Chitosan Fibers Loaded with Limonite as Catalyst for Decolorization of Organic Dye via Persulphate-based Advanced Oxidation Process

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Abstract: Wastewater generated from industries had resulted in serious impact to the environment. Conventional biological and physiochemical treatment methods for wastewater containing organic molecules have some limitations, therefore, the selection of other alternative methods or processes that are more suitable to degrade organic molecules and lower COD in wastewater. Heterogeneous Fenton processes and persulfate oxidation are advanced oxidation processes (AOPs) to degrade organic pollutants via reactive radical species. Therefore, in this study, limonite powder was incorporated into porous regenerated chitosan fibers and further used as heterogeneous catalyst to decompose methylene blue via sulfate radical-based AOPs. Limonite is used as a Fenton catalyst in this process to generate the persulfate radicals that initiate the decolorization process. Limonite-chitosan fibers were produced to effectively recover the limonite powder so that the catalyst can be reused repeatedly. The formation of limonite-chitosan fibers viewed under FESEM shows the limonite powder were well distributed in both surface and cross section area. The effectiveness of limonite-chitosan fiber as a Fenton catalyst under persulfate activation can achieve MB decolorization of 78.9% under 14 min. The stability and reusability of chitosan-limonite fibers were evaluated and measured in cycles 1 to 11 under optimal conditions. After 11 cycles of repeated use, the limonite chitosan fiber can maintain the performance up to 86% showed that the limonite containing chitosan fiber is a promising reusable catalyst material.

***Keywords*:** Advanced oxidation process; Wastewater treatment; Persulfate oxidation; Decomposition.

INTRODUCTION

Rapid industrialization, which utilizes organic dyes in the agriculture, food technology, leather, and textile industries, has caused major environmental issues [1]. Several technologies have been employed to tackle the wastewater issues, such as physical adsorption methods, chemically advanced oxidation processes (AOPs), biodegradation approaches, and traditional flocculation and coagulation methods [2–4]. Among all of these, AOPs have gained popularity due to their ability to degrade non-biodegradable organic molecules[5].

AOPs utilize powerful free radicals such as hydroxyl radicals (OH·) and sulfate radicals ($SO_4^{-}\cdot$), generated via homogenous or heterogenous catalysis, photocatalysis, electrocatalysis, etc, which decompose organic molecules in water (mineralization to CO_2, H_2O, and inorganic ions) [6]. Previous studies show that limonite is an efficient catalyst for Fenton/H_2O_2 reactions to degrade organic molecules [7]. However, its potential in AOPs reactions is yet to be discovered. In this study, we prepared regenerated chitosan fibers containing various amounts of limonite and further used them as a recyclable catalyst to decolorize methylene blue in an aqueous solution via $SO_4^{-}\cdot$-based AOPs. Immobilization of limonite powder into the chitosan fibers offers several advantages, such as the easy recovery and separation of the catalyst [8].

MATERIALS AND METHODS

A 2 wt% of chitosan dissolved in 2.5 wt% acetic acid was prepared by heating the mixture solution using a hotplate at 90 ºC for 1 h. The limonite powder was added to the chitosan solution with different weight percentages (1%, 10%, and 20%) and then stirred for 1 h using a magnetic stirrer to homogenize the mixture. The chitosan–limonite mixture was then loaded into a syringe attached with a 21G needle (inner diameter 0.51 mm) and then the solution was injected manually into a 50 mL NaOH (0.1 M) solution to yield regenerated chitosan–limonite fibers continuously. Characterization: Fourier transform infrared (FTIR) spectrometer, field emission scanning electron microscope (FESEM), and X-ray diffraction (XRD). The density functional theory calculation was conducted in Materials Studio using the DMol3 module (Biovia Discovery Studio 2021 (License Keys: LKO 1986646).

RESULTS AND DISCUSSION

Chitosan–limonite fibers to study the effect of limonite content and PS concentration as in figure 1a. The decolorization percentage of The effect of MB concentration on the decolorization via $SO_4^{-}\cdot$-based AOPs showed that the higher the MB concentration, the greater the percentage of decolorization as in Figure 1b.

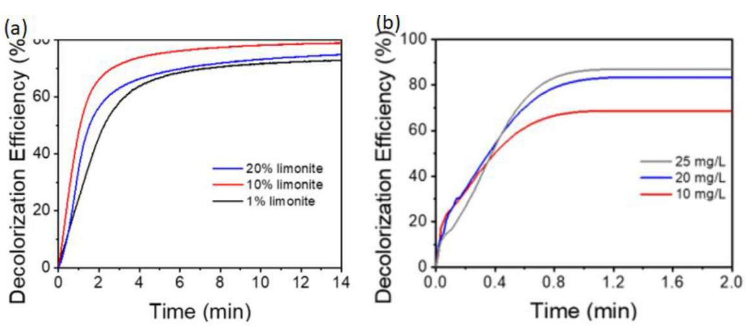

Fig. 1. (a) Decolorization kinetics of MB with 4 mM PS using chitosan–limonite fibers (1%, 10%, and 20% limonite). **(b)** Decolorization kinetics of MB at different concentrations of MB, 4 mM PS and chitosan–limonite fibers (10% limonite).

Figure 2a shows the effect of pH on the MB solution showed that the MB decolorization by $SO_4^{\cdot -}$-based AOPs was favored at pH 5.78, neutral (pH 7), and alkaline (pH 9.3), with decolorization percentages of 79, 72%, and 69%, respectively. The MB decolorization dropped drastically at a low pH medium (pH 2.7), with 21% of MB decolorization. This could be due to the highly acidic medium deactivating the $SO_4^{\cdot -}$ radicals that form the acid intermediates [9]. The stability and reusability of the chitosan–limonite fibers were evaluated for 10 consecutive cycles for the decolorization of MB at pH 5.78 for 15 min (Figure 2b). The decolorization efficiency was maintained at 86% for up to 10 consecutive cycles relative to the first decolorization percentage.

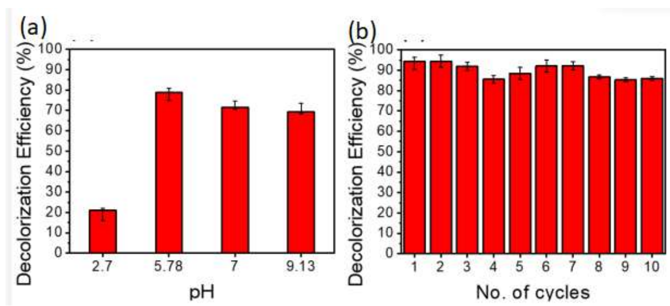

Fig. 2. (a) Effect of pH on the decolorization efficiency (4 mM PS and chitosan–limonite fibers (10% limonite)) **(b)** The recyclability of the chitosan fibers with 10% limonite on the MB decolorization with 4 mM PS and 5 mg/L MB (plotted relative to the first cycle of the decolorization experiment).

CONCLUSIONS

We successfully synthesized chitosan–limonite fibers loaded with limonite powder and further used the fibers as heterogeneous catalysts for the $SO_4^{\cdot -}$-based AOPs to decolorize methylene blue. The chitosan–limonite fibers also showed good recyclability up to 10 cycles with a decolorization efficiency greater than 86%. Persulfate was more favorably adsorbed onto hematite than goethite, suggesting that hematite is more dominant in catalyzing the generation of $SO_4^{\cdot -}$radicals from persulfate. The produced chitosan–limonite fibers could be also potentially used for other oxidation reactions which require iron or iron hydroxide compounds as a heterogeneous catalyst.

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