Preparation of Particle Reusable Heterogeneous Catalyst Fe_3O_4/ATP for Methylene Blue Decolorization

Ting Zhang, Chunyuan Qian, and Lingyu Dong

***Abstract*—New simple wet-ultrasonic method was employed to synthesize akind of particle heterogeneous catalyst Fe_3O_4/attapulgite (Fe_3O_4/ATP), which used attapulgite particles as catalyst carrier and Fe_3O_4 as active component loaded on the carrier. The catalyst is low cost and easy to prepare, and the effects of various preparing factors on its catalytic performance were investigated and discussed. The heterogeneous catalyst was characterized using SEM, FT-IR and XRD for its structure and catalysis properties. Fe_3O_4/ATP was used as the catalyst to decolorize high concentration (100mg/L) methylene blue (MB) in the heterogeneous Fenton system. Box-Behnken design (BBD) method was used for experimental design, data analysis and optimization. The influences of catalyst dosage, H_2O_2 initial concentration and pH value on MB decolorization ratios in Fe_3O_4/ATP/H_2O_2 heterogeneous Fenton system were studied. The heterogeneous catalyst Fe_3O_4/ATP has excellent catalytic performance and more than 99%MB decolorization were achieved under the optimum conditions. Higher decolorization ratio was obtained for recycled use of Fe_3O_4/ATP. Comparison experiments showed MB decolorization in Fe_3O_4/ATP/H_2O_2 system is really a catalytic process. Furthermore, Fe_3O_4/ATP can be easily separated from the solution and reused due to its particle form.**

***Index Terms*—Fe_3O_4/attapulgite, particle catalyst, heterogeneous Fenton system, methylene blue decolorization.**

I. Introduction

The types and quantity of manufactured dyes are increasing with the rapid development of dye industry in China. This leads to increasing discharged dye wastewater into nature water systems annually. China has the most dye production in the world, but disposal rate of dye wastewater was less than 30% of the total, and most of that was not properly disposed. Various methods can be used for dye wastewater decolorization and degradation, including biological treatment [1], flocculation precipitation [2], adsorption [3], chemical oxidation [4], and catalytic oxidation [5], etc. In recent years, more and more researchers focused on advanced oxidation Fenton method and Fenton-like method to treat dye wastewater [6]-[9], especially the heterogeneous Fenton method. For examples, Valero - Luna *et al*. [10] prepared $BaFe_{12}O_{19}$ catalyst by coprecipitation method, which was used for dye wastewater treatment containing methylene blue. The 70.8% decolorization of methylene blue and 63.7% TOC removal was obtained with catalyst dosage of 0.75 g/L and hydrogen peroxide dosage of 12 mmol. Jiang *et al*. [11] synthesized novel Fe_2O_3 nanosheets with double-shell hollow morphology by replica molding from diatomite framework, which was applied to dispose malachite green dye wastewater. Palas *et al*. [12] tested the catalytic performance of $LaCuO_3$ in photo Fenton-like oxidation in treating the food dye, Tartrazine under visible and UV light irradiation. Ma *et al*. [13] prepared the Fe-g-C_3N_4/GMC catalyst to treat acid red dye wastewater, which showed excellent catalytic properties in the range of pH 4 ~ 10.

Clay minerals have been used as the catalyst carrier, including montmorillonite, kaolin, bentonite, etc. Among those, attapulgite has gained a lot of research attention [14]-[16] due to its peculiar structural characteristics suitable for adsorbent and catalyst carrier [17], [18]. Zhang and Nan. [19], [20] prepared Fe_2O_3/attapulgite heterogeneous Fenton catalyst, and used it to degrade or decolorize surfactant SDBS and dyes MB and CR. More than 99% degradation or decolorization ratios can be obtained under the optimal conditions.

