



## Preparation of Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx biocatalyst: Feasibility study of MG decolorization

Vahide Elhami<sup>1</sup>, Afzal Karimi<sup>\*2</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Chemical and Petroleum Engineering, University of Tabriz, Tabriz, Iran

<sup>2</sup>Faculty of Advanced Technologies in Medicine, Iran University of Medical Sciences, Tehran, Iran

### ARTICLE INFO

#### Article history:

Received 13 June 2015

Received in revised form

19 November 2016

Accepted 22 January 2017

#### Keywords:

Decolorization

Glucose oxidase

Kissiris

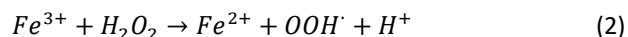
Heterogeneous Bio-Fenton

### ABSTRACT

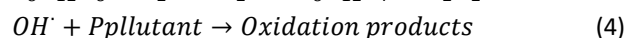
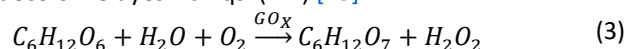
Titanium dioxide (TiO<sub>2</sub>) and Fe<sub>3</sub>O<sub>4</sub> magnetite particles were coated on spherical Kissiris; glucose oxidase (GOx) enzyme was immobilized on Kissiris/Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> by physical adsorption. This catalyst was analyzed by a scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray (EDX) measurements. The performance of the prepared biocatalyst in the decolorization of Malachite Green dye was investigated. The optimal operation parameters were 20 mg/L, 20 mM, 5.5 and 40 °C for initial dye concentration, initial glucose concentration, pH and temperature, respectively. Under these conditions, a 95% Malachite Green decolorization efficiency was obtained after 150 min of reaction by using 1 g of prepared heterogeneous bio-Fenton catalyst. In this process, in contrast to a conventional Fenton's reaction, external hydrogen peroxide and ferrous ion sources were not used. The effect of various reaction parameters such as initial concentration of dye, amount of catalyst, concentration of glucose, pH value and temperature on MG decolorization efficiency was studied.

### 1. Introduction

Synthetic dyes are 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<sup>5</sup> tons of dyestuff are produced per year [2, 3]. Malachite green (MG) is a triphenylmethane dye that is extensively used in the above mentioned industries. MG has some damaging effects on the ecosystem and its contact with skin leads to irritation, redness, and pain [4, 5]. Therefore, the 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 [6-10]. Fenton's reaction is a well-known method for the elimination of organic pollutants [11]. Fenton and Fenton like reactions can be demonstrated according to Equations (1) and (2) [10]:



Hydroxyl radicals have high oxidizing potential ( $E^0 = 2.8$  v) in terms of oxidizing various organic materials such as dyestuffs [12]. H<sub>2</sub>O<sub>2</sub> 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 [13, 14]. 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 via Eqs. (1-4) [15].



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

\*Corresponding author. Tel: +98 41 3339 31467

E-mail address: akarimi@tabrizu.ac.ir

area to volume ratio provided by the nanoparticles, such as TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>, favors high binding capacity and high catalytic specificity of the conjugated enzyme [16]. However, the main problem of the suspended biocatalyst is in the separation of nanoparticles after the treatment [18]. To solve the separation problem of carriers, this study used Kissiris for the TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx immobilization. Kissiris is formed by foam thickening of volcanic lava and has micropores which are irregularly distributed throughout the surface. This natural mineral with a highly porous structure, good mechanical strength and stability toward chemical agents could be a very attractive material for enzyme immobilization [19-22]. In order to provide a better medium for the GOx enzyme, this research used TiO<sub>2</sub> nanoparticles due to their chemical inertness, rigidity, thermal stability, good adhesion to carriers, and high surface area [23]. Fe<sub>3</sub>O<sub>4</sub> was coupled with TiO<sub>2</sub> to make a TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> adequate composite for GOx immobilization, the capacity of which is usually higher than pure TiO<sub>2</sub> and pure Fe<sub>3</sub>O<sub>4</sub> [24]. Moreover, Fe<sub>3</sub>O<sub>4</sub> was a ferrous source for the heterogeneous Fenton's reaction and the adherence property of TiO<sub>2</sub> nanoparticles caused Fe<sub>3</sub>O<sub>4</sub> nanoparticles to be strongly linked to Kissiris carriers. Therefore, the prepared carrier had the advantage of being enzyme compatible and included a ferrous source for the commencement of bio-Fenton reactions.

