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Facile synthesis of silver nanoparticles and their application in dye degradation

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ABSTRACT

The present article reports a simple, facile and eco-friendly method based on microwave irradiation for the synthesis of silver nanoparticles in aqueous medium using starch as stabilizing agent and a new reducing agent namely hexamine. The silver nanoparticles were characterized by UV–vis, FTIR, XRD and HR-TEM analysis. UV–vis spectroscopic studies provided sufficient evidences for the formation of nanoparticles. The role of starch in the synthesis and stabilization of the nanoparticles was obtained from FTIR studies. The XRD and HR-TEM investigations clearly demonstrated the crystalline nature of the nanoparticles. From the TEM images, the silver nanoparticles were found to be spherical and of nearly uniform size with an average diameter of 18.2 ± 0.97 nm. The nanoparticles showed excellent catalytic activity in the degradation of methyl orange and rhodamine B by $NaBH_4$.

1. Introduction

Synthetic organic dyes are extensively used in various industries such as textile, paper, plastic, food, cosmetic and pharmaceutical [1]. The discharges from these industries result in substantial environmental pollution. Studies have shown that many of the dyes are carcinogenic, mutagenic and harmful to the environment [2]. These coloured dyes are toxic to aquatic organisms and perturb the aquatic life. Various physical, chemical and biological water treatment methods have been used for removing the dye wastes. These include methods such as adsorption, membrane filtration, chemical oxidation and reduction, photochemical and electrochemical treatment, anaerobic treatment etc. [3–8]. Since the dye pollutants are chemically stable, traditional water treatment methods are found to be ineffective. They are highly resistant to microorganisms and hence the water soluble dyes are not generally decolourized effectively by conventional biological treatment [9]. Recently, nanotechnology has been extended to the area of waste water treatment [10]. Nanocatalysis has undergone a remarkable growth in recent years and seems to be a revolution in the field of catalysis. Metallic nanoparticles exhibit physical and chemical properties that differ considerably from those of the bulk materials [11]. This is largely due to their finite size and large surface area to volume ratio and the reactivity that depends mostly on their size. The size dependent reactivity and large surface area have made them efficient catalysts [12]. Several researchers have reported the use of nanocatalysts for the effective removal of dye stuffs [12–15].

Among metal nanoparticles, silver nanoparticles (AgNPs) continue to be interesting in nanotechnology due to their excellent optical and electronic properties as well as their strong toxicity to a wide range of microorganism. Several synthetic approaches have been developed for the synthesis of silver nanoparticles including chemical [16], photochemical [17], sonochemical [18], radiolytic [19], polyol [20] and biological methods [21]. Most of these production routes involve the use of toxic chemicals and require harsh reaction conditions. Among these, the most popular method for the preparation of Ag colloids is still the chemical reduction of a silver salt in presence of a stabilizing agent because of its short reaction time. The synthesis and application of silver nanoparticles requires the stabilization of them in suitable stabilizing systems. However, the chemical reagents used as reducing and stabilizing agents in this method are usually highly toxic and poses huge environmental hazards which limits their utility.

In recent years, immense amount of research has been carried out in the area of nanosynthesis by using non-toxic and easily available materials with the aim to reduce environmental threats. Microwave-assisted synthesis of nanoparticles in aqueous medium using green chemicals is receiving much consideration in recent times due to the adherence of this method to the three

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principles of green nanoparticle synthesis which are (i) the selection of a non-toxic reducing agent, (ii) a cost-effective and easily renewable stabilizing agent and (iii) an environmentally benign solvent system. Furthermore it has several attractive features over conventional thermal heating methods such as short reaction time, lower energy consumption and better product yield [22]. Microwave irradiation offers rapid and uniform heating of the reaction medium and thus provides homogeneous nucleation and growth conditions for nanoparticles. Many successful reports on microwave-assisted green synthesis of silver nanoparticles have been published in recent years [23–26].

In this work, we report the microwave-assisted synthesis of silver nanoparticles in aqueous medium using a new reducing agent namely hexamine in presence of starch as stabilizing agent. Hexamine is a low-cost chemical that finds application in medicine and food industry. It has been observed that when a strong reducing agent like $NaBH_4$ is used, the reaction is very fast and has to be cooled to control the rate of reduction in many cases. Moreover, it is highly toxic and synthesis of larger nanoparticles has been found to be difficult [27]. On the other hand, when a mild reducing agent like sodium citrate or ascorbic acid is used, the reduction reaction is slow and has to be carried out at elevated temperatures to enhance the rate of reduction. In addition, they usually yield relatively larger nanoparticles of varying size and shape [28]. In contrast, hexamine is non-toxic, easy to handle, and yields spherical nanoparticles with narrow size distribution at a moderately fast rate. Since all materials used in this method are environment friendly, this may be regarded as a green approach for nanoparticle synthesis. In addition, this method is simple, fast and economic. We have investigated the catalytic utility of the starch stabilized silver nanoparticles (AgNP-starch) in the dye degradation reactions by taking the reduction reactions of methyl orange and rhodamine B by $NaBH_4$ as model reactions.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$), hexamine, methyl orange, rhodamine B and sodium borohydride ($NaBH_4$) were purchased from Merck India Ltd and used without further purification. All aqueous solutions were made by using double distilled water.