Some composites containing Fe_3O_4 and attapulgite were synthesized, such as attapulgite /Fe_3O_4 /Au nanocomposites [21], attapulgite /Fe_3O_4 magnetic nanoparticles [22] and attapulgite /Fe_3O_4 /polyaniline nanocomposites [23], [24], for water treatment or water analysis. As can be seen, most Fe_3O_4/ATP composites were made to nanoparticle form in order to obtain high surface area. But nanocomposites have an obvious defect: it is difficult for nanocomposites to separate and reuse when they were used as adsorbents and catalysts. Although some nanocomposites can be separated by magnetic properties, the process is not as easy as that of particle composites.

To obtain a high-efficient, low-cost and easy-to-separate catalyst, in this study, attapulgite clay was used as a raw material to prepare a kind of particle heterogeneous catalyst Fe_3O_4/ATP, and its preparation conditions, reacting conditions and recycling properties of MB decolorization were studied.

II. Experimental

A. Chemicals

Attapulgite clay (ATP), obtained from Jiangsu province of China, is industrial grade with ATP content of 60%–70%. Its chemical components (%) are as follows: SiO_2, 57.006; Al_2O_3, 8.583; MgO, 8.456; Fe_2O_3, 4.641; Na_2O, 0.948; TiO_2, 0.893; CaO, 0.216; K_2O, 0.094; MnO, 0.034 and SO_3, 0.007.

Experimental chemicals, including three acetylacetone

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The authors are with the Department of Petrol-Chemical Engineering, Lanzhou University of Technology, Lanzhou, China (e-mail: zhangting@lut.cn, author@lamar. colostate.edu, author@nrim.go.jp).

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iron ($Fe(acac)_3$ or $C_{15}H_{21}FeO_6$), methylene blue (MB, $C_{16}H_{18}ClN_3S\ 3H_2O$), anhydrous ethanol ($C_2H_5OH$), hexane ($C_6H_{14}$), oleylamine ($CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2NH_2$), sulfuric acid ($H_2SO_4$) and sodium hydroxide (NaOH), are analytical pure.

B. Preparation and Characterization of Heterogeneous Catalyst Fe_3O_4/ATP

20 g of ATP clay were weighed and mixed with water evenly and then aged for 24 h at room temperature. The aged ATP was granulated to small particle (D=1mm) and dried for 2 h at 105 ℃, then roasted for 2 h at 600 ℃. 5mmol $Fe(acac)_3$was added into a 250 mL conical flask contained 80 mL oleylamine (or ethanol) and 20 mL n-hexaneinto, fully mixing. 5 gram spherical ATP particles were immersed in the mixture solution for a certain time in an ultrasonic water bath. The ATP particles were then separated from solution before being dried at a vacuum drying oven for 2 h under 0.07 Mpa and 40 ℃. After that, the particles were placed into muffle furnace and roasted without air for 2 h at 190 ℃. Thus, the particles heterogeneous catalyst Fe_3O_4/ATP was obtained. The process of preparing Fe_3O_4/ATP catalyst is shown in Fig. 1.

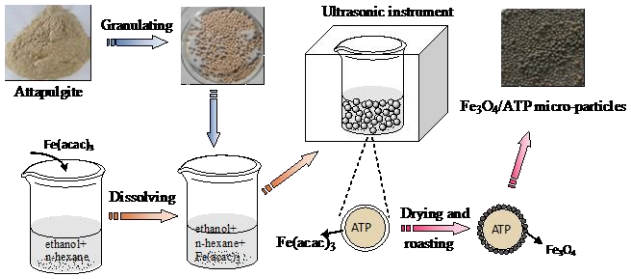


Fig. 1. The schematic of Fe_3O_4/ATPcatalyst preparation.

Scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT–IR) and X-ray diffraction (XRD) were used to characterize Fe_3O_4/ATP catalyst sample. A field-emission scanning electron microscope was utilized to determine the crystal morphology. Measurements were made on a JSM-5500 SEM instrument using a digital imaging process in room temperature at an acceleration voltage of 20 kV. To avoid charge accumulations, the samples were prepared electrically conductive by sputter coating with a thin layer of gold in vacuum conditions. And all samples were dispersed in ethanol before tests. A transmission electron microscopy was utilized to investigate the micromorphology and microstructure. Measurements were made on a JEM-1200EX TEM instrument. FT-IR spectroscope was used to confirm the chemical structure, any changes in the compositional or functional group during preparation of ATP-base catalyst. Measurements were made on a Nicolet AVTAR 360 FT-IR spectrometer after samples were mixed with 300mg of spectroscopic grade KBr and ground in an agate mortarin the range of 4000-400 cm^{-1} at room temperature. To investigate the crystalline structure and stability of ATP and Fe_3O_4/ATP composites, powder X-ray diffraction patterns wererecorded by X-ray diffract meter (Panalytical X Pert PRO XRD) using Cu K_α radiation (λ=0.1542nm) at a rate of 0.02 °/s in the range of 5 ° to 80 °with an operating voltage of 40 kV and electric current of 150 mA.

C. Experimental Methods

Methylene blue (MB) was chosen as a target pollutant as a common cationic dye and its molecular weight of 373.90. A stock solution containing MB (1000mg/L), which can be diluted to the required concentrations for later degradation experiments, was prepared using distilled water. To obtain 100mg/L MB dye solution, 10mL MB solution (1000mg/L) was added in a conical flask and diluted with 90mL distilled water. The pH of the solution was adjusted by adding sodium hydroxide solution or sulfur acid. ATP-base catalyst samples with required dosage of hydrogen peroxide (30%w/w) were then added into the conical flask contained 100mL, 100mg/L MB solution .After being sealed the conical flasks were placed in a constant-temperature water bath. For H_2O_2 solution, solid catalyst and MB solution, metric units of concentration used in this study were mmol/L, g/L and mg/L, respectively. The MB concentration was measured using a INESA 752N type ultraviolet-visible spectrophotometer by methylene blue spectrophotometry at λ of 664nm. The degradation ratio, i.e. the removal degree of MB can be calculated using the equation of $\eta=(C_0-C_t)/C_0\times100\%$ (Eq. 1), where C_0 is the initial concentration of MB wastewater and C_t is the concentration at contact time t.

Box-Behnken design (BBD) is a three-level incomplete factorial design extensively used in experimental design. BBD is performed to optimize the initial reaction rate andthe derivative of the initial portion of the kinetic curve, and it can be used to arrange in order the importance of the various influencing factors.

In order to explore the possibility of recycling and the stability of Fe_3O_4/ATP as a catalyst, at least 10 times repeated decolorization experiments were performed. To guarantee the same experimental conditions, for each run, the initial concentration of MB and H_2O_2 were 100mg/L and 9.8mmol/L separately, and reused 0.5 g catalyst which was just washed by distilled water after reaction. The analytical methods for each run were also the same as mentioned above.

III. Result and Discussion

A. Optimization of Fe_3O_4/ATP Preparation

Catalysis effect of Fe_3O_4/ATP was influenced by many factors during the process of synthesis, such as solvent used, ultrasonic time, ultrasonic frequency, ultrasonic temperature and precursor concentration.

Solvents are very important during the preparation of Fe_3O_4/ATP. They might influence the dispersing condition of active components thereby they will influence the loading capacity of active components on the catalyst. We compared the MB decolorization ratios when using two different mixed solvents (alcohol and n-hexane, oleylamine and n-hexane) during the catalyst preparation. It can be seen from Fig. 2 that it achieves higher MB removal ratio (over 80%) as using alcohol and n-hexane solvents than that (70%) while using oleylamine and n-hexane. Furthermore, oleylamine has high

viscosity, which is difficult to be mixed evenly with other solvent. The truth that it also generates a lot of waste indissolvable liquid, can't meet the low carbon demand. As a result, using ethanol + n-hexane as solvents is more efficient and friendlier to environment.

