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Silver nanoparticles catalyzed reductive decolorization of spent dye bath containing acid dye and its reuse in dyeing

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ABSTRACT

Decolorization of spent dye baths after dyeing of nylon, silk and wool fabrics with C.I. Acid Red 249 was attempted followed by their reuse in repeated dyeing. The system comprised of a non-sulfur reducing agent, sodium borohydride, along with silver nanoparticles synthesized by plant mediation technique using fresh curry leaves (*Murraya koenigii*). Response surface methodology was used to optimize the conditions of decolorization for reproducibility of results. Box-Behnken design matrix with three variables namely, dosage of nanoparticles, concentration of reducing agent and time of treatment, was employed to design the experimental runs. Analysis of variance was employed to estimate the statistical parameters and evaluate the statistical significance of the model. Fisher's F- test was used to evaluate the quality and model terms. Three-dimensional response surface plots were used to study the interactive effect of operating variables on the response. Decolorized spent dye bath solutions were reused up to five times to dye fresh samples of nylon, silk and wool with the same dye. Negligible difference was observed in color depth and the fastness properties were identical for all the dyed samples even with respect to that dyed using dye liquor made from fresh water. Phytotoxicity studies revealed considerable reduction in toxicity of Acid Red 249 dye due to degradation. Thus, the treatment system for dye decolorization and repeated use of decolorized dye bath in dyeing was successful.

1. Introduction

Water is one of the most important resources of Mother Nature, which is essentially required to cater the agricultural, industrial and domestic needs. All activities require good quality water and its scarcity is on the rise day by day as large volumes are consumed and discarded along with a variety of pollutants [1]. It is essential to reuse water as far as possible in order to conserve it. Chemical processing of textile materials is carried out in aqueous medium and the discharge of unused/unfixed chemicals and colorants along with large volumes of left over baths and wash liquors causes high levels of pollution. Among various pollutants of the textile processing industry, the dye containing colored wastewater is most notorious from the point of view of its treatment as well as reusability.

Azo dyes are most commonly used for textile colorationand comprise 60–70% of all synthetic dyestuffs [2]. Water soluble acid dyes are widely used for dyeing of polyamide fibers, such as natural fibers wool and silk and synthetic fiber nylon [3]. The unused dye concentration present in the textile effluent has been estimated to be around 10–200 mg/L [4].

With increasingly stringent norms about environmental protection, there is an urgent necessity to minimize the use of natural resources without affecting the needs of the consumer. Lots of efforts have been taken so far by the processing industry to minimize the use of water in dyeing operations. Now the focus lies on the reuse of spent dye bath to further reduce the consumption of fresh water and save on the cost of operation as well as wastewater treatment. Processes like photo–Fenton [5], ozonation [6], photocatalysis [7], coupled nanofiltration membranes and electrochemical processes [8], gamma radiations [9], microbial decolorization [10], combined chitosan adsorption and UV-Fenton advanced oxidation process (CAAOP) [11], etc. have been employed for dye containing wastewater treatment for reuse. However, each of these methods has specific pros and cons. Advanced oxidation processes are gaining importance for their non-polluting characteristics and cost effectiveness [12]. Although reducing agents are mostly sulfur based and hence unacceptable, the azo chromophore based dyes are known to undergo reductive degradation easily, as compared to other types of chromophores. Nanocatalysis has emerged as a substitute for conventional water treatments. High surface area to volume ratio and size dependent reactivity have made metal nanoparticles suitable candidate for catalysis [13]. Among the metal nanoparticles, silver nanoparticles (AgNP) are extensively used in various catalytic applications. In degradation of dyes, they act as a redox catalyst by electron relay

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effect between donor and acceptor molecules [14]. AgNP synthesized using aqueous extract of waste tea have been reported to exhibit catalytic activity in decolorization of cationic organic dye solutions with hydrogen peroxide [15]. AgNP synthesized using *Trigonella foenum-graecum* seeds [16] and *Terminalia cuneata* [17] have been used as catalyst for decolorization of cationic and direct dye solutions along with $NaBH_4$. Silver-sulfur-oxido vanadium cluster (AgVT-catalyst) was used as an effective catalyst for quick reduction of methylene blue, methyl orange and hexavalent Cr (VI) to Cr (III) [18]. Recent researches have focused on employing Ag/Ag halides NPs as photocatalysts through modification in their band gap. Studies showed that enhanced photocatalytic activity was obtained by either supporting or doping Ag/AgCl-NPs in various metal oxides such as ZnO,WO_3 or TiO_2 [19–21] etc. AgCl@VO_x and Ag/AgCl@VO_x NPs were formed by encapsulating AgCl and Ag/AgCl − NPs into amorphous vanadium oxides (VO_x). These nanocomposites were successfully used in photooxidation of methylene blue and methyl orange under direct sunlight [22].

The present study focuses on the reuse of decolorized dye bath for similar dyeing repeatedly up to five times. For this, the exhausted dye bath after dyeing of different polyamide fabrics with azo chromophore based acid dye, Acid Red 249, was decolorized using a non-sulfur reducing agent, sodium borohydride, catalyzed by AgNP. The AgNP were synthesized by environment friendly technique of plant mediation using fresh curry leaves.

The parameters of reaction were optimized using response surface methodology. To our knowledge, no study has been reported on reuse of decolorization of spent dye bath containing azo dye with sodium borohydride catalyzed with AgNP for dyeing.

