



Room-temperature synthesis of air stable cobalt nanoparticles and their use as catalyst for methyl orange dye degradation



Arijit Mondal^a, Bibhutosh Adhikary^b, Debkumar Mukherjee^{a,*}

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

^b Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, India

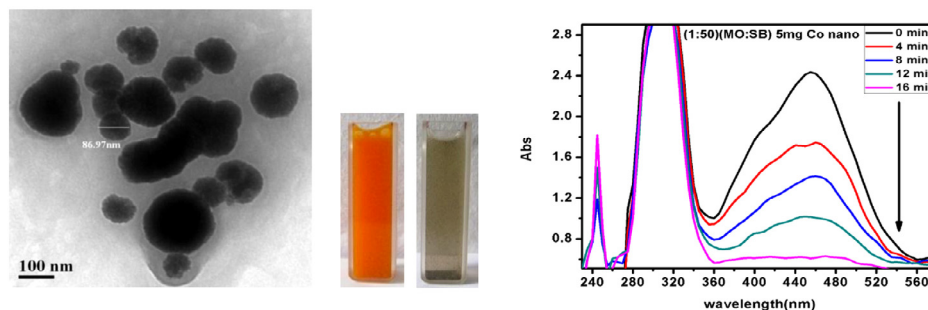
HIGHLIGHTS

- Tetrabutyl ammonium bromide stabilized cobalt nanoparticles prepared at room temperature.
- Methyl orange dye solution can be completely degraded within 16 min.
- The used nanoparticles can be recovered from the aqueous solution by applying a magnet.
- Catalytic activity of cobalt is superior to palladium nanoparticles under similar situations.
- Tentative reaction mechanism has been predicted based on chemical and kinetic studies.

GRAPHICAL ABSTRACT

Cobalt nanoparticles catalytically degrade methyl orange dye in presence of NaBH₄.

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ABSTRACT

An easy, green and economically viable approach has been made to synthesize highly active and ordered structures of cobalt nanoparticles. The air stable nanoparticles were prepared from cobalt sulphate using tetra butyl ammonium bromide as surfactant and sodium borohydride as reductant. The cobalt nanocolloids in aqueous medium were found to be efficient as catalysts for the degradation of toxic organic dyes. Our present study involves degradation of methyl orange 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 was found to degrade the organic dye effectively but lose their catalytic activity after recovery. Based on chemical and kinetic studies an attempt has been made to elucidate the mechanism of dye degradation using the nanoparticles.

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1. Introduction

In recent years several wet-chemical approaches such as pyrolysis [1,2], solvothermal [3], hydrothermal decomposition [4], modified polyol processes [5] and template-based methods [6]

have been developed to synthesize cobalt crystals with different morphologies. Some efforts have been focused on exploring the relations between their shapes and properties. There is however no report of a very simple and quick method to prepare cobalt nanoparticles [7,8].

In recent years considerable attention has been paid to the environmental problem involving water treatment [9]. The pollution of water sources by dyes from the textiles and mining industries has become a serious environmental concern now-a-days. The textile

* Corresponding author. Tel.: +91 033 24029402.

E-mail address: debkumarmukherjee@rediffmail.com (D. Mukherjee).

dyes with high aromatic content and low biodegradability have emerged as major environmental pollutants [10,11]. Nearly 10–15% of the dye is lost in the dyeing process and is released in the wastewater. The wastewater 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 of workers. Skin diseases, chemical burns, irritation, ulcers and respiratory problems are common among workers involved in water treatment plants [12]. Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades for the treatment of textile wastewater. Although most of them were found to be effective, the cost involved in the process is rather expensive [13,14]. Shao et al. [15] and Zhang et al. [16] 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. [17] employed silver nanoparticles supported on silica spheres to reduce eosin and methylene blue. Pal et al. [18] used silver particles in aqueous surfactant media and studied their catalytic properties towards the reduction of a number of dyes. Unfortunately, silver nitrate the raw material for production of silver nanoparticles is also expensive. However in none of these articles the mechanism of dye degradation has been discussed. In the present case we have made an attempt to find the mechanistic pathway of dye degradation based on chemical and kinetic studies conducted on them.

Nanosized magnetic particles are considered to be potential adsorbents for aqueous pollutants due to their high surface areas and the unique advantage of easy separation using external magnetic fields. Several reports have been published on the use of various types of magnetic nanoparticles like iron [19,20], cobalt [2,21], etc. along with reducing agents for degradation and removal of dyes. The magnetic particles mentioned are almost all iron-based oxides [19,22]. 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 [23].

Herein, we used tetrabutyl ammonium bromide stabilized cobalt nanoparticles, prepared at room temperature, as an adsorbent in aqueous solution. Aqueous solution of methyl orange (MO) can be completely degraded within 16 min by the cobalt nanoparticles. 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 (CoSO_4), tetrabutyl ammonium bromide (TBAB), sodium borohydride (SB), methyl orange (MO), 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 NaBH_4

To a screw-capped glass bottle equipped with a stirring bar were added 64 mg of cobalt sulphate (225 μmole), 100 mg tetrabutyl

