Degradation of malachite green solution using combined microwave and ZnFe₂O₄ powder

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ABSTRACT

Dyestuff malachite green MG in aqueous solution can be degraded rapidly assisted by microwave irradiation (MW) in the presence of ZnFe₂O₄ powder. ZnFe₂O₄ acted as a MW as well as the catalyst for MG degradation, and could be used repeatedly. The effects of MW time, initial concentration of MG, addition amount, pH value and used times of ZnFe₂O₄ powder were discussed in details using UV-Vis spectra, FT-IR spectra, ion chromatography and TOC analysis technologies. The results showed that the degradation percentage of MG was nearly 100%, corresponding to 92% of TOC removal, when the mass fraction of ZnFe₂O₄ was 1.2%, MW 500 W and the irradiation time 2 min. Additionally, the above method using ZnFe₂O₄ powder as catalyst combined with MW has high degradation ratios, short reaction time, low costs, no intermediates and no secondary pollution. Therefore, it may be available for the treatment of various dyestuff wastewaters on a large scale.

Key words | malachite green, microwave assisted degradation, MW absorbing materials, ZnFe₂O₄ induced oxidation

INTRODUCTION

Synthetic dyestuffs like MG, a triphenyl methane dye, are used extensively in textile, paper-making, printing industries and dyehouses. The effluents of these industries are highly colored and the disposal of these wastes into receiving waters can cause damage to the environment. Dyes may significantly affect photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics and metals, chlorides, etc. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to decompose.

Many feasible methods, such as ozonation, photodegradation, adsorption, froth flotation, reverse osmosis, ion exchange, membrane filtration and flocculation, are often applied for the removal of MG from textile effluents (Daneshvar et al. 2004; Horikoshi et al. 2004). In some cases, traditional biological procedures are combined with chemical or physical treatment processes to achieve decolorization (Kumar et al. 2005; Srivastava et al. 2006).

Recently, several researchers have reported that MG can be effectively degraded from aqueous solution. Sirés et al. (2008) showed that MG could be degraded from wastewater by in situ electrogenerated Fenton’s reagent at carbon-felt cathode. The study of single-compound MG solutions was completed with the analysis of COD at different electrolysis times during the oxidation process of solutions containing 0.5 mM of the selected MG with 0.2 mM Fe³⁺ at 400 mA. Total 420 min were required to obtain 93% of the MG degradation ratio. Diorio et al. (2008) indicated that the decolorization of MG was 94–100% in 120 min. Pérez-Estrada et al. (2008) used the photolytic degradation to make MG totally disappeared after 210 h. These methods can be very effective for the degradation of the MG, but a long time was needed and lots of intermediate products were produced in the degradation process.

doi: 10.2166/wst.2009.497
Recently, as a viable alternative, MW processes have received increasing interest owing to their low cost, effectiveness and environmental friendly (Jones et al. 2002). Therefore, MW processes possess potential to convert or degrade the pollutants into water, carbon dioxide and various salts of inorganic nature. MW absorbing materials also play an important role in the application of MW techniques and the treatment of organic pollutants (Tai & Jou 1999). In the MW magnetic field, absorbing materials can reach quickly a higher temperature, and promote oxidation and degradation processes of organic pollutants adsorbed. Some materials including activated carbon (Liu et al. 2004), metal oxidation (Li et al. 2002), sulfide power (Mall et al. 1996), ash (Gupta et al. 2004), CoFe2O4 (Zhang et al. 2008) and ferrite (Mane et al. 2007) are very popular MW absorbing materials.

In this study, ZnFe2O4 as MW absorbing material combined with MW was prepared and applied to degradation of the dye in wastewater. The processes of three systems (MW combined with ZnFe2O4, MW, and ZnFe2O4) for the degradation of MG were compared and discussed. It was found that the most effective for the degradation of MG was an integrated MW combined with ZnFe2O4 process.

**EXPERIMENTAL**

**Reagents and instruments**

The initial concentration of MG solution in all experiments was 20 mg L$^{-1}$. Fe(NO$_3$)$_3$, Zn(NO$_3$)$_2$ and NaOH (2.5 mol L$^{-1}$) are of analytical grade. Doubly distilled water was used to prepare all the solutions. FT-IR spectra of ZnFe$_2$O$_4$ were measured using FT-IR 5700 (Nicolet company, USA). The ZnFe$_2$O$_4$ powders X-ray diffraction (XRD) patterns were recorded on Siemens D5000 Diffractometer. The MG solution was irradiated using NJL07-3 model MW apparatus (Jiequan equipment Ltd. China), and MW output power ranged from 100 to 900 W. The pH of the MG solution was measured by S-3C model pH-meter (China). UV-Vis-NIR Cary 5000 (Varian, USA) was used to check the degradation efficiency of MG. Total organic carbon (TOC) in the solutions was measured with a TOC-VSCN analyzer (Shimadzu Co, Japan) to investigate the mineralization of MG. Ion Chromatography (2020ii, USA) were used to inspect the degradation process of MG.