2.2. Methods

2.2.1. Synthesis of silver nanoparticles (AgNPs)

To 90 mL of aqueous solution containing 0.1 g starch which was taken in a 250 mL beaker, 10 mL 0.05 M $AgNO_3$ solution was added in a drop wise manner and was stirred for 15 min. Followed by this, 0.028 g (0.002 M) hexamine was added and the reaction mixture was subjected to microwave irradiation for 4 min by placing in a domestic microwave oven (Sharp R-219T (W)) operating at a power of 800 W and frequency 2450 MHz. The nanoparticle formation was monitored using UV–vis spectrophotometer by scrutinizing the reaction mixture after 1, 2, 3 and 4 min of microwave irradiation in the scan range 300–700 nm. Upon microwave irradiation, the colour of the reaction medium changed into yellowish-brown due to nanoparticle formation.

2.2.2. Catalytic reduction of methyl orange

The catalytic reduction of methyl orange by $NaBH_4$ was studied as follows. To 2 mL of aqueous methyl orange solution (0.01×10^{-2} M) taken in a quartz cell of 1 cm path length, 0.5 mL recently prepared $NaBH_4$ solution (0.06 M) was added. Then 0.5 mL of AgNP-starch colloidal solution of a definite concentration was added to start the reaction. The variation in the concentration of methyl orange with time was monitored using UV–vis spectrophotometry by following the change in the absorbance of the peak at 464 nm. The absorption spectra were recorded in 1 min intervals in the range of 200–600 nm at ambient temperature.

2.2.3. Catalytic reduction of rhodamine B

To study this reaction, 0.5 mL freshly prepared $NaBH_4$ solution (0.06 M) was added to 2 mL of rhodamine B solution (0.06×10^{-3} M) contained in a quartz cuvette. Subsequently, 0.5 mL of nanocatalyst solution of a definite concentration was added and UV–vis spectra were recorded every 1 min in the range of 300–700 nm. The kinetics of the reaction was studied by measuring the change in intensity of the peak at 554 nm with time.

2.2.4. Characterization

UV–vis spectroscopic studies were carried out on a Shimadzu UV-2450 spectrophotometer. FTIR spectra were recorded using Perkin Elmer-400 spectrometer with ATR facility. The sample for XRD measurement was prepared by depositing a thin film of the sample on a microscopic glass slide and the diffraction pattern was recorded on a PANalytic X'PERT-PRO X-ray spectrometer. High resolution-transmission electron microscopic (HR-TEM) measurements were done using a JEOL JEM-2100 microscope.

3. Results and discussion

3.1. Synthesis and UV–vis spectroscopic investigation of silver nanoparticles

UV–vis spectrophotometric analysis is used to follow and confirm the formation of starch stabilized silver nanoparticles (AgNP-starch). The reduction of Ag^+ ions into Ag nanoparticles was monitored by recording the absorption spectrum of the reaction mixture with time in the range of 300–700 nm. The spectra obtained during the synthesis AgNP-starch are depicted in Fig. 1. It is well known that silver nanoparticles show an absorption band in the range of 350–450 nm due to surface plasmon vibrations of conducting electrons [29]. As is evident, initially no band was observed in the range 350–450 nm. But after 2 min of microwave heating, the colourless solution began to change into yellowish brown and a small absorption band appeared around 409 nm suggesting the formation of silver colloids. The intensity of this absorption band increased rapidly with increase in reaction time up to 4 min due to the continuous formation of silver nanoparticles.

However, further increase in reaction time did not cause any appreciable change in the intensity of the SPR band. The sharp

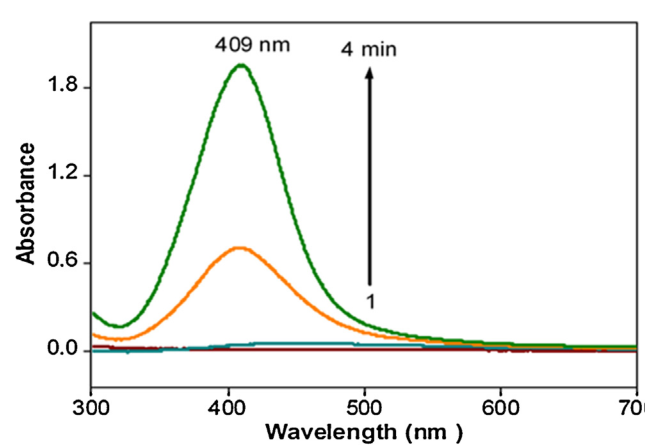

Fig. 1. UV–vis absorption spectra recorded at 1 min interval during the course of microwave-assisted AgNP-starch synthesis.