## 2. Materials and methods

### 2.1. Materials and equipment

TiO<sub>2</sub> nanoparticles (commercial Degussa P25) were a mixed phase containing 80% anatase and 20% rutile with an 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 the solutions were prepared using distilled water. A UV-vis spectrophotometer (1700 UV-vis Shimadzu, Japan) was used to determine dye concentration. Scanning electron microscopy (SEM) images and EDX analysis were taken by MIRA3FEG-SEM (Tescan Brno, Czech Republic). FTIR spectrums were obtained by Tensor 27 (Bruker, Germany). A Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) was used for sonication.

### 2.2. Coating TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> on Kissiris

A suspension of 0.5 g TiO<sub>2</sub> nanoparticles in 25 mL of methanol was sonicated for 15 min. The desired amount of HCl (1 N) was added to the solution to reach a 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 [25]. The coated Kissiris were washed with distilled water to remove weakly attached particles. The deposited

amount of TiO<sub>2</sub> was measured by the difference in the mass of Kissiris before and after TiO<sub>2</sub> deposition. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using a chemical coprecipitation method [26]. Kissiris, coated with TiO<sub>2</sub> were dispersed in 100 mL of deionized water and then 2.7 g of FeSO<sub>4</sub>·7H<sub>2</sub>O and 5.4 g of FeCl<sub>3</sub>·4H<sub>2</sub>O were added. The mixed solution was continuously stirred under nitrogen gas at 80°C for 1 h. Subsequently, 30 mL of NH<sub>3</sub>·3H<sub>2</sub>O 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 allowed to dry in a vacuum condition for 1 h.

### 2.3. Immobilization of GOx on Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>

1 g of the carrier was dispersed in 10 mL of GOx solution in a phosphate buffer at a 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 [17].

### 2.4. Decolorization

Experiments were carried out at a certain temperature and a constant stirring rate of 160 rpm in a 100 mL Erlenmeyer flask, which contained 20 mL of reaction mixture. The reaction mixture contained a certain concentration of MG and glucose with the desired amount of bio-Fenton catalyst to measure MG concentration in the sample solutions. The dye absorbance was measured at a maximum wavelength ( $\lambda_{\max}$ =617 nm). The decolorization percentage was calculated by the following equation:

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

Where C<sub>0</sub> 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 was analyzed using EDX (energy dispersion X-ray) patterns (Figure 1). According to the figure, the applied Kissiris contained Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, 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 the Figure 1, implying the successful deposition of TiO<sub>2</sub> and the synthesis of Fe<sub>3</sub>O<sub>4</sub>.

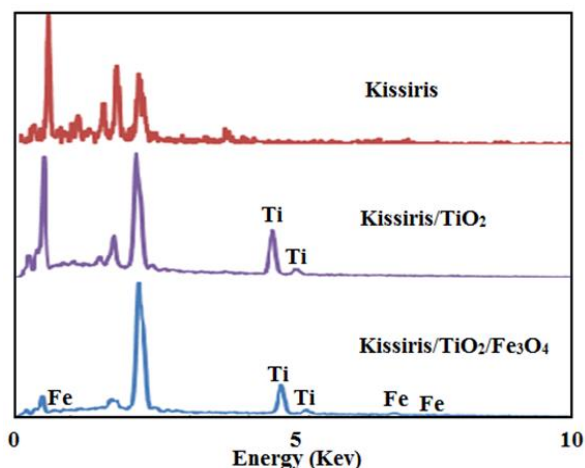


Fig. 1. EDX spectrum of Kissiris, Kissiris/TiO<sub>2</sub> and Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>