Precursor ($Fe(acac)_3$) solution concentration also had a great influence on the catalytic performance of Fe_3O_4/ATP. Fig. 3 shown that when precursor $Fe(acac)_3$ solution concentrations changed from 10 to 60 mmol/L during catalyst preparation, the decolorization ratios of MB firstly increased then went down. And $Fe(acac)_3$ solution concentrations of 30 mmol/L showed the highest catalytic performance in this heterogenous Fenton system. High precursor concentration enhances the number of Fe species loaded on ATP particles, but too much Fe species loaded would decrease the specific surface area of ATP particles which is tightly associated with catalytic and degrading performance.

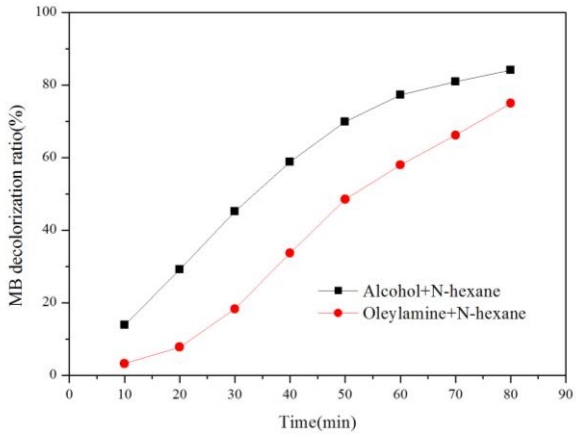


Fig. 2. The influences of solvents on MB removal ratio.

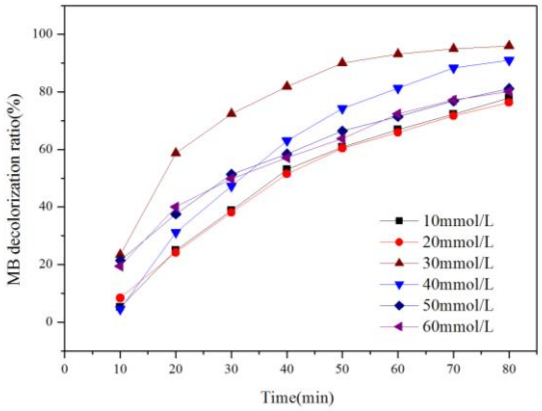


Fig. 3. The influences of precursor $Fe(acac)_3$ concentration on MB removal ratio.

In order to introduce Fe species into ATP and gain enough Fe_3O_4 nano-particles on ATP surface, ATP particles should be immersed in precursor solution for almost 12 hours. While using ultrasonic can significantly reduce the immersing time. Ultrasonic frequency, ultrasonic time and ultrasonic temperature significantly affected the performance of catalyst, as can be seen in Fig. 4. From Fig. 4(a) and 4(b), the MB removal efficiency increased with increasing of the ultrasonic frequency and ultrasonic time. It is believed that higher frequency and longer time can cause the fast and efficient mass exchange, leading to high-load capacity. But the ultrasonic frequency and the ultrasonic time should better not be more than 100 kHz and 40min separately, due to safety considerations. As can be seen from Fig. 4(c), high ultrasonic temperature does not result in high-load capacity and high MB decolorization. It has the highest MB decolorization at 25℃ because too high temperature is not good for adsorption and too low temperature is not good for thermal motion of molecule.

