



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Modified wool-iron biopolymer-based complex as an active heterogeneous decontamination photocatalyst

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ARTICLE INFO

Article history:

Received 28 July 2016

Revised 22 September 2016

Accepted 14 October 2016

Available online xxx

Keywords:

Heterogeneous catalysis

Photo-Fenton catalysis

Decontamination

Biopolymer

Wool-iron complex

ABSTRACT

A series of biopolymer based complex were manufactured by coordinating iron ions to the abundant amino- and sulfur-containing groups in the modified wool and used as heterogeneous Fenton-like photocatalyst for 4-chlorophenol (4-CP) degradation in the presence of H₂O₂. Hydroxylamine hydrochloride (NH₂OH·HCl) or acrylic acid was employed to modify the natural wool to strengthen the interaction with iron and to reinforce the structural stability. The NH₂OH·HCl modified wool based complex showed the best catalytic performance for 4-CP degradation. The strong coordination between iron and great number of hydroxamic acid in this modified complex leads to the least iron leaching during the tests. HO· species was confirmed to be the dominant reactive oxidant in the decontamination process. The approach presented in this study can provide a new approach for developing novel biopolymer-based photocatalysts for efficient degradation of toxic organic pollutants such as 4-CP.

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1. Introduction

As a powerful method for solving the problems of energy crisis and environmental pollution, heterogeneous photocatalysis has become a comprehensively studied area during the past several decades. It can use clean and renewable natural solar light as the energy and work at low temperature, usually at room temperature. Among them, heterogeneous photo-Fenton catalysis has proven to be an efficient and powerful process for degradation of various organic pollutants in water, in which most of organics can be mineralized to CO₂, H₂O and other inorganic matters [1].

The Fenton reagent was first reported over 100 years ago [2]. The Fenton process can generate highly reactive hydroxyl radicals (HO·), which could oxidize the nonbiodegradable pollutants, such as chlorophenols (CPs), which was generated in many industrial processes in manufacturing herbicides, fungicides, pesticides, insecticides, pharmaceuticals, dyes, and so on [3,4]. The traditional homogeneous Fenton process was so attractive but could not be used on a large scale owing to its low degradation efficiency, strict pH range limits and precipitation sludge of ferric oxyhydroxide, which required a further separation step [5,6]. Therefore, develop-

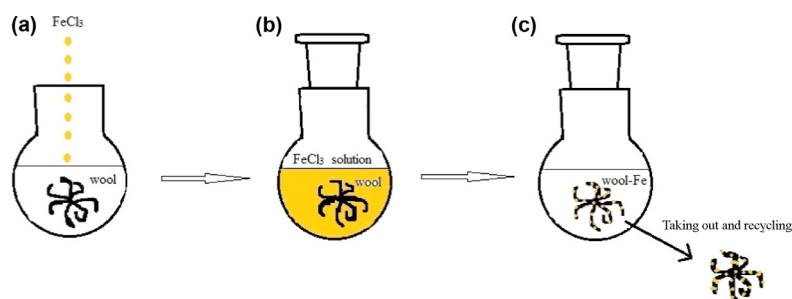
ment of solid state catalysts is a promising alternative to overcome these barriers of application.

In recent years, some natural biopolymers, such as silk and wool, are becoming modern fashion in the green combination of aqueous media and active metal as heterogeneous catalysts. Among them, the wool-metal complexes, especially wool-Pd and wool-Fe system, are widely used in various catalytic processes, such as advanced oxidation [7], Heck reaction [8,9], water splitting [10], Suzuki reaction [11] and hydration reaction [12,13]. Wool is the representation of most biopolymers because of its special structure with numerous N- and S-containing groups. There are two main kinds of nitrogen-containing groups, namely -NH-CO- and -NH₂, and three kinds of sulfur-containing groups, namely -SO₃H, -S-S- and -SH involved in the structure of wool [7]. The obvious interaction and affinity between the groups in wool and some transition metals render it with some fantastic properties, such as the evenly distribution of loaded elements on the surface of fibers and the possibility to take organic reaction in aqueous phase with assistance of this hydrophilous polymer.

There have been some researches using wool as support to form a biopolymer-metal complex, such as wool-Pd/CdS photocatalysts [7] or wool-Pd catalyst [8], which exhibited high activity for photocatalysis reaction under visible light irradiation. In general, the keratin in pure wool does not dissolve in cold water. However, it can dissolve slowly in hot water and strong acid/alkali conditions.

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Scheme 1. The route for preparation of wool-Fe complex.

Moreover, the keratin structure can be damaged in the presence of some oxidant species, which severely limit its applications. Therefore, it is highly desirable to modify the pure wool with special treatment to reinforce its structural stability and to enhance its capability of coordination.