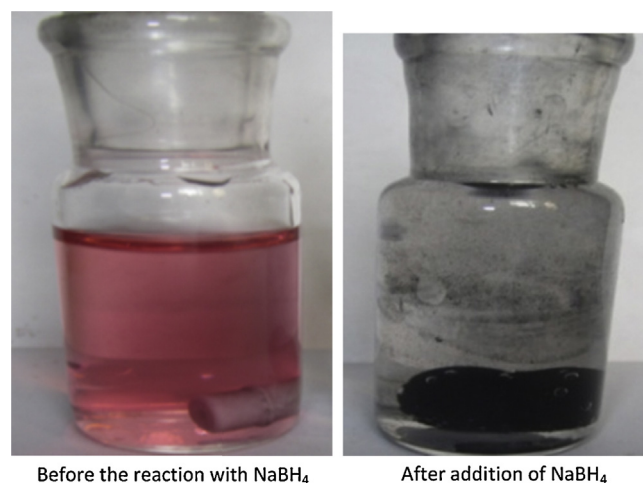


Fig. 1. Preparation of magnetic cobalt nanoparticles.

ammonium bromide (300 μmole) and 8 ml of deionized water. After adding deionized water solution of NaBH_4 (0.1 M) dropwise, the mixture was stirred at room temperature for 15 min and then aqueous solution was decanted off. The TBAB-stabilized CoNPs (132 mg) were washed with water ($5 \times 2.0 \text{ ml}$) and acetone ($5 \times 2.0 \text{ ml}$) and dried under vacuum. The particles thus prepared can be stored at room temperature for several days (Fig. 1).

2.3. Catalytic degradation process

In a representative degradation experiment, 5 mg of TBAB-stabilized CoNPs and an aqueous solution of NaBH_4 (2 ml, $1 \times 10^{-4} \text{ M}$) were rapidly added one by one into an aqueous solution of MO (2 ml, $2 \times 10^{-6} \text{ M}$). The whole mixture was then subjected to UV-vis spectral analysis at room temperature. The concentrations of methyl orange were quantified by measuring the absorption intensities at λ_{max} 465 nm.

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 CoNPs in acetone for 45 min 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 room temperature on INTECH spectrophotometer using solutions in 1 cm quartz absorption cell at wavelength 200–700 nm. XRD patterns were obtained from Bruker-Nonius FR-590 Mach 3 instrument after treatment of the samples at 300 $^{\circ}\text{C}$ in nitrogen atmosphere for 30 min. Specific surface area of particles by BET analysis was made using Quantachrome instrument in the relative pressure range 0.05–0.3.

3. Results 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

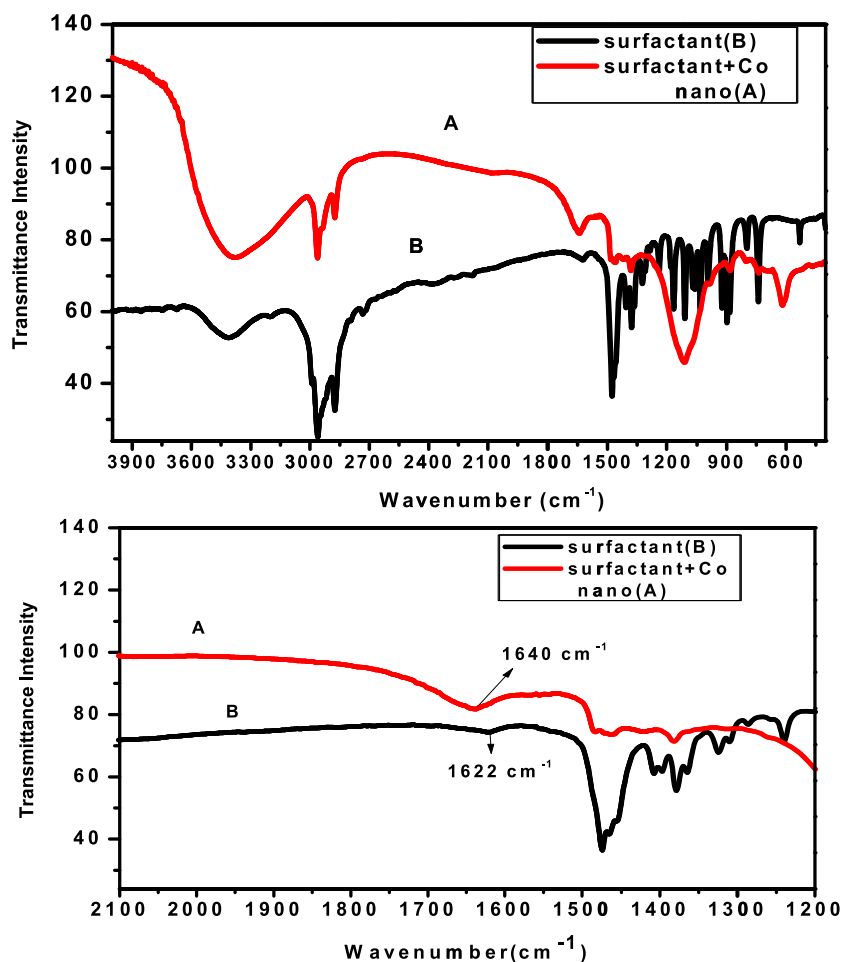
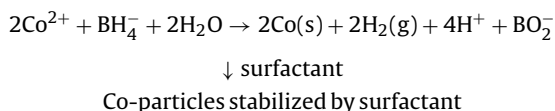


Fig. 2. FTIR spectra of TBAB surfactant (B) and TBAB capped CoNPs (A).

the reducing agent is introduced. The overall reaction proposed for this process is:



