Research Article

Degradation of FBL Dye Wastewater by Magnetic Photocatalysts from Scraps

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Magnetic photocatalyst solves the separation problem between wastewater and TiO_2 photocatalysts by the application of magnetic field. This research investigates the treatment of simulated FBL dye wastewater using Mn-Zn ferrite/ TiO_2 magnetic photocatalyst. The magnetic Mn-Zn ferrite powder was first produced by a chemical coprecipitation method from spent dry batteries and spent pickling acid solutions. These two scraps comprise the only constituents of Mn-Zn ferrite. The as-synthesized Mn-Zn ferrite was then suspended in a solution containing $\text{Ti}(\text{SO}_4)_2$ and urea. Subsequently a magnetic photocatalyst was obtained from the solution by chemical coprecipitation. The prepared Mn-Zn ferrite powder and magnetic photocatalyst (Mn-Zn ferrite/ TiO_2) were characterized using XRD, EDX, SEM, SQUID, BET, and so forth. The photocatalytic activity of the synthesized magnetic photocatalysts was tested using degradation of FBL dye wastewater. The adsorption and degradation studies by the TOC and ADMI measurement were carried out, respectively. The adsorption isotherm and Langmuir-Hinshelwood kinetic model for the prepared magnetic TiO_2 were proved to be applicable for the treatment. This research transforms waste into a valuable magnetic photocatalyst.

1. Introduction

Wastewaters from textile and dyeing industries are highly colored by various nonbiodegradable dyes which cause serious environmental problems [1]. Advanced oxidation processes such as $\text{UV}/\text{H}_2\text{O}_2$ [2], ozonation [1, 3–5], Fenton processes [5–8], ozone/Fenton [9], TiO_2 , and modified TiO_2 [10–17] are promising alternatives for the mineralization of textile dyes or other pollutants. Among them, the semiconductor TiO_2 's simultaneous photocatalytic oxidation and reduction process show the significant potential due to its being photoreactive, nontoxic, chemically and biologically inert, photostable, and lower in cost. Among different advanced oxidation processes (AOPs), a relatively new AOP, sonolysis or hybrid AOPs with combination of sonolysis, has drawn increasing attention as it generates the $\bullet\text{OH}$ -free radical through the phenomenon of transient cavitation by ultrasound irradiation [18–20].

Cavitation is essentially nucleation, growth, and transient implosive collapse of gas bubbles driven by ultrasound wave.

Manganese zinc ferrites are important ferrimagnetic materials because of their high magnetic permeability and low magnetic hysteresis loss [21]. Ferrites are commonly produced using a ceramic process that involves a high temperature calcination of oxide and/or carbonates. Their main disadvantages are their large and nonuniform size distribution, poor reproducibility, contamination, and a need for the application of high temperature for production [22]. Therefore, several wet chemical methods have been used to prepare fine Mn-Zn ferrite powders, such as the citrate precursor method [23, 24], the autocombustion method [25], the hydrothermal method [26], the sol-gel method [27], and the coprecipitation method [28]. A rather new technique for the ferrite synthesis is the sonochemical method in

which ferrite nanoparticles are prepared using ultrasound irradiation or sonication of the reaction mixture [29, 30].

