

UNGLAZED WASTE POTTERY SCRAPS AS A HETEROGENEOUS CATALYST FOR FENTON-LIKE DECOLORIZATION OF METHYL ORANGE

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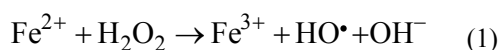
Abstract

Unglazed waste pottery scraps (UPS), obtained from the pottery manufacturing process, could be used as a Fenton-like catalyst for the decolorization of methyl orange dye (MO) because it contains an iron active species. The effect of various experimental parameters such as the catalyst dosage, initial pH of the dye solution, the initial concentration of the hydrogen peroxide (H₂O₂) and the dye, and the reaction temperature on the decolorization efficiency of the process was studied. The best performance of the MO decolorization was found to be 98.6% after 90 min of reaction by using a 10 g/L catalyst dosage and 10 mM of H₂O₂ at pH 3 for 60 mg/L of the MO solution with a 30°C of reaction temperature. Moreover, the catalyst can be reused at least 3 times. The leaching of the Fe active species resulted in a decreasing percentage of the MO decolorization.

Keywords: Unglazed pottery scraps waste, heterogeneous Fenton-like catalyst, wastewater treatment, methyl orange

Introduction

Nowadays, Fenton technology is widely used for the treatment of industrial wastewater containing non-biodegradable organic pollutants. Generally, the homogeneous Fenton process is well known with iron(II) ions (Fe²⁺) reacting with hydrogen peroxide (H₂O₂) to produce hydroxyl radicals (•OH), according to Equation (1):



and the •OH radicals can consequently oxidize organic compounds to carbon dioxide (CO₂) and water (H₂O) (Fenton, 1894; Walling, 1975), while there are Fenton-like reactions in which iron(III) ions (Fe³⁺) or other transition metal ions are utilized.

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The homogeneous Fenton process has some disadvantages. The removal or treatment of the sludge-containing iron ions at the end of the wastewater treatment process requires the use of expensive reagents, extensive time, and labor. In addition, the reaction occurs in a narrow pH range and the deactivation of the catalyst can occur from the complexation of iron with phosphate anion and intermediate oxidation products (Caudo *et al.*, 2006; Kasiri *et al.*, 2008). To overcome these problems, heterogeneous Fenton catalysts have been investigated as potential replacements for homogeneous Fenton catalysts. Among the heterogeneous solid catalysts for the Fenton process, clay has recently received much attention because it is abundant in nature and inexpensive. Combined with the functionality of iron, it can serve as a heterogeneous catalyst (Cheng *et al.*, 2008; Garrido-Rom  rez *et al.*, 2010). Moreover, clay can be used as support for iron to increase the active sites which leads to higher catalytic activity (Xu *et al.*, 2009a; Ramirez *et al.*, 2007, 2008; Chen and Zhu, 2007; Hassan and Hameed, 2011a, 2011b; Platon *et al.*, 2011; Hartmann *et al.*, 2010; Rodriguez *et al.*, 2010; Azmi *et al.*, 2014).

In Thailand, Dan Kwian pottery is a well-known product of Nakhon Ratchasima Province. It has special characteristics such as shape, color, and toughness. Dan Kwian pottery is made of Dan Kwian clay which is commonly found near the banks of the Moon River where they have been worn away or eroded, creating areas of a swamp-like deposits. The most special feature is its natural red color which is due to the iron oxide content present in the clay (Chimnakom, 1999; Rattanachan, 2007). Unglazed waste pottery scraps (UPS) are the broken pieces that occur during the pottery manufacturing process. Thus, UPS contain iron species that could be used as a heterogeneous catalyst in the Fenton process for wastewater treatment. With the use of UPS, reduction of the cost of wastewater treatment could be achieved.

In this work, we studied the decolorization of an active commercial dye, methyl orange (MO), in an aqueous solution using UPS as a heterogeneous catalyst in the presence of H₂O₂. The influence factors on the MO decolorization, such as the initial concentration of the H₂O₂ and dye, the catalyst

dosage, the temperature, and the pH of the solutions were investigated. Moreover, the UPS were tested in the decolorization of real textile wastewater obtained from Pak Thong Chai District, Nakhon Ratchasima.