**Preparation of ZnFe$_2$O$_4$**

ZnFe$_2$O$_4$ was synthesized using chemical co-precipitation method in our laboratory. The preparation of ZnFe$_2$O$_4$ was performed as follows: Add Zn(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ salts with a molar ratio of 1:2 in 200 mL doubly distilled water with vigorous mechanical stirring. Meanwhile, drop 2.5 mol L$^{-1}$ NaOH in the solution to adjust the pH to 11. Stop stirring and filter the precipitate and then rinse many times with doubly distilled water. ZnFe$_2$O$_4$ crystals could be obtained by calcination in Muffle furnace at 700°C for 3.0 h.

**Adsorption experiments**

Adsorption capacities and kinetics were conducted using the batch method at a temperature of 25 ± 1°C. Add 5 to 50 mg L$^{-1}$ of the dye solution and an accurately weighed amount of ZnFe$_2$O$_4$ into the reactor with a thermostatic mechanical shaker. Separate ZnFe$_2$O$_4$ from the solution by centrifugation after different adsorption time intervals and determine the concentration of the dye in the solution. Adsorption isotherm tests were carried out with different concentrations of MG at a fixed concentration of ZnFe$_2$O$_4$.

**Procedure**

MG was oxidized using the following methods including MW method, MW combined with ZnFe$_2$O$_4$ and ZnFe$_2$O$_4$ (without MW), respectively. The experiments of MW degradation were performed using the glass reactors placed inside a MW oven. The output power of MW varied from 100 to 900 W. The samples were taken out periodically for the analysis of MG degradation efficiency.

All spectra of MG solutions were recorded by UV-Vis spectrophotometer at the wavelength from 190 to 800 nm (Figure 1). The absorbance (A) at maximum absorption peak ($\lambda_{max}$) observes Lambert-Beer’s law within 0–50 mg L$^{-1}$ MG solutions. The calibration curve of standard MG solution was used to estimate the degradation efficiency of MG. The efficiency of color removal was
calculated according to the concentration percentage ratio of decolorized dye to that of initial one (Equation (1)).

\[
\text{Degradation efficiency (\%)} = \frac{c_0 - c}{c_0} \times 100
\]  

(1)

where \(c_0\) is the initial concentration of MG (mg L\(^{-1}\)) and \(c\) the concentration of MG at time \(t\).

RESULTS AND DISCUSSION

The UV-Vis spectra of MG

The UV-Vis spectra of MG were given in Figure 1. It could be found that the several maximum absorbance peaks of MG solution at 253, 318, 424 and 618 nm declined rapidly when using MW combined with ZnFe\(_2\)O\(_4\) (curve d). The removal efficiency for MG was nearly 100% within 1.5 min. It indicates that there are synergistic effects of MW and ZnFe\(_2\)O\(_4\) on the removal of MG.

Adsorption property of ZnFe\(_2\)O\(_4\)

ZnFe\(_2\)O\(_4\) has a strong adsorption capacity for many polar organic compounds. In this study, we are interested in the degradation of MG by MW together with the existence of ZnFe\(_2\)O\(_4\). Therefore, the adsorption capacity of MG on the ZnFe\(_2\)O\(_4\) should be evaluated in terms of adsorption isotherm.

The adsorption capacity of 1.0 g of ZnFe\(_2\)O\(_4\) on MG ranged from 2.5 to 25 mg L\(^{-1}\) in solution (pH 6.82) could be determined. There was a gradual increase of adsorption on MG until the equilibrium was reached. The distribution of dye between the sorbent and the solution at equilibrium has been expressed using the Langmuir and Freundlich models (Wan Ngah et al. 2004). The former is valid for monolayer sorption on a surface with a finite number of identical sites, is given by:

\[
\frac{c_e}{q_e} = \frac{c_e}{q_{\text{max}}} + \frac{1}{bq_{\text{max}}}
\]  

(2)

where \(c_e\) is the concentration of MG in the solution at equilibrium (mg L\(^{-1}\)), \(q_e\) is the amount of sorbed MG on one gram of ZnFe\(_2\)O\(_4\) at equilibrium (mg g\(^{-1}\)), \(q_{\text{max}}\) is the maximum adsorption at monolayer (mg g\(^{-1}\)), and \(b\) is the Langmuir constant related to the affinity of binding sites (L mg\(^{-1}\)).

