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Methyl Orange removal by a novel PEI-AuNPs-hemin nanocomposite

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ABSTRACT

A novel poly(ethyleneimine)/Au nanoparticles/hemin nanocomposite (PEI-AuNPs-Hemin) acting for Methyl Orange (MO) removal has been synthesized. PEI-AuNPs was prepared firstly and it was then linked to hemin through the coupling between carboxyl groups in hemin and amino groups in PEI without the activation of carboxyl groups. The high reactivity and stability of AuNPs contributed greatly in the formation of the amido bonds in the nanocomposite. Fourier transform infrared spectroscopy, transmission electron microscopy and UV–visible spectroscopy were used to characterize the PEI-AuNPs-Hemin. Results show that PEI-AuNPs-Hemin has strong adsorption for MO. Adsorption and degradation experiments were carried out at different pHs, nanocomposite concentrations and UV irradiation times. Removal of MO in acidic solutions was more effective than in basic solutions. The real-time study showed that the MO degradation with the nanocomposite under UV irradiation was a fast process. In addition, the photocatalytic degradation mechanism was proposed. The study suggests that the PEI-AuNPs-Hemin may have promising applications in environmental monitoring and protection.

Introduction

Synthetic dyes are commonly used in industries, such as food, medicine, paper, textile and cosmetics. Most of them are toxic, carcinogenic, and mutagenic for human body. Each year a large amount of dyes in untreated wastewater are discharged into the ecological systems, resulting in adverse effects on human and animal health. Therefore, they must be carefully removed from the environment (Goscianska et al., 2014; Zhang et al., 2014). Some new chemical and biological methods for dye removal have been reported, such as oxidation (Meriç et al., 2004), electrolysis (Cui et al., 2012), membrane separation (Zhong et al., 2012), coagulation and flocculation (Verma et al., 2012). However, due to the complex molecular structures and high stability of dyes, these methods are not always successful. Development of nanocomposites for dye removal has increased tremendously, such as multi-walled carbon nanotube functionalized with chitosan and poly-2-hydroxyethyl methacrylate for Methyl Orange (MO) removal (Mahmoodian et al., 2015), γ-Fe_2O_3 nanoparticles integrated $H_2Ti_3O_7$ nanotubes for Methylene Blue removal (Harsha et al., 2015), reduced grapheme oxide enwrapped AgI nanocomposites for Rhodamine B removal (Reddy et al., 2015), magnetic nickel zinc ferrite nanocomposite for organic synthesized dyes removal (Afkhami et al., 2015), *etc.*

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Nanocomposites have the advantages of large specific surface area, small diffusion resistance, high adsorption capacity and faster adsorption equilibrium (Ahmad et al., 2015).

Hemin, a biologically active iron-porphyrin compound, is considered a potential biomimetic catalyst for water purification (Xue et al., 2012). However, despite the prominent properties of hemin, difficulties remain in the direct application of hemin as a catalyst in aqueous solution due to its oxidative self-destruction in the oxidizing reaction system, and molecular aggregation which results in catalytically inactive dimers (Yao et al., 2014). Thus there is a growing demand for overcoming these problems. One potential method is to immobilize hemin on various supports, such as TiO_2 (Tang et al., 2013), β-cyclodextrin (Lin et al., 2012) or graphene (Guo et al., 2011) to improve reactivity and stability in oxidation reactions. However, TiO_2-hemin showed weak reactivity, and β-cyclodextrin-hemin or grapheme-hemin was difficult to separate from the reaction system. Consequently, the development of novel materials as supports to immobilize hemin for dye removal with improved reactivity, stability, dispersion, separability and easy synthesis is highly desired.

