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"Green" synthesis of Cu_2S nanoparticles from (*Z*)-1-methyl-2-(pyrrolidin-2-ylidene)thiourea ligand for the preparation of Cu_2S-chitosan nanocomposites for the removal of Cr(VI) ion from wastewater

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ABSTRACT

Synthesis of copper sulfide nanoparticles through homogeneous precipitation method and the preparation of Cu_2S–chitosan nanocomposites for the removal of Cr(VI) ions from wastewater samples has been achieved. The absorption studies revealed a blue shift in the wavelengths of the band edges when the starch or PVA was introduced into the nanoparticles. The structural studies of the particles were carried out using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD patterns presented the cubic $Cu_{1.8}S$ phase for all the synthesized copper sulfide nanoparticles. TEM images showed spherical shaped particles which became agglomerated when the stabilizers were introduced into the nanomaterial. The adsorption studies proved that the parameters such as pH, dosage and contact time plays an important part during the water treatment.

1. Introduction

The utilization of heavy metals and chemicals in process industries have resulted in the generation of large quantities of sewages that comprises of high level of toxic materials which is causing problems to the environment. The availability of these harmful substances in higher percentages into our water systems can be a threat to the life of humans and animals, which can lead to serious diseases. The treatment of these toxic substances from water streams can be expensive [1]. Chromium(VI) is regarded as the most harmful and toxic substance due to its high carcinogenic and resistant properties [2]. Numerous methods have been applied for the removal of Cr(VI) from water. These methods include ion exchange, precipitation, adsorption, chemical oxidation, reverse osmosis methods etc. [3]. Adsorption is considered to be the most effective technique among these methods since it is more appropriate and ease to manage [4].

Nanomaterials have been used in our days to treat wastewater. Copper sulfide nanoparticles in particular, have been used by biomedical researchers across the globe as sensors [5] and drug delivery [6]. The incorporation of copper sulfide nanoparticles can increase the surface charge of the composite. Recently, we have reported the synthesis of silver sulfide nanoparticles and the preparation of the Ag_2S-chitosan nanocomposites for the removal of iron(II) ion from wastewater [7].

This article reports the synthesis of copper sulfide nanoparticles through simple and eco-friendly homogeneous precipitation technique. Cu_2S nanoparticles were then integrated with chitosan to form nanocomposites. The polymer nanocomposites were used in the treatment of Cr(VI) from wastewater sample and the percentage removal of this heavy metal from the solution was determined. The effect of pH, adsorbent dosage, and contact time were investigated.

2. Experimental

2.1. Materials

Thiourea, 1-methyl-2-pyrrolidine, copper acetate monohydrate, starch, PVA, ammonium hydroxide, chitosan, potassium dichromate, methanol, and acetone were reagents from Sigma-Aldrich and were all used without further purification.

2.2. Preparation of the ligand

The (*Z*)-1-methyl-2-(pyrrolidin-2-ylidene) thiourea ligand was prepared according to the procedure described previously [7,8]. In a typical preparation, 1-methyl-2-pyrrolidone (1 mmol) in hot methanolic (20 mL) was mixed with (20 mL) hot methanolic solu-

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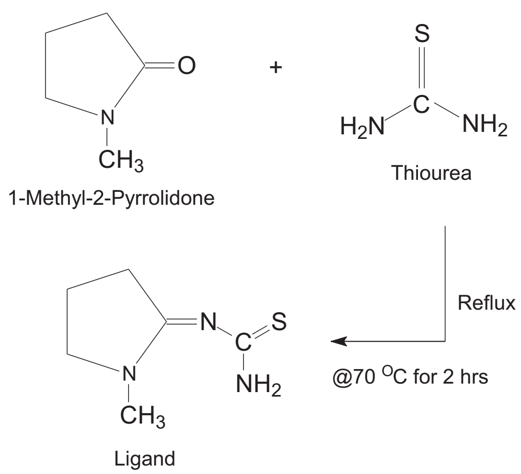
tion of thiourea (1 mmol). The mixture was refluxed for 2 h on the water bath at 70 °C. The precipitate was separated out on cooling the contents at room temperature. The white crystals were then filtered, washed with acetone and dried in a desiccator. *Elemental analysis: calculated (found) % C 45.83(44.52), H 7.05(7.32), N 26.72 (26.65), S 20.39(21.03) for $C_6H_{11}N_3S$. Percentage yield: 78%; melting point: 113–119 °C. Significant FTIR bands: ν(N–H): 3282 cm^{-1}; ν (C=N): 1621 cm^{-1}; ν(C–N): 1087 cm^{-1}; ν(C=S): 720 cm^{-1}.*



Scheme 1. Preparation of the (*Z*)-1-methyl-2-(pyrrolidin-2-ylidene)thiourea ligand.