Figure 2 presents the FTIR spectrum of Kissiris, Kissiris/TiO<sub>2</sub>, Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, and Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx. In the measured spectra, the bonds at about 3400-3500 cm<sup>-1</sup> were attributed to the vibration of the OH group. The bending vibration of H<sub>2</sub>O molecules was observed within 1400-1700 cm<sup>-1</sup> [27]. In the spectrum of volcanic Kissiris, the peaks at 400-600 cm<sup>-1</sup> were assigned to the vibration of Al-O bonds of Al<sub>2</sub>O<sub>3</sub> and those at 600-900 cm<sup>-1</sup> and 1100-1250 cm<sup>-1</sup> corresponded to the vibration of Si-O-Si and Si = O, respectively [28]. The peaks at 400-700 cm<sup>-1</sup> in the spectra of Kissiris/TiO<sub>2</sub> corresponded to the stretching vibration of Ti-O and Ti-O-Ti [28]. The peaks at 400-700 cm<sup>-1</sup> were assigned to the vibration of Fe-O-Fe and Fe-O in the spectra of synthesized Fe<sub>3</sub>O<sub>4</sub> [27]. In Figure 2, the Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx represents the FTIR spectra of immobilized GOx on the carrier, in which the peaks at 1645.82 and 1513.17 cm<sup>-1</sup> correspond to amide I and amide II bonds of GOx, respectively [29]. Thus, the results proved the successful preparation of the bio-Fenton catalyst of Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx. Scanning electron microscopy (SEM) images of the Kissiris, thin deposited layers of TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, and immobilized GOx were taken. Figure 3(b) and (c) clearly shows the attachment of TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the Kissirises. Figure 3d shows that GOx was successfully immobilized on the carrier.

### 3.2. Catalytic activity of the Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx

To ensure that the enzyme was acting, the new catalyst was used to decolorize 5 mg/L of malachite green aqueous solution with and without adding glucose. In the absence of glucose, the decolorization was only 33% at 60 min. The GOx enzyme did not produce H<sub>2</sub>O<sub>2</sub> without substrate (e.g., glucose) and it was physical adsorption that caused the disappearance of dye in this case. When glucose was added to the reaction medium, the decolorization percentage increased to 99.9% at 60 min.

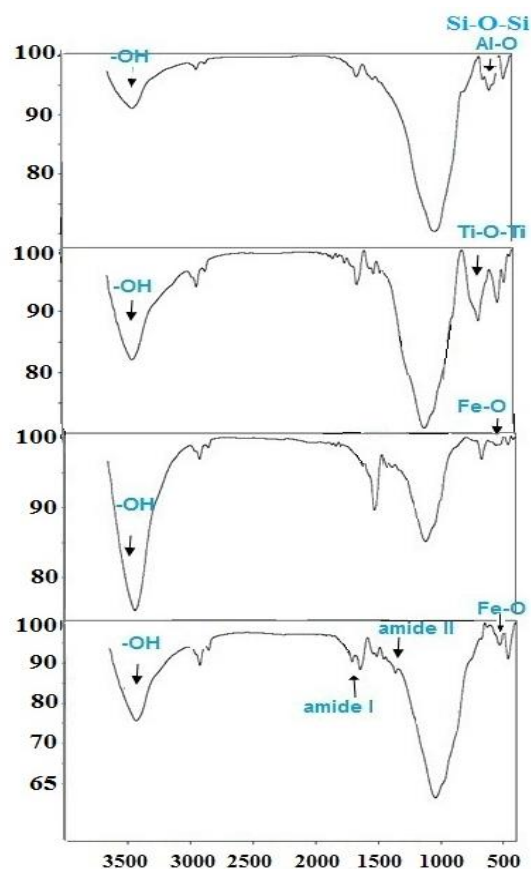
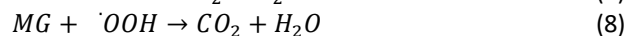
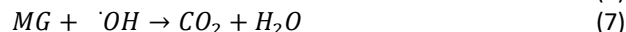
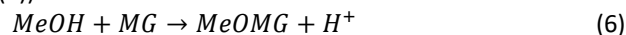


Fig. 2. FT-IR spectrum of Kissiris, Kissiris/TiO<sub>2</sub>, Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, and Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx.

A possible mechanism of decolorization can be outlined as the following reactions [30]. First, MG was adsorbed onto the catalyst surface, Eq. (6), where Me refers to the Fe or Ti on the surface of catalyst. The enzymatic reaction produced in-situ hydrogen peroxide according to Eq. (3). Then, Fenton and Fenton-like processes took place and active radicals such as hydroxyl and perhydroxyl radicals (<sup>•</sup>OH and <sup>•</sup>OOH) were generated, as shown in Eqs. (1) and (2), respectively. Finally, the produced radicals oxidized the organic molecules of dye, leading to MG decolorization (Eqs. (7) and (8)).



#### 3.2.1. Effect of dye concentration

The experiments were conducted at an initial concentration of MG in the range of 20 – 100 mg/L, while maintaining agitation rate, catalyst loading, initial glucose concentration and temperature at 160 rpm, 1 g, 20 mM and 35°C, respectively. Figure 4 shows that MG disappearance efficiency decreased with a decrease in initial dye concentration. It can be seen that the decolorization rate was faster at the start of the reaction for each initial concentration, which was mainly due to the higher number

of available dye molecules for reaction and the rapid engagement of active radicals with organic molecules decreased the chance of undesired reactions between

radicals in the first minutes of the reaction [31]. Table 1 shows the overall decolorization rate.