In the past few decades, a variety of nanomaterials have been developed for immobilization and stabilization of biomolecules (Ansari and Husain, 2012). Among these exploited nanomaterials, gold nanoparticles (AuNPs) are highly attractive because of their unique properties including high stability and reactivity, biocompatibility, excellent electronic conductivity and surface plasma characteristic (Jans and Huo, 2012; Saha et al., 2012). AuNPs have been successfully applied for the immobilization of biomolecules such as DNA (Pei et al., 2012), enzyme (He et al., 2011), antibody (Stuchinskaya et al., 2011) and polymer (Coulston et al., 2011). Polyethyleneimine (PEI) is a typical water-soluble and mono-disperse polyamine with regular branched dimensional structure. There are a large number of nitrogen atoms in its macromolecular chain. It has been widely used for modification, catalysis and reduction (Kim et al., 2008; Liu et al., 2013). Wang et al. (2005) reported that the secondary amino groups of the PEI as linear units are related to the reduction process, and the primary amino groups as terminal units are responsible for the particle stabilization. Brondani et al. (2013) have successfully applied PEI-coated AuNPs (PEI-AuNPs) for laccase immobilization. Given that AuNPs can also serve as photocatalysts for dye degradation under UV irradiation (Cheng et al., 2013; Zhu et al., 2009), we synthesized PEI-AuNPs using PEI as a reductant and stabilizer to immobilize the hemin through the formation of amido bonds.

In this work, a novel PEI-AuNPs-Hemin nanocomposite applied for MO removal has been successfully synthesized. The nanocomposite was easily dispersed and stable in aqueous solutions, and exhibited strong adsorption for MO. MO removal experiments were carried out at different pH, nanocomposite concentrations and UV irradiation times. Compared with other nanocomposites reported before (Afkhami et al., 2015; Harsha et al., 2015; Mahmoodian et al., 2015; Reddy et al., 2015), PEI-AuNPs-Hemin is easier to synthesize and more effective (degrading 80% MO within 2 min with only 0.5 mg/mL PEI-AuNPs-Hemin), which make it potentially applied in environmental monitoring and protection.

1. Experimental

1.1. Chemicals

Branched PEI (weight-average molecular weight, 25 kDa), $HAuCl_4{\cdot}4H_2O$ and Hemin (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). N,N-dimethylformamide (DMF) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents used were of analytical grade. Ultrapure water was prepared through a Millipore Milli-Q water purification system (≥18.25 MΩ).

1.2. Instruments

UV–visible absorbance spectra were measured on an UV-3600 UV–VIS-NIR spectrophotometer (Shimadzu, Japan) with a sample volume of 3 mL. Infrared spectra were carried out on Fourier transform infrared spectroscopy (FTIR-8400S, Shimadzu, Japan). Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-8100 EM transmission electron microscope (Hitachi, Japan). TEM samples were prepared by spin coating 10 μL of the mixture onto carbon-coated copper grid substrates, which were then baked at 70°C.

1.3. Preparation of PEI-AuNPs-hemin

The AuNPs were synthesized following the procedure described by Brondani et al.2013). Firstly, 500 μL of PEI solution was added to 5 mL of 1 mmol/L $HAuCl_4$ solution with stirring. The mixture was then heated to 80°C with a ramping of 5°C/min and held at 80°C until the characteristic ruby red color appeared (generally 2 min). The PEI-AuNPs nanocomposite was obtained after cooling down to the ambient temperature under stirring. Then, 1 mL PEI-AuNPs solution was mixed with 500 μL of 0.1 mmol/L hemin. After stirring for 1 hr, the mixture was centrifuged at 14,000 r/min for 30 min, then washed and

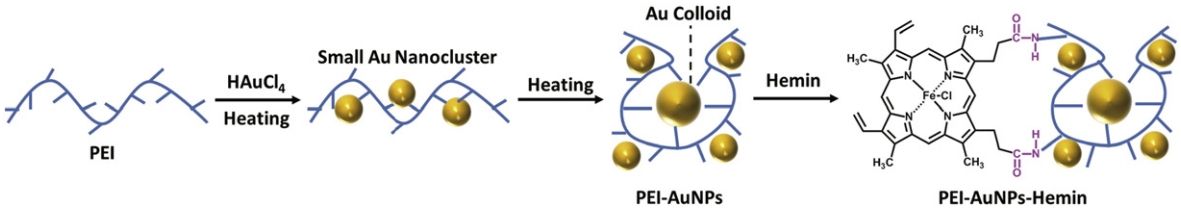

Fig. 1 – Schematic representation for the formation of poly(ethyleneimine)/Au nanoparticles/hemin nanocomposite (PEI-AuNPs-Hemin).