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

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Abstract: We demonstrate here a simple and versatile route to prepare nickel nanoparticles from nickel sulphate using a surfactant and sodium borohydride as the reductant. These active and ordered structures of nickel nanoparticles were found to be efficient catalysts for degradation of methyl orange in aqueous medium. The particles remaining in solution were found to possess excellent catalytic activity even after several recycling attempts and have little propensity to coalesce or aggregate into inactive bigger lumps. Size selectivity was found to be one major reason of catalytic reusability using metal nanoclusters for similar dye degradation under identical reaction conditions.

Keywords: synthesis; nickel nanoparticles; methyl orange; dye degradation; recyclability.


Biographical notes: Arijit Mondal has graduated from the University of Calcutta in 2009, Master’s degree from Guru Ghasidas University in 2011 and enrolled as a PhD scholar in IIEST (Indian Institute of Engineering Science and
Transition metal nanoparticles by virtue of their novel optical, electronic, magnetic and chemical properties, have myriads of applications as pigments in the field of electronics, in catalysis and in biological systems as important drug delivery components. Nickel nanoparticles have applications as biosensors, fuel-cell layers, composites and solar energy materials and also as nanofluids [1]. Recently, it has been described that nickel nanoparticles are potential candidates for catalysts, magnetic materials, conducting inks, and ferrofluids [2]. One certain way to enhance the applicability of nano-particles is to modify their surface in such a way so that they can be easily re-dispersed for recyclability reactions.

Synthesis of metal nanoparticles employing salts of transition metals like nickel, copper and iron is relatively difficult because they are easily oxidised under reaction conditions. Many techniques have been used for the synthesis of nanoparticles including micro-emulsion [3,4] solvothermal reduction [5] thermal decomposition of organic complexes [6–8] use of microwave [9] and even gas phase condensation reactions [10]. Cordente et al. [11] used the thermal decomposition of organic complex technique to synthesise nickel nanorods in tetrahydrofuran (THF) solution. The textile dyes with high aromatic content and low biodegradability have emerged as major environmental pollutants [12,13]. Pollution of water sources by dye discharge from the textiles and mining industries has become a serious environmental threat now-a-days. Several 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 effluents. Although most of them were found to be effective, the cost involved in the process is rather expensive due to want of suitable catalysts that could sustain the regeneration techniques followed after dye degradation [14,15]. 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 recent reports have been published on the use of various types of magnetic nanoparticles like iron [16,17] cobalt [18,19], etc. along with reducing agents for effective degradation.
and removal of dyes. There are however very few reports about use of nickel nanoclusters for the purpose of dye degradation mainly because of their difficulty in preparation and stabilisation [20]. In the present case we have made an attempt to synthesise nickel nanosized particles from nickel sulphate using TBAB as surfactant and NaBH₄ as the reducing agent under ambient laboratory conditions. These particles were then employed as catalysts for dye degradation to satisfy environmental demands.

2 Experimental

2.1 Chemicals and materials

All chemicals were of reagent grade and used without further purification. Nickel sulphate hexahydrate (NiSO₄, 6H₂O), tetrabutyl ammonium bromide (TBAB), sodium borohydride (SB), Methyl Orange (MO), and acetone were purchased from Merck-India. Nickel nanoparticles, cobalt nanoparticles have been abbreviated as NiNPs, CoNPs respectively in the manuscript.

2.2 Preparation of TBAB stabilised nickel nanoparticles reduced by NaBH₄

To a screw-capped glass bottle equipped with a stirring bar were added 64 mg of nickel sulphate hexahydrate (243.4 μmole), 100 mg tetrabutyl ammonium bromide (310 μmole) and 8 ml of deionised water. After adding deionised water solution of NaBH₄ (0.1 M) dropwise, the mixture was stirred at room temperature for 15 min and then aqueous solution was decanted off. The TBAB-stabilised NiNPs (125 mg) were washed with water (5 × 2.0 ml) and acetone (5 × 2.0 ml) and dried under vacuum. The particles thus prepared can be stored at room temperature for several days.

2.3 Catalytic degradation process

In a representative degradation experiment, 5 mg of TBAB-stabilised NiNPs and an aqueous solution of NaBH₄ (2 ml, 1 × 10⁻⁴ M) were rapidly added one by one into an aqueous solution of MO (2 ml, 2 × 10⁻⁶ M). The whole mixture was then subjected to UV-vis spectral analysis at room temperature. The concentrations of MO were quantified by measuring the absorption intensities at λₘₐₓ, 465 nm.

2.4 Characterisation

Transmission Electron Microscopy (TEM) images of nickel nanoparticles were obtained using CM30 microscope operating at 200 kV and expanded to 470 pixels/cm resolutions. TEM samples were prepared by dispersing NiNPs in acetone for 45 min using 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 range 200–700 nm.
3 Results and discussion

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

\[
2\text{Ni}^{2+} + \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{Ni}(s) + 2\text{H}_2(g) + 4\text{H}^+ + \text{BO}_2^-
\]

\[
\downarrow \text{surfactant (TBAB)}
\]

Ni-particles stabilised by the surfactant

Without the surfactant, the black colloidal particles immediately agglomerate into a big size lump and catalytic studies were made even with these aggregated lump materials. The presence of the surfactant on the surface of metal nanoparticles can be explained by comparing their FTIR data (Figure 1).