Despite existing technologies, nanosized TiO_2 particles remain difficult to separate from treated wastewater. Fixed-film- TiO_2 systems are undermined by their own immobility, while magnetic TiO_2 systems offer to overcome this limitation. For example, Ma et al. [31] synthesized titania-coated Mn-Zn ferrite by hydrolysis of titanium chloride (TiCl_4) in the presence of Mn-Zn ferrite nanoparticles, which were prepared by a stearic acid sol-gel method. The magnetization of the TiO_2 -coated Mn-Zn ferrite particles was reduced, unlike the uncoated ferrite nanoparticles, and high coercivity was obtained ($H_c > 100$ Oe) for both prepared uncoated and coated ferrite particles. It was also found that the synthesized photocatalysts were not superparamagnetic. Chen and Zhao [32] reported a magnetically separable photocatalyst of $\text{TiO}_2/\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ which was prepared using the solid phase synthesis method. The addition of a SiO_2 membrane between the $\gamma\text{-Fe}_2\text{O}_3$ core and the TiO_2 shell weakened the adverse effects of $\gamma\text{-Fe}_2\text{O}_3$ on the photocatalysis of TiO_2 . The photocatalyst described in Chen and Zhao's article showed good photocatalytic activity and it was able to separate from the solution through the use of a magnetic field. Gao et al. [33] synthesized a magnetically separated photocatalyst of $\text{TiO}_2/\gamma\text{-Fe}_2\text{O}_3$ by a sol-gel method. The sample sintered at 500°C showed the highest activity for the degradation of an acridine dye aqueous solution, with the optimal supporting amount of TiO_2 approximating 50%. Fu et al. [34] successfully prepared $\text{TiO}_2/\text{NiCuZn}$ ferrite composite powder as a magnetic photocatalyst. The core NiCuZn ferrite powder was synthesized using waste material from steel and electroplating industries. The shell of the TiO_2 nanocrystal was prepared by a sol-gel hydrolysis method of titanium isopropoxide with NiCuZn ferrite powder, followed by heat treatment. In their study [34], the optimum dosage of the magnetic photocatalyst was 2.67 g/L for treating a methylene blue solution.

In this research, a simple magnetic photocatalyst preparation method was undertaken. First, Mn-Zn magnetic ferrite powder was prepared from spent Mn-Zn dry batteries and ferrous sulfate containing spent acid solution from steel plants by using coprecipitation method. Then, the magnetic powder was added to a titanium sulfate solution and the hydroxides of titanium were precipitated at desired pH using urea solution. After filtration, drying, and grinding, the precipitates were sintered at 500°C under N_2 atmosphere to form the magnetic photocatalyst, Mn-Zn ferrite/ TiO_2 . The adsorption and degradation of simulated FBL (Everdirect Supra Turquoise Blue) dye wastewater were carried out by applying self-prepared magnetic photocatalysts under dark as well as under solar irradiation. The adsorption isotherm and L-H kinetic model were also studied.

2. Materials and Methods

2.1. Preparation of Magnetic Mn-Zn Ferrite Powder and Magnetic Photocatalyst. The flow diagram for preparing the Mn-Zn ferrite powder and ferrite is shown in Figure 1.

The designed composition used was $\text{ZnO}:\text{MnO}:\text{Fe}_2\text{O}_3 = 12.5:35:52.5$ by molar ratio and $8.56:20.89:70.55$ by weight percentages or $\text{Zn}:\text{Mn}:\text{Fe} = 0.25:0.7:2.1$ by moles and $\text{Zn}:\text{Mn}:\text{Fe} = 9.3:22.4:68.3$ by weight percentages. The reactions are shown as follows:

Due to the presence of Cu^{+2} in the waste acid, iron powder was added to replace copper by reaction (2).

The magnetic photocatalyst was prepared by adding Mn-Zn ferrite magnetic powder 10 g and urea ($\text{N}_2\text{H}_4\text{CO}$) of 150 g into 92 mL of $\text{Ti}(\text{SO}_4)_2$ solution. The ratio of Mn-Zn ferrite powder to TiO_2 was 1:1 (wt%). The flow chart for the preparation of the magnetic photocatalyst of Mn-Zn ferrite/ TiO_2 is shown in Figure 2. The reactions followed would be

2.2. Characterization. The crystalline structure of both magnetic powder and magnetic photocatalyst was examined by XRD (X-ray diffractometer, XRD-6000, Shimadzu, Japan). Their M-H loops were measured by SQUID (superconducting quantum interference device, MPM57, Quantum Design, USA). The chemical compositions of the particles were analyzed by XRF (X-ray fluorescence, XEPOS/XEPO1, Spectro Co., Germany). Their microstructure was observed by SEM (scanning electron microscopy, S-3000N, Hitachi, Japan). The specific area was measured by BET (Brunauer-Emmett-Teller, Model-ASAP 2012, Micromeritics, USA).

