

# Room-temperature synthesis of cobalt nanoparticles and their use as catalysts for Methylene Blue and Rhodamine-B dye degradation

Arijit Mondal, Asish Mondal and Debkumar Mukherjee\*

Department of Chemistry, Ramsaday College, Amta, Howrah 711 401, India

(Received March 7, 2015, Revised June 27, 2015, Accepted June 30, 2015)

**Abstract.** Air stable nanoparticles were prepared from cobalt sulphate using tetra butyl ammonium bromide as surfactant and sodium borohydride as reductant at room temperature. The cobalt nanocolloids in aqueous medium were found to be efficient catalysts for the degradation of toxic organic dyes. Our present study involves degradation of Methylene Blue and Rhodamine-B using cobalt nanoparticles and easy recovery of the catalyst from the system. The recovered nanoparticles could be recycled several times without loss of catalytic activity. Palladium nanoparticles prepared from palladium chloride and the same surfactant were found to degrade the organic dyes effectively but lose their catalytic activity after recovery. The cause of dye colour discharge by nanocolloids has been assigned based on our experimental findings.

**Keywords:** nanoparticles; chemical synthesis; dye degradation; catalytic properties; transmission electron microscopy

---

## 1. Introduction

In recent years wet-chemical approaches such as pyrolysis (Guo *et al.* 2007, Liu *et al.* 2010), solvothermal process (Wang *et al.* 2008), hydrothermal decomposition (Cao *et al.* 2011), modified polyol process (Dakhlaoui *et al.* 2008) and template-based methods (Xia *et al.* 2011) have been developed to synthesize cobalt crystals with different morphologies and applications. Some efforts have been focused on exploring the relations between their shapes, properties and uses. There is however no report of a very simple and quick method to prepare cobalt nanoparticles (Cao *et al.* 2011, Zhang *et al.* 2013) due to their propensity to easy oxidation even at ambient temperatures.

In recent years considerable attention has been paid to the environmental problem involving water treatment (Sanchez-Martin *et al.* 2010). The pollution of water sources by dyes from the textiles and mining industries has become a serious environmental concern now-a-days. The textile dyes with high aromatic content and low biodegradability have emerged as major environmental pollutants (Arslan *et al.* 2000, Sauer *et al.* 2002). The waste-water from textile mills causes serious impact on natural water bodies and in the surrounding lands. The improper handling of hazardous chemicals in the textile water also has some serious impact on the health and safety standard of workers. Skin diseases, chemical burns, irritation, ulcers and respiratory problems are common

---

\*Corresponding author, Associate Professor, E-mail: [debkumarmukherjee@rediffmail.com](mailto:debkumarmukherjee@rediffmail.com)

among workers involved in water treatment plants (Arslan 2001). Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades for the treatment of textile waste-water. Although most of them were found to be effective, the cost involved in the process is rather expensive (Kositzki *et al.* 2004, Patil *et al.* 1988). Shao *et al.* (2009), Zhang *et al.* (2007) employed Pd nanoparticles deposited on silicon nanowires to degrade Eosin Y and Methylene blue, respectively. During the degradation of Eosin Y or Methylene blue in presence of sodium borohydride, the Si/Pd nanoparticles offer several advantages such as rapid reaction rate, high catalytic activity, and reuse. However palladium chloride, the raw material required for preparing the Pd nanoparticles, is very expensive. Liu *et al.* (2005) employed silver nanoparticles supported on silica spheres to reduce eosin and methylene blue. Jana *et al.* (1999) produced silver particles in aqueous surfactant media and studied their catalytic properties toward the reduction of a number of dyes. Unfortunately, silver nitrate the raw material for production of silver nanoparticles is also expensive.

Nanosized magnetic particles are useful adsorbents for aqueous pollutants due to their high surface areas and the added advantage of easy separation using external magnetic fields. Several reports have been published on the use of various types of magnetic nanoparticles like iron (Shih *et al.* 2010, Fau *et al.* 2009), cobalt (Liu *et al.* 2010, Liang and Zhao 2012) etc along with reducing agents for degradation and removal of dyes. The magnetic particles mentioned are almost all iron-based oxides (Shih *et al.* 2010, Dutta *et al.* 2014). There are very few reports about use of cobalt materials for the purpose of dye degradation mainly because of their difficulty in preparation and stabilization.

Herein, we used tetrabutyl ammonium bromide stabilized cobalt nanoparticles, prepared at room temperature, as an adsorbent in aqueous solution. Aqueous solution of methylene blue (MB) can be completely degraded within 2 minutes by the Cobalt nanoparticles. We have selected two different dye molecules which have absorbance maxima well within the visible range suitable for spectral studies and have different cationic moieties. The chloride anion is however common in both the structures. The used cobalt nanoparticles can be recovered by applying a magnet from outside to the aqueous solution. TEM studies before and after the dye degradation process reveals no aggregation or disintegration of particles. Our endeavour to use cobalt nanoparticles in the field of dye degradation may become important in the treatment of industrial effluents.

## 2. Experimental

### 2.1 Chemicals and materials

All chemicals were of reagent grade and used without further purification. Cobalt sulphate ( $\text{CoSO}_4$ ), tetrabutyl ammonium bromide (TBAB), Sodium borohydride ( $\text{NaBH}_4$ ), Methylene Blue (MB), Rhodamine-B, acetone were purchased from Merck-India. Cobalt nanoparticles and palladium particles have been abbreviated as CoNPs and PdNPs respectively in the manuscript.

### 2.2 Preparation of TBAB stabilized cobalt nanoparticles reduced by $\text{NaBH}_4$

To a screw-capped glass bottle equipped with a stirring bar were added 64 mg of cobalt sulphate ( $225 \mu\text{mole}$ ), 100 mg tetrabutyl ammonium bromide ( $300 \mu\text{mole}$ ) and 8 ml of deionized