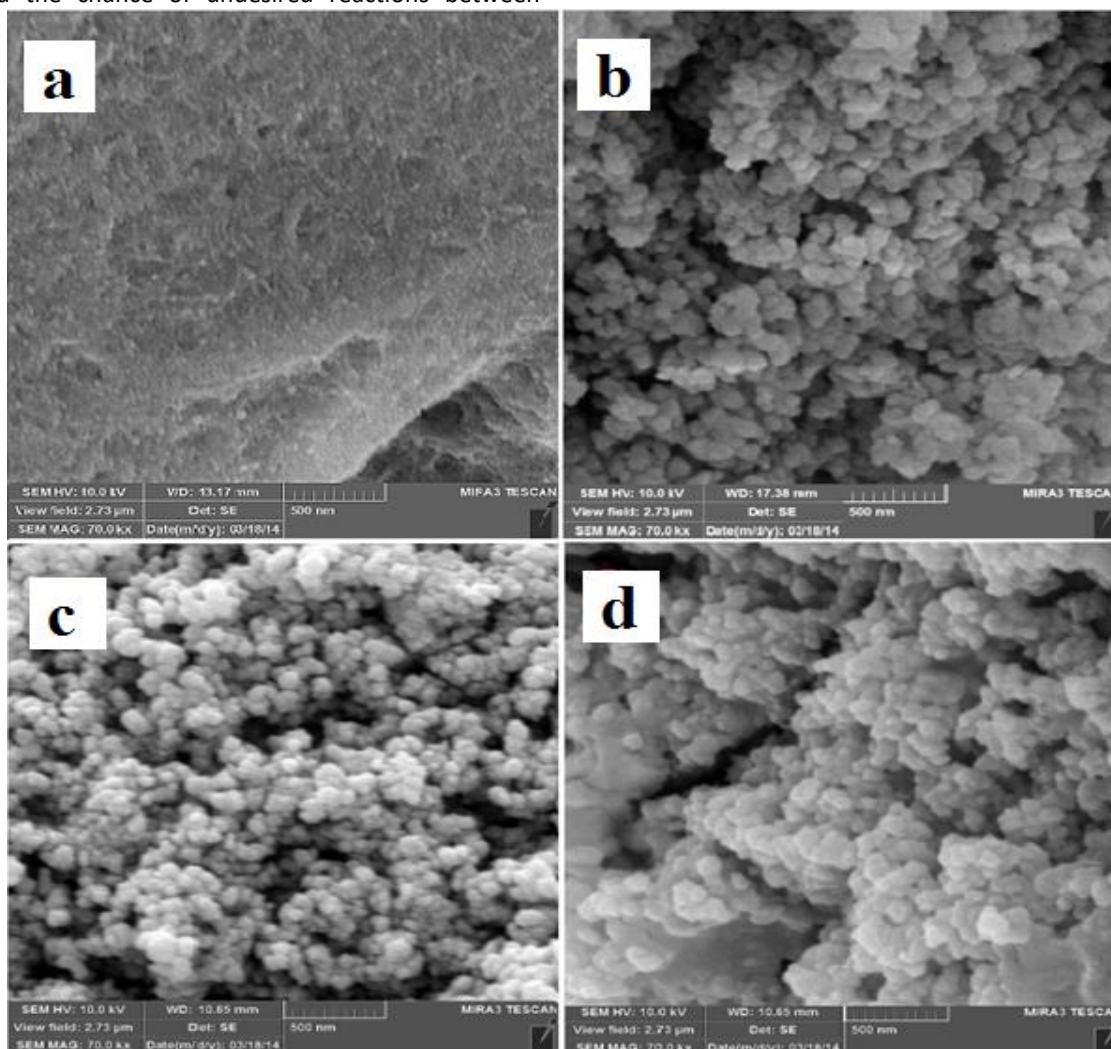


Fig. 3. SEM images of (a) Kissiris, (b) Kissiris/TiO<sub>2</sub>, and (c) Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, (d) Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx.