Experimental Procedure

Materials

The UPS were obtained from Dan Kwian, Chokchai District, Nakhon Ratchasima Province, Thailand. The UPS were ground and sieved to obtain a particle size of less than 500 µm. Methyl orange (C₁₄H₁₄N₃NaO₃S, Carlo Erba, Dasit Group SpA, Milan, Italy), hydrogen peroxide (30% H₂O₂, Merck, Merck KGaA, Darmstadt, Germany), and sulfuric acid (H₂SO₄, Merck, Merck KGaA, Darmstadt, Germany) were of analytical reagent grade.

Catalyst Characterization

The morphology of the UPS was observed using scanning electron microscopy (SEM) (SEM-JEOL-JSM5800LV, JEOL Ltd., Tokyo, Japan). Some metal species in the UPS were determined by using an energy dispersive X-ray fluorescence (EDXRF) spectrometer (Oxford ED2000, Oxford Instruments plc, Abingdon, UK). The crystalline structure of the UPS was analyzed by an X-Ray diffractometer (Bruker D2 PHASER, Bruker Corp., Billerica, MA, USA) using CuK α radiation at 40 kV and 40 mA. Data were collected from 5° to 80° with a step size of 0.02. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer (PerkinElmer Inc., Waltham, MA, USA). The surface area of the UPS was determined by N₂ adsorption–desorption analysis (Micromeritics ASAP 2010, Micromeritics Instrument Corp., Norcross, GA, USA) from the Brunauer–Emmett–Teller (BET) method.

Catalytic Activity Measurements and Analytical Methods

All experiments were carried out in 125 mL-Erlenmeyer flasks with 50 mL of 60 mg/L MO. The pH of the solutions was adjusted to the desired values by using 3M H₂SO₄ and after that the UPS were added. The reactions

were initiated by adding a predetermined amount of H_2O_2 solution to the flask. The mixture solution was stirred with a magnetic stirrer. After the study period, the reaction mixture was centrifuged to remove the catalyst. The concentrations of the MO were measured using a double beam UV-vis spectrophotometer (Shimadzu model UV-2450, Shimadzu Corp., Kyoto, Japan) at 510 nm.

The decolorization efficiency of the MO was calculated using the following equation:

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 (mg/L) is the initial concentration of the MO and C_t (mg/L) is the concentration of the MO at the time, t (min).

To evaluate the potential application of the UPS, the decolorization of real textile wastewater was tested. The wastewater sample, which was collected from an equalization tank of an industrial textile plant located in Nakhon Ratchasima (Thailand), showed a dark brown

color associated with the mixture of several classes of dyes, as well as other pollutants used in the textile process. The sample was refrigerated at approximately 4°C . Before starting any testing with the sample, the temperature of the sample was adjusted back to the ambient raw water temperature and was used without dilution. The treated wastewater was diluted 10 times before detection with a UV-vis spectrophotometer (Shimadzu model UV-2450, Shimadzu Corp., Kyoto, Japan).

Catalyst stability and leaching test

The spent catalyst was reused in order to evaluate the catalytic activity during successive experiments and, thus, to observe the possibility of reusing the catalyst. The catalyst was tested in 4 consecutive cycles using fresh solutions at the optimum condition ($[\text{MO}]_0 = 60 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, catalyst = 10 g/L , $\text{pH} = 3$, and reaction time = 90 min at the reaction temperature of 27°C). After each experiment, the catalyst was removed by centrifugation and dried at 60°C for 2 h .

Table 1. Chemical composition of UPS

Component content (%)									
SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	CaO	MnO_2	Cr_2O_3
70.75	13.65	7.63	4.29	1.51	0.92	0.77	0.38	0.07	0.03