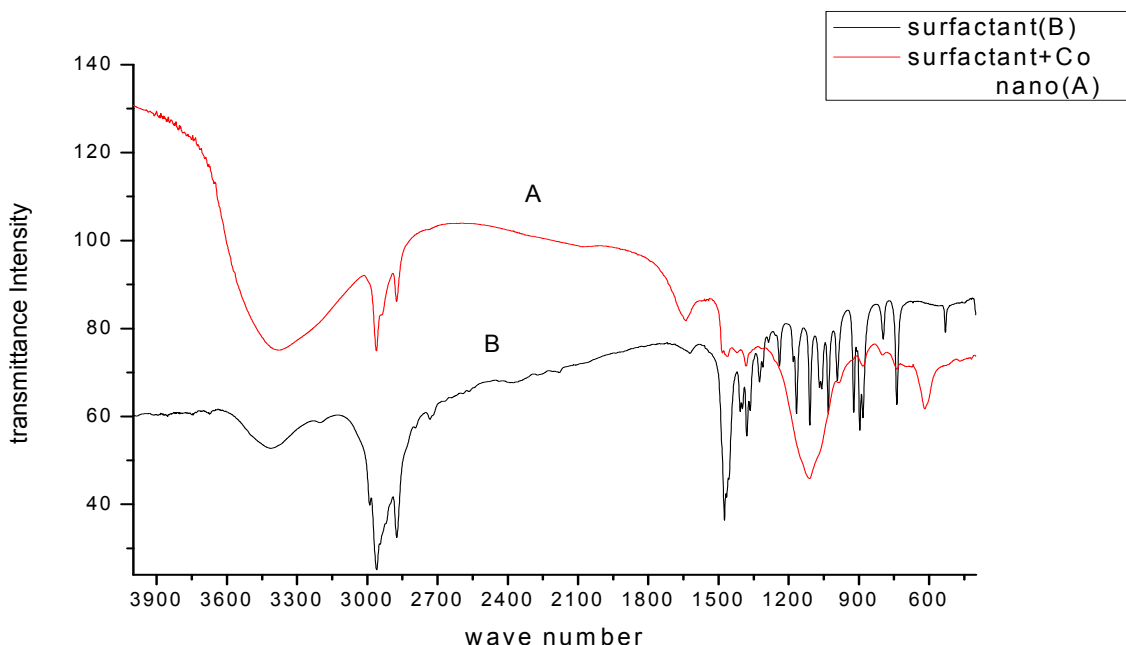


Fig. 1 FTIR spectra of TBAB surfactant (a) and TBAB capped CoNPs (b)

water. After adding deionized water solution of  $\text{NaBH}_4$  (0.1 M) dropwise, the mixture was stirred at room temperature for 15 minutes and then aqueous solution was decanted off. The TBAB-stabilized CoNPs (132 mg) were washed with water ( $5 \times 2.0$  ml) and acetone ( $5 \times 2.0$  ml) and dried under vacuum. The particles thus prepared can be stored at room temperature for several days.

### 2.3 Dye degradation process

In a representative degradation experiment, 5 mg of TBAB-stabilized CoNPs and an aqueous solution of  $\text{NaBH}_4$  (2 ml,  $2 \times 10^{-2}$  M) were rapidly added one by one into an aqueous solution of MB or Rhodamine-B (2 ml,  $4 \times 10^{-5}$  M). The whole mixture was then subjected to UV-Vis spectral analysis at room temperature. The concentrations of Methylene Blue and Rhodamine B were quantified by measuring the absorption intensities at  $\lambda_{\text{max}}$  664 nm and 550 nm respectively.

### 2.4 Characterization

High Resolution Transmission Electron Microscopy (HRTEM) images of cobalt nanoparticles were obtained using CM30 microscope operating at 200 kV and expanded to 470 Pixels/cm resolutions. HRTEM samples were prepared by dispersing CoNP<sub>s</sub> in acetone for 45 minutes in a sonicator. The solution was withdrawn using hypothermal syringe and one drop of the solution was put in a carbon-coated copper grid and left to dry. The UV-Vis absorption spectra were measured at 25°C on INTECH spectrophotometer using solutions in 1 cm quartz absorption cell at wavelength 300-750 nm.

### 3. Result and discussion

The formation of cobalt nanoparticles during the reaction of cobalt(II) sulphate and sodium borohydride could be easily followed by dramatic colour change from pink to black as soon as the reducing agent is introduced. The overall reaction proposed for this process is-



↓ surfactant

Co-particles stabilized by surfactant

These cobalt nanocolloids are generally stabilized by Tetraethylammoniumbromide (TEAB) against aggregation by electrostatic or steric protection. The presence of the surfactant on the surface of cobalt nanoparticles can be explained by comparing their FTIR data (Fig. 1).

The surface binding interaction study of TEAB capped CoNPs was carried out by recording FTIR spectra in the range of 4000-500  $\text{cm}^{-1}$ . The characteristic bands of pure TEAB can be divided into two regions. Two absorption bands in the range 2958-2874  $\text{cm}^{-1}$  are assigned to symmetric and antisymmetric stretching of  $\text{CH}_2$  of the aliphatic group (tail) and another band at 1622  $\text{cm}^{-1}$ , is attributed to Nitrogen group(head group) of TEAB molecules. The 1622  $\text{cm}^{-1}$  band in pure TEAB shifted to 1640  $\text{cm}^{-1}$  in capped cobalt nanoparticles. This clearly showed that the capping was due to positively charged nitrogen head group moieties (Mondal *et al.* 2015).

#### 3.1 TEM pictures

The morphology and size of the as-synthesized particles on the carbon coated Cu grid were characterized by HRTEM (Fig. 2). The size distribution of Co nanoparticles fall between 80-100 nm estimated on the basis of studying 32 such particles. EDX (Energy Dispersive X-ray spectroscopy) spectrum shows 18.6 % cobalt (weight %) present in the isolated nanoparticles (Fig. 3).