The dosage of H_2O is an important factor to synthesize the air-stable TBAB stabilized CoNPs. The release of hydrogen gas (H_2) as shown in the above equation can protect the cobalt particles from being oxidized during the reaction process. De-aired water by using inert gases can also protect the Co-particles from oxidation. We have however used double distilled water during the preparation steps without facing any problem. These cobalt nanocolloids are generally stabilized by TBAB 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. 2)

The surface binding interaction study of TBAB capped CoNPs was carried out by recording FTIR spectra in the range of $4000\text{--}500\text{ cm}^{-1}$. The characteristic bands of pure TBAB can be divided into two regions. Two absorption bands in the range $2958\text{--}2874\text{ cm}^{-1}$ are assigned to symmetric and antisymmetric stretching of CH_2 of the aliphatic group (tail) and another band at 1622 cm^{-1} , is attributed to nitrogen group(head group) of TBAB molecules. The 1622 cm^{-1} band in pure TBAB shifted to 1640 cm^{-1} in capped cobalt nanoparticles. This clearly showed that the capping was due to positively charged nitrogen head group moieties.

3.1. TEM pictures

The morphology and size of the as-synthesized particles on the carbon coated Cu grid were characterized by HRTEM (Fig. 3). The size distribution of Co nanoparticles fall between 80 and 100 nm estimated on the basis of studying 64 such particles. EDX (energy dispersive X-ray spectroscopy) spectrum shows 18.6% cobalt (weight%) present in the isolated nanoparticles (Fig. 4).

3.2. MO 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 MO in the presence of sodium borohydride at 25°C and at pH 10.2. The progress of the catalytic degradation of MO can be easily monitored by the decrease in its optical density at the wavelength of the absorbance maximum of MO. Fig. 5 shows the UV–vis spectra of the degradation of MO ($2 \times 10^{-6}\text{ M}$) at sodium borohydride concentration of $1 \times 10^{-4}\text{ M}$. It can be seen that the absorption band of MO at 465 nm decreases gradually with the reaction time and the orange colour of the mixture vanished completely in 16 min when the spherical cobalt nanoparticles were used (Fig. 5). The absorbance band at 465 nm originates from a conjugated structure formed by the azo bond under the strong influence of the electron-donating dimethylamino group and the band at 300 nm is due to the $\pi\text{--}\pi^*$ transition of the aromatic moiety.

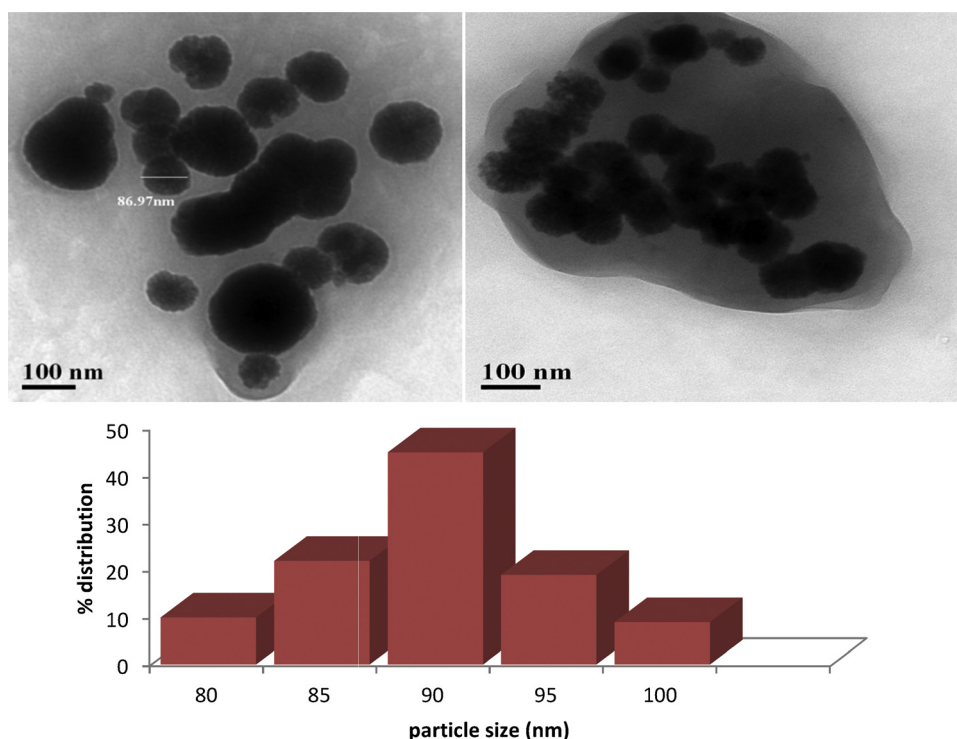


Fig. 3. HRTEM Images of Co nanoparticles and particle size distribution.

In the control experiment without any catalyst, an intense absorption peak at 465 nm was still observed even after 600 min (Fig. 6). The reaction rate of MO 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 MO. Cobalt sulphate used as catalyst in place of cobalt nanoparticles has no effect and the spectrum is almost similar to that obtained in Fig. 6. It is important to state that both sodium borohydride and nanoparticles are involved in the process of dye degradation as absence of any one in the reaction medium does not lead to any noticeable colour change.

