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

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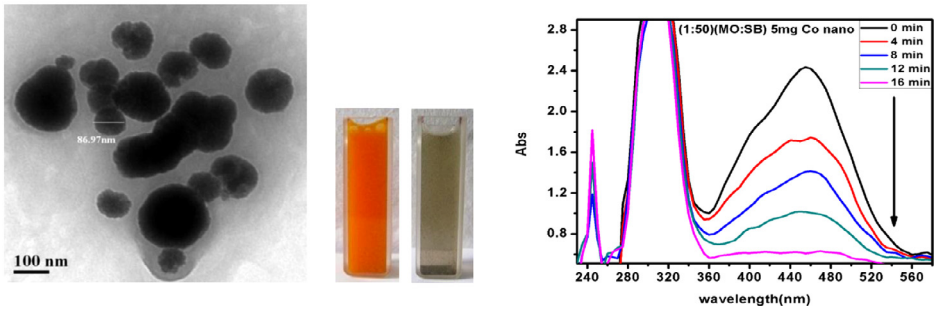
HIGHLIGHTS

- 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 $NaBH_4$.



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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.

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

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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 waste-water. 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 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 waste-water. 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 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× 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 (Fig. 1).

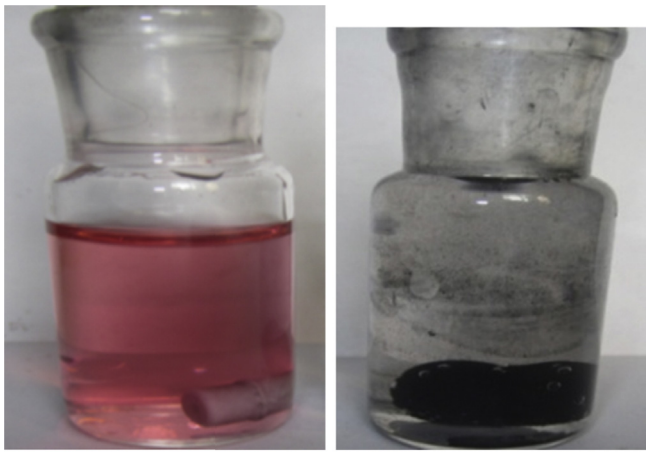

Fig. 1. Preparation of magnetic cobalt nanoparticles.

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, 1×10^{-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 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 $CoNP_S$ 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 °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