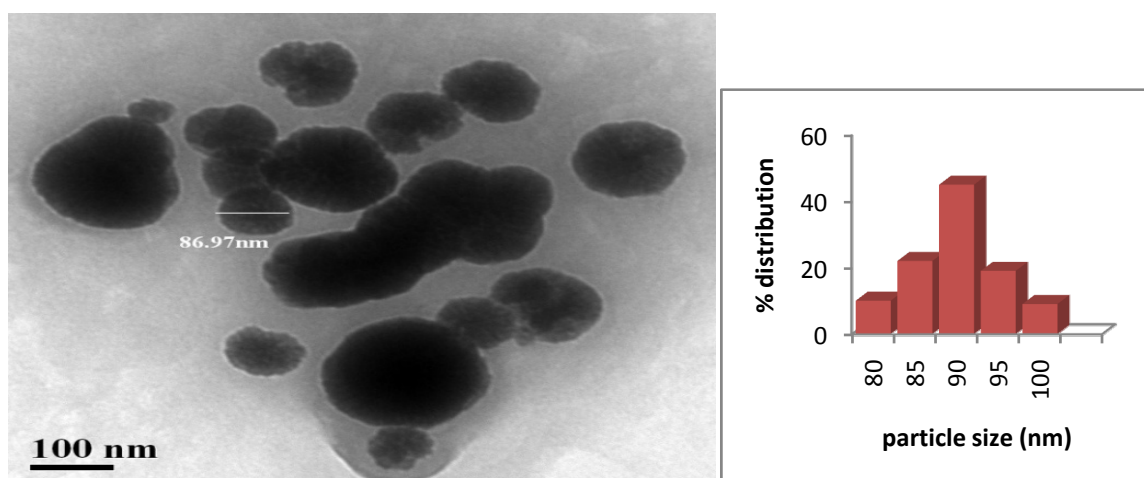


Fig. 2 HRTEM images of Co nanoparticles

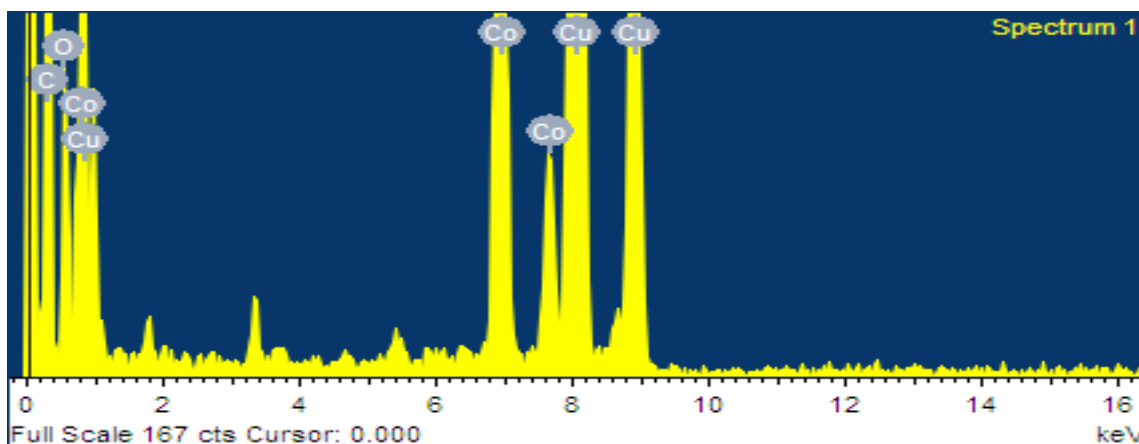


Fig. 3 EDX spectrum of cobalt nanocolloids on carbon coated copper grid

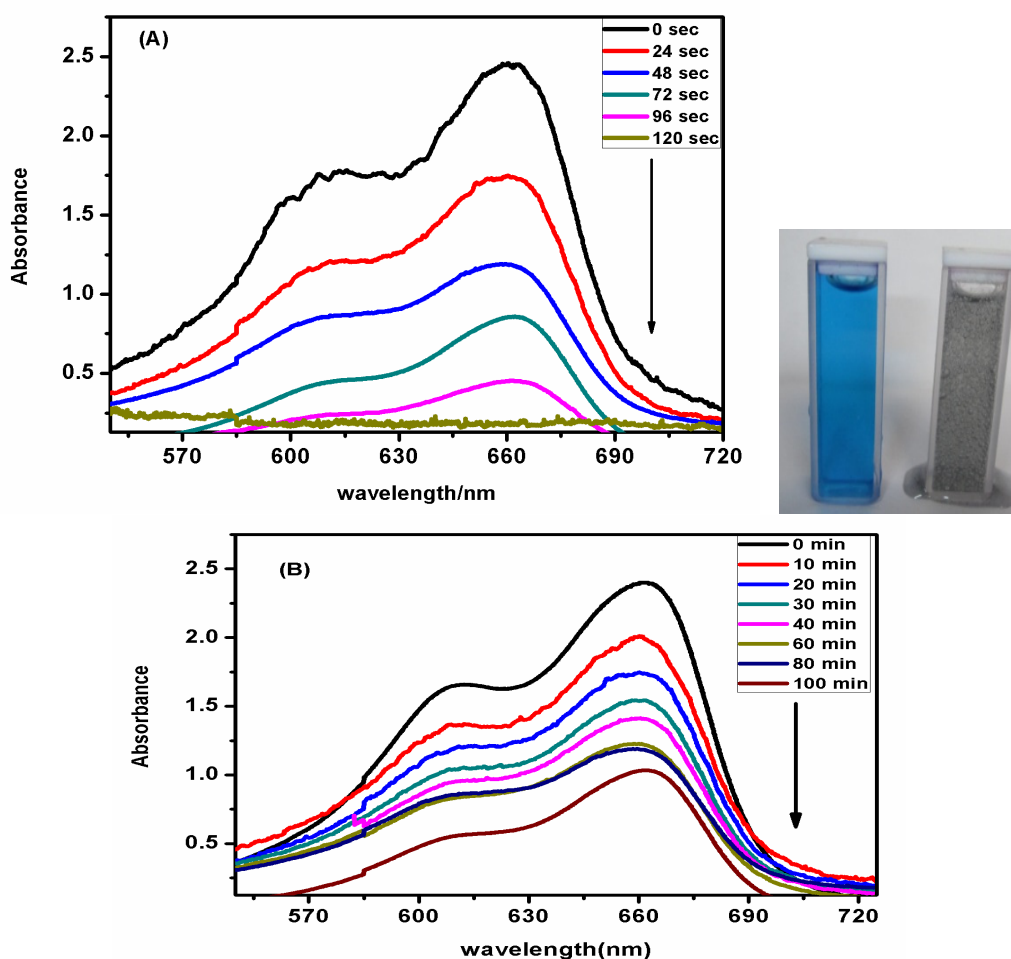


Fig. 4 UV-Vis spectra, (A) MB degradation in presence of CoNPs (B) MB degradation without presence of CoNPs