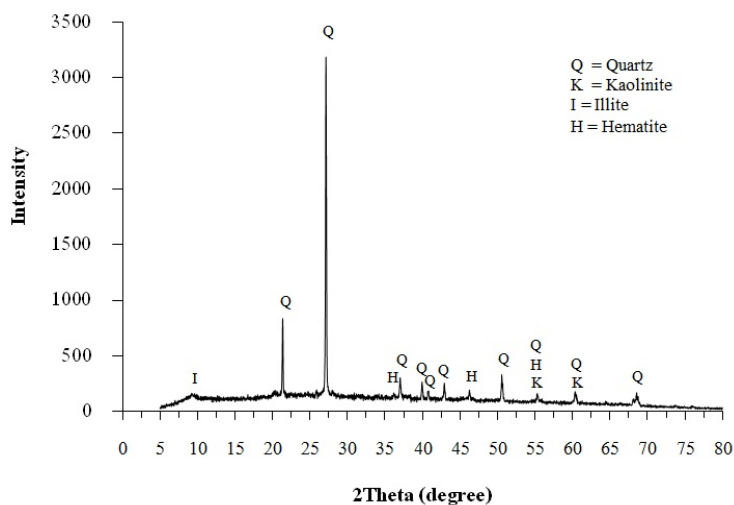


Figure 1. XRD pattern of UPS

The leaching of iron ions in the MO solution after the oxidation with H_2O_2 was determined by using an atomic absorption spectrophotometer (AAS) (Shimadzu AA-6300, Shimadzu Corp., Kyoto, Japan). Prior to the measurements, a calibration curve was constructed by using the known concentrations of standard iron solutions.

Results and Discussion

Characterization of the UPS

From the X-ray fluorescence (XRF) analysis, the main constituents of the UPS are silicon oxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), and sodium oxide (Na_2O), as shown in Table 1. The X-ray powder diffraction (XRD) pattern of the UPS is shown in Figure 1. The main crystalline phase observed in the UPS is quartz ($2\theta = 21.4^\circ$,

27.1° , 37.0° , 39.9° , 40.8° , 50.6° , 55.3° , 60.3° , and 68.5° , JCPDS 01-078-1256). Moreover, the presence of illite ($2\theta = 9.2^\circ$), kaolinite ($2\theta = 55.3$ and 60.3°), and hematite (Fe_2O_3) ($2\theta = 35.2^\circ$, 46.3° , and 55.3° , ICDD PDF card 33-0664) was observed with low intensity peaks. In this study, the UPS contained the mineral form of iron(III) oxide (Fe_2O_3), the so-called Fenton-like catalyst. The FTIR absorption spectrum of the UPS is shown in Figure 2(a). The wavenumber and assignment of the vibration modes observed are listed in Table 2. The main constituent of the minerals in the UPS was quartz with the bands detected at 798, 779, 695, and 467 cm^{-1} . Kaolinite (3699 , 3620 , and 1035 cm^{-1}) and hematite (913 and 535 cm^{-1}) were inferred from the IR absorption bands (Farmer, 1974; Gadsden, 1975; Sathya and Velraj, 2011; Azmi *et al.*, 2014). The particles have various shapes and sizes which are in the range of 10-20 micrometers, seen by

Table 2. Positions and assignments of the IR vibration bands observed

Position (cm^{-1})	Assignments	Position (cm^{-1})	Assignments
3699	O-H stretching of Kaolinite	798	Si-O bending of quartz
3620	O-H stretching of Kaolinite	779	Si-O-Si stretching of quartz
3437	O-H stretching of water	695	Si-O bending of quartz
1632	O-H bending of water	535	Fe-O bending of hematite
1035	Si-O stretching of Kaolinite	467	Si-O bending of quartz
913	Fe-O-Fe bending		

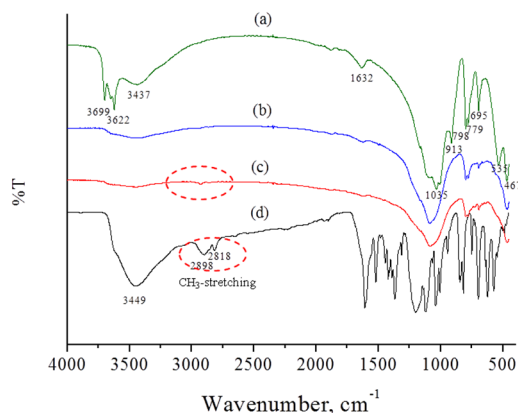


Figure 2. FTIR spectra of UPS (a), UPS in the Fenton process (b), UPS adsorbed with MO (c), and MO (d)

SEM. The BET surface area of the UPS is 13 m²/g.