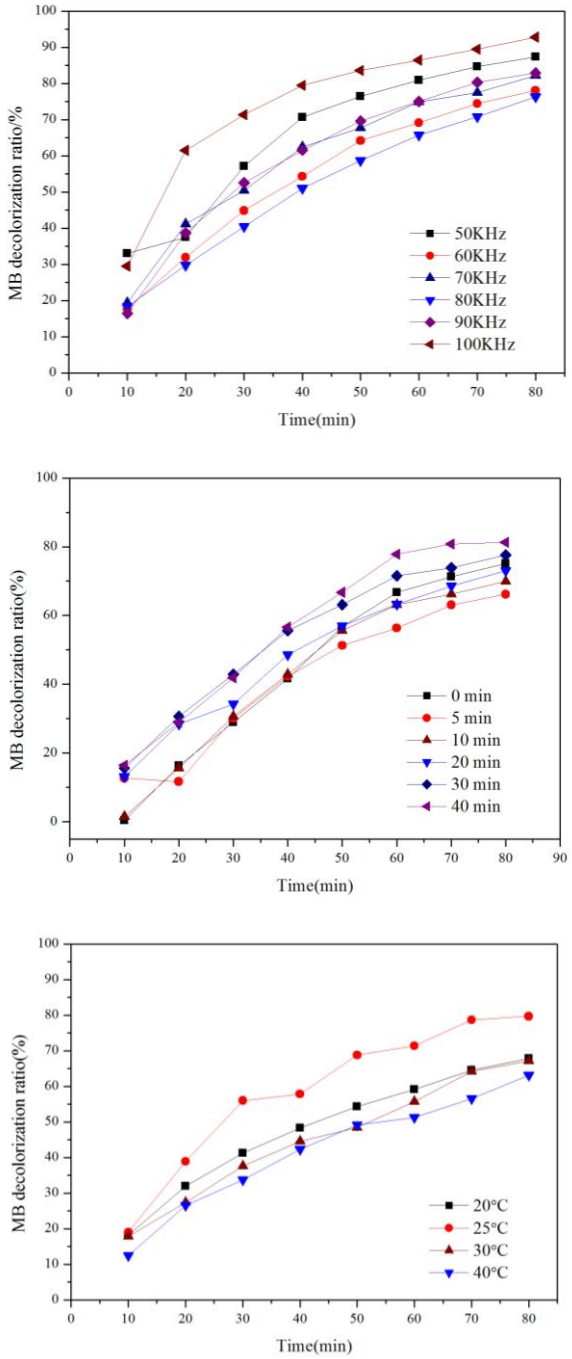


Fig. 4. The influences of ultrasound (a-ultrasound frequency; b-ultrasound time; c-ultrasound temperature) on MB removal ratio/

B. Characterization

SEM micrographs were collected to illustrate the morphologies of ATP and Fe_3O_4/ATP samples, as depicted in Fig. 5. Rod-shaped particles with lengths of 500~700nm and widths of 100~150nm are visible (Fig. 5a). After the introduction of iron species into ATP, nano-Fe_3O_4 particles

were coated evenly onto the surface of ATP (Fig. 5b).

The FT-IR results of ATP and Fe_3O_4/ATP can be seen in Fig. 6. The strong wide absorption bands appeared at 3420cm^{-1} associated with the surface hydroxyl groups. The weak sharp absorption bands at 1630cm^{-1} is flexural vibrations of water H-O-H. The strong wide absorption bands at 1040cm^{-1} is dissymmetry stretching vibrations of Si-O-Si, and the absorption bands at 777cm^{-1} and 476cm^{-1} are symmetry stretching and flexural vibrations of Si-O. Some peaks were observed at lower wavenumbers (480cm^{-1} and 565cm^{-1}) corresponding to vibration modes of Fe-O bonds of Fe_3O_4 nanoparticles on the surface of ATP.