The sorption data were analyzed according to the linear form of the Langmuir isotherm (Equation (2)). The plot of \(C_e/q_e\) versus \(C_e\) gives a straight line of slope \(1/q_{\text{max}}\) and intersects \(1/bq_{\text{max}}\), where \(q_{\text{max}}\) presents the theoretical monolayer saturation capacity. The Langmuir constant \(b\), the monolayer saturation capacity \(q_{\text{max}}\) were 0.064 L mg\(^{-1}\) and 2.45 mg g\(^{-1}\). The isotherm was found to be linear over the entire concentration range studied (correlation coefficient, \(r = 0.990\)), showing that data correctly agreed the Langmuir relation.

The Empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

\[
\log q_e = \log K_F + \frac{1}{n}\log C_e
\]  

(3)

where \(K_F\) and \(n\) are Freundlich constants indicating sorption capacity (mg g\(^{-1}\)) and intensity, respectively.

Based on Freundlich isotherm (Equation (3)), \(K_F\) and \(n\) can be obtained from linear plot of \(\log q_e\) against \(\log C_e\). The \(K_F\) and \(n\) are 0.51 mg g\(^{-1}\) and 1.21, respectively. The correlation coefficient, \(r\) was 0.537 suggesting that the Langmuir model is much agreeable with the adsorption behavior compared to the Freundlich model.
FT-IR spectra of MG on the surface of ZnFe$_2$O$_4$ powder

To evaluate the degradation behavior of MG on the surface of ZnFe$_2$O$_4$ particles, the FT-IR spectrograms of ZnFe$_2$O$_4$ was shown in Figure 2. Curve a, b and c was the IR spectrograms of ZnFe$_2$O$_4$, ZnFe$_2$O$_4$ by MW degradation and ZnFe$_2$O$_4$ by MG adsorption, respectively. It was found that the wave number for the main MG function group is between about 1,750–800 cm$^{-1}$. It could be seen from Figure 2 that the main function groups of MG had disappeared after MW degradation, which demonstrates that MG could be adsorbed by ZnFe$_2$O$_4$ and degraded by MW.

Based on the analysis of the above UV-Vis and IR spectra (MW/ZnFe$_2$O$_4$, 2.0 min), not only the MG dyes adsorbed on the surface of ZnFe$_2$O$_4$ were degraded by MW, but also those in the solution were done. It is possible that MG in the solutions may first be adsorbed on the surface of ZnFe$_2$O$_4$ particles, and then immediately degraded by microwave irradiation. Moreover, it was found that ZnFe$_2$O$_4$ power could be used repeatedly more than 9 times and the high efficiency (94%) of the dye removal was maintained.

Effect of irradiation time and reaction kinetics

It could be observed from Figures 3 and 4 that the degradation efficiency of MG for MW and MW/ZnFe$_2$O$_4$ systems gradually increased with irradiation time. Both systems have the highest removal efficiencies in 2 min. Nearly 100% degradation efficiency of MG was achieved at 2.0 min in MW/ZnFe$_2$O$_4$ system. However, only 13% in MW system could be achieved. As shown in Figure 3, 47% of MG was adsorbed on ZnFe$_2$O$_4$ power in 1 h. It indicated that the integrated MW/ZnFe$_2$O$_4$ has stronger degradation ability to MG dye.

Based on the experimental data, curve fitting was performed by the first order and second order reaction models, respectively (Figure 4). The kinetic equations corresponding to MW/ZnFe$_2$O$_4$ and MW are $\ln \frac{c_i}{c_0} = -2.720t + 4.59$ ($r = 0.9985$), $\ln \frac{c_i}{c_0} = -0.0714t + 4.60$ ($r = 0.9947$), the pseudo first-order rate constants are 2.720 and 0.0714 min$^{-1}$, and half-lives ($t_{1/2}$) are 0.25
and 9.71 min, respectively. The kinetic results showed that these processes should belong to the pseudo first-order reaction model.