Catalytic Activity of the UPS in Heterogeneous Fenton Process

Effect of the Catalyst Dosage

The effect of the catalyst dosage on the decolorization of the MO is shown in Figure 3. The results indicate that the MO decolorization was significantly affected by the dosage of

the catalyst. The higher catalyst dosage corresponded with the higher active sites of Fe²⁺/Fe³⁺ for H₂O₂ decomposition. This resulted in faster decomposition of H₂O₂ which led to an increase in the number of •OH radicals (Hassan and Hameed, 2011a). When the amount of the catalyst increased up to 10.0 g/L, the decolorization of the MO was 99%. However, there was no apparent effect on the MO oxidation rate when using 20.0 g/L of catalyst. Hence, a suitable catalyst dosage

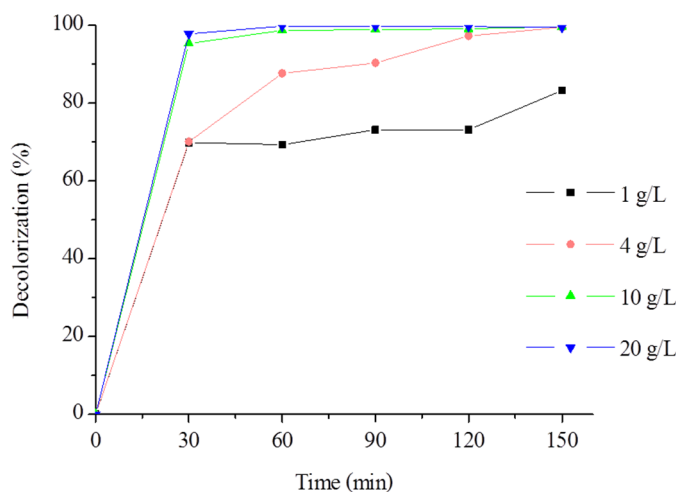


Figure 3. Effect of catalyst dosage on the decolorization of MO. Reaction conditions: [MO]₀ = 60 mg/L; volume of MO solution = 50 mL; [H₂O₂]₀ = 19 mM; pH = 3; and temperature = 27°C

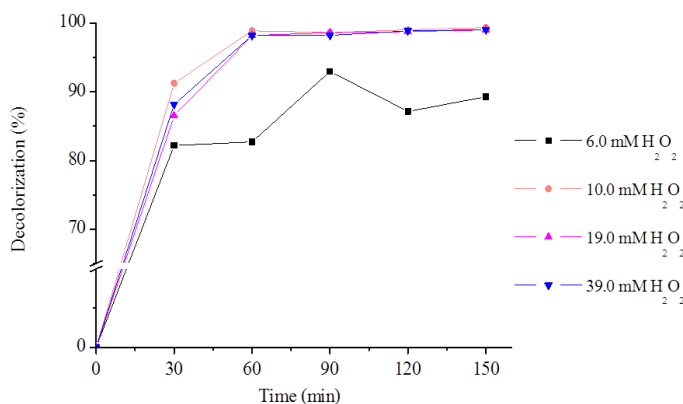


Figure 4. Effect of initial concentration of H₂O₂ on the decolorization of MO. Reaction conditions: [MO]₀ = 60 mg/L; volume of MO solution = 50 mL; catalyst dosage = 10 g/L; pH = 3; and temperature = 27°C

for the decolorization of MO by the heterogeneous Fenton-like process is 10.0 g/L.

Effect of the Initial H_2O_2 Concentration

Figure 4 shows the MO decolorization under different H_2O_2 concentrations (6–39 mM H_2O_2). The increase of the H_2O_2 concentration led to increasing decolorization of the MO due to more $\bullet OH$ radical generation. At the low concentration of H_2O_2 , lower decolorization efficiency was observed due to insufficient

$\bullet OH$ radical generation to catalyze the organic matter. However, it should be pointed out that when the concentration of H_2O_2 was over 10.0 mM, the removal of the MO decreased slightly. This can be explained by the scavenging of $\bullet OH$ radicals at a higher concentration of H_2O_2 , leading to a decrease in the number of $\bullet OH$ radicals in the solution. Hence, a dosage of 10.0 mM H_2O_2 can be used as the optimum dosage for the decolorization of MO.