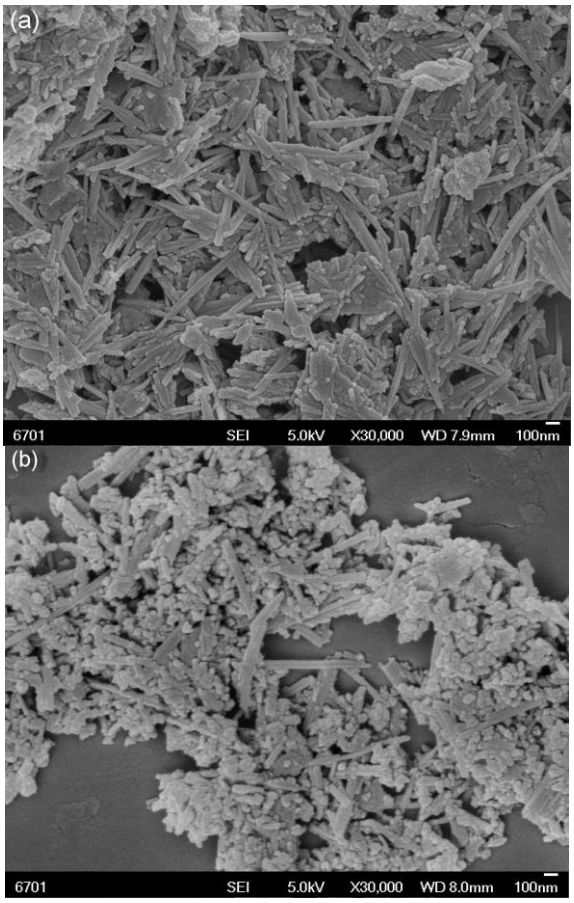


Fig. 5. SEM micrographs of samples(a-ATP, b-Fe_3O_4/ATP).

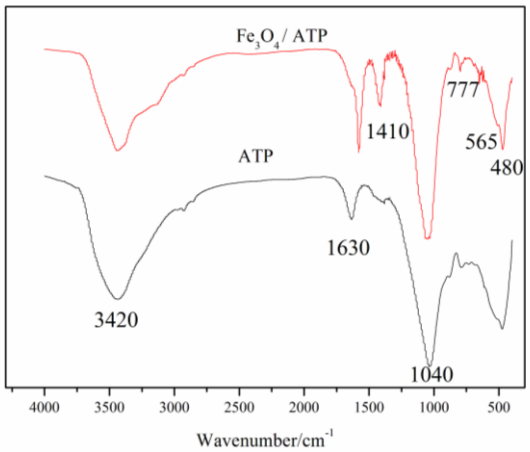


Fig. 6. FT-IR spectra of ATP and Fe_3O_4/ATP samples.

The phase structures of samples were investigated by XRD, and the obtained results are shown in Fig. 7. XRD patterns of Fe_3O_4/ATP are contrasted with those of ATP. The characteristic peaks of cubic spinel structure known from bulk Fe_3O_4 phase on ATP support, which should be at 18.28 °, 30.18 °, 35.57 °,43.13 °, 53.408 °, 57.04 ° (Wang *et al*. 2013), appear at 20.78 °, 29.36 °, 36.5 °,42.38 ° , 50.06 ° and 59.66 ° due to the imperfect crystallization of Fe_3O_4.

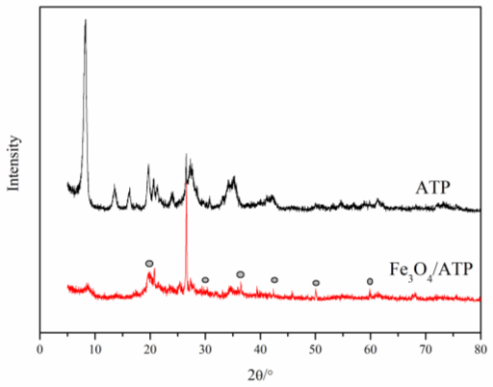


Fig. 7. XRD patterns of ATP and Fe_3O_4/ATP samples.