2.3. Adsorption and Photocatalytic Degradation. The adsorption and photocatalytic reaction were carried out by mixing 1 L of a FBL dye solution with 5 g of magnetic Mn-Zn ferrite/ TiO_2 photocatalysts inside a 2 L photoreactor beaker, using a teflon agitator under dark and under solar irradiation for 8 hrs, respectively. The structure of the FBL dye was shown in [8]. The initial dye concentrations were COD =

FIGURE 1: Flow chart for preparation of Mn-Zn ferrite by coprecipitation process from zinc-carbon waste dry batteries and waste sulfuric acid.

100, 200, 300, and 400 mg/L for each experiment. To prepare COD = 100 mg/L, 0.0956 g of FBL dye was measured to make 1 L solution. The sampling time was 0 to 480 min with interval of 40 min, and each sample was taken under mixture condition. After filtration by 0.45 μm MFS, the TOC (total organic carbon, Model 1010, O.I. Analytical, USA) and ADMI (American Dye Manufacturers Institute, Model DR/4000V, HACH, USA) were measured for each sample. COD was determined by the potassium dichromate titration method as described in standard methods [35]. Solar intensities were measured by a radiometer (Lutron Co., Taiwan). All solar intensities at 0.5, 1, 2, 3, 4, 5, 6, 7, and 8 hours were measured and averaged and expressed as I_{av} (mW/cm^2).

FIGURE 2: Flow chart for the preparation of magnetic photocatalyst of Mn-Zn ferrite/ TiO_2 .

3. Results and Discussion

3.1. Characterization of Magnetic Photocatalyst of Mn-Zn Ferrite/ TiO_2 . The XRF analysis of Mn-Zn ferrite powder and Mn-Zn ferrite/ TiO_2 is shown in Table 1. It is clear that the experimental values of magnetic powder from waste are close to the quantity used by predetermined value. The designed molar ratio would be $\text{ZnO} : \text{MnO} : \text{Fe}_2\text{O}_3 = 12.5 : 35 : 52.5$. By SEM micrographs, the particle size for the magnetic Mn-Zn ferrite powder is around 0.24 μm and agglomerates into a secondary particle size of approximately 2 μm [36]. TiO_2 is precipitated on the surface of the secondary particle and its size is approximately 2.5 μm (Figure 3). The EDX diagram for the Mn-Zn ferrite powder and the Mn-Zn ferrite/ TiO_2 photocatalyst indicates the presence of Mn, Zn, Fe, and titanium as shown in Figure 4. The minor Zn amount existed in the magnetic photocatalysts causing the absence of Zn in Figure 4(b). The X-ray diffraction patterns of the Mn-Zn ferrite powder, sintered Mn-Zn ferrite, and magnetic photocatalysts in Figure 5 revealed that the spinel cubic ferrites and the anatase form of TiO_2 exist. All the peaks in the pattern match well with the Joint Committee of Powder Diffraction Standard (JCPDS). The sintered Mn-Zn ferrite at 1200°C (N_2) in Figure 5(b) showed the only existence of the spinel cubic structure which can be used directly in the magnetic industry. A small amount of hematite also existed in the specimens. The surface area of Mn-Zn ferrite powder by BET measurement was 8.24 m^2/g and that of Mn-Zn ferrite/ TiO_2 is increased to 84.98 m^2/g which shows more active sites for photoreaction.

3.2. Magnetic Property. The magnetic properties of Mn-Zn ferrite powder, Mn-Zn ferrite, and Mn-Zn ferrite/ TiO_2 are presented by magnetic hysteresis loops using SQUID as shown in Figure 6. The saturation magnetizations (M_s) of Mn-Zn ferrite powder (with and without calcinations) and Mn-Zn ferrite/ TiO_2 are 63.15, 99.37, and 14.33 emu/g , respectively. The corresponding coercive forces (H_c) are 7.66, 4.60, and 6.13 Oe, respectively. Due to the minimal hysteresis

FIGURE 3: SEM images of self-prepared magnetic photocatalyst of Mn-Zn ferrite/TiO₂ (a) $\times 10000$, (b) $\times 25000$.