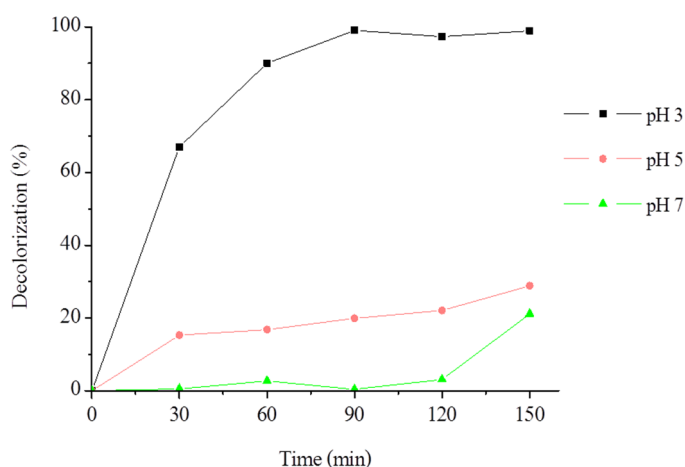


Figure 5. Effect of pH on the decolorization of MO. Reaction conditions: $[MO]_0 = 60$ mg/L; volume of MO solution = 50 mL; catalyst dosage = 10 g/L; $[H_2O_2]_0 = 10$ mM; and temperature = 27°C

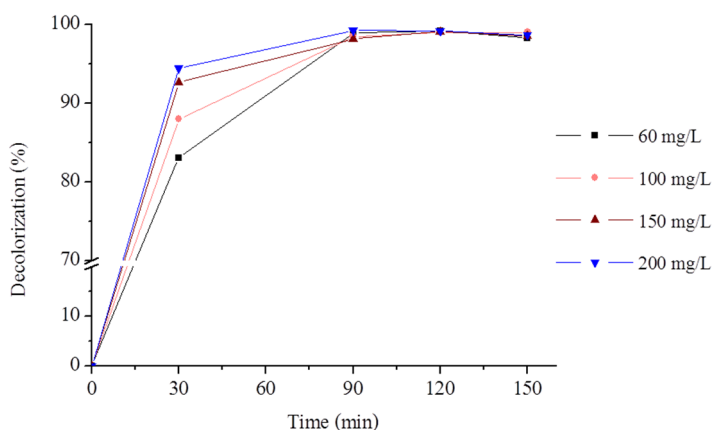


Figure 6. Effect of initial concentration of MO on the decolorization of MO. Reaction conditions: $[H_2O_2]_0 = 10$ mM; volume of MO solution = 50 mL; catalyst dosage = 10 g/L; pH = 3; and temperature = 27°C

Effect of Solution pH

The effect of the initial pH of the solution on the decolorization of the MO was studied at pH 3, 5, and 7 and the results are shown in Figure 5. The decolorization of the MO was the highest at pH 3 within 90 min. This is consistent with the work of Chen *et al.* (2008) that proved that the optimum pH of Fenton oxidation mostly falls in the pH range of 2.5–3.5. At pH 5 and 7, the decolorization efficiency of the MO decreased rapidly. This

could be explained by the decrease of the oxidation efficiency as a result of H_2O_2 decomposing into molecular oxygen and water, losing some of its oxidation ability. It is known that the generated O_2 would not be capable of efficiently oxidizing the organics in the mild operating conditions used (Gou and Al-Dahhan, 2003). On the other hand, the MO in acidic solution preferred the quinoid structure which undergoes degradation by $\bullet\text{OH}$

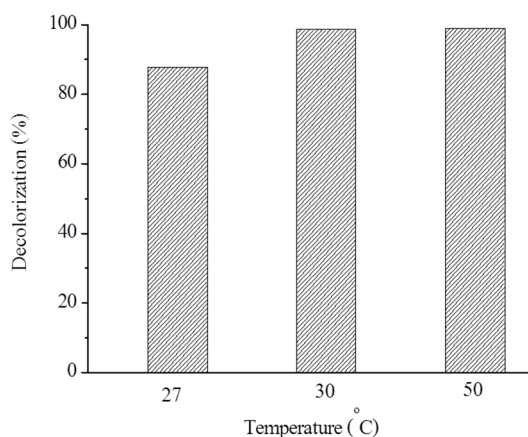


Figure 7. Effect of temperature on the decolorization of MO. Reaction conditions: $[\text{MO}]_0 = 60 \text{ mg/L}$; volume of MO solution = 50 mL; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; catalyst dosage = 10 g/L; pH = 3; and reaction time = 90 min