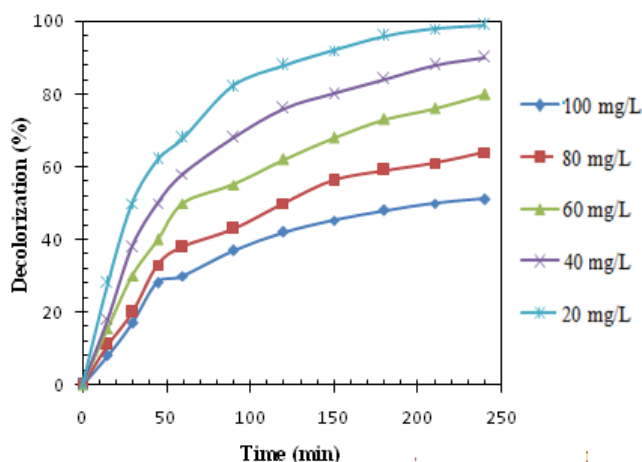


Fig. 4. Effect of initial concentration of dye on pseudo-first order rate constant during heterogeneous bio-Fenton oxidation treatment; [glucose]<sub>0</sub>=20 mM, 1 g Kissiris/Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>/GOx, T= 35°C.

Table 1. Overall pseudo-first order kinetic rate constant for different dye concentration

MG concentration	$k_{app}(\text{min}^{-1})$	$R^2$
20	0.0029	0.9074
40	0.0041	0.9439
60	0.0063	0.9714
80	0.0093	0.9802
100	0.0182	0.9935

### 3.2.2. Effect of glucose concentration

To study the effect of glucose concentration on MG degradation, different concentrations of glucose (5-25) mM were tested (Fig. 5). The experiments were performed at a fixed initial Malachite Green concentration of 20 mg/L, 1 g of heterogeneous bio-Fenton catalysts, and a temperature of 35°C. The increase in decolorization rate, shown in Figure 5, was related to the H<sub>2</sub>O<sub>2</sub> generation rate, which was produced by enzymatic reaction using immobilized GOx. This in-situ production of H<sub>2</sub>O<sub>2</sub> was the main advantage of

the immobilized enzyme. By the increase of glucose amount, the in-situ production and consumption rate of hydrogen peroxide increased. The decolorization efficiency was raised, as a result of the increased glucose concentration from 5 to 20 mM. However, at 25 mM, the degradation efficiency decreased; this can be due to the adverse reactions caused by hydrogen peroxide scavenging (Eqs. (10)- (11)) at such a high concentration of  $H_2O_2$  [32].

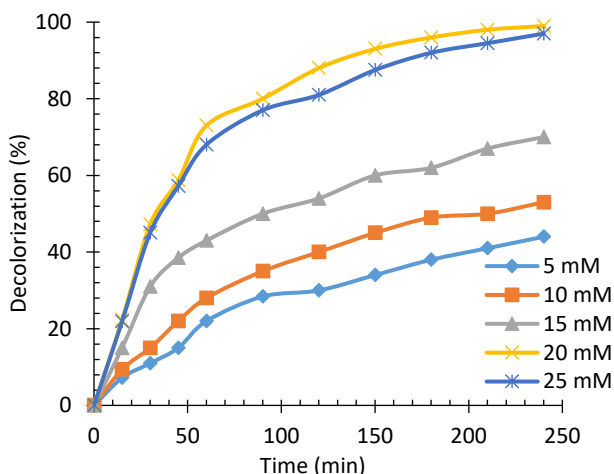
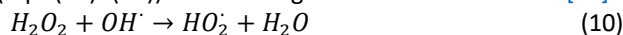


Fig. 5. Effect of initial glucose concentration on pseudo-first order rate constant during heterogeneous bio-Fenton oxidation treatment;  $[MG]_0 = 20 \text{ mg/L}$ , 1 g Kissiris/ $Fe_3O_4/TiO_2/GOx$ ,  $T = 35^\circ \text{C}$ .

### 3.2.3. Effect of pH

As can be seen in Figure 6, the MG disappearance efficiency was influenced by the pH value of the solution. The efficiency increased by raising the pH value from 3.5 to 5.5 and decreased significantly above a pH of 5.5. These changes of decolorization efficiency can be attributed to the stability of  $H_2O_2$  in the acidic medium. The decrease in efficiency at pH values higher than 5.5 was due to  $Fe(OH)_3$  formation; in this form, iron disintegrated hydrogen peroxide to water and oxygen [31]. On the other hand, the higher and lower pH values disrupted the enzymatic reaction, so that there was an optimal pH value of 5.5 for enzyme activity and decolorization process.

