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Green synthesis of Ag-Au bimetallic nanocomposites using a biodegradable synthetic graft copolymer; hydroxyethyl starch-g-poly (acrylamide-*co*-acrylic acid) and evaluation of their catalytic activities

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ABSTRACT

An eco-friendly method for the synthesis of Ag-Au bimetallic nanocomposites from aqueous solution using a novel biodegradable graft copolymer hydroxyethyl starch-g-poly (acrylamide-*co*-acrylic acid) acting as a reducing and stabilising agent was reported. The graft copolymer was prepared using a solution polymerization technique using potassium perdisulfate as the initiator at 70 °C and was characterized by measuring its molecular weight and molecular weight distribution using size exclusion chromatography, FTIR spectroscopy, XRD and SEM studies. Biodegradation study was carried out by enzyme hydrolysis. Ag-Au nanocomposites prepared by using the synthesised graft copolymer was characterized by using UV–VIS and FTIR spectroscopy, HR-TEM with SAED analysis, FESEM and EDAX analysis. Catalytic activities of the bimetallic nanocomposites were evaluated for the reduction of 4-nitrophenol to 4-aminophenol, degradation of 'N=N' (azo bond) bond in some azo dyes in presence of sodium borohydride. Three commercial azo dyes namely congo red, sudan-1 and methyl orange were used for azo bond degradation. The kinetics of catalytic activities were studied using UV–VIS spectroscopy.

1. Introduction

Bimetallic nanocomposites/nano structures gained enormous interest nowadays because of their potential applications in various fields particularly in improved catalytic activities [1–3]. The physical properties like surface area, shape, density, size etc gained by the bimetallic nanoparticles are much different from their monometallic forms [4]. The most important applications of metal nanoparticles which were widely studied are their role in catalysis. Bimetallic catalysts show unique catalytic activities in comparison to their parent metals which offers the opportunity for getting new catalysts with enhanced activities and selectivity [5,6]. The catalytic activity of metal nanoparticles greatly depends on their preparative methods which control their size, shape and morphologies which are gain controlled by the synthetic methods used as well as by the compounds used for their preparation.

Bimetallic nanoparticles are mainly synthesised by involving simultaneous or successive reduction of two metal components which generates either core shell or alloy nano structures. The successive reduction or sequential reduction method

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yields core shell nano structures [7,8] where as simultaneous reduction or co reduction method forms alloy nanoparticles predominantly [9,10]. Various methods have been developed to synthesize the bimetallic nanoparticles such as sol-gel method [11], aerosol technique [12], micro-emulsion technique [13], sono-chemical method [14], etc. However all these methods require sophisticated instrumental techniques, time consuming, requirement of hazardous substances and expensive. Therefore, there is increasing interest to synthesize metal nanoparticles by green procedure which is eco-friendly and free from the use of toxic chemicals. Several works of biosynthesis of bimetallic nanoparticles have been reported till now [1,3,15–17].

In recent years graft copolymers, based on natural polysaccharides and acrylic monomers have been used in wide variety of applications like flocculating agents [18–20], metal adsorbing [21–23] agents, drug reducers [24] and matrices for controlled drug release [25]. Such graft copolymers are eco-friendly and biodegradable [26]. Synthesis of metal nanoparticles (monometallic or bimetallic) using polysaccharide based graft copolymers have attracted wide spread attention nowadays. In the authors' laboratory monometallic gold and silver nanoparticles were prepared by polysaccharide based graft copolymers and their antibacterial activities were evaluated [27–29]. In the present investigation a green synthesis of Ag-Au bimetallic nanocomposites by using graft copolymer based on hydroxyethyl starch (HES) and a mixture of acrylamide and acrylic acid is reported. The structure of HES was given in our previous communication [20].

The azo dyes constitute the largest and most varied group of synthetic organic dyes used today in dyeing industries. Such azo compounds have unique characteristics due to their particular structure and exhibit extraordinarily high stability. Pure water is very much essential for the survival of living organisms. Waste water and industrial effluent treatment requires removal of harmful contaminants and possible reuse. The coloured waste water discharged from dyeing industries contains such azo dyes which are toxic to aquatic life and impose destructive impact on the environment. So it is necessary to destroy the azo dyes before disposal to aqueous stream. Destruction of azo bond (—N═N—) present in such dye molecules can be done by hydride donors in presence of metal catalyst as hydride ion can not it self reduce such —N═N— linkage. Previously it was shown that gold and silver nanoparticles [30,31] catalyze such reduction process but reduction rate is slow. In the present study an attempt was made to reduce (cleave) the azo bond present in azo dyes by hydride ion in presence of Ag-Au bimetallic nanocomposites prepared from a mixture of silver nitrate and chloroauric acid solution by the graft copolymer hydroxyethyl starch-g-poly(acrylamide-*co*-acrylic acid) [HES-g-poly(AM-*co*-AA)]. Three potentially toxic dyes congo red (CR), sudan-1 and methyl orange (MO) were used for this study. The structures are given in Fig. 1. Again, reduction of 4-nitrophenol to 4-aminophenol is environmentally and industrially important. The so prepared Ag-Au nanocomposites showed an excellent catalytic activity for the reduction of 4-nitrophenol to 4-amminophenol.

The graft copolymer was prepared by using solution polymerization technique using potassium perdisulfate ($K_2S_2O_8$) as the initiator at 70 °C. The synthesised graft copolymer was characterized by measuring its molecular weight and molecular weight distribution by size exclusion chromatography (SEC), FTIR spectroscopy, SEM and XRD studies. Biodegradation of the graft copolymer was carried out by the enzymatic cleavage and the number of carboxylic acid (—COOH) group incorporated was determined by measuring its neutralisation equivalent using standard alkali. The Ag-Au bimetallic nanocomposites was characterized by UV–VIS and FTIR spectroscopy, X-ray diffraction pattern, high resolution transmission electron microscopy (HR-TEM) along with selected area electron diffraction patterns (SAED), Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDAX). The catalytic activities of the bimetallic nanocomposites for azo bond cleavage and 4-nitrophenol reduction were studied using UV–VIS spectroscopy.

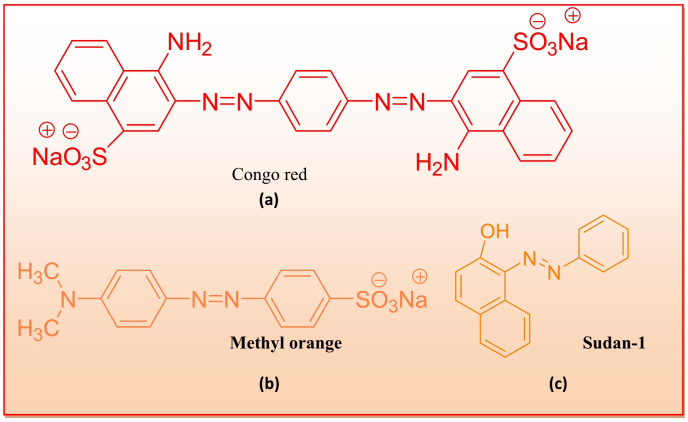

Fig. 1. Structures of (a) Congo red, (b) Methyl orange and (c) Sudan-1.