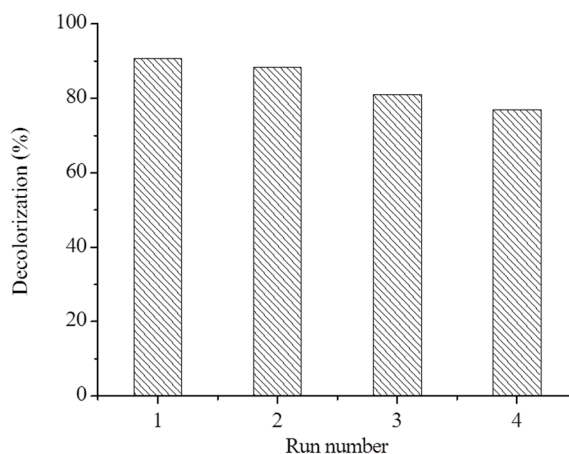


Figure 8. Reusability of the UPS catalyst on the decolorization of MO. Reaction conditions: $[\text{MO}]_0 = 60 \text{ mg/L}$; volume of MO solution = 50 mL; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; catalyst dosage = 10 g/L; pH = 3; reaction time = 90 min; and temperature = 27°C

and $\bullet\text{OOH}$ radicals more easily than the azo structure (Panda *et al.*, 2011).

Effect of Initial MO Concentration

The decolorization efficiency of the Fenton-like process affected by the initial concentration of the MO was evaluated. The results indicated that the decolorization efficiency increased when the initial MO concentration increased (Figure 6). This could

be explained by the lifetime of $\bullet\text{OH}$ radicals. As the lifetime of $\bullet\text{OH}$ radicals is very short (only a few nanoseconds), they can only react where they are formed. Moreover, the increase of the quantity of MO molecules per volume unit logically enhances the probability of collision between organic matter and the oxidizing species, leading to an increase in the decolorization efficiency (Hassan and Hameed, 2011b).

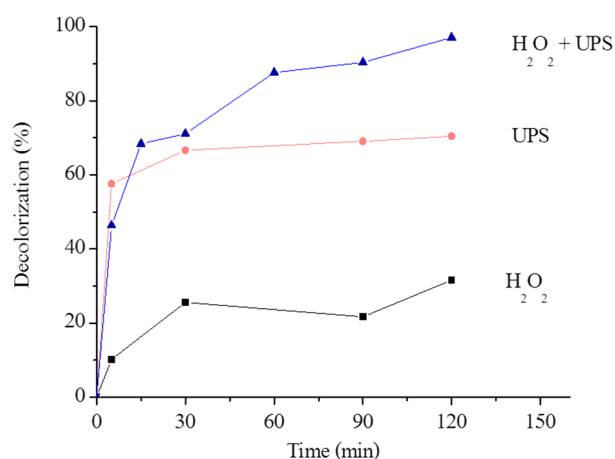


Figure 9. Effect of various experimental parameters on the decolorization of MO. Reaction conditions: $[\text{MO}]_0 = 60 \text{ mg/L}$; volume of MO solution = 50 mL; $[\text{H}_2\text{O}_2]_0 = 19 \text{ mM}$; catalyst dosage = 4 g/L; pH = 3; and temperature = 27°C

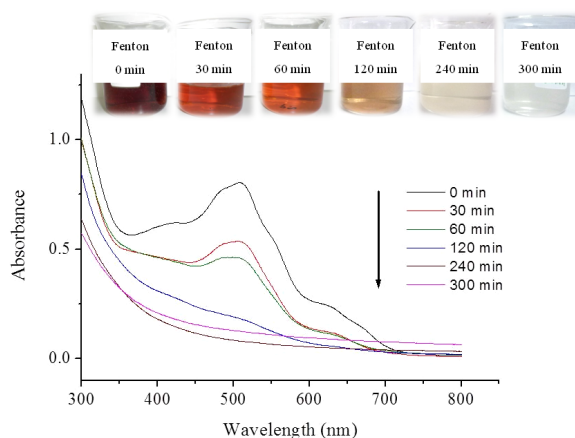


Figure 10. Absorption spectra of dye wastewater at different reaction times. Reaction conditions: volume of dye wastewater = 50 mL; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; catalyst dosage = 10 g/L; pH = 3; and temperature = 27°C

Effect of Temperature

The influence of the reaction temperature on the decolorization of the MO was investigated at 27, 30, and 50°C. The results are illustrated in Figure 7. It can be seen that the decolorization efficiency increased with the temperature. This was due to the higher temperature which increased the reaction rate for generating the oxidizing species such as •OH radicals or high-valence iron species (Sun *et al.*, 2006). In addition, a high temperature can provide more energy for the reactant molecules to overcome the activation energy barrier (Xu *et al.*, 2009b, 2010).