3.3. Effect of pH, temperature and amount of nanoparticles on degradation of MO

3.3.1. Effect of pH

The degradation of methyl orange was carried out at 25 °C and at pH 10.2 in most cases. The effect of high and low pH on degradation rate was studied keeping the amount of cobalt nanoparticles same

and other conditions unchanged. The pH of the aqueous solution was adjusted by adding requisite amounts of HCl (0.1 N) and NaOH (0.1 N) solutions. It is quite evident that the degradation of the dye occurs effectively at low pH but at pH < 8, the rate of degradation of MO is fast enough to be monitored by concentration changes at different time intervals (Fig. 7). The sodium borohydride aqueous solution is however stable in the alkaline medium and the chances of protonation of the amine groups is considerably reduced at pH > 9. The enhanced reduction of azo dyes with an increase in H⁺ concentration has also been reported by Shih et al. [19] and Soomro et al. [23].

3.3.2. Effect of temperature

Rate of degradation of methyl orange at different temperatures has been shown in Fig. 8. With increasing temperatures the rate of dye degradation increases and above 50 °C the rate becomes high enough to be carefully monitored or measured. In general, all our dye degradation reactions have however been carried out at 25 °C. It is to be mentioned that the temperature of discharged dye waste

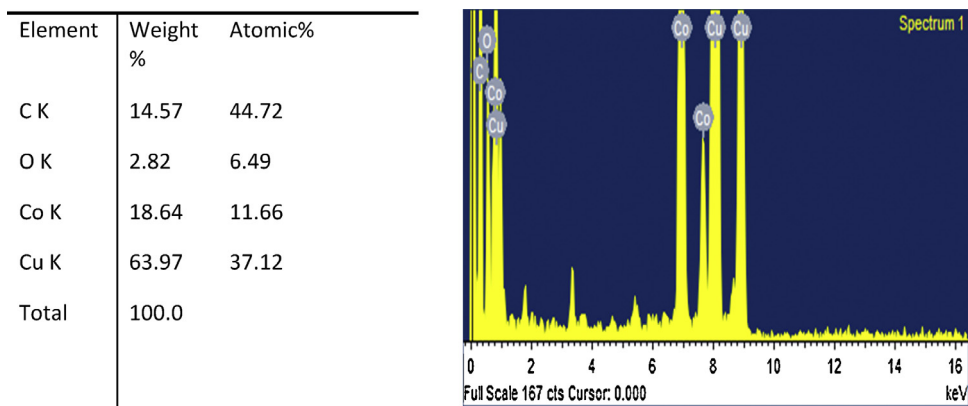


Fig. 4. EDX Spectrum of Co nanostructure.

Molecular Structure of Methyl Orange

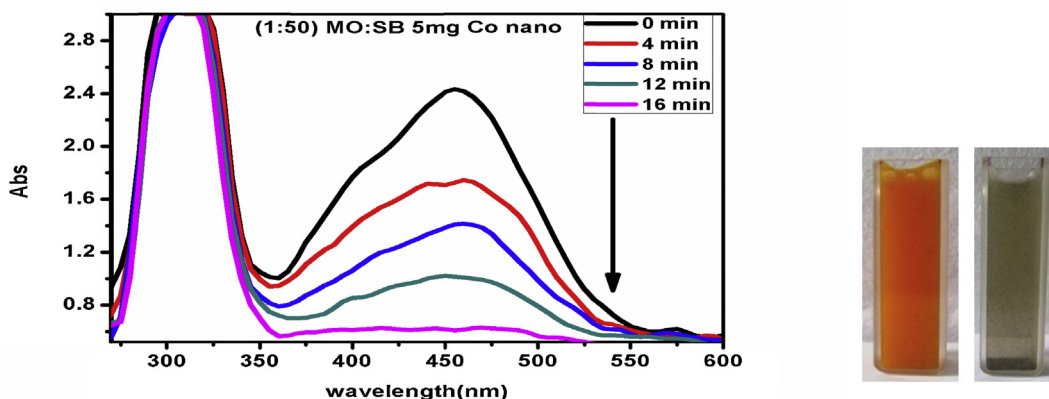
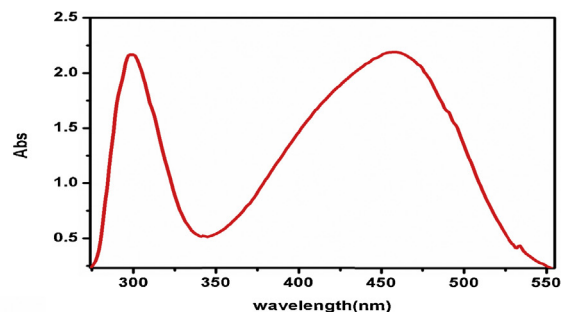
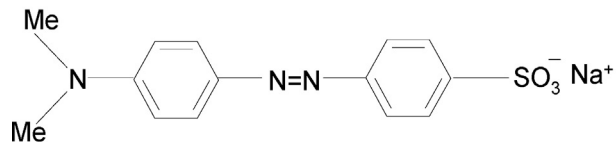


Fig. 5. MO degradation in the presence of CoNPs and neat MO spectrum with structure.