### 3.2.4. Effect of temperature

To determine the effect of temperature on MG decolorization, experiments were conducted at a temperature range of 298 to 318 K. According to Figure 7, the decolorization efficiency increased by increasing temperature to  $20^\circ \text{C}$ ; this was due to an increase in GOx activity by temperature which consequently enhanced the hydrogen peroxide production rate. Also, the reaction of hydrogen peroxide with Fe ions was accelerated by an increase in temperature. Decolorization efficiency decreased above  $20^\circ \text{C}$ , which was due to the denaturation

of the protein molecules in the structure of the enzyme. Thus, excessive temperature deactivated glucose oxidase and disrupted its bio-catalytic activity; as a result, the in-situ generation of hydrogen peroxide decreased and consequently, decolorization efficiency decreased.

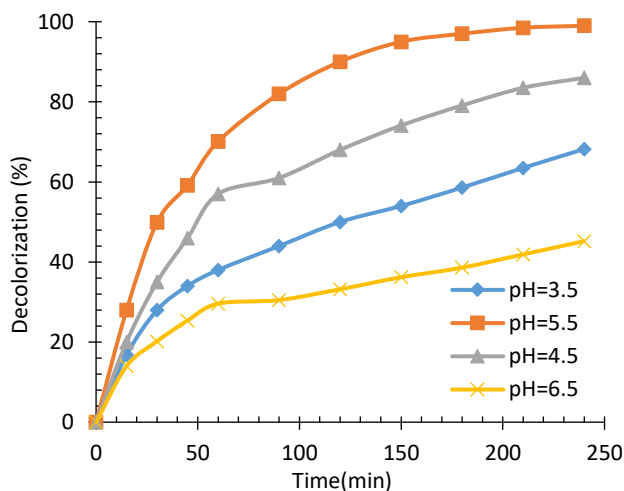


Fig. 6. Effect of pH value on pseudo-first order rate constant during heterogeneous bio-Fenton oxidation treatment;  $[MG]_0 = 20 \text{ mg/L}$ ,  $[glucose]_0 = 20 \text{ mM}$ , 1 g Kissiris/ $Fe_3O_4/TiO_2/GOx$ ,  $T = 35^\circ \text{C}$ .

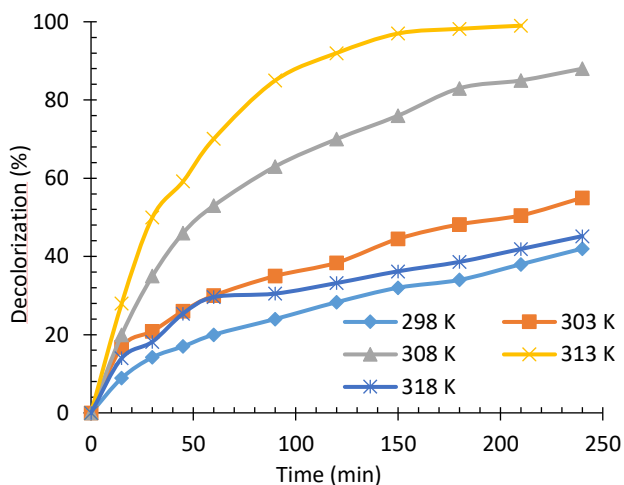


Fig. 7. Effect of temperature on pseudo-first order rate constant during heterogeneous bio-Fenton oxidation treatment;  $[MG]_0 = 20 \text{ mg/L}$ ,  $[glucose]_0 = 20 \text{ mM}$ , 1 g Kissiris/ $Fe_3O_4/TiO_2/GOx$ ,  $\text{pH} = 5.5$ .

## 4. Conclusions

Bio-Fenton is a newly introduced method for the elimination of organic pollutants. In this technique, hydrogen peroxide is generated by an enzymatic reaction and reacts with a  $Fe^{2+}$  ion to produce a hydroxyl radical. The glucose oxidase enzyme was immobilized on the Kissiris/ $TiO_2/Fe_3O_4$  carrier to enhance enzyme reusability. The results of EDX, FTIR, and SEM analyses showed that the synthesis of the hybrid heterogeneous bio-Fenton catalyst (e.g., Kissiris/ $TiO_2/Fe_3O_4/GOx$ ) was successful. The best MG

decolorization efficiency, by using 1 g of prepared heterogeneous bio-Fenton catalyst, was 95% after 150 min at an optimal operating condition of 20 mg/L MG initial concentration, 20 mM glucose, a pH value of 5.5 and a temperature of 40 °C. It was observed that Kissiris/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>/GOx is a promising catalyst for the bio-*P*-values of 0.0020 and 0.0066, respectively. In other words, increasing pH had a greater influence on the removal efficiency.