C. Process Optimization of MB Decolorization by Fe_3O_4/ATP/H_2O_2 System

BBD method is used for the experimental design, data analysis and optimization. Reaction conditions of heterogeneous catalysis system such as temperature, pH value, H_2O_2 dosage and catalyst dosage have great effect on MB decolorization ratio. It is known that there is a positive correlation between temperature and MB decolorization. It takes 24 h to obtain 99% MB decolorization ratio at 20℃, while it takes only 1 h to obtain the same ratio at 60 ℃when using heterogeneous Fenton system to decolorize MB (Zhang *et al*., 2017). Thus all the experiments were conducted at 60℃. Parameters chosen for process optimization are pH (2~12), Fe_2O_3/ATP dosage (2g/L~10g/L) and H_2O_2 dosage (19.8 mmol/L~98 mmol/L). The data of 17 experimental runs of BBD method were analyzed by Design Expert 8.0.6.1 software. The optimized parameters for maximizing the initial rate were also obtained using the established equation.

TABLE I: ANOVA RESULTS OF THE QUADRATIC MODEL OF THE DECOLORIZATION RATIO

Source	Sum of squares	Degree of freedom	Mean square	F value	p-value (prob>F)
Model	10867.79	9	10867.79	59.78	<0.0001
X_1 (pH)	2110.23	1	2110.23	104.47	<0 .0001
X_2 (H_2O_2 concentration)	1535.69	1	1535.69	76.02	<0 .0001
X_3 (catalyst dosage)	458.29	1	458.29	22.69	0 .0021
Residual	141.40	7	20.20		
Lack of fit	123.96	3	41.32	9.48	0.0273
Pure error	17.44	4	4.36		
Corrected total	11009.19	16			

R^2=0.9872; adjusted R^2=0.9706

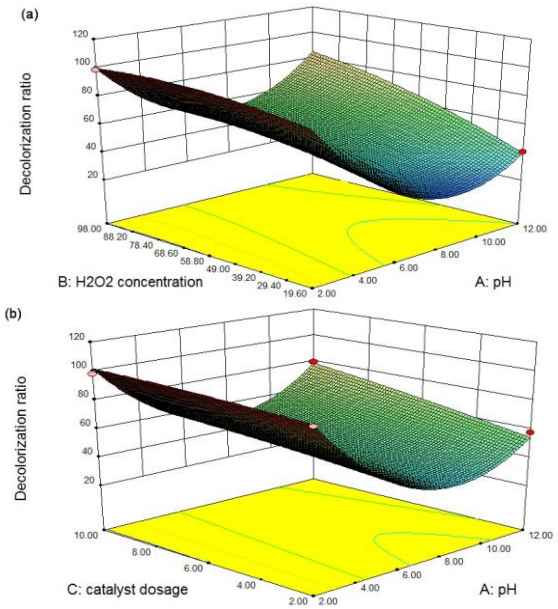
According to the analysis by Design Expert 8.0.6.1 software, the analysis of variance (ANOVA) results of the quadratic model of the decolorization ratio was shown in Table I. The calculated F value of 59.78, much larger than the critical value of 3.68 for $F_{0.05}$ (9, 7), implying that the derived quadratic polynomial model is significant. The model correlation coefficient of R^2=0.9872, suggests that the there is good agreement between the experimental and predicted

values of the degradation efficiency of MB. The function presented below was employed as the prediction model:

$$Y=126.79-29.02X_1+0.42X_2+0.98X_3+0.046X_1X_2+0.23X_1X_3 +9.25\times10^{-4}X_2X_3+1.55X_1^2-3.36\times10^{-3}X_2^2-0.065X_3^2$$

where Y is the decolorization ratio of MB (%), X_1 is pH value, X_2 is H_2O_2 concentration, X_3 is Fe_3O_4/ATP dosage. The derived model is adequate to perform the process variables optimization of Fe_3O_4/ATP/H_2O_2 system for the decolorization of MB, significant at 95% confidence level (p=0.0273<0.05).

