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Efficient degradation of organic dyes by heterogeneous cefdinir derived silver nanocatalyst

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ABSTRACT

Cefdinir derived silver nanocatalyst (Cef-Ag (0) NPs) was successfully synthesized in aqueous solution by efficient one-pot method and effectively employed for the ultrafast catalytic degradation of Rose Bengal and Eosin Gelblich dyes. The improvement was achieved in percent degradation of toxic dyes by varying and optimizing reaction time, and amount of catalyst reducing agent concentration. The catalytic study revealed that complete reduction $\sim$99.9% of dye was accomplished in short period of reaction time (60 s) by efficient cefdinir derived silver nanoparticles. The calculated K (rate constant) value for RB and EG catalytic degradation was achieved 7×10^{-2} and 10×10^{-2} s^{-1}, respectively by plotting lnC vs time (s) and result show that reaction is following first order kinetics.

Introduction

Nowadays, it is important to continue research toward synthesis of metal nanoparticles (MNPs) by using inexpensive and nontoxic chemicals [1,2], environmentally benign solvents, and clean and renewable/biodegradable materials [3,4]. These nanoparticles were utilized in most of chemical reactions of degradation of pollutant compounds [5–8]. Among the different noble metal nanoparticles, stabilized silver nanoparticles (AgNPs) have been widely employed as catalysts for a wide range of reactions [9,10].

Degradation of dyes effluent is a crucial and sensitive issue for industries [6]. Continuous exposure to these dyes has been exposed to exert influence on anaerobic biomass, irritation of the respiratory system, and gastro intestinal track. Hence, physical or chemical advanced treatment processes are essential and useful for the treatment of waste waters containing these dyes [11]. On the other hand, most of the dyes are useful for different industries purposes like pigmentation of textiles, cosmetics, paper, leather, ceramics, inks, and food processing products, which are derived from AZO dyes. About 15% of the dyes are discharged in the natural streams. This waste signals a great hazard and cause much harm to human and environmental health due to the toxicity of effluent of these dyes [12]. Many techniques are available for the removal of these dyes such as adsorption [13], nanofiltration [14], biological treatment [15] and so on.

Dyes consist of one of the major groups of chemicals besides fertilizers, pharmaceuticals, and petrochemicals. During ancient times, people used dyes from natural resources like tesu flowers, so that they can make their clothes bright and colorful likewise, indigo, logwood, madder, etc. [6]. The dyeing and textile printing industry is a water-intensive industry requiring a large volume of freshwater at various steps of printing and therefore, the volume of wastewater produced is equally large. These effluents, with their high BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand), and poised solids, are very toxic in nature as they contain large quantities of dyes (azoic, indigo, and aniline), bleaching agents, acids/alkalis, and heavy metals in very high concentration [16].

Some textile dyes are relatively challenging to microbial degradation, besides that anaerobic microorganisms when degrading some dyes give birth to aromatic amines that might be dangerous and carcinogenic [17]. Therefore, in recent years, there have been many researches done on fungal depolarization of textile waste water. The use of fungi is a promising alternative to replace or add current treatments [18–20]. Textile industry is one of the most common and essential industrial sectors in the world that plays significant role in nation's economy [21]. Because of drastic changes in customers' demands, the textiles finishing

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industry is a challenge to use high quantity of dyes and auxiliaries that are necessary for modern textile processing [22].

Among all these dyes, Rose Bengal and Eosin Gelblich dyes are highly toxic [23], which contains heterocyclic aromatic compound due to its cationic in the nature [24], Rose Bengal and Eosin Gelblich functional groups pretense a hazard as pollutants to water resources [11]. The emergence applications of heterogeneous catalysts include metal and metal oxide nanoparticles for advanced techniques of waste water treatments so that it could produce successful result [25–28]. Therefore, it is the urge of time for the requirement of a technique which endorses very simple, cost-effective, green, and prompt methods to use nano-based catalytic degradation/reduction of organic dyes pollutants. Previously, antibiotic-based silver nanoparticles were synthesized and used as catalyst for the degradation of some pharmaceutical drugs [29].

Herein, we report a very simple one-pot method for the synthesis of silver nanocatalysts by green method using cefdinir antibiotic and their effective application as heterogeneous, recoverable, and reusable catalyst for remarkably faster and complete degradation of Rose Bengal and Eosin Gelblich dyes in the presence of LiAlH4. The entire research work is based on excellent economy of the process in terms of using cheaper chemicals, facile, and simpler synthesis of catalyst, with shorter time for product formation (quicker procedure) and easy recovery and recycle of this catalyst.

