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Fluorescence quenching and photocatalytic degradation of textile dyeing waste water by silver nanoparticles

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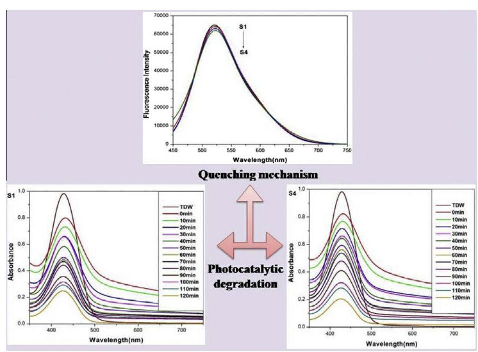
HIGHLIGHTS

- Silver nanoparticles (Ag NPs) have been synthesized by chemical method.
- Spherical shaped Ag NPs were obtained.
- Low fluorescence quantum yield was obtained.
- Apparent rate constants were determined.
- Ag NPs acts as a good nanocatalyst for waste water.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles (Ag NPs) of different sizes have been prepared by chemical reduction method and characterized using UV–vis spectroscopy and transmission electron microscopy (HRTEM). Fluorescence spectral analysis showed that the quenching of fluorescence of textile dyeing waste water (TDW) has been found to decrease with decrease in the size of the Ag NPs. Experimental results show that the silver nanoparticles can quench the fluorescence emission of adsorbed TDW effectively. The fluorescence interaction between Ag NPs (acceptor) and TDW (donor) confirms the Förster Resonance Energy Transfer (FRET) mechanism. Long range dipole–dipole interaction between the excited donor and ground state acceptor molecules is the dominant mechanism responsible for the energy transfer. Furthermore, photocatalytic degradation of TDW was measured spectrophotometrically by using silver as nanocatalyst under UV light illumination. The kinetic study revealed that synthesized Ag NPs was found to be effective in degrading TDW.

Introduction

Water is one of the important enablers of life on earth. It is one of the purest symbols of wealth, health, serenity, beauty and originality. Pure water, which is free of toxic chemicals and pathogenic bacteria, is necessary for human health [1]. Water and environment gets contaminated by the organic matters liberated from textile industries. Textile waste water includes a large variety of dyes and chemicals additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition [2]. Main pollution in TDW came from dyeing and finishing processes and these processes require the input of a wide range of chemicals and

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dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in TDWs are generally caustic soda, detergents, urea, ammonia, wax, starch, pigments, azo and vat dyes that increases its high suspended solids, chemical oxygen demand, heat, color, acidity, toxicity and other soluble substances [3]. These effluents cause a lot of damage to the environment. The removal of color from textile industry and dyestuff manufacturing industry waste waters represents a major environmental concern [4]. Besides high water consumption, this process generates colored waste waters that are particularly difficult to treat [5].

It is well known that colloidal metal nanoparticles exhibit special catalytic, structural, chemical, electronic and novel optical properties from bulk materials [6] owing to quantum sizes and surface effects. NPs have been proven very good candidates for applications in commercial products such as textiles will most likely result in these materials reaching waste water treatment plants. Technological applications of Ag NPs, generally associated with their antibacterial properties, have been continually increasing over the last decade. Ag NPs are currently used in a number of consumer products ranging from room fresheners to shampoos, biomedical products, laundry products and textiles. This latter application is thought to be one of the most important sources of Ag NPs to the environment [7].

The quenching of fluorescence provides useful information on the nature of interaction between the fluorophore and the quencher. The fluorescence of fluorophore might be enhanced or quenched due to the presence of nearby metallic NPs. The strength of the enhancement/quenching is influenced by many factors such as size and shape of the metal NPs, the orientation of the fluorophore dipole moments relative to the NPs, the radiative decay rate and quantum yield of the fluorophore. The quenching is usually observed if the fluorescence is located at a very short distance (<5 nm) from the metal surface. When the fluorophore–metal distance is increased, both fluorescence quenching and enhancement have been observed [8,9].