FIGURE 4: EDX of Mn-Zn ferrite powder (a) and Mn-Zn ferrite/TiO₂ (b).

TABLE 1: XRF analysis of magnetic powder and magnetic photocatalyst.

Samples	Fe ₂ O ₃ (wt%)	MnO (wt%)	ZnO (wt%)	TiO ₂ (wt%)
Mn-Zn ferrite powder (predetermined)	70.55%	20.89%	8.56%	—
Mn-Zn ferrite powder (experimental)	66.2%	26.2%	7.5%	—
Mn-Zn ferrite/TiO ₂ (N ₂ 500°C) (experimental)	28.4%	8.5%	2.9%	60.1%

FIGURE 5: XRD pattern of Mn-Zn ferrite powder (a), Mn-Zn ferrite sintered at 1200°C (N_2) (b), and Mn-Zn ferrite/ TiO_2 (N_2 , 500°C) (c).

and small H_c , the prepared magnetic materials are all soft-magnetic materials. The magnetic property of the magnetic photocatalysts prepared from waste allows its recovery by the applied magnetic field.

3.3. Adsorption and Solar Photodegradation. The TOC and color ADMI removal percentage through the adsorption of Mn-Zn ferrite/ TiO_2 from FBL simulated dye wastewater, having initial dye COD concentrations of 100, 200, 300, or 400 mg/L and the weight ratio of ferrite powder: TiO_2 maintained at 1:1, are shown in Figures 7 and 8. It is clear that adsorption by magnetic photocatalyst is much efficient for diluted solution but shows low efficiency for concentrated dye wastewater.

The photodegradation for simulated FBL dye wastewater with initial COD of 100, 200, 300, and 400 mg/L under solar irradiation by using self-produced magnetic photocatalysts from waste and also TiO_2 prepared is shown in Figures 9 and 10. TiO_2 was also produced by the same coprecipitation method. The degradation efficiency increased as the concentrations of pollutants decreased. For dilute pollution of FBL

dye (COD = 100 ppm), the TOC removal can reach 87.85% and color or ADMI removal can reach 96.17%. The treatment efficiency by Mn-Zn ferrite/ TiO_2 from waste is very close to that of self-prepared TiO_2 by treating dilute simulated dye wastewater. By using TiO_2 only, TOC removal is 88% and color ADMI removal reached 96%. Both dosages of TiO_2 and magnetic photocatalysts were all 5 g/L.

3.4. Adsorption Isotherm. The Langmuir adsorption isotherm has the following equation [37]:

$$Y = \frac{y_m K C_e}{1 + K C_e} \quad \text{or} \quad \frac{C_e}{Y} = \frac{1}{K y_m} + \frac{C_e}{y_m}, \quad (8)$$

where Y is the mass adsorbed per mass of adsorbent (mg/g), y_m is the mass of the adsorbed solute required to completely saturate a unit mass of adsorbent or monolayer coverage (mg/g), K is the adsorption constant (L/mg), and C_e is the equilibrium TOC concentration of solute dye (mg/L). By plotting C_e/Y against C_e for different dye concentrations, straight line was obtained as shown in Figure 11. Adsorption

FIGURE 6: Hysteresis loop of Mn-Zn ferrite calcined at 1200°C (a), Mn-Zn ferrite powder without calcinations (b), and Mn-Zn ferrite/TiO₂ calcined at 500°C (c).

FIGURE 7: TOC removal % versus time by adsorption of magnetic photocatalyst of Mn-Zn ferrite/TiO₂ (N₂, 500°C) (FBL, COD = 100–400 ppm).

constants were determined by the y -intercepts of the lines and $1/y_m$ were obtained from the slope. Their values were 11.53 (mg/g) for y_m and 0.1014 (L/mg) for K , respectively.