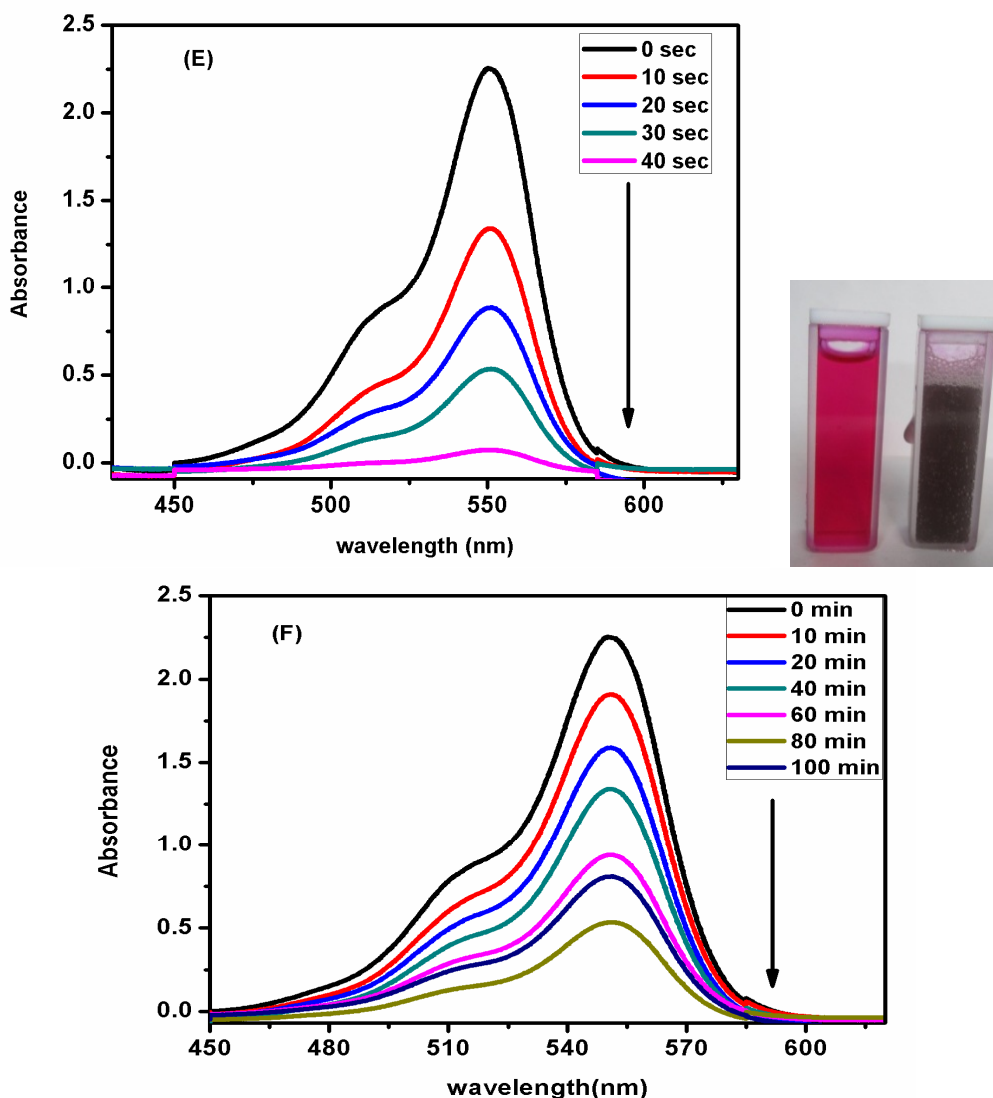


Fig. 5 (e) UV-vis spectra of Rhodamine B degradation in presence of CoNPs; (f) degradation without presence of CoNPs

### 3.2 MB dye degradation in presence and without presence of CoNPs

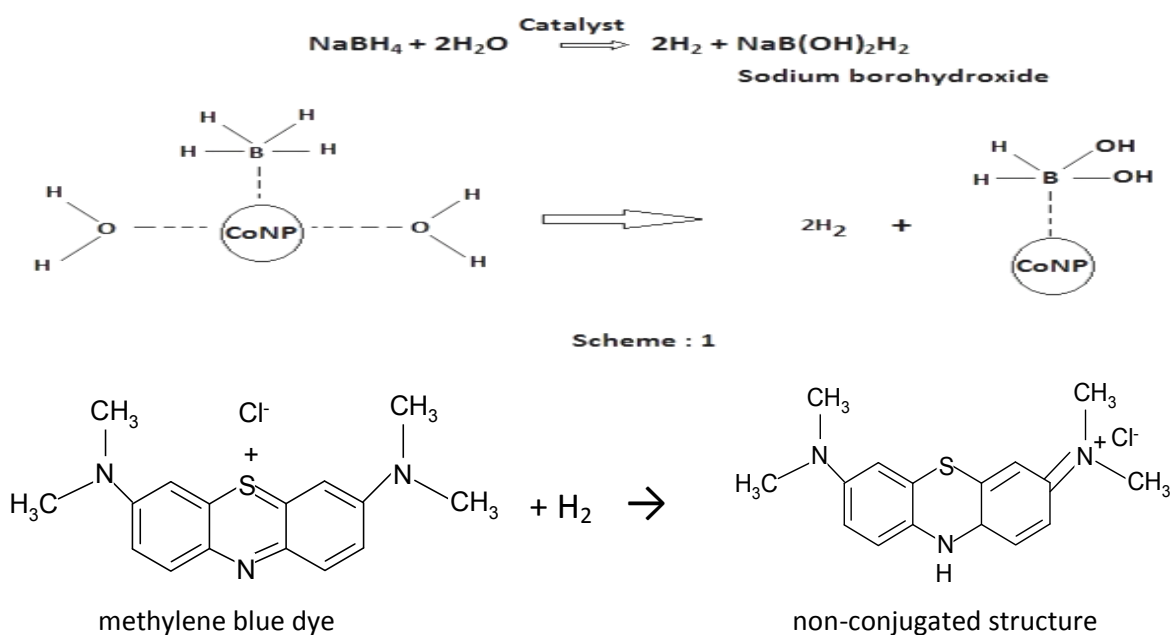
To investigate their catalytic activity, the cobalt nanosized particles were first employed in the degradation of MB in the presence of sodium borohydride. The progress of the catalytic degradation of MB can be easily monitored by the decrease in its optical density at the wavelength of the absorbance maximum of MB. Fig. 4 shows the UV-Vis spectra of the degradation of MB ( $2 \times 10^{-5} \text{M}$ ) at sodium borohydride concentration of ( $2 \times 10^{-2} \text{M}$ ). It can be seen that the absorption band of MB at 664 nm decreases gradually with the reaction time and the blue colour of the mixture vanished in 120 seconds when the spherical cobalt nanoparticles were used. In the control

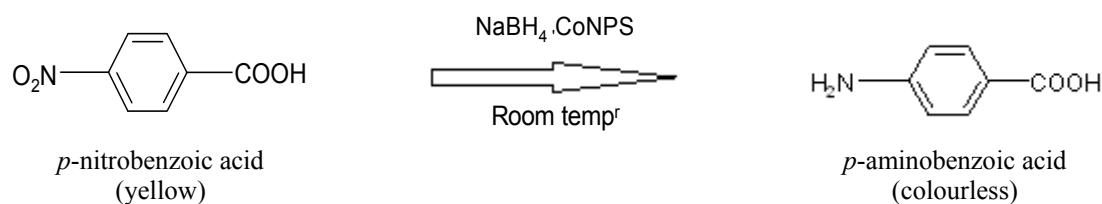
experiment without any catalyst, an intense absorption peak at 664 nm was still observed even after 100 minutes (Fig. 4(b)). The reaction rate of MB degradation with cobalt catalyst is at least 50 times faster than the results of the control test. This clearly indicates that the spherical cobalt nanoparticles have high activity in degradation of MB. Cobalt sulphate used as catalyst in place of nanoparticles has no effect and the spectrum is almost similar to that obtained in Fig. 4(b).