Waste waters from textile industry contain various pollutants including a high content of organic matter, surfactants, additives and dyes. Dyes have obtained notoriety as hazardous substances, because most of them are toxic and considered to be resistant to biodegradation. The discharge wastes containing organic matters are toxic to micro organisms, aquatic organisms and human beings. These matters when discharged into rivers or lakes they cause non-aesthetic pollution, biological magnification eutrophication, toxicity and perturbation in aquatic life. These discharged pollutants are chemically stable, so traditional water treatment methods are ineffective. Various methods have been proposed for the treatment of colored waste waters, namely, oxidation [10], electrolysis [11], biodegradation [12], adsorption [13], chemical coagulation [14] and membrane filtration [15] are currently used, which work by direct precipitation and separation of pollutants, or elimination by adsorption on activated carbon or similar materials. Among them, combination of UV radiation has received considerable attention because it is possible to degrade organic compounds and color from waste waters. UV process destroys the chromophore structure of these matters, and leads to complete decolorization. In the degradation process, hydroxyl radicals (OH°) are generated when the photo catalyst is illuminated in the presence of water and air [16], these ultra reactive species associated with oxygen are able to achieve a complete mineralization of organic pollutants into carbon dioxide, water and other non-hazardous products [17].

Our group has studied the fluorescence quenching of quinone derivatives in Ag NPs environment [18–22]. Though there are number of articles which illustrate the fluorescence quenching of fluorophore dyes by nanoparticles, no one has attempted to study the fluorescence quenching of textile waste water by silver nanoparticles. Therefore, we got interested to investigate the effect of Ag nanoparticles on the fluorescence quenching of TDW. Additionally, photocatalytic degradation of TDW was measured by using silver as nanocatalyst under UV irradiation. The prepared nanoparticles will be used to quench and degrade the organic compounds present in waste water.

Experimental

Dyeing waste water sampling

Dyeing waste water sample was collected from Textile Dyeing Industry, Erode, Tamilnadu, India.

Materials

Silver nitrate ($AgNO_3$, 99.5%) sodium borohydride ($NaBH_4$, 95%) and Rhodamine 6G were purchased from MERCK. Spectral grade methanol (C_2H_5OH) was purchased from NICE. All the chemicals were of Analytical Grade and used as purchased without further purification. Doubly distilled water was used throughout the experiment. All glasswares were properly washed with distilled water and dried in hot air oven before use.

Preparation of colloidal silver

Silver colloid was prepared by boro-reduced method [23]. In brief, $AgNO_3$ solution and $NaBH_4$ solution were prepared by dissolving 0.0294 mM of $AgNO_3$ in 100 ml of distilled water and 0.0096 mM of $NaBH_4$ in 300 ml of distilled water. 100 ml of $AgNO_3$ solution was added dropwise to 300 ml of ice-cold $NaBH_4$ solution and the mixture was stirred vigorously for 1 h until glassy yellow color was obtained (S1). It was repeated for different concentration of $AgNO_3$ solution (0.2649, 0.5003 and 0.7358 mM) (S2, S3 and S4) at constant concentration of sodium borohydride solution (0.0096 mM). The silver colloid was stored in a dark place, which was stable for several days or weeks. To investigate the influence of Ag NPs on TDW, the above waste water and silver sol have been taken in 1:1 volume ratio.

Methods of characterization

Shimadzu UV-1700 pharmaspec UV–vis spectrophotometer was used to record the absorption spectra. Jobin Yvon Flurolog-3-11 Spectrofluorometer was used to record the emission spectra. The excitation wavelength of concentrated TDW is 430 nm. The morphology and particle size of Ag NPs were obtained by High resolution transmission electron microscopy (HRTEM), which was performed on a JEOL JEM-2100 high resolution electron microscope operating at 200 kV. The photocatalytic activity of TDW in presence of Ag NPs was studied using UV irradiation (254 nm) at different time intervals (0–120 min).

Fluorescence quantum yield

The relative fluorescence quantum yield $(\omega_r el)$ [8] of the sample in terms of reference sample (ϕ_o) is $(\phi_{rel}) = \left(\frac{F}{F_0}\right)\left(\frac{OD_0}{OD}\right)\left(\frac{n}{n_0}\right)\phi_0$ Where F and F_0 are the integrated fluorescence intensities, OD and OD_0 are the optical densities and n and n_0 are the refractive indexes for Rhodamine 6G in methanol. The relative fluorescence quantum yield (ϕ_{rel}) in which Rhodamine 6G was used as fluorescence standard (ϕ = 0.94). In the present case, the fluorescence quantum yield of TDW was found to be 0.0173.