**Effects of the calcination temperature of ZnFe$_2$O$_4$**

The performance of crystal ZnFe$_2$O$_4$ can be influenced by calcination temperature. Total 5 kinds of ZnFe$_2$O$_4$ particles were prepared using the calcination temperatures at 300, 500, 600, 700 and 800°C for 3 h. One gram of the above ZnFe$_2$O$_4$ particles was used for the MG removal (MW power, 500 W; initial concentration of MG, 20 mg L$^{-1}$ MG, 50 mL). The result showed that ZnFe$_2$O$_4$ particles prepared at 700°C had the highest removal ability to MG. The intensities of peak and the diffraction angles confirmed by XRD that crystal ZnFe$_2$O$_4$ particles at 700°C had better crystallinity and crystalline state.

**Effects of several parameters on the degradation**

To study the effects on the degradation of MG dye in aqueous solution, several dominant parameters including the percentage of ZnFe$_2$O$_4$, the concentration of MG and pH value were discussed. The experimental results were presented in Figures 5–7, it could be found that there are the highest removal ratios when the percentage of ZnFe$_2$O$_4$ was 1.2%, initial concentration of MG solution was lower than 50 mg L$^{-1}$ and pH was in the range of 6–10, respectively.

Among these parameters, pH could influence greatly the degradation of MG dye. The pH can affect the adsorption on dye cation. Generally, the positive charge is carried easily on surface of sorbent at lower pI_E, whereas, the negative one is done at higher pI_E. The surface charges for ZnFe$_2$O$_4$ are neutral at isoelectric point (IEP) thus the pH at IEP (pI_E) is 7.0–8.0 which can enhance the electrostatic attachment to dye cations.

**Effect of MW output power**

The MW output power was regarded as the most important factor in the experiment, since the temperature that the
ZnFe$_2$O$_4$ could reach was directly related to the power level. The investigated power levels were 200, 400, 500, 600, 700 and 800 W, and other parameters remained constant, namely, MG aqueous solution (20 mg L$^{-1}$) and 0.2% (w/w) ZnFe$_2$O$_4$, irradiation time 2 min. The test results shown in Figure 8 indicated that degradation efficiency of MG gradually increased with the MW power from 200 to 500 W; whereas the degradation efficiency was not changed for higher power (>500 W). So the output power of 500 W was chosen throughout the experiments.

The effect of MW on MG degradation

MW and its power may be the other factor on the MG degradation in this study. The experimental results showed that there was the highest removal efficiency on the MG when MW power was 500 W or above. Routine heating up to 100$^\circ$C can not decompose MG, indicating that the increase of solution temperature by MW is not dominant on the removal of MG (Zhang et al. 2007). Thus, the synergistic effects from MW thermal cracking caused by highly localized super heating and MW absorbing material may be the dominant actions on the MG degradation. MW radiation can generate $\cdot$OH radicals which involved advanced oxidation process and can be further enhanced at the presence of ZnFe$_2$O$_4$ and dissolved oxygen, in aqueous solution.

As mentioned above, the results using IR and UV-Vis analyses informed that the high adsorption capacity on ZnFe$_2$O$_4$ particle surface can produce great amount of “heat point” which could lead to the more rapid oxidations MG molecules. Also, MG molecules itself in the solution were decomposed effectively due to the decrease of the activation energy and the increase of reaction activity of MG molecules.

In order to farther prove and explore the degradation process of MG, the degradation products including nitrate ions and TOC removal percentage were determined using Ion Chromatograph and TOC analyzer. The concentration of NO$_3^-$ was 3.7 mg L$^{-1}$ and TOC removal percentage was up to 92.2%. The results showed that the most of organic MG molecules has been converted into inorganic NO$_3^-$ ions and higher TOC removal percentage could be obtained.

CONCLUSION

High crystallinity and adsorption capacity of ZnFe$_2$O$_4$ particles were obtained by the co-precipitation method and confirmed by the XRD and FT-IR spectra technologies. The maximum adsorption capacity for MG on ZnFe$_2$O$_4$ was 2.45 mg g$^{-1}$. The adsorption behavior agrees Langmuir isotherms and the degradation kinetics were observed by the fist-order rate expression. The degradation efficiency for MG dye was highly pH and microwave radiation dependent to obtained up to 100% removal efficiency within 2 min; It is available in the removal of dyes in wastewater using ZnFe$_2$O$_4$ powder combined with microwave assisted technique.

ACKNOWLEDGEMENTS

The authors greatly acknowledge the Science Foundation of Education Department of Liaoning Province and the Natural Science Foundation of Liaoning Province of China (No. 2009R30 and No. 20082050) for financial support. The authors also thank our colleagues and other students participating in this work.

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