed. We have used bio-synthesized GNP to verify the catalytic activity of it by reducing p-nitrophenolate to p-aminophenolate. The reduction of p-nitrophenolate to p-aminophenolate is evidenced by a decrease in absorbance at 400 nm and simultaneous growing of a new peak at 295 nm associated with formation of p-aminophenolate .The reduction progress was monitored for a period of 300 S. The plot of natural log of the absorbance at 400 nm (ln A_{400nm}) versus time produced a straight line. As the reduction reaction is pseudo-first-order in the presence of excess $NaBH_4$ and

catalyst, the slope of the plot mentioned above, yields the apparent reaction rate, $k_{app} = 3.13\times10^{-3}$ s^{-1}. Thus, this is found to be an easy method for determining reaction rate by UV−Visible spectroscopy.

Acknowledgements

We are thankful to Central Research Facility of IIT Kharagpur, India for HR-TEM and XRD measurements.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N. Toshima, T. Yonezawa, "Bimetallic nanoparticles—novel materials for chemical and physical applications", New J. Chem., 22, pp.1179−1201, 1998.

[2] M. Valden, X. Lai, DW. Goodman, "Gold Clusters on Titania with the Appearance of Nonmetallic Properties", Science, 281, pp.1647−1650, 1998.

[3] GJ. Hutchings, S. Carrettin, P. Landon et al, "New approaches to designing selective oxidation catalysts: Au/C a versatile catalyst", Top Catalysis, 38, pp.223–230, 2006.

[4] H. Ago, K. Murata, M. Yumura et al, "Ink-Jet Printing of Nanoparticle Catalyst for Site-Selective Carbon Nanotube Growth," Appl Phys Lett., 82, pp.811-813, 2003.

[5] T. Mitsudome, Y. Mikami, H. Funai et al, "Oxidant-Free Alcohol Dehydrogenation Using a Reusable Hydrotalcite-Supported Silver Nanoparticle Catalyst," Angew Chem, 120 pp.144−147, 2008.

[6] L. Prati, F. Porta, "Oxidation of alcohols and sugars using Au/C catalysts: Part 1. Alcohols," Appl Catalysis A, 291, pp.199–203, 2005.

[7] P. Waszczuk, TM. Barnard, C. Rice et al, "A Nanoparticle Catalyst with Superior Activity for Electrooxidation of Formic Acid. Electrochem Commun, 4, pp. 599−603, 2002.

[8] G. Vijayaraghavan, KJ. Stevenson, "Synergistic Assembly of Dendrimer Templated Platinum Catalysts on Nitrogen-Doped Carbon Nanotube Electrodes for Oxygen Reduction," Langmuir, 23, pp. 5279−5282, 2007.

[9] G. Barman, S. Maiti, J. KonarLaha, "Bio-fabrication of gold nanoparticles using aqueous extract of red tomato and its use as a colorimetric sensor", Nanoscale Res Lett., 8, pp.181-189, 2013.

[10] G. Barman, S. Maiti, J. KonarLaha, "Trichloroacetic acid assisted synthesis of gold nanoparticles and its application in detection and estimation of pesticide," J anal Sci Tech, 4 ,pp. 3-9, 2013,

[11] T. Vincent, E Guibal, "Chitosan-Supported Palladium Catalyst. Influence of Experimental Parameters on Nitrophenol Degradation. Langmuir 19:8475−848 (2003)

[12] K. Hayakawa, T. Yoshimura, K. Esumi, "Preparation of Gold- Dendrimer Nanocomposites by Laser Irradiation and Their Catalytic Reduction of 4-Nitrophenol", Langmuir, 19, pp. 55−175521, 2003.

[13] K. Kuroda, T. Ishida, M. Haruta, "Reduction of 4-Nitrophenol to 4-Aminophenol Over Au Nanoparticles Deposited on PMMA," J Mol Catal A Chem, 298, 7−11, 2009.

[14] N. Pradhan, A. Pal, T. Pal, "Catalytic Reduction of Aromatic Nitro Compounds by Coinage Metal Nanoparticles," Langmuir, 17, pp. 1800−1802, 2001.

[15] A T. Scott, N. Rafaela, M. Martine et al., "Accelerating the initial rate of hydrolysis of methyl parathion with laser excitation using monolayer protected 10 nm Au nanoparticles capped with Cu(bpy) catalyst", *Chem Comm*, 48, pp.4121-4123 ,2012.

[16] C. Chen, DH. Chen, "Spontaneous synthesis of gold nanoparticles on gum arabic–modification iron oxide nanoparticles as a magnetically recoverable nanocatalyst" Nanoscale Res Lett, 7, pp. 1-7, 2012.

[17] B. Hammer, Y. Morikawa, JK. CO. Nørskov, "Chemisorption at Metal Surfaces and Overlayers," Phys Rev Lett, 76, pp.2141− 2144, 1996.

[18] B, Hammer, JK, Nørskov, "Electronic Factors Determining the Reactivity of Metal Surfaces", Surf Sci 343, pp.211−220 ,1995.

[19] W. Lv, Y. Wang, W. Feng et al., "Robust and smart gold nanoparticles: one-step synthesis, tunable optical property, and switchable catalytic activity," J Mater Chem, 21, pp.6173–6178. 2011.

[20] B. Hammer, "Special Sites at Noble and Late Transition Metal Catalysts,' Top Catal, 37, pp.3−16, 2006

[21] GL. Hallett-Tapleya, COL. Crites, M. Gonzalez-Bejara et al., "Dry photochemical synthesis of hydrotalcite, g-Al2O3 and TiO2 supported gold nanoparticle catalysts," J Photochem Photobiol A, 224, pp. 8–15, 2011.

[22] DP. Zachary, ER. Stacia, K. Emily et al, "A Systematic Investigation of p-Nitrophenol Reduction by Bimetallic Dendrimer Encapsulated Nanoparticles," J Phys Chem C, 117, pp.7598−7604, 2013.

[23] C. Majee, BK. Gupta, R. Mazumder GS. "Chakraborthy HPLC Method Development and Characterization of Bio-Active Molecule Isolated from Andrographis paniculata," Int J Pharm Tech Res 3, pp.1586-1592, 2011.

GNP assisted hydrolysis of Methyl Parathion and catalytic reduction of its hydrolysed product

Gadadhar Barman and J. Konar Laha*

Department of Chemistry, Midnapore College, Midnapore-721101, W.B, India

- *Gadadhar Barman is currently pursuing Ph. D degree program in Midnapore College (Vidyasagar University), India, PH-+91 8900642399. E-mail:bgadadhar@rediffmail.com*
- *Dr. Jayasree Konar Laha is Faculty as Head and associate Professor in Midnapore College (Vidyasagar University), India, PH-+91 9434029182. E-mail: j.laha@yahoo.co.in, Fax: +91 3222275847*