### 3.2 Rhodamine-B dye degradation in presence and without presence of CoNPs

To examine the universality of spherical cobalt nanoparticles as catalysts for dye degradation, we then chose rhodamine B as test target. Fig. 5 shows the UV-Vis spectra for the degradation of rhodamine-B ( $2 \times 10^{-5} \text{M}$ ) at same concentration of sodium borohydride as employed in case of methylene blue. Fig. 5(e) shows that the intensity of the absorption band of rhodamine-B at 550 nm decreases gradually with the reaction time, and the colour of the mixture changes in only 40 seconds when the spherical cobalt nanoparticles were used as catalyst. In the control experiment without any catalyst, an intense absorption peak at 550 nm was observed even after 100 minutes (Fig. 5(f)). The reaction rate of rhodamine B degradation with nanoparticles as catalyst is at least 150 times faster than the results of the control test. The pale pink solution obtained at the end of 1 minute of reaction time was filtered off and the test for presence of carboxylic acid group was performed using saturated sodium bicarbonate solution. No effervescence of  $\text{CO}_2$  indicates absence of the  $\text{COOH}$  group in the dye molecule. Presence of the catalyst therefore can reduce the carboxylic acid moiety either to the aldehyde or to the alcoholic stage. The fate of the unsaturation groups in the dye molecules could not be clearly ascertained using GC/MS and all our attempts to isolate the fragments out of dye degradation reaction proved unsuccessful.

### 3.3 Reason of colour change of dye molecules





Dyes are coloured because of the presence of chromophores which are part of the conjugated system in the molecule. In addition to one or more chromophores (examples are Nitro-, Azo, Anthraquinone or Phthalocyanine moiety, Anthracene, Phenanthrene etc.) most dyes contain colour enhancing groups like carboxylic, sulphonic or hydroxyl groups classified as auxochromes. If any of the features mentioned above are missing or altered, the colour of the dye is lost or weakened. The research group of Kojima (Kojima *et al.* 2002) has shown that an aqueous solution of sodium borohydride in presence of a catalyst liberates hydrogen. The hydrogen thus liberated in our case by reaction of cobalt nanocolloids and borohydride in aqueous medium by virtue of scheme 1 is responsible for change of structure of methylene blue dye to its nonconjugated structure and hence loss of colour is observed.

In case of Rhodamine B, the carboxylic acid group is reduced to alcohol while the main framework of the dye molecule seems to remain unaltered. The colour of the dye therefore changes from bright red to pale pink within 1 minute. We have also studied the reduction of *p*-nitrobenzoic acid in aqueous solution (pale yellow colour) under similar conditions. Chemical studies indicate that the colourless solution obtained within a few minutes contains *p*-aminobenzoic acid by virtue of reduction of the  $-\text{NO}_2$  group under the experimental conditions.

It is therefore imperative that if the chromophore which is part of the conjugation system is destroyed, the colour of the dye will be discharged and if there is change in the auxochrome group, the intensity of the colour will be reduced considerably.

### 3.4 Separation of CoNPs and recyclability study

The catalyst can be easily separated from the reaction medium. As cobalt nanoparticles possess magnetic property, they get stuck into the magnetic stirrer used in the system. Aqueous solution was slowly decanted from the reaction vessel and cobalt nanocolloids containing the magnetic stirrer were dispersed in deionised water using a sonicator. The solution was centrifuged when all nanoparticles settled at the bottom of the centrifuge tube. The aqueous solution was finally decanted out. The process was repeated two times when finely dispersed black particles were obtained. Recycling experiments were then performed to test the reuse of the spherical Co nanoparticles. Catalytic experiments under similar conditions suggest that the regenerated particles still possess relatively good activity even after 7 cycles. The time of degradation of methylene blue dye with every cycle however increases and gets doubled during the 7<sup>th</sup> recycle experiment (Fig. 6). After 4 consecutive cycles the cobalt nanoparticles were collected for HRTEM image to study their particle size distribution and to verify whether agglomeration or further degradation of particles has occurred. TEM image (Fig. 7) of the recycled particles clearly show that no such phenomena have happened.

For comparison, another group of experiments were carried out using Pd nanoparticles as catalysts for dye degradation reactions. Palladium nanoparticles were prepared and characterized



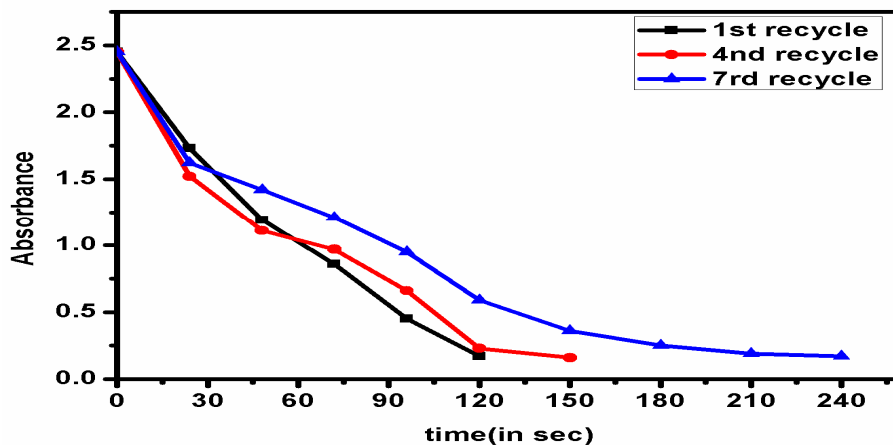


Fig. 6 Plot of the absorbance at  $\lambda_{\max}$  of MB versus time during degradation for the 1<sup>st</sup>, 4<sup>th</sup>, 7<sup>th</sup> reuse of the CoNPs.  $[\text{NaBH}_4]=2\times 10^{-2}\text{M}$  and  $[\text{Methylene Blue}]=2\times 10^{-5}\text{M}$

