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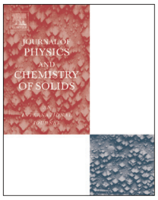

Copper-containing polyvinyl alcohol composite systems: Preparation, characterization and biological activity

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ABSTRACT

The present investigation reports, the complex formation of Cu(II) with polyvinyl alcohol (PVA) and the synthesis of PVA-stabilized Cu_2O particles. This PVA–Cu_2O composite has been prepared via chemical reduction method using PVA–Cu(II) complex as precursor. At first, Cu(II) ions were stabilized in PVA matrix via complex formation with OH groups; subsequently, this PVA–Cu(II) macromolecular complex as precursor reacted with ascorbic acid as reducing agent at $pH = 12$ to prepare PVA–Cu_2O composite. The products were characterized by FTIR, XRD, FE-SEM, HRTEM, Visible Spectroscopy and atomic absorption. In the following, the antibacterial properties of as-prepared composites were examined against Gram-positive (*Bacillus thuringiensis*) and Gram-negative bacteria (*Escherichia coli*), and the results showed excellent antibacterial activity of these materials.

1. Introduction

The chemistry of polymer-metal complexes and polymer-matrix composites has attracted considerable attention in the past decade, and a large number of studies have been devoted to evaluate these materials and investigate some their physical and chemical behavior [1–5]. Some polymers due to availability, having simple methods to building polymeric structures from simple molecules; solubility in water and compatibility with biological condition are used in this field for different purposes [6,7]. Polyvinyl alcohol ($-[CH_2-CHOH]-n$: PVA) is recognized as an eco-friendly vinyl polymer soluble in water [8]. Some groups have investigated binary complexes between PVA and metal ions Cu(II), Co(II), Ni(II) and Zn(II) [9]. The chemistry of chelation of metal ions by PVA is different from other polymers commonly used as self-template organic matrix. PVA undergoes a complexation with metal ions by the assistance of –OH groups; and the metal ions physically and/or chemically are entrapped [9]. Many groups have studied complex formation and gelation in polyvinyl alcohol solutions in the presence of copper ions [10–15]. Complex formation takes place in two stages, with the formation of a corresponding positively charged blue complex and a green deprotonated complex [10]. According to data obtained by other authors [10,11], aqueous solutions of cupric ions and PVA show a green coloration at $pH > 7$. Some researchers believe that at $pH > 7$, the reaction of the Cu^{2+} ion with four OH groups takes place, and it is accompanied by compacting of the macromolecular chains [12–14]. Yokoi et al. [11] have reported an interaction mode in the chemistry of polymer-metal complexes. They believe that cupric ions exist as the polynuclear complex of $Cu(OH)_2$ solubilized by PVA at $pH > 6$ and as ordinary hydrated ions at $pH < 6$.

Copper oxide (CuO) nanoparticles have many significant applications due to its multifunctional properties [16]. Mahapatra et al. generated copper hydroxide as a precursor which was thermally decomposed to CuO nanoparticles [17].

Cuprous oxide (Cu_2O) is a p-type semiconductor and recently, much attention has been paid to this and related materials because of its potential applications in fields such as solar cells, [18] pigments, [19] catalysts and photocatalysts [20]. Several successful methods have been reported for the production of Cu_2O [21,22]. Chemical reduction is a method, in which the preparation of Cu_2O from Cu^{2+} salts involves the reduction of Cu^{2+} ions to Cu^{+} ions with a reducing agent.

Ram et al. [23] have reported ion exchange reaction of $Cu^{2+} \rightarrow Cu \rightarrow Cu^{+}$. They found that the reduction of the Cu^{2+} resulted in Cu without formation of Cu^{+} as an intermediate phase. Also, the sequential reduction process $CuO \rightarrow Cu_2O \rightarrow Cu$ has been reported by Pike et al. [24] with CuO reducing completely to the intermediate Cu_2O phase before further reduction to metallic copper.

Antibacterial materials have been developed as ecological important materials, and become one of the hot topics within the

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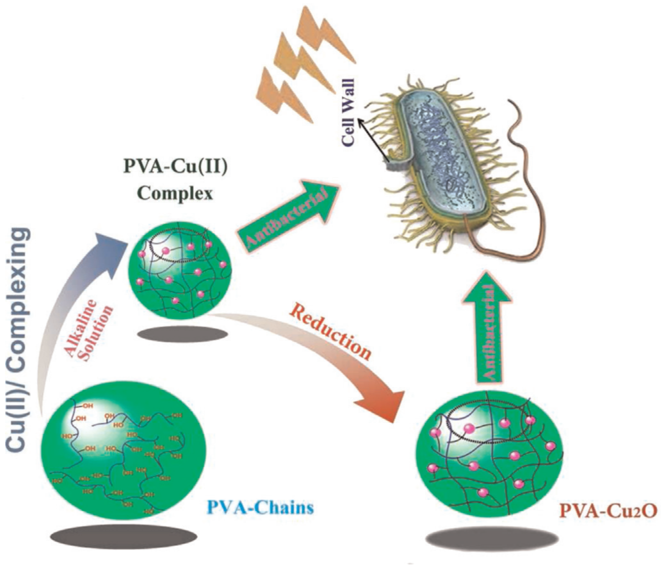

Scheme 1. Preparation and antibacterial activity of copper-containing polyvinyl alcohol composite systems.

fields of functional materials [17,25].