2.3. Synthesis of copper sulfide nanoparticles

Cu_2S nanoparticles were synthesized by mixing copper acetate (5 mmol) in warm 50% methanol (20 mL) with 20 mL warm 50% methanolic solution of the ligand (10 mmol) in a 100 mL two necked flask. The warm mixture was refluxed inside the water bath at 70 °C for an hour to produce a black solution. Exactly 0.5% starch or PVA solution was added into the black solution to stabilize the nanoparticles. The pH of the solution was adjusted to pH = 11 with ammonia hydroxide solution and further stirred for an hour. The synthesized Cu_2S nanoparticles were separated from the solution using centrifuge technique, washed with methanol and dried in an open air.

2.4. Preparation of Cu_2S-chitosan nanocomposites

The synthesized Cu_2S-PVA capped nanoparticles (~3 mg) were dispersed in 10 mL of distilled water. The filtered copper sulfide nanoparticles solution was then transferred into a small beaker with 0.5% chitosan (50 mL) solution. The mixture was then covered with a foil and ultra-sonicated for 4 h to ensure a complete incorporation. The prepared Cu_2S nanocomposite solutions were then used in water treatment.

2.5. Batch adsorption experiments

A stock solution of heavy metal (1000 ppm) was prepared by dissolving 2.83 g of potassium dichromate in 1 L of distilled water. The desired concentrations ranging from 20 to 100 ppm where

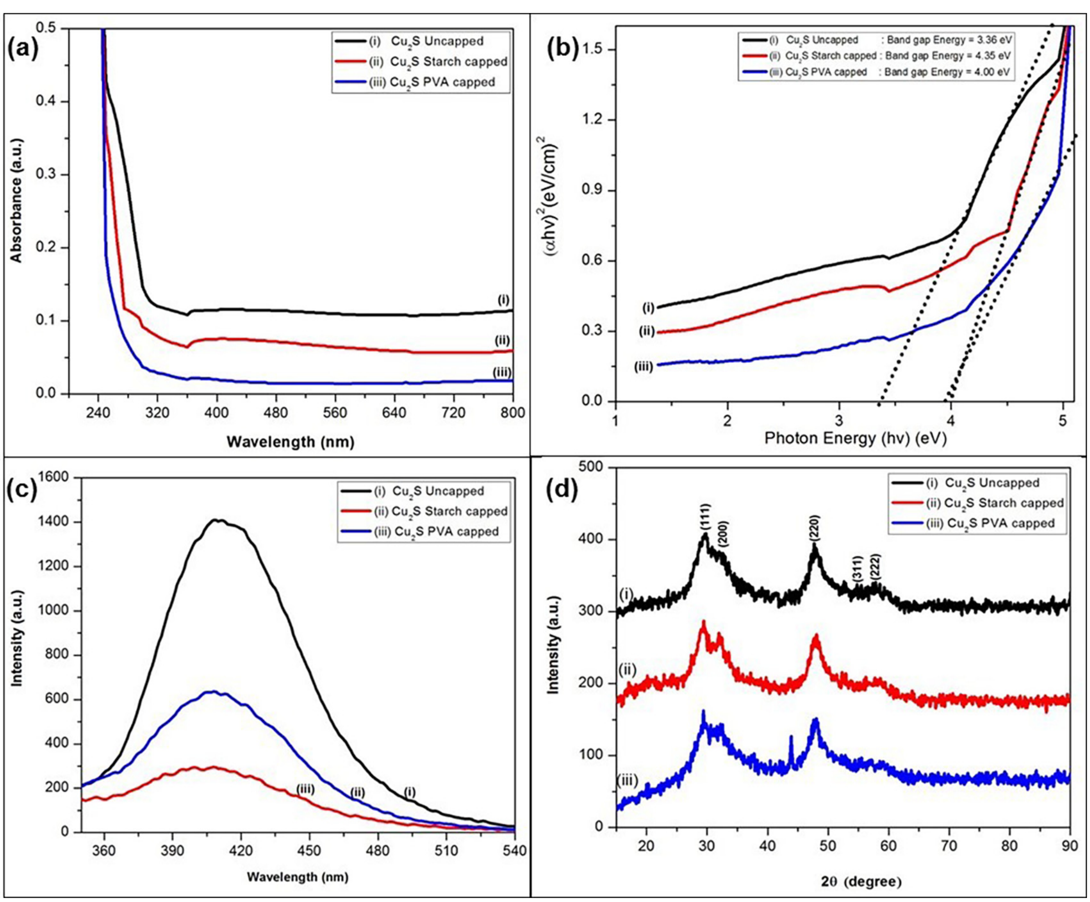


Fig. 1. Absorption (a), Tauc plot (b), emission (c) spectra, and X-ray diffraction patterns (d) of Cu_2S nanoparticles.