2. Materials and methods

2.1. Materials

Commercially available sample of C.I. Acid Red 249 dye (AR 249, λ_{max} = 552 nm) was procured from Archroma Pvt. Ltd. India and was used without further purification (Fig. 1). Fresh curry leaves (*Murraya koenigii)*, used for imparting specific flavor to Indian curry are abundantly available in local market at cheaper rate. Silver nitrate and sodium borohydride of LR grade were procured from SD Fine-Chem Ltd. Ready-for-dyeing plain weave fabrics, nylon (75 GSM, Grasim Bhiwani Textile Ltd.), wool (200 GSM, Raymonds India Ltd.) and Eri silk (86 GSM, Jharcraft Silk Textiles and Handicraft Development Corp. Ltd. Mumbai) were used for dyeing.

2.2. Synthesis of silver nanoparticles

Silver nanoparticles (AgNP) were synthesized using the method reported by Philip et al. [23] with slight modification. Briefly, 9 g of fresh green curry leaves (*Murraya koenigii*) were thoroughly washed with distilled water, chopped, added to 200 mL of distilled water and stirred at room temperature (32° C) for 1 min. A pale yellow extract was obtained by filtering the mixture with Whatman filter paper 1 (UK, 11 μm) and stored in a refrigerator for further use. For plant mediated synthesis of AgNP, the filtered extract was added drop wise to 1 mM aqueous solution of silver nitrate in the ratio of 1:1. After complete addition of the extract, the mixture was stirred further for 10 min at room temperature. The reaction solution turned brown from pale yellow in 30 min indicating the formation of AgNP.

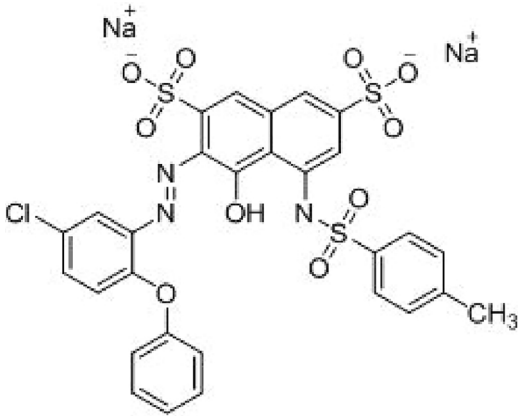

Fig. 1. Chemical structure of C.I. Acid Red 249 dye.

2.3. Characterization of AgNP

UV–visible spectral study was performed to ascertain the formation of AgNP on Shimadzu UV-1800 UV–vis spectrophotometer (Shimadzu, Japan). The surface plasmon resonance (SPR) peak was observed in the range of 400–450 nm in visible region. X – Ray diffraction analysis of powdered AgNP was carried out on XRD – 6100 (Shimadzu, Japan) with Cu Kα radiation (K = 1.54056 Å). The morphology and size of nanoparticles were analyzed using HR –TEM (Tecnai G2, F30) with an accelerating voltage of 300 kV.

2.4. Dyeing with acid dye

Nylon, silk and wool fabrics were dyed with AR 249 using standard dyeing procedure at 1.5, 2 and 5% shades on the mass of fiber (omf), respectively, in a Rota dyer machine (RB Electronics and Engineering Pvt. Ltd., Mumbai). The shades were selected such that, after completion of dyeing in each case, sufficient amount of unutilized dye remains in the spent dye bath for decolorization experiment. Thus, the spent dye baths after dyeing of nylon, silk and wool with the above-mentioned shades contained 6.6×10^{-5} M, 8.0×10^{-5} M and 21.4×10^{-5} M of dye, respectively, estimated as per the procedure given in section 2.8. The dye baths were prepared using requisite amounts of dye and fresh water and the pH was adjusted to 4 with 30% H_2SO_4. Fabric samples were dyed using a liquor ratio of 40:1 at 90 °C for 45 min. Soaping of dyed samples was done with a nonionic detergent (2 g/L) at 70 °C for 20 min followed by thorough washing, first with hot and then with cold water. Resultant dyed fabrics were air dried and marked as control samples. After the completion of dyeing, the spent dye baths containing unutilized dye were decolorized under optimized parameters, determined by applying Box-Behnken design. The same dyeing procedure was followed for repeated cycles of dyeing using decolorized dye baths.

2.5. Treatment of spent dye bath and its reuse

The absorbance values of all the spent dye baths were estimated at λ_{max} of the dye using Shimadzu UV-1800 UV–vis spectrophotometer (Shimadzu, Japan). All the decolorization experiments were carried out in batches of 50 mL at room temperature with a constant stirring of 70 rpm. Prior to decolorization, the pH values were determined and adjusted to 4. Synthesized colloid of AgNP was diluted with distilled water in the ratio of 1:10. Various concentrations of the reducing agent ($NaBH_4$) were prepared ranging from 0.05 to 0.5 M. For the reaction, 1 mL of $NaBH_4$ (various concentrations) and various dosages (0.1–2 mL) of AgNP colloid were added to 50 mL of spent dye bath, as given in supplementary material (ESM, Table S2). Samples were withdrawn at the specific time intervals and the absorbance was measured. After the completion of decolorization process, individual dye baths were reconstituted using decolorized solutions alone by the addition of requisite amounts of dye for 1.5, 2 and 5% shades and reused for dyeing of nylon, silk and wool fabrics, respectively. The procedure of decolorization- reconstitution- dyeing was repeated for five times.