It is well-known that copper ions are able to kill bacteria, and to date, there have been some studies on the production and application of the copper or copper oxide as antibacterial materials [17,25,26]. Also, some researchers have studied the antibacterial mechanism of Cu(II) species [26]. Perelshtein et al. [27] investigated the antibacterial properties of the CuO-fabric composite. The activity of CuO-doped phosphate glass fibers was studied by Abou Neel. [28]. Recently, Zhao et al. [22] have reported the antibacterial activity of cuprous oxides with different morphologies. However, rare studies have carried out on the investigation of antibacterial properties of the copper-based composites, especially, Cu_2O-containing composites.

Here, the complex formation of cupric ions with PVA and the synthesis of Cu_2O particles embedded in PVA matrix were investigated by XRD, TEM, FE-SEM, FTIR, Visible Spectroscopy and atomic absorption. The as-prepared composites were examined as antibacterial agents against Gram-positive and Gram-negative bacteria (Scheme 1).

2. Experimental

2.1. Synthesis procedures

2.1.1. Preparation of PVA–CU(II) complexes

1 g of polyvinyl alcohol (crystalline powder, high molecular weight) was initially dissolved in 50 ml distilled water. In another beaker, a solution of NaOH (4 g in 25 ml distilled water) was prepared and this solution was added to the PVA solution under stirring. The mixture was heated at 70 °C for 3 h, and after cooling, $CuSO_4$ solution (sample B_7: 7 mmol, sample B_5: 5 mmol and sample B_2: 2.5 mmol $CuSO_4 \cdot 5H_2O$ in 20 ml distilled water) was added dropwise to the PVA solution under quickly stirring. A green gel was produced when $CuSO_4$ solution was added, and then, the mixture was heated at 90 °C for 10 h. The reaction mixture was cooled down to room temperature followed by centrifugation (6000 rpm) to produce the PVA–Cu(II) complex. After that, the product was collected, washed with distilled water and ethanol several times to remove the impurities and dried in an oven at 80 °C.

2.1.2. Preparation of PVA-stabilized Cu_2O particles: reduction of PVA–Cu(II) complex (B5) by ascorbic acid

Ascorbic acid (0.89 g) was dissolved in 10 ml of distilled water and was added dropwise into the cooled reaction mixture of sample B_5 (without work-up and purification) at room temperature, under very slow stirring. After several seconds, the orange–red particles appeared in the reaction mixture. The resulting mixture was then left in air at room temperature for 15 h. A reddish product obtained which was then washed with distilled water and ethanol several times to remove impurities and dried in air.

3. Results and discussion

The complex formation of PVA with different amounts of Cu(II) ions occurred at pH = 12 and a green product which was insoluble in water appeared. Some molecular structures for the PVA–Cu(II) complexes have been reported, including polynuclear [11], binuclear [12], and mononuclear [14] complexes of Cu(II) ion with hydroxyl groups of PVA.

The PVA chains consist of two parts hydrophobic backbones and hydrophilic alcoholic OH groups. In aqueous solutions the hydrophobic backbones of PVA chains lie toward the inside but hydrophilic OH groups lie toward the outside of bulk water and rush out to encounter water (Fig. 1).

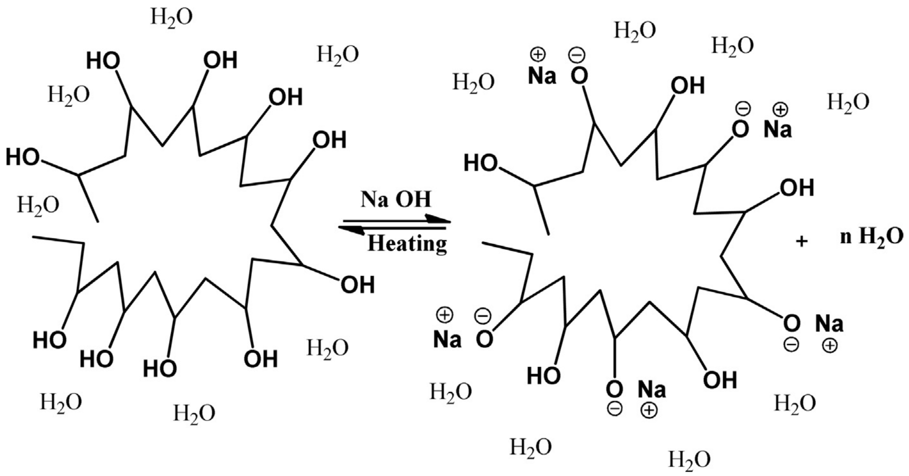

Fig. 1. Possible structures for PVA in high alkaline aqueous solutions.