Fig. 8 shows the 3D response surface modeling representing the effects of catalyst dosage, initial H_2O_2 concentration and the initial pH on the decolorization of MB by heterogeneous Fenton Fe_3O_4/ATP/H_2O_2 system. It can be seen from Fig. 8(a) and Fig. 8(b) that pH is a crucial operating factor for Fe_3O_4/ATP/H_2O_2 system to decolorize MB. That means pH directly affects the catalytic performance. Unlike the decreasing trend of MB decolorization ratio with increasing pH value in Fe_2O_3/ATP/H_2O_2 system [25], the decolorization of MB decreased firstly, and then rise along with the increasing pH value in Fe_3O_4/ATP/H_2O_2 system, and the lowest decolorization ratio is at pH of 8. This is due to different decomposing mode of H_2O_2 influenced by different surface charge of different catalysts. In Fe_3O_4/ATP/H_2O_2 system, more hydrogen peroxide decomposed into O_2 and H_2O (80% approximately) at neutral conditions instead of generating OH. H_2O_2 did not decompose at pH under 3.5, while at alkaline pH of 12, H_2O_2 decomposition ratios were about 60%, not as high as that at neutral pH conditions (8 or 9). From Fig. 8(c), H_2O_2 concentration and catalyst dosage have little influences on decolorization ratio of MB. On the whole, higher catalyst dosage and higher H_2O_2 concentration will lead to a higher decolorization of MB. According to Fig. 4, the order of influence is pH>Fe_3O_4/ATP dosage>H_2O_2 dosage. The model predicted that the optimal conditions are pH value of 2, Fe_3O_4/ATP dosage of 10g/L and H_2O_2 concentration of 98mmol/L.



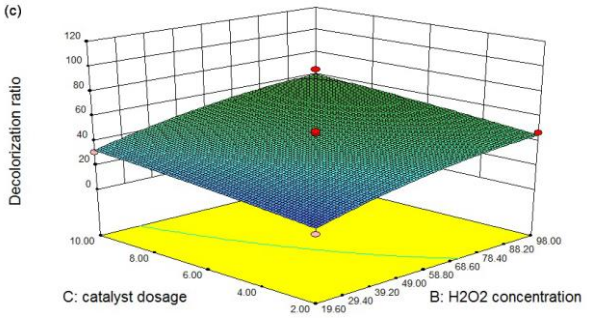


Fig. 8. 3D response surface plot and contour plot of the decolorization ratio of MB.

D. Repeated Decolorization Experiments

10 times repeated decolorization experiments were performed to test the recycling ability of Fe_3O_4/ATP as a catalyst, as shown in Fig. 9. At the first run, the decolorization efficiency of MB is only 64.6%, in subsequent runs, the decolorization efficiency increases. At the fifth, sixth and seventh runs, the ratios are almost 100%, and at next several runs, the efficiency decreases a little, but still is over 90%. This phenomenon could be explained that the products of MB degradation in the first several runs, such as acetic acid, ethyl alcohol, etc., gradually activate the Fe_3O_4/ATP and make it more efficient than before. The decreasing of decolorization ratio in the last several runs may be explained by that adsorbing too more MB or its degradation products on catalyst hinder the surface catalytic reactions between Fe_3O_4 and H_2O_2.

E. Comparison Experiments

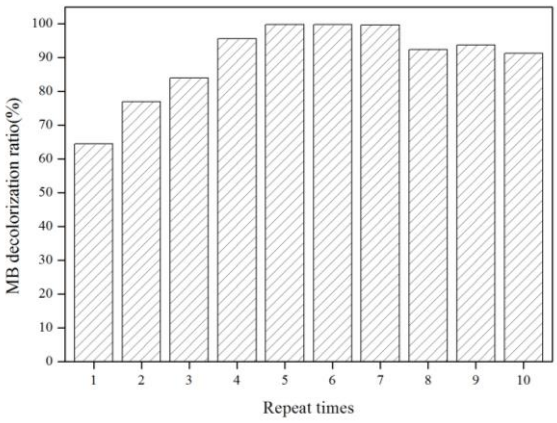


Fig. 9. Influences of recycle times on MB removal ratio.

To get a clear understanding of the MB degradation process by Fe_3O_4/ATP/H_2O_2 system, comparison experiments about the MB removal experiments are conducted with H_2O_2, Fe_3O