**Figure 1** FTIR spectra of TBAB surfactant (A) and TBAB capped NiNPs (B) (see online version for colours)

The surface binding interaction study of TBAB capped NiNPs was carried out by recording FTIR spectra in the range of 4000–500 cm\(^{-1}\). Two absorption bands in the range 2958–2874 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 1638 cm\(^{-1}\) in capped nickel nanoparticles. This clearly showed that the capping was due to positively charged nitrogen head group moieties [21].

**TEM images**

The morphology and size of the as-synthesised particles on the carbon coated Cu grid were characterised by TEM (Figure 2). The size distribution of Ni nanoparticles falls mainly between 100–160 nm (1 \(\mu\)m = 1000 nm) estimated on the basis of studying 64 such particles. Energy dispersive X-ray spectroscopy (EDX) spectrum shows 46.32% nickel (weight %) present in the isolated nanoparticles.
The XRD pattern of the fresh nickel nanoparticles and after the reaction, shown in Figure 3, shows definite patterns for nickel and peaks are extremely broad. The characteristic peaks at 44.49, 51.75, 76.40 for nickel (JCPDS, No.04-0850) marked by their indices (111), (200) and (220) have been observed. This revealed that the as-synthesised nanocrystals were pure nickel with fcc structure [22]. The crystallite size of the as-synthesised nickel, $D_c$, was calculated from the major diffraction peaks of the base of (111) using the Scherrer equation (1)

$$D_c = \frac{K \lambda}{\beta \cos \theta}$$

where $K$ is a constant (ca.0.9) [22]; $\lambda$ is the X-ray wavelength used in XRD (1.5405 Å); $\theta$ is the Bragg angle; $\beta$ is the pure diffraction broadening of a peak at half-height, that is, broadening due to the crystallite dimensions. The diameter of the nanoparticles calculated by Scherrer formula is 125.2 nm (0.125 μm).
3.1 Catalytic activity of nickel nanoclusters

To investigate their catalytic activity, the nickel nanosized particles were first employed in the degradation of MO in the presence of sodium borohydride at 28°C and at pH 10. 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 (Figure 4). Figure 5 shows the UV-vis spectra of the degradation of MO ($2 \times 10^{-6}$ M) at sodium borohydride concentration of ($1 \times 10^{-4}$ 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 24 min when the spherical nickel nanoparticles were used (Figure 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 dimethyl amino group and the band at 300 nm is due to the $\pi-\pi^*$ transition of the aromatic moiety.

In the control experiment without any catalyst, an intense absorption peak at 465 nm was still observed even after 660 min (Figure 6). The reaction rate of MO degradation with nickel catalyst is at least 50 times faster than the results of the control test. This clearly indicates that the spherical nickel nanoparticles have high activity in degradation of MO. It is important to state that both sodium borohydride and nanoparticles are involved in the process of dye degradation as absence of either in the reaction medium does not lead to any noticeable colour change.
Another reaction was performed when in situ degradation of the dye was done using nickel sulphate and sodium borohydride in aqueous medium under similar conditions. The dye lost its orange colour completely in 24 min and the spectrum was similar to that obtained using the capped nanoparticles. The importance of using TBAB as protective coating surrounding the nickel particles could however be illustrated during recycling experiments. The black lump collected at the end of the degradation after the in situ reaction was found to be completely inactive and no degradation was noticed even after the first cycle.

**Effect of temperature**

The effect of temperature on the reaction kinetics of methyl orange with NiNPs was investigated over the temperature range of 10–48°C. The degradation efficiencies increased with increasing temperature in the reaction time. With increasing temperature, 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 been carried out at 28°C. It is to be mentioned that the temperature of discharged dye waste
water is usually higher than 30°C and so it would be convenient to apply this technology for water treatment.

3.2 Mechanism of dye degradation

Dyes are generally coloured because they absorb light in the visible spectrum (350–700 nm), contain at least one chromophore (such as 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 –COOH, SO₃H or –OH groups which also influence dye solubility. If any of these features gets affected or is lacking from the molecular structure, the colour of the dye is lost [23]. 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 [24] that an aqueous solution of sodium borohydride in presence of a catalyst liberates hydrogen with formation of sodium borohydroxide as given in Scheme 1.

Scheme 1  Role of nanoparticles for formation of borohydroxide species

The liberated H₂ reduces the azo group of methyl orange first to imine and finally to the amine stage. The final product of degradation in our case is the sulphanilic acid (p-aminobenzenesulphonic acid) and the p-phenylenediamine.

3.3 Separation of NiNPs and recyclability study

Aqueous solution was slowly decanted from the reaction vessel and nickel 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 process was repeated two times when finely dispersed black particles were obtained. Recycling experiments were then performed to test the reuse of the spherical Ni nanoparticles. Catalytic experiments under similar conditions suggest that the regenerated particles still possess relatively good activity even after three cycles. The time of degradation of methyl orange dye with every cycle however increases during the fifth recycle experiment (Figure 7). After three consecutive cycles the nickel nanoparticles were collected for TEM image to study their particle size distribution and to verify whether agglomeration or further degradation of particles has occurred. TEM image (Figure 8) of the recycled particles (32 particles studied) shows no appreciable changes in size distribution (Figure 8(b)).
4 Conclusion

It is evident that the spherical NiNPs can catalyse the degradation reaction of dyes in the presence of sodium borohydride and produce a remarkable enhancement in the reaction rate. They are highly air stable and represent an inexpensive, eco-friendly alternative noble metal catalyst suitable for waste water treatment. Further degradation reactions involving various organic functional groups will be undertaken in future using the nickel nanoclusters.

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References

Room-temperature synthesis of nickel nanoparticles and their use