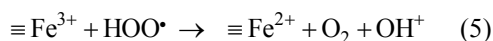
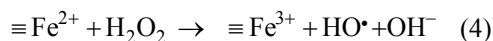
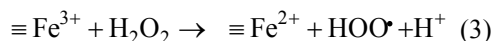
Catalyst Stability and Leaching Test

Reusability of the the UPS catalyst on the decolorization of MO is shown in Figure 8. As expected, the decolorization efficiency was considerably higher in the first run followed by 4 gradually decreasing successive runs. The MO decolorization only decreased from 91 to 77 in 4 cycles. The reason for this initial loss in activity could be attributed to the small amount of iron leached from the catalyst surface. Regarding iron leaching, the concentration leached was 1.83 mg/L. In conclusion, the UPS catalyst exhibited higher activity for the MO oxidation within 3 cycles of reuse.

Mechanism for MO Decolorization

Figure 9 shows the decolorization of the MO as a function of time. The results showed that in the case of MO and H₂O₂ only, the MO decolorization is the lowest (20% decolorization of the MO after 120 min) due to the low oxidation potential of hydrogen peroxide compared to •OH radicals (Bigda, 1995). With the presence of the UPS only, about 60%

decolorization of the MO was achieved, which is due to the adsorption of the MO on the surface of the UPS, as evidenced by the presence of C-H stretching in an IR spectrum of the MO on the UPS shown in Figure 2(c). When the UPS and H₂O₂ were added to the solution of the MO, more than 90% of the MO was decolorized in 120 min. The IR analysis of the UPS after use in the reaction shows no features of MO (Figure 2(b)). The results suggested that the decolorization of the MO should occur via the catalytic reaction. The generation of •OH radicals based on the presence of Fe₂O₃ oxide has been proposed by Ali *et al.* (2014) and are shown in the following equations:



The symbol $\equiv$ represents the iron species bound to the surface of the catalyst. The $\equiv \text{Fe}^{2+}$ ions generated from (Equation (3)) react with H₂O₂ to form •OH that consequently reacts with the dye.

In Table 3, the decolorization efficiency of the MO using several heterogeneous Fenton catalysts with different systems is given. It was found that the UPS can serve as a potential Fenton catalyst for Mo decolorization, as compared to the synthesized catalysts. The UPS has an advantage over many other catalysts due to its having low cost and being environmentally friendly.

Table 3. Comparison of decolorization efficiency of MO with different heterogeneous Fenton catalysts

Catalyst	[Dye] ₀ , (mg/L)	[H ₂ O ₂] ₀ , (mmol/L)	pH	Reaction time, (min)	Temperature, (°C)	Catalyst dosage, (g/L)	Decolorization efficiency, (%)	References
NdFeB	20	0.6	3	60	20	10	97.8	Yang <i>et al.</i> (2014)
Goethite	75	3.88	3	70	20	0.3	98.9	Wang <i>et al.</i> (2015)
Fe ₂ MnO ₄ /AC-H	50	18	4	120	29	2.5	100	Nguyen <i>et al.</i> (2015)
UPS	60	10	3	90	30	10	98.6	Present study

Decolorization of Real Textile Wastewater

The representative UV-Vis spectra changes in the real textile wastewater sample solution at various reaction times were observed and the corresponding spectra are shown in Figure 10. Within 300 min of the oxidation reaction, the treated dye sample was colorless and did not show significant absorbance at the maximum wavelength indicating that the dye was completely removed. As is evident from the results, the UPS have the potential to act as a heterogeneous Fenton-like catalyst which can remove dye from industrial wastewater.

Conclusions

1. The UPS sample was successfully used as a heterogeneous Fenton catalyst for the decolorization of dye wastewater containing MO.

2. The optimal reaction condition was found to be $[H_2O_2]_0 = 10$ mM, $[MO]_0 = 60$ mg/L, an amount of UPS = 10 g/L, the pH = 3, and the temperature was 30°C. Under optimal conditions, the 98.6% decolorization efficiency of the MO in the aqueous solution was achieved within 90 min of reaction.

3. The catalyst stability and leaching test showed that over 80 % decolorization of the MO was still achieved within 90 min and after the catalyst was used for 3 cycles.

4. The UPS sample showed a high catalytic activity toward the decolorization of real dye wastewater in the presence of H_2O_2 and in the acidic pH range. Thus, this study may provide useful information for the use of waste materials as catalysts in the heterogeneous Fenton-like process.

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