3.5. Langmuir-Hinshelwood Kinetic Model (L-H Model). The L-H model can be expressed by the following equation [31]:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} = \frac{k_d C}{1 + KC}, \quad (9)$$

where k_r is the photocatalytic reaction constant [mg/(L·min)], k_d is the apparent degradation rate constant (min⁻¹),

FIGURE 8: ADMI removal % versus time by adsorption of magnetic photocatalyst of Mn-Zn ferrite/TiO₂ (N₂, 500°C) (FBL, COD = 100–400 ppm).

FIGURE 9: TOC removal % versus time by using Mn-Zn ferrite/TiO₂ (COD_{|t=0} = 100–400 ppm) and TiO₂ (COD_{|t=0} = 100 ppm) of FBL dye (dosage, 5 g/L; $I_{av.} = 0.8289$ mW/cm²).

and C is the dye concentration, TOC (mg/L). Combining zero-order and first-order reactions, the L-H model becomes

$$-\ln\left(\frac{C}{C_0}\right) + K(C_0 - C) = K_r K t. \quad (10)$$

Let $C = 0.87C_0$ and $t = t_{0.87}$; the equation becomes

$$t_{0.87} = \frac{0.1393}{k_r K} + \frac{0.13C_0}{k_r}. \quad (11)$$

FIGURE 10: ADM removal % versus time by using Mn-Zn ferrite/TiO₂ (COD_{t=0} = 100–400 ppm) and TiO₂ (COD_{t=0} = 100 ppm) of FBL dye (dosage, 5 g/L; I_{av} = 0.8289 mW/cm²).

FIGURE 11: Langmuir adsorption isotherm for Mn-Zn ferrite/TiO₂.

By plotting $t_{0.87}$ against $0.13C_0$, the straight line was obtained and shown as in Figure 12. From the slope and intercept, the kinetic constants can then be calculated.

The constants obtained from adsorption isotherm and L-H model were summarized in Table 2. The adsorption constants for both isotherm and L-H model were very close. It means that adsorption by magnetic photocatalysts occurred first and then photodegradation followed. The result also shows that the L-H kinetic model fits well for the photodegradation of FBL simulated dye wastewater.

FIGURE 12: L-H kinetic model for the magnetic photocatalysts of Mn-Zn ferrite/TiO₂.

TABLE 2: Adsorption constant for Langmuir isotherm and constants for L-H model.

Constants	Langmuir	Langmuir-Hinshelwood
k_r (mg/L min)	—	3.1614
k_d (min ⁻¹)	—	0.3212
K (L/mg)	0.1014	0.1016

4. Conclusions

Mn-Zn ferrite magnetic powder and the sintered Mn-Zn ferrite were successfully prepared from spent dry batteries and steel picking sulfuric waste acid. The composition obtained is close to the designed value as molar ratio of ZnO : MnO : Fe₂O₃ = 12.5 : 35 : 52.5. The sintered Mn-Zn ferrite can be used directly in magnetic industry. The magnetic photocatalyst of Mn-Zn ferrite/TiO₂ was also successfully produced by using magnetic powder, titanium sulfate, and urea as raw material and then followed by simple coprecipitation method. Comparing with JCPDS data, the XRD patterns of the photocatalyst contain Mn-Zn ferrite, anatase TiO₂, and a small amount of hematite. The magnetic photocatalyst falls into the category of soft-magnetic materials by SQUID study which can be recycled by the application of magnetic field. The treatment efficiency by magnetic photocatalyst of Mn-Zn ferrite/TiO₂ for dilute simulated FBL dye wastewater can reach 87.85% of TOC removal and 96.17% of color removal and is very close to the efficiency of using TiO₂ alone. The Mn-Zn ferrite and magnetic photocatalyst produced from waste not only solve the pollution problems but also create the possibility of the benefits for the commercial applications. Both the Langmuir adsorption isotherm and L-H model fit well for the prepared magnetic photocatalyst and can be used successfully in AOP.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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