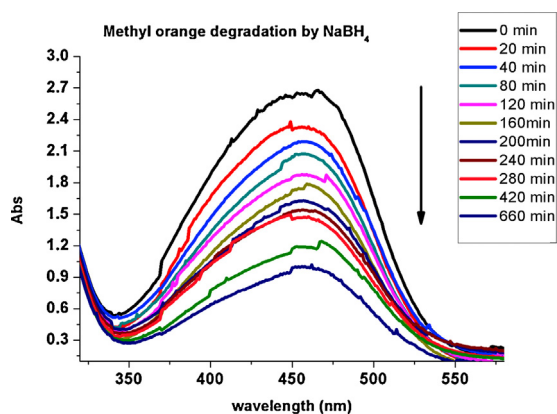


Fig. 6. Degradation of methyl orange without use of cobalt nanoparticles.

water is usually higher and so it would be convenient to apply this technology

Fig. 9A depicts degradation of methyl orange using different amounts of cobalt nanoparticles but at constant MO/sodium borohydride molar ratio and temperature maintained at 25 °C. Fig. 9B shows that the rate of decolorization of the dye also increases as the concentration of sodium borohydride increases.

3.4. Kinetic study of the MO dye degradation in presence of CoNPs [24]

UV-vis spectral results (Fig. 10) were used to study the kinetics of the catalytic reaction [24]. The experiment was carried out by adding 5, 4 and 2 mg of CoNPs into an aqueous solution of MO (2×10^{-6} M) and NaBH₄ (1×10^{-4} M) at 25 °C and pH 10.2. The degradation rate of MO was monitored at a maximum wavelength of 465 nm visible region and was found to follow first order kinetics

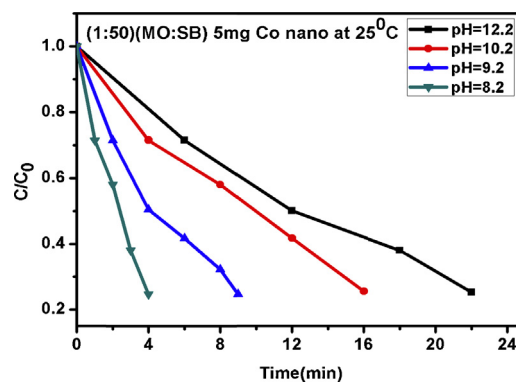


Fig. 7. Degradation of MO by CoNP at different pH values.

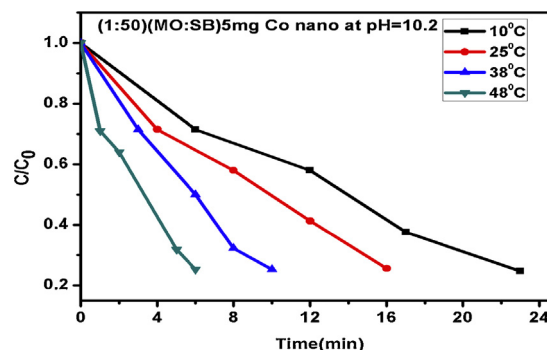


Fig. 8. Degradation of MO by CoNP at different temperatures.

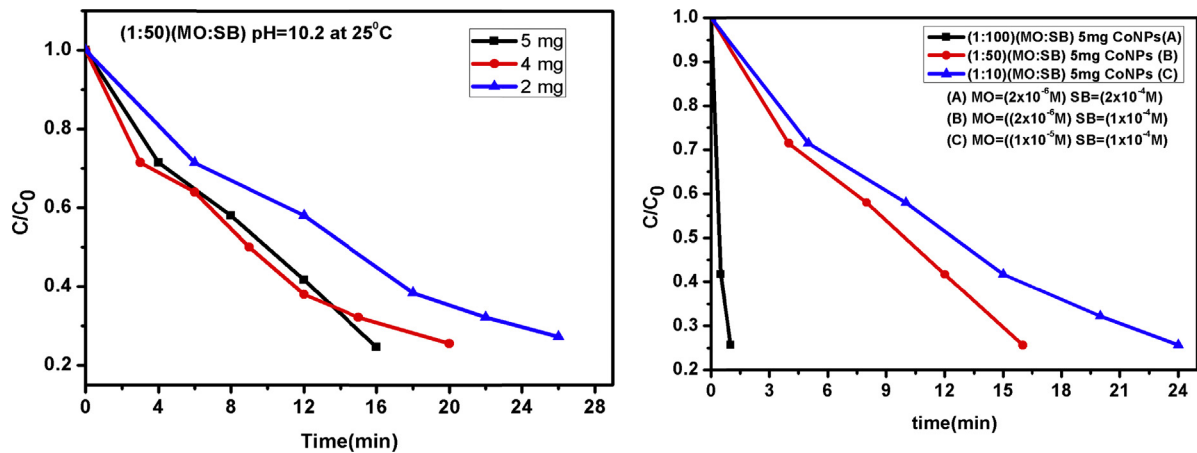


Fig. 9. Effect of degradation of MO using different amounts of cobalt nanoparticles (A) and sodium borohydride (B).

as given by Eq. (1). The first order rate constant (*k*) for degradation of MO was calculated and found to be 0.064 s⁻¹ (3.84 min⁻¹).

$$\ln \left(\frac{C}{C_0} \right) = -kt \quad (1)$$

Kinetic studies of MO degradation at different temperatures was carried out using 5 mg CoNPs and aqueous solution of NaBH₄ (1 × 10⁻⁴ M) at pH 10.2 to measure the activation energy of the

process. The *E_a* value estimated to be 62.42 kJ/mol i.e. 15.1 kcal/mol is comparable to double bond hydrogenation of common organic azo compounds [25].