## References

- [1] Doğan, M., Abak, H., Alkan, M. (2009). Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. *Journal of hazardous materials*, 164(1), 172-181.
- [2] Gupta, V. K., Mittal, A., Krishnan, L., Gajbe, V. (2004). Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and purification technology*, 40(1), 87-96.
- [3] Jasińska, A., Różalska, S., Bernat, P., Paraszewicz, K., Długoński, J. (2012). Malachite green decolorization by non-basidiomycete filamentous fungi of *Penicillium pinophilum* and *Myrothecium roridum*. *International biodeterioration and biodegradation*, 73, 33-40.
- [4] Srivastava, S., Sinha, R., Roy, D. (2004). Toxicological effects of malachite green. *Aquatic toxicology*, 66(3), 319-329.
- [5] Nethaji, S., Sivasamy, A., Thennarasu, G., Saravanan, S. (2010). Adsorption of Malachite Green dye onto activated carbon derived from *Borassus aethiopum* flower biomass. *Journal of hazardous materials*, 181(1), 271-280.
- [6] Khataee, A. R., Vatanpour, V., Ghadim, A. A. (2009). Decolorization of CI Acid Blue 9 solution by UV/Nano-TiO<sub>2</sub>, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study. *Journal of hazardous materials*, 161(2), 1225-1233.
- [7] Aleboye, A., Kasiri, M. B., Olya, M. E., Aleboye, H. (2008). Prediction of azo dye decolorization by UV/H<sub>2</sub>O<sub>2</sub> using artificial neural networks. *Dyes and pigments*, 77(2), 288-294.
- [8] Rauf, M. A., Meetani, M. A., Hisaindee, S. (2011). An overview on the photocatalytic degradation of azo dyes in the presence of TiO<sub>2</sub> doped with selective transition metals. *Desalination*, 276(1), 13-27.
- [9] Xu, N., Zhang, Y., Tao, H., Zhou, S., Zeng, Y. (2013). Bio-electro-Fenton system for enhanced estrogens degradation. *Bioresour. Technol.*, 138, 136-140.
- [10] Zhang, G., Qin, L., Meng, Q., Fan, Z., Wu, D. (2013). Aerobic SBR/reverse osmosis system enhanced by Fenton oxidation for advanced treatment of old municipal landfill leachate. *Bioresour. Technol.*, 142, 261-268.
- [11] Yalfani, M. S., Contreras, S., Medina, F., Sueiras, J. (2009). Phenol degradation by Fenton's process using catalytic in situ generated hydrogen peroxide. *Applied catalysis B: Environmental*, 89(3), 519-526.
- [12] Barreca, S., Colmenares, J. J. V., Pace, A., Orecchio, S., Pulgarin, C. (2014). Neutral solar photo-Fenton degradation of 4-nitrophenol on iron-enriched hybrid montmorillonite-alginate beads (Fe-MABs). *Journal of Photochemistry and Photobiology A: Chemistry*, 282, 33-40.
- [13] Osegueda, O., Dafinov, A., Llorca, J., Medina, F., Sueiras, J. (2012). In situ generation of hydrogen peroxide in catalytic membrane reactors. *Catalysis today*, 193(1), 128-136.
- [14] Torabi, S. F., Khajeh, K., Ghasempour, S., Ghaemi, N., Siadat, S. O. R. (2007). Covalent attachment of cholesterol oxidase and horseradish peroxidase on perlite through silanization: activity, stability and co-immobilization. *Journal of biotechnology*, 131(2), 111-120.
- [15] Karimi, A., Aghbolaghy, M., Khataee, A., Shoa Bargh, S. (2012). Use of enzymatic bio-Fenton as a new approach in decolorization of malachite green. *The scientific world journal*, 2012.
- [16] Ansari, S. A., Husain, Q. (2012). Potential applications of enzymes immobilized on/in nano materials: a review. *Biotechnology advances*, 30(3), 512-523.
- [17] Karimi, A., Mahdizadeh, F., Salari, D., Niaei, A. (2011). Bio-deoxygenation of water using glucose oxidase immobilized in mesoporous MnO<sub>2</sub>. *Desalination*, 275(1), 148-153.
- [18] Khataee, A. R., Fathinia, M., Aber, S., Zarei, M. (2010). Optimization of photocatalytic treatment of dye solution on supported TiO<sub>2</sub> nanoparticles by central composite design: intermediates identification. *Journal of hazardous materials*, 181(1), 886-897.
- [19] Ghasemzadeh, R., Kargar, A., Lotfi, M. (2011). Decolorization of synthetic textile dyes by immobilized white-rot fungus. In *international conference on chemical, ecology and environmental sciences, Pattaya* (pp. 434-438).
- [20] Jamshidian, H., Khatami, S., Mogharei, A., Vahabzadeh, F., Nickzad, A. (2013). Cometabolic degradation of para-nitrophenol and phenol by *Ralstonia eutropha* in a Kissiris-immobilized cell bioreactor. *Korean Journal of chemical engineering*, 30(11), 2052-2058.
- [21] Karimi, A., Vahabzadeh, F., Bonakdarpour, B. (2006). Use of *Phanerochaete chrysosporium* immobilized on Kissiris for synthetic dye decolorization: involvement of manganese peroxidase. *World journal of microbiology and biotechnology*, 22(12), 1251-1257.
- [22] Tsoutsas, T., Kanellaki, M., Psarianos, C., Kallifas, A., Koutinas, A. A. (1990). Kissiris: A mineral support for the promotion of ethanol fermentation by *Saccharomyces cerevisiae*. *Journal of fermentation and bioengineering*, 69(2), 93-97.
- [23] Xiao, P., Zhang, Y., Cao, G. (2011). Effect of surface defects on biosensing properties of TiO<sub>2</sub> nanotube