In this paper, in order to search for a natural products-based green chemical process to degrade the organic pollutants in water, we prepared a series of photo-Fenton catalysts with NH₂OH·HCl or acrylic acid treated wool as the biopolymer support and iron as the active metal. 4-chlorophenol (4-CP) was selected as a model pollutant for the photocatalytic tests. Besides, the photodegradation mechanisms of 4-CP was also discussed and proposed in this work.

2. Experimental

2.1. Wool pretreatment

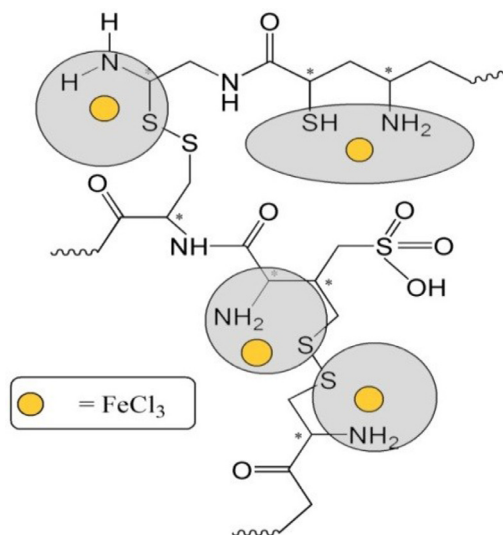
All the materials and reagents were of analytical grade and used without further purification. Wool was cut from domestic sheep from Changji City, Xinjiang province. Common white wool was washed with distilled water and, and then cut into pieces. Then the pieces were washed in the solution with a certain amount of washing power under ultrasound at 35 °C for 40 min. Subsequently, the wool pieces were oxidized by H₂O₂ with water bath at 80 °C for 40 min, and the wool turned to be black-brown. Thereafter, the black-brown wool was treated by the mixture of urea (1 mol/L) and NaHSO₃ (0.38 mol/L), stirred at 100 °C for 40 min. After the wool returned to white, it was washed with water several times, dried at 80 °C. Finally, the wool was collected by ball-milling at a speed of 3000 r/min for 5 min.

2.2. Synthesis of wool-Fe complex

1.0 g of treated wool power was dipped in water with ultrasound for 1 h, and the pH was adjusted to 3.0 before adding excess FeCl₃·6H₂O (3.27 mmol), and then vigorously stirred for 12 h at ambient temperature. The final product was filtered and obtained with water wash several times (Scheme 1), dried in a vacuum oven at 60 °C for hours to get the wool supported iron complex. The structure of wool-Fe may be shown as Scheme 2.

2.3. Synthesis of NH₂OH·HCl modified wool-Fe complex

1.0 g of treated-wool power was dipped in water (50 mL) by sonication for 1 h at 35 °C, followed by adding NH₂OH·HCl (3 g), then adjusted pH to 11 with NaOH solution (30 wt%). After vigorously stirring at room temperature for 3 h, the pretreatment wool was washed with water for several times. Then the pH for the solution containing pretreated wool was adjusted to 3.0 using dilute H₂SO₄. Excess FeCl₃ was added with vigorous stirring. The following steps reference to the part of 2.2. The catalyst was denoted as wool-Fe/NH₂OH·HCl.



Scheme 2. The possible structure of wool-Fe complex.

2.4. Synthesis of acrylic acid modified wool-Fe complex

The acrylic acid (CH₂=CHCOOH) modified wool was prepared reference to the existing study reported by Reddy et al. [14]. The wool was grafted with acrylic acid as the following steps. About 1 g of wool was dipped into deionized water (50 mL) by sonication for 1 h at 35 °C, then the acroleic acid (0.5 g) was added. The graft reaction was initiated with adding the oxidant (potassium persulfate, K₂S₂O₈, 0.05 g) and the reductant (sodium bisulfite, NaHSO₃, 0.019 g) followed by deoxygenating through passing nitrogen gas for 30 min. The grafting reaction was performed at pH 5.5 and 60 °C for 4 h. The whole reaction was terminated and the modified wool product was collected by centrifuging, washed with deionized water. Then the pH for the solution containing pretreated wool was adjusted to 3.0 using dilute H₂SO₄. Excess FeCl₃ was added with vigorous stirring. The following steps reference to the part of 2.2. The catalyst was denoted as wool-Fe/CH₂=CHCOOH.

These two kinds of modified samples was denoted as wool-Fe/X (X = no modify, NH₂OH·HCl and CH₂=CHCOOH).

2.5. Degradation of 4-CP

The catalytic performance of wool-Fe complex was evaluated by 4-CP oxidation in the presence of H₂O₂. All photocatalytic experiments were carried out in a jacketed cylindrical quartz tube reactor with vigorous stirring and the temperature was controlled at 35 ± 0.2 °C. A 250 W high pressure mercury lamp (λ_{max} = 365 nm) was used as the source of irradiation with a quartz jacket to water-cooling, and the light flux at the liquid level was tested to be ca. 90 μW/cm².

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