3.5. Mechanism of dye degradation

Dyes are generally coloured because they absorb light in the visible spectrum (350–700 nm), contain at least one chromophore

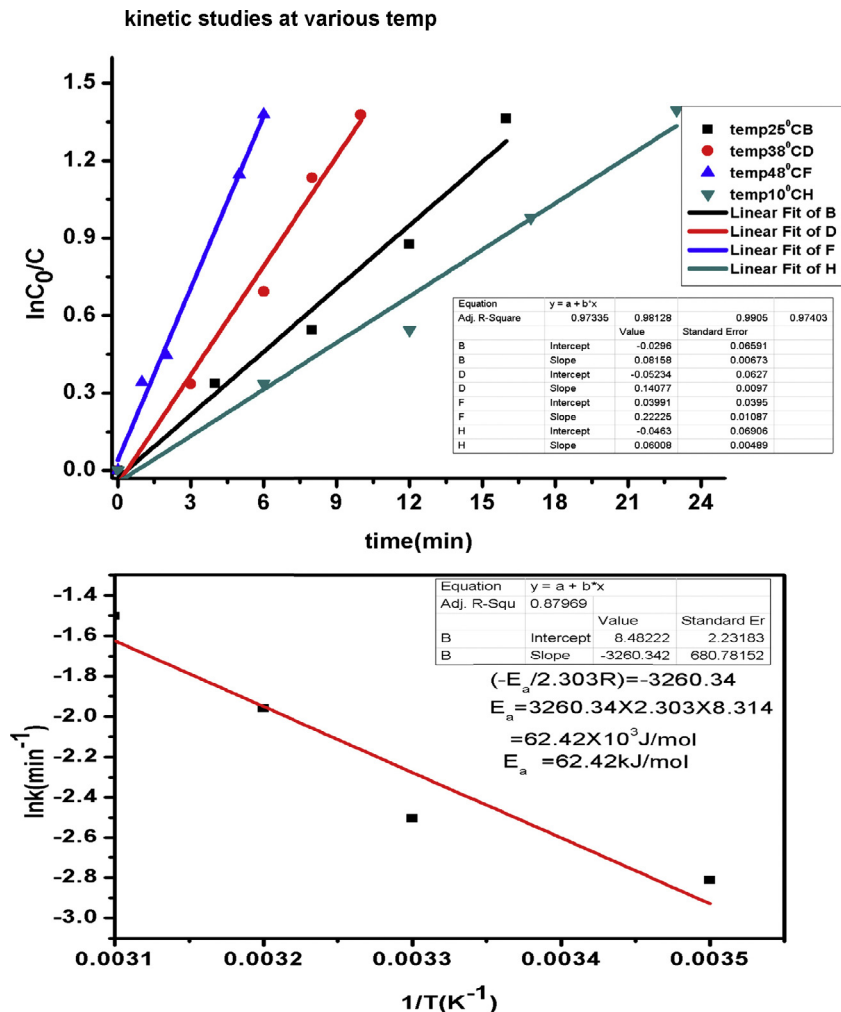


Fig. 10. Kinetic studies of methyl orange dye degradation at various temperatures.

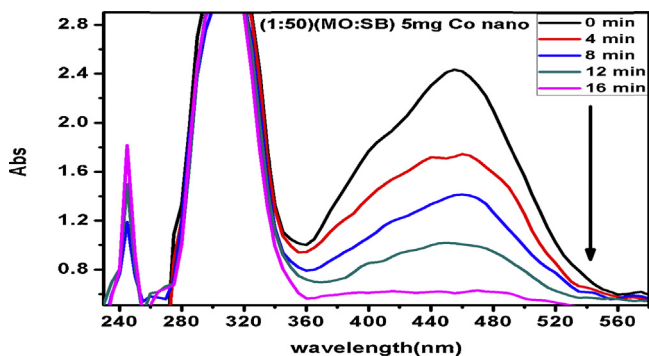


Fig. 11. MO degradation using cobalt nanocolloids in aqueous medium with formation of sulphanic acid.

(like nitro, azo, anthraquinone moiety, phthalocyanine, methine group, etc.) and have a conjugated system. In addition to chromophores, most dyes contain colour enhancing groups known as auxochromes, like $-\text{COOH}$, SO_3H or $-\text{OH}$ groups which also influence dye solubility. If any of these features get affected or is lacking from the molecular structure, the colour of the dye is lost. Regarding the requirement of a chromophore generating colour in organic compounds, it is important that the chromophore must be part of a conjugated system and if there occurs coupling that results in doubling the length of the conjugated system then there will be bathochromic shift i.e. to a darker colour [26].

The molecular structure of methyl orange contains an azo group in conjugation with benzene rings and a sulphonic acid moiety that imparts an orange colour to the dye. It is well known [27] that an aqueous solution of sodium borohydride in presence of a catalyst liberates hydrogen with formation of sodium borohydroxide as given in Scheme 1.

The liberated H_2 reduces the azo group of methyl orange first to imine and finally to the amine stage as proposed in Scheme 2. We have reported that both borohydride and cobalt nanocolloids must act together to be effective in discharging the colour of the dye. The final product of degradation in our case is the sulphanic acid (*p*-aminobenzenesulphonic acid) and the *p*-phenylenediamine. The peak of sulphanic acid at 246 nm [20] gradually increases with time in our case (Fig. 11) as the absorption maxima at 465 nm diminishes. All our attempts to isolate the fragments from the dye degradation however failed but we were able to recycle the nanocolloids for subsequent reactions.