- arrays. *sensors and actuators B: Chemical*, 155(1), 159-164.
- [24] Meng, H., Wang, B., Liu, S., Jiang, R., Long, H. (2013). Hydrothermal preparation, characterization and photocatalytic activity of TiO<sub>2</sub>/Fe–TiO<sub>2</sub> composite catalysts. *Ceramics international*, 39(5), 5785-5793.
- [25] Shoaebargh, S., Karimi, A., Dehghan, G. (2014). Performance study of open channel reactor on AO<sub>7</sub> decolorization using glucose oxidase/TiO<sub>2</sub>/polyurethane under UV–vis LED. *Journal of the Taiwan institute of chemical engineers*, 45(4), 1677-1684.
- [26] Ozmen, M., Can, K., Arslan, G., Tor, A., Cengeloglu, Y., Ersoz, M. (2010). Adsorption of Cu (II) from aqueous solution by using modified Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles. *Desalination*, 254(1), 162-169.
- [27] Mesgari, Z., Gharagozlou, M., Khosravi, A., Gharanjig, K. (2012). Spectrophotometric studies of visible light induced photocatalytic degradation of methyl orange using phthalocyanine-modified Fe-doped TiO<sub>2</sub> nanocrystals. *Spectrochimica acta part A: Molecular and biomolecular spectroscopy*, 92, 148-153.
- [28] Fan, Y., Ma, C., Li, W., Yin, Y. (2012). Synthesis and properties of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanocomposites by hydrothermal synthetic method. *Materials science in semiconductor processing*, 15(5), 582-585.
- [29] Zuo, S., Teng, Y., Yuan, H., Lan, M. (2008). Direct electrochemistry of glucose oxidase on screen-printed electrodes through one-step enzyme immobilization process with silica sol–gel/polyvinyl alcohol hybrid film. *Sensors and actuators B: Chemical*, 133(2), 555-560.
- [30] Abbas, M., Rao, B. P., Reddy, V., Kim, C. (2014). Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> core/shell nanocubes: Single-batch surfactantless synthesis, characterization and efficient catalysts for methylene blue degradation. *Ceramics international*, 40(7), 11177-11186.
- [31] Hameed, B. H., Lee, T. W. (2009). Degradation of malachite green in aqueous solution by Fenton process. *Journal of hazardous materials*, 164(2), 468-472.
- [32] Romanias, M. N., El Zein, A., Bedjanian, Y. (2012). Heterogeneous interaction of H<sub>2</sub>O<sub>2</sub> with TiO<sub>2</sub> surface under dark and UV light irradiation conditions. *The journal of physical chemistry A*, 116(31), 8191-8200.