Experimental

Cleaning of glassware

All glassware were soaked in 1 M HNO_3 solution overnight followed by washing with detergent containing solution, tap water, and ultrapure water. The glassware were finally washed several times with deionized water and put in an oven at 100 °C for 1 h. The dried glass wares were properly cooled in room temperature before use.

Chemicals and reagents

Analytical grade 99% $AgNO_3$, 99% NaOH, 98% $LiAlH_4$ and 99%Cefdinir, 97% Rose Bengal (RB), and 97% Eosin Gelblich (EG) were purchased from Sigma–Aldrich and Merck respectively, and utilized without further purification. All solutions that is acidic, basic, and salt solutions were prepared in ultrapure water (conductivity below than 0.05 μS/cm).

Preparation of standard stock solutions

To prepare the standard solutions of compound such as 0.01 M cefdinir, $AgNO_3$, NaOH Rose Bengal and Eosin Gelblich, and 0.1 M $LiAlH_4$, the exact masses of each reagent was taken in 100 ml of volumetric flask and dissolved in ultrapure water.

Synthetic procedure for cefdinir capped-Ag NPs

Highly efficient cefdinir capped-Ag NPs were successfully synthesized by following protocol. In typical procedure 0.4 ml of $AgNO_3$ solution was taken in 20 ml test tube and 0.3 ml cefdinir and 0.2 ml NaOH was added. Solution was shaken properly and final volume was made up to 10 ml with ultrapure water.

Instrumentations

The resulting Cef-AgNPs solution was analyzed by ultraviolet–visible (UV–vis) spectrometer model Shimadzu UV–vis 2600 in the range of 300–800 nm.

The FTIR (Fourier transform infrared) spectra of AgNPs and cefdinir were performed by model (Perkin Elmer BX FTIR) after incorporating the dried sample in solid state KBr disk. FTIR spectra in the range 4000–400 cm^{-1} were recorded, so that it would be easy to investigate the nature of the chemical bonds formed.

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA by using Cu Ka radiation.

High-resolution transmission electron microscopy (HRTEM) analysis was studied by using a JEOL JEM 2100 microscope. A drop of diluted sample in alcohol was dripped on a TEM grid.

Sample preparation for XRD and FTIR and TEM

In each case, the yellow colloidal solution of Cef-AgNPs was poured into petri dish and heated on temperature controlled electric water bath set at 100 °C until solvent evaporation. The dried product was washed several times with both deionized water and ethanol in order to remove any unreacted cefdinir. The product was carefully dried in an oven at 100 °C at least for 60 min. The black particles adsorbed on the glass of petri dish were removed with a clean glass slide. The resulting sample was collected in a small sample ampoule before each analysis.

Procedure for catalytic degradation of dyes

The catalytic activity of cefdinir derived silver nanoparticles was experienced by reduction of RB and EG dyes with an excessive quantity of $LiAlH_4$ only with the quantity of Cef-AgNPs. Under optimized conditions, 10 mg/l dyes (100 μl) along 0.1 M LiAlH4 (100 μl) were taken in a 3.0 ml capacity quartz cuvette and then, the volume of the mixture was adjusted 3.0 ml with distilled water and after that the catalytic degradation of dyes was monitored by recording UV–vis spectra. For application studies, NPs were placed on a piece of glass cover slip by drop casting method followed by solvent evaporation on hot plate at the temperature of 100 °C. The weight of glass cover slip was measured before and after NPs deposition to check out the weight of NPs deposited by difference.

Results and discussion

UV–vis spectroscopy

UV–vis spectrometry was performed to follow and confirm the formation of cefdinir stabilized silver nanoparticles (Cef-Ag (0) NP). 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 300–900 nm. It is observed in UV–vis spectrum of the Cef-Ag (0) NPs that the colloidal silver exhibits a strong absorption between 400 and 415 nm, which corresponds to the surface Plasmon resonance (SPR) of AgNPs [9,30] suggesting the formation of NPs as shown in Fig. 1. The appearance of absorption band in the range of 350–450 nm is due to surface plasmon vibrations of conducting electrons [9,31]. Cef-AgNPs were synthesized with very slow kinetics and showed excellent stability until several months and no significant change is observed in the intensity of the SPR band. The sharp intense band evident the formation of monodispersed and spherical nanoparticles and the absence of any absorption peak in the range of 450–900 nm indicate the no apparent aggregation of nanoparticles [32].

HRTEM analysis

Fig. 2 shows the typical HRTEM image of the AgNPs prepared using chemical reduction approach. TEM analysis on the sample indicated crystalline spherical Cef-AgNPs with 6.80 ± 2.1 nm