The proposed scheme could also explain why high H^+ concentration facilitates azo dye degradation because hydride ion from the borohydride species and H^+ from coordinated water are involved in the reduction of the azo group. Also it is expected that with more cobalt nanoparticles used, there will be more surface sites for coordination of borohydride, water molecules and the dye which will favour the reduction steps shown in Scheme 2. Specific surface area of as-prepared CoNPs and those recovered after two catalytic runs were measured on the basis of the Brunner–Emmett–Teller analysis of the particles in the relative pressure range 0.05–0.3. (BET plots and data supplied as supplementary material). BET data for Co particles before ($33.91 \text{ m}^2/\text{g}$) and after reaction ($32.96 \text{ m}^2/\text{g}$) shows negligible change in surface area which is eminent from the recyclability nature of recovered nanoparticles.

3.6. 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

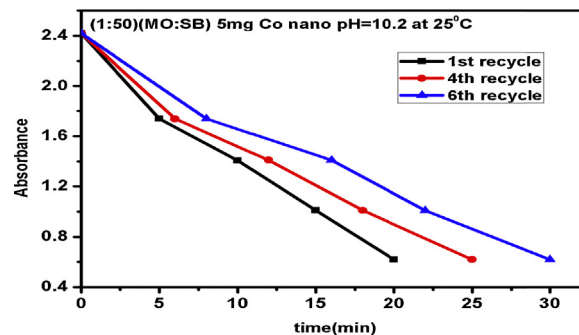


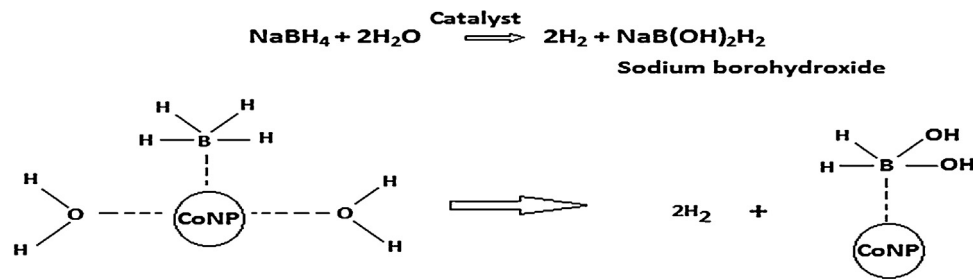
Fig. 12. Recycle test of MO dye degradation using recovered CoNPs.

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 methyl orange dye with every cycle however increases and gets doubled during the 6th recycle experiment (Fig. 12). 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. 13) of the recycled particles alleviated our fear as no such phenomena were noticed. XRD patterns of cobalt particles before and after two catalytic cycles were also identical which emphasizes the stable nature of CoNPs (figures provided as supplementary material).

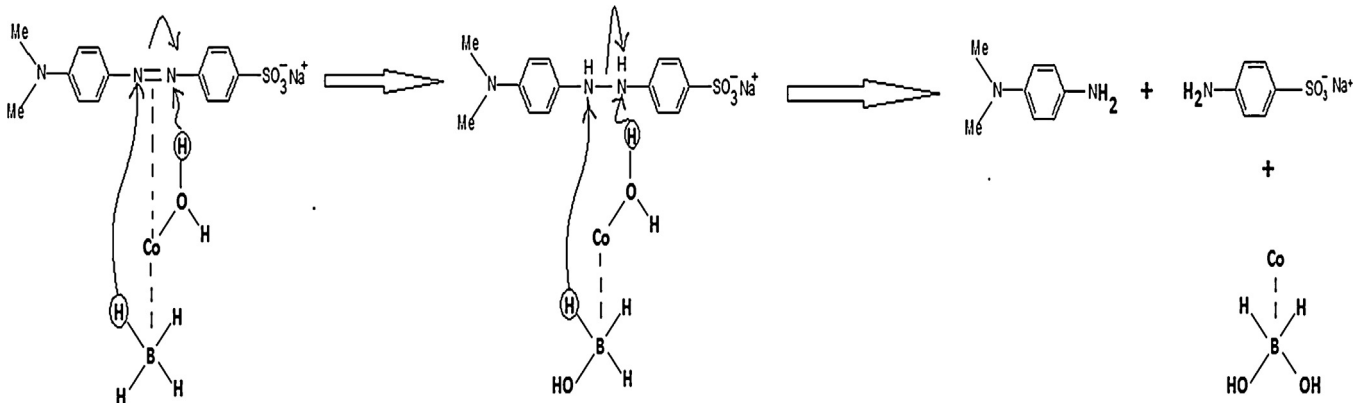
For comparison, another group of experiments were carried out using Pd nanoparticles as catalysts for dye degradation reactions. Palladium nanoparticles were prepared and characterized as described in our previous work [28]. The morphology and size of the Pd nanoparticles are shown below (Fig. 14). Specific surface area measurement done on as-prepared palladium particles show an average area $47.4 \text{ m}^2/\text{g}$ which is high compared to those measured for cobalt particles.

