



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Preparation of heterogeneous bio-Fenton catalyst for decolorization of Malachite Green

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ARTICLE INFO

Article history:

Received 4 January 2015

Revised 27 March 2015

Accepted 3 May 2015

Available online xxx

Keywords:

Heterogeneous bio-Fenton

Kissiris

Glucose oxidase

Decolorization

Malachite Green

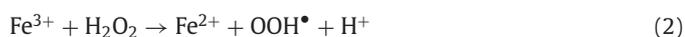
ABSTRACT

Titanium dioxide (TiO₂) and Fe₃O₄ magnetite particles were coated on spherical Kissiris; and glucose oxidase (GOx) enzyme was immobilized on Kissiris/Fe₃O₄/TiO₂ by physical adsorption. Performance of the prepared biocatalyst in decolorization of Malachite Green dye was investigated. Ninety-nine percent Malachite Green decolorization was obtained after 120 min by using 2 g of the heterogeneous bio-Fenton catalyst at initial dye concentration of 20 mg/L, initial glucose concentration of 20 mM, pH 5.5 and temperature of 40 °C. In this process, in contrast to conventional Fenton's reaction, external hydrogen peroxide and ferrous ion sources were not used.

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1. Introduction

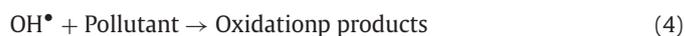
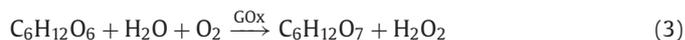
Synthetic dyes are mostly used in many industries such as textile, leather tanning, paper, plastics, pharmaceuticals, and foods [1]. There are more than 100,000 types of mercantile dyes and over 7×10^5 tons of dyestuffs are produced per year [2,3]. Malachite Green (MG) is a triphenylmethane dye that is extensively used in the mentioned industries. MG has some damaging effects on the ecosystem and its contact with skin leads to irritation, redness, and pain [4,5]. Therefore, elimination of MG from industrial wastewaters has become environmentally important. Many methods such as advanced oxidation, ozonation, adsorption, reverse osmosis, ion exchange, and membrane filtration have been utilized to remove dyes from waste effluents [6–11]. Fenton's reaction is a well-known method for the elimination of organic pollutants [12]. Fenton and Fenton like reactions can be demonstrated according to the following mechanisms (Eqs. (1) and (2)) [11]:



Hydroxyl radicals have high oxidizing potentials ($E^0 = 2.8$ V) in terms of oxidizing various organic materials such as dyestuffs [13]. H₂O₂ is widely used as a source of hydroxyl radicals. Recently,

in-situ production of hydrogen peroxide within the reaction medium has been developed in order to increase the efficiency of wastewater treatment and decrease the risk of hydrogen peroxide transportation and storage [14,15].

Glucose oxidation, a simple enzymatic reaction, is catalyzed by glucose oxidase and applied for the *in-situ* generation of hydrogen peroxide. Therefore, simultaneous bio-Fenton's reactions can be done to decolorize dyes through the following equations (Eqs. (3), (1) and (4)) [16]:



To increase the efficiency of bio-Fenton process, a proper carrier should be prepared to enhance GOx loading, activity, and stability and decrease the enzyme usage cost in continuous reactors [17,18].

High surface area to volume ratio, provided by the nanoparticles such as TiO₂ and Fe₃O₄, favors high binding capacity and high catalytic specificity of the conjugated enzyme [17]. However, the main problem of suspended biocatalyst is in the separation of nanoparticles after the treatment [19]. To solve the separation problem of carriers, in this study Kissiris was used for the TiO₂/Fe₃O₄/GOx immobilization. Kissiris is formed by foam thickening of volcanic lava and has micro-pores which are irregularly distributed throughout the surface. This natural mineral with a highly porous structure, good mechanical

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strength and stability toward chemical agents could be a very attractive material for enzyme immobilization [20–23].

In order to provide a better medium for GOx enzyme, in this research TiO₂ nanoparticles were used owing to their chemical inertness, rigidity, thermal stability, good adhesion to carriers, and high surface area [24]. Fe₃O₄ was coupled with TiO₂ to make a TiO₂/Fe₃O₄ adequate composite for GOx immobilization, the capacity of which is usually higher than pure TiO₂ and pure Fe₃O₄ [25]. Moreover, Fe₃O₄ is a ferrous source for heterogenic Fenton reaction and adherence property of TiO₂ nanoparticles causes Fe₃O₄ nanoparticles to be strongly linked to Kissiris carriers. Therefore, the prepared carrier has advantage of being enzyme compatible and includes a ferrous source for the commencement of bio-Fenton reactions.

2. Materials and methods

2.1. Materials

TiO₂ nanoparticles (commercial Degussa P25) were a mixed phase containing 80% anatase and 20% rutile with average crystal size of 21 nm. Methanol (99.9%), glucose oxidase (EC 1.1.3.4, from *Aspergillus niger*), β-D-glucose and Malachite Green oxalate (MG) were obtained from Sigma Aldrich. Iron (III) chloride tetrahydrate, iron (II) sulfate heptahydrate, ammonia trihydrate (Merck) and nitrogen gas were used to prepare magnetite nanoparticles. All solutions were prepared by distilled water.

2.2. Coating TiO₂ and Fe₃O₄ on Kissiris

Suspension of 0.5 g TiO₂ nanoparticles in 25 mL of methanol was sonicated for 15 min using Sonoplus Ultrasonic Homogenizer HD 2200 (Germany). Desired amount of HCl (1 N) was added to the solution to reach the pH value of 5. The suspended solution was poured onto 5 g of Kissiris at 90 °C and was allowed to dry at the mentioned temperature for 5 h [26]. The coated Kissiris were washed with distilled water to remove weakly attached particles. The deposited amount of TiO₂ was measured by the difference in the mass of Kissiris before and after TiO₂ deposition.