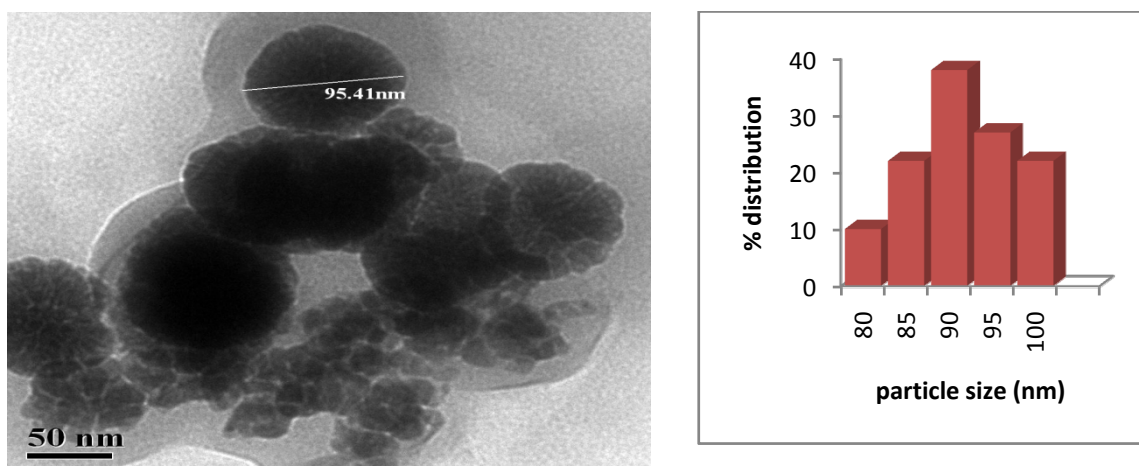


Fig. 7 TEM of recovered cobalt nanoparticles after 4<sup>th</sup> recycle

as described in our previous work (Mondal *et al.* 2014). The morphology and size of the Pd nanoparticles are shown below (Fig. 8).

#### 4. Catalytic activity of PdNPs in dye degradation reactions

Fig. 9 shows the UV-Vis spectra for the degradation of methylene blue and rhodamine-B using palladium catalyst. For MB, the absorption intensity of the system utilizing Pd nanoparticles decreases rapidly and the reaction is completed within 3 min 40 second (Fig. 9(a)). For Rhodamine-B, the absorption intensity of the system utilizing Pd nanoparticles as catalyst (same mmole metal concentration as cobalt nanoparticles) also decreases with time and the reaction is completed within 5 minutes. The reaction rate of methylene blue and rhodamine B degradation

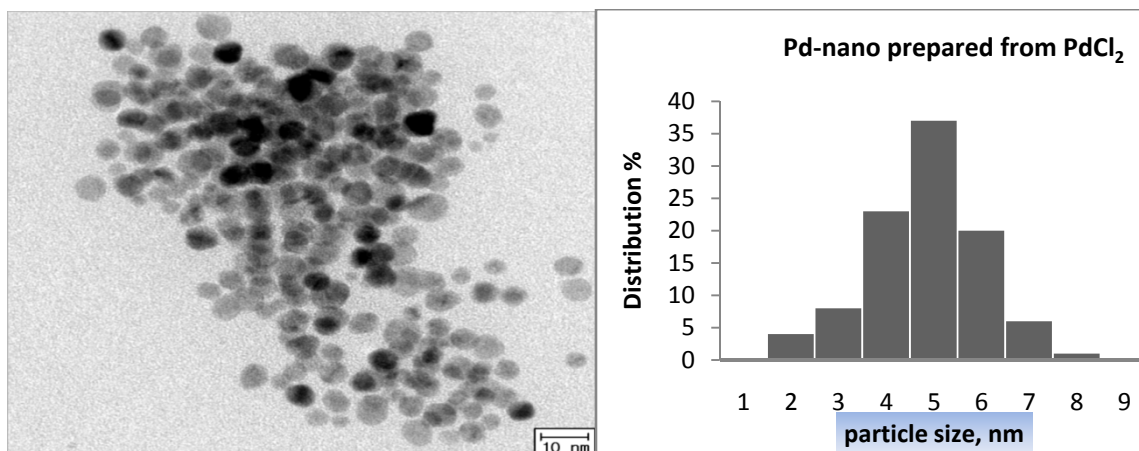


Fig. 8 TEM picture of palladium nanoparticles and their size distribution

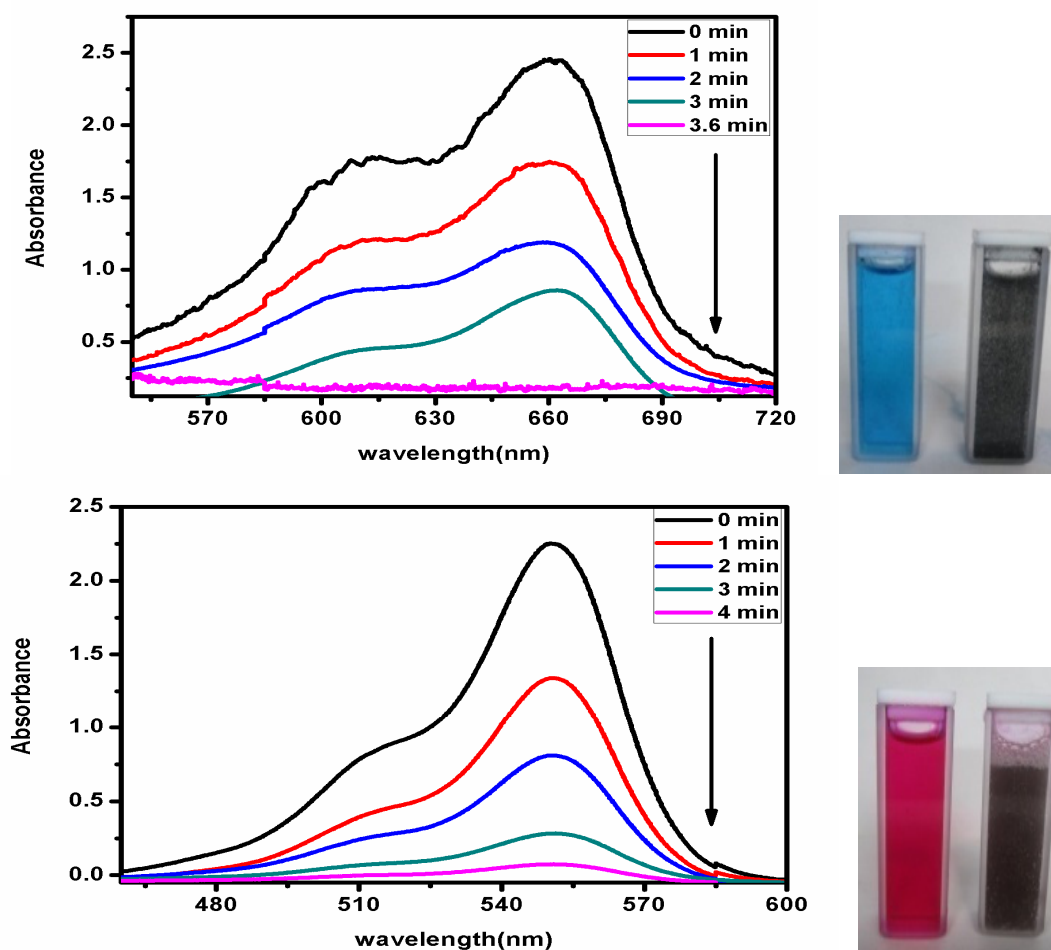


Fig. 9(a) UV-vis spectra of MB degradation in presence of PdNPs (b) Rhodamine-B degradation in presence of PdNPs

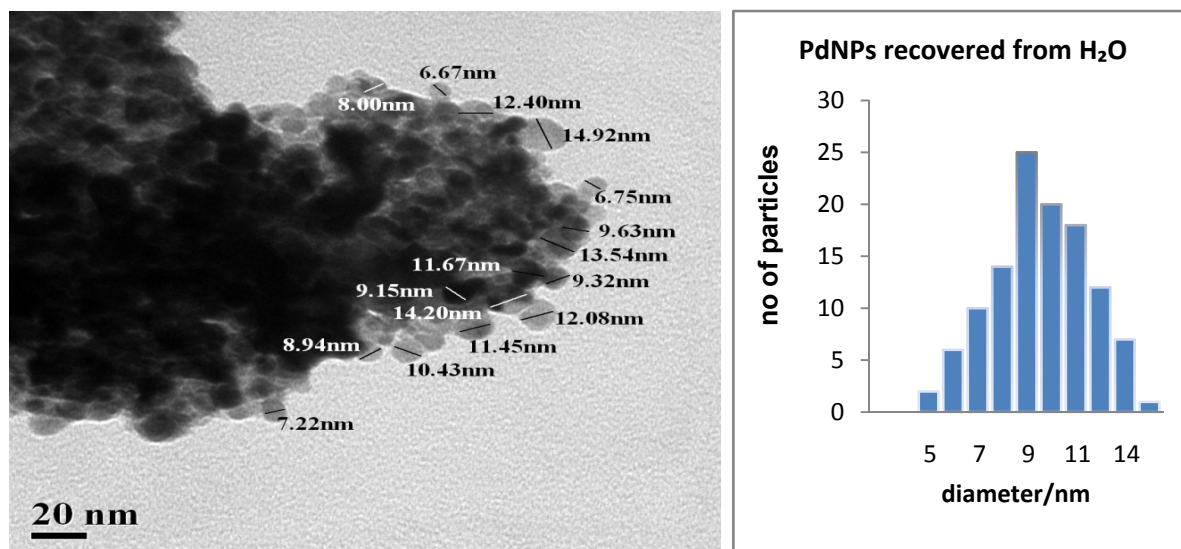


Fig. 10 Recovered TEM picture of palladium nanoparticles after 1<sup>st</sup> recycle of dye (MB) degradation

with cobalt nanoparticles is therefore much faster compared to palladium nanoparticles under similar conditions. The reaction is however incomplete when no palladium nano particles were used or when palladium chloride was added in place of nanoparticles. In all cases sodium borohydride was used as the reducing agent in the aqueous system. In absence of  $\text{NaBH}_4$ , no degradation of dye molecules occur and simple use of molecular hydrogen (under gas balloon pressure) does not yield any result.

To recover the palladium particles for recycling process the aqueous solution was first decanted off and similar steps were followed as employed in case of cobalt particles. To our surprise we notice that after second cycle, the catalytic activity was completely lost. This is evident as even after 15 minutes there was no change in colour of the dye solutions. HRTEM of the nanoparticles collected after first dye degradation show considerable changes as far as average particle size distribution is concerned. Micrographs reveal considerable aggregation of the palladium particles on use and this is reflected in the increase in average size of recovered particles. Palladium particles freshly prepared from  $\text{PdCl}_2$  had on an average a diameter of  $5 \pm 0.5$  nm and this increased to around  $10 \pm 1$  nm (almost 100%) at the end of the first cycle (Fig. 10). TEM micrograph reveals considerable closeness of particles and even agglomeration. So from industrial point of view it is pertinent that palladium particles are not good catalysts for dye degradation processes. On the other hand cobalt is a much cheaper material and its catalytic activity and reusability is superior to palladium nanoparticles under similar situations.

## 5. Conclusions

It is evident that the spherical cobalt nanoparticles can catalyze the degradation reaction of dyes in the presence of sodium borohydride and produces a remarkable enhancement in the reaction rate. It is highly air stable and represents an inexpensive, eco-friendly alternative noble metal catalyst suitable for waste water treatment. A common belief that smaller the particles better

is their behaviour as surface catalysts has been proved wrong in the present case as palladium particles of much smaller size distribution were found to be inactive compared to larger cobalt particles for same set of degradation reactions. More degradation reactions of organic dyes involving various functional groups will be undertaken in future to elucidate the degradation mechanism using these cobalt nanocolloids.

## Acknowledgements

The authors are grateful to the department of Chemistry, R.S College and Indian Institute of Engineering Science & Technology (IEST) for all instrumental support and to the University Grants Commission-New Delhi for providing financial support and scholarship to A.M.

## References

- Arslan, I. (2001), "Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation, and ferrous iron-catalyzed ozonation", *J. Hazard. Mater.*, **85**, 229-241.
- Arslan, I., Balcioglu, I.A. and Bahnemann, D.W. (2000), "Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel TiO<sub>2</sub>-photocatalysts", *Appl. Catal. B: Environ.*, **26**, 193-206.
- Cao, F., Deng, R.P., Tang, J.K., Song, S.Y., Lei, Y.Q. and Zhang, H.J. (2011), "Cobalt and Nickel with various morphologies: mineralizer-assisted synthesis, formation mechanism, and magnetic properties", *Cryst. Eng. Comm.*, **13**, 223-229.
- CaO, Y.B., Zhang, X., Fan, J.M., Hu, P., Bai, L.Y., Zhang, H.B., Yuan, F.L. and Chen, Y.F. (2011), "Synthesis of Hierarchical Co micro/nano-composites with hexagonal plate and polyhedron shapes and their catalytic activities in Glycerol hydrogenolysis", *Cryst. Growth Des.*, **11**, 472-479.
- Dakhlaoui, A., Smiri, L.S., Babadjiam, G., Schoenstein, F., Molinié, P. and Jouini, N. (2008), "Controlled elaboration and magnetic properties of submicrometric cobalt fiers", *J. Phys. Chem. C*, **112**, 14348-14354.
- Dutta, A.K., Maji, S.K. and Adhikary, B. (2014), "Fe<sub>2</sub>O<sub>3</sub> nanoparticles: An easily recoverable effective photo-catalyst for the degradation of rose Bengal and methylene blue dyes in the waste-water treatment plant", *Mater. Res. Bull.*, **49**, 28-34.
- Fan, J., Guo, Y., Wang, J. and Fan, M.H. (2009), "Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles", *J. Hazard. Mater.*, **166**, 904-910.
- Guo, L., Liang, F., Wen, X.G., Yang, S.H., He, L., Zheng, W.Z., Chen, C.P. and Zhong, Q.P. (2007), "Uniform Magnetic chains of hollow cobalt mesospheres from one-pot synthesis and their assembly in solution", *Adv. Funct. Mater.*, **17**, 425-430.
- Jana, N.R., Sau, T.K. and Pal, T. (1999), "Growing small silver particles as redox catalyst", *J. Phys. Chem. B*, **103**, 115-121.
- Kalwar, N.H., Sirajuddin, Soomro, R.A., Sherazi, S.T.H., Hallam, K.R. and Khaskheli, A.R. (2014), "Synthesis and characterization of highly efficient nickel nanocatalysts and their use in degradation of organic dyes", *Internat. J. Metals*, **20**, 10-14.
- Kojima, Y., Suzuki, K.I., Fukumoto, K., Sasaki, M., Yamamoto, T., Kawai, Y. and Hayashi, H. (2002), "Hydrogen generation using sodium borohydride solution and metal catalysts coated on metal oxide", *Int. J. Hyd. Eng.*, **27**, 1029-1034.
- Kositzi, M., Antoniadis, A., Poullos, I., Kiridis, I. and Malato, S. (2004), "Solar photocatalytic treatment of simulated dyestuff effluents", *Sol. Energy*, **77**, 591-600.
- Liang, X.M. and Zhao, L.J. (2012), "Room temperature synthesis of air-stable cobalt nanoparticles and their highly efficient adsorption ability for Congo red", *RSC Adv.*, **2**, 5485-5487.
- Liu, C.Y., Jiang, Z.J. and Sun, L.W. (2005), "Catalytic properties of silver nanoparticles supported on silica

- spheres”, *J. Phys. Chem. B*, **109**, 1730-1735.
- Liu, S.H., Gao, H.T., Ye, E.Y., Low, M., Lim, S., Zhang, S.Y., Lieu, X.H., Tripathy, S., Tremel, W. and Han, M.Y. (2010), “Graphitically encapsulated cobalt nanocrystal assemblies”, *Chem. Commun.*, **46**, 4749-4751.
- Mondal, A., Das, A., Adhikhari, B. and Mukherjee, D.K. (2014), “Palladium nanoparticles in ionic liquids: reusable catalysts for aerobic oxidation of alcohols”, *J. Nanopart. Res.*, **16**, 1-10.
- Mondal, A., Adhikhari, B. and Mukherjee, D.K. (2015), “Room temperature synthesis of air stable Cobalt nanoparticles and their use as catalyst for Methyl Orange dye degradation”, *Coll. Surf. A: Physiochem. Eng. Aspect.*, **482**, 248-257.
- Patil, S.S. and Shinde, V.M. (1988), “Biodegradation studies of aniline and nitrobenzene in aniline plant waste water by gas chromatograph”, *Environ. Sci. Technol.*, **22**, 1160-1165.
- Sánchez-Martin, J., González-Velasco, M., Beltrán-Heredia, J., Gragera-Carvajal, J. and Salguero-Fernández, J. (2010), “Novel tannin-based adsorption in removing cationic dye (Methylene Blue) from aqueous solution. Kinetics and equilibrium studies”, *J. Hazard. Mater.*, **172**, 9-16.
- Sauer, T., Neto, G.C., José, H.J. and Moreira, R.F.P.M. (2002), “Kinetics of Photocatalytic degradation of a reactive dye in a TiO<sub>2</sub> slurry reactor”, *J. Photochem. Photobiol. A: Chem.*, **149**, 147-154.
- Shao, M.W., Wang, F.X., Cheng, L., Chen, D.Y., Fu, Y. and Ma, D. (2009), “Si/Pd nanostructure with high catalytic activity in degradation of eosin Y”, *Mater. Res. Bull.*, **44**, 126-129.
- Shih, Y.H., Tso, C.P. and Tung, L.Y. (2010), “Rapid degradation of methyl orange with nanoscale zerovalent iron particles”, *J Environ. Eng. Manag.*, **20**, 137-143.
- Soomro, R.A., Sherazi, S.T.H., Sirajuddin, Memon, N., Shah, M.R., Kalwar, N.H., Hallam, K.R. and Shah, A. (2014), “Synthesis of air stable copper nanoparticles and their use in catalysis”, *Adv. Mat. Lett.*, **5**, 191-198.
- Wang, X., Yuan, F.L., Hu, P., Hu, L.J. and Bai, L.Y. (2008), “Self assembled growth of hollow spheres with octahedron-like Co nanocrystals via one-pot solution fabrication”, *J. Phys. Chem. C*, **112**, 8773-8778.
- Xia, L.X., Zhao, H., Liu, G., Hu, X., Liu, Y., Li, J., Yang, D. and Wang, X. (2011), “Degradation of dyes using hollow copper microspheres as catalyst”, *Coll. Surf. A: Physiochem. Eng. Aspect.*, **384**, 358-362.
- Zhang, P., An, Q., Guo, J. and Wang, C.C. (2013), “Synthesis of mesoporous magnetic Co-NPS/carbon nanocomposites and their adsorption property for methyl orange from aqueous solution”, *J. Coll. Interf. Sci.*, **389**, 10-15.
- Zhang, W., Hu, H., Shao, M.W., Lu, L., Wang, H. and Wang, S. (2007), “Synthesis of layer deposited silicon nanowires, modification with Pd nanoparticles, and their excellent catalytic activity and stability in the reduction of methylene blue”, *J. Phys. Chem. C*, **111**, 3467-3470.