3.7. Catalytic activity of PdNPs in dye degradation reactions

Fig. 15 shows the UV–vis spectra for the degradation of methyl orange using palladium catalyst. For MO, the absorption intensity of the system utilizing Pd nanoparticles decreases rapidly and the reaction is completed in 20 min. The reaction is incomplete when no palladium nano particles were used or when palladium chloride was added in place of nanoparticles. In all cases sodium borohydride was however used as the reducing agent in the aqueous system. The reaction rate of methyl orange degradation with cobalt nanoparticles is therefore slightly faster compared to palladium nanoparticles. 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 noticed that after second cycle, the catalytic activity was completely lost. This is evident as even after 480 min there was no change in colour of the dye solution. 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 PdCl_2 had on an average a diameter of $5 \pm 0.5 \text{ nm}$ and this increased to around



Scheme 1. Generation of hydrogen by coordination of borohydride and water to CoNPs.



Scheme 2. Hydrogenation of the azo bond and degradation of the dye.

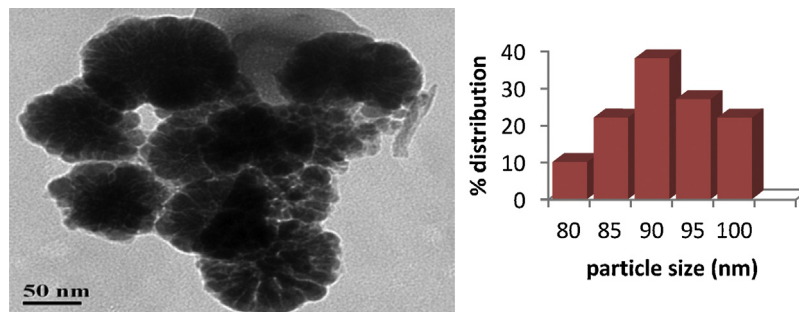


Fig. 13. TEM of recovered cobalt nanoparticles after 4th recycle.

8 ± 1 nm (almost 60%) at the end of the first cycle (Fig. 16). Also BET analysis for surface area measurement of recovered nanoparticles show a reduced value $21.8 \text{ m}^2/\text{g}$ from an initial $47.4 \text{ m}^2/\text{g}$. 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.

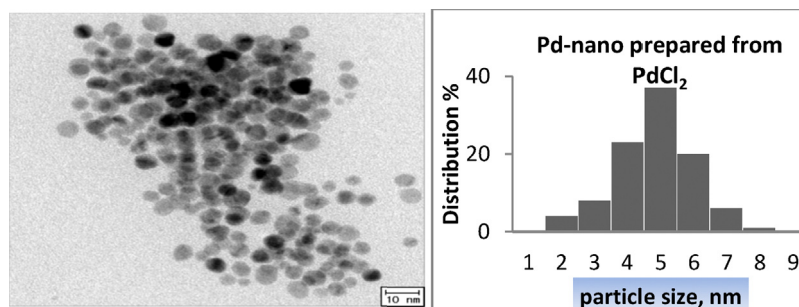


Fig. 14. TEM picture of palladium nanoparticles and their size distribution.

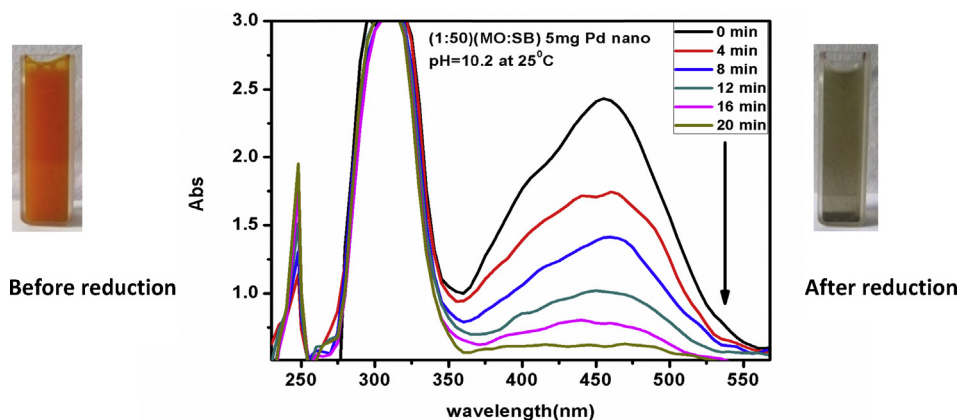


Fig. 15. MO degradation using palladium nanoparticles.

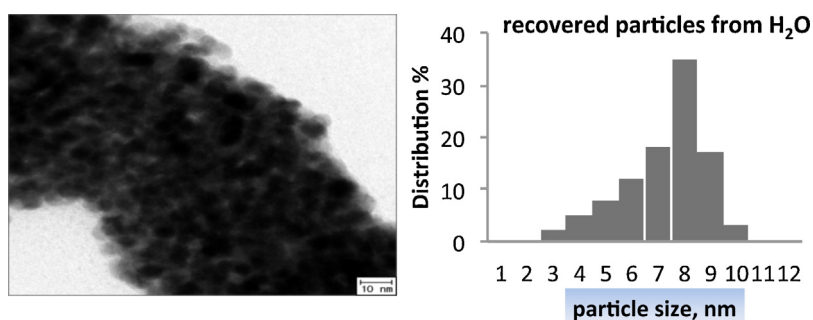


Fig. 16. Recovered TEM picture of palladium nanoparticles after 1st recycle of dye (MO) degradation.

4. Conclusion

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. Another common belief that smaller particles behave as good catalysts because of their high surface area and more active centres 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 as far as their catalytic behaviour is concerned. Further degradation reactions involving various organic functional groups will be undertaken in future using the cobalt nanoclusters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2015.05.011>

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