Fe₃O₄ nanoparticles were synthesized using chemical coprecipitation method [27]. Kissiris, coated with TiO₂, were dispersed in 100 mL of deionized water and then 2.7 g of FeSO₄·7H₂O and 5.4 g of FeCl₂·4H₂O were added. The mixed solution was continuously stirred under the nitrogen gas at 80 °C for 1 h. Afterward, 30 mL of NH₃·3H₂O was rapidly added to the mixture and stirred for another 1 h. Finally, the carriers were washed with 100 mL of deionized water to remove impurities and were allowed to dry in the vacuum condition for 1 h.

2.3. Immobilization of GOx on Kissiris/TiO₂/Fe₃O₄

One gram of the carrier was dispersed in 10 mL of GOx solution in phosphate buffer at pH value of 5.5 by stirring in a shaker incubator for 2 h at 30 °C. The prepared heterogeneous bio-Fenton catalyst was separated from the solution and washed with distilled water to remove weakly attached GOx [18]. The catalyst was stored at 4 °C until use.

The enzyme immobilization efficiency was calculated from difference between the initial and final enzyme activities in the reaction media. Also, the amount of released GOx into the washing solution was accounted in calculation of the amount of immobilized enzyme. In this process, the hybrid catalyst directly transforms the produced H₂O₂ to hydroxyl radical. Therefore, the decreased DO concentration in one min was measured by using DO meter sensor (Extech, DO600, USA) to assay catalyst activity [28]. One unit of catalyst activity has been defined as the amount of required catalyst to consume 1 μmol O₂ during 1 min at 25 °C has been.

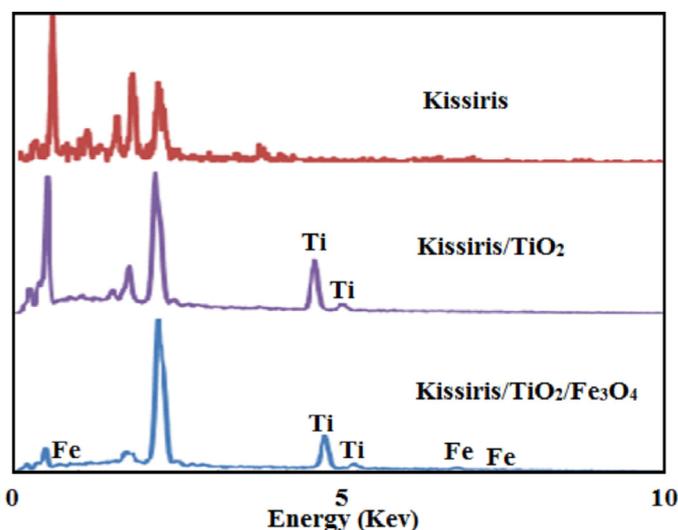


Fig. 1. EDX spectrum of Kissiris, Kissiris/TiO₂ and Kissiris/TiO₂/Fe₃O₄.

2.4. Decolorization

Experiments were carried out in 100 mL Erlenmeyer, which contained 20 mL of reaction mixture at certain temperature and constant stirring rate of 160 rpm. The reaction mixture contained certain concentration of MG and glucose with desired amount of bio-Fenton catalyst. To measure MG concentration in the sample solutions, UV–vis spectrophotometer (1700 UV–vis Shimadzu, Japan) was used. Dye absorbance was measured at maximum wavelength ($\lambda_{\max} = 617$ nm). Decolorization percentage was calculated by the following equation:

$$\text{Decolorization (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (5)$$

where C_0 and C are the concentrations of the sample solution at times 0 and t , respectively.

3. Results and discussion

3.1. Characterizing of the catalysts

Mineral composition of the prepared support could be analyzed using EDX (energy dispersion X-ray) patterns (Fig. 1). According to the figure, the applied Kissiris contained Al₂O₃, SiO₂, CaO, etc. The sharp peak was assigned to Au, since the samples were coated by gold in the analysis procedure. The appearance of Ti and Fe can be clearly observed in Fig. 1, implying successful deposition of TiO₂ and synthesis of Fe₃O₄.

Fig. 2 presents the FT-IR spectrum of Kissiris, Kissiris/TiO₂, Kissiris/TiO₂/Fe₃O₄, and Kissiris/TiO₂/Fe₃O₄/GOx. In the measured spectra, the broad peak at about 3400–3500 cm⁻¹ was attributed to the vibration of OH group. Bending vibration of H₂O molecules was observed within about 1400–1700 cm⁻¹ [29]. In the spectrum of volcanic Kissiris, the peaks at 400–600 cm⁻¹ are assigned to the vibration of Al–O bonds of Al₂O₃ and those at 600–900 cm⁻¹ and 1100–1250 cm⁻¹ correspond to the vibration of Si–O–Si and Si=O, respectively [30].

The peaks at 400–700 cm⁻¹ in the spectra of Kissiris/TiO₂ correspond to the stretching vibration of Ti–O and Ti–O–Ti [30]. The peaks at 400–700 cm⁻¹ are assigned to the vibration of Fe–O–Fe and Fe–O in the spectra of synthesized Fe₃O₄ [29]. In Fig. 2, the Kissiris/TiO₂/Fe₃O₄/GOx represents the FT-IR spectra of immobilized GOx on the carrier, in which the peaks at 1645.82 and 1513.17 cm⁻¹ correspond to amide I and amide II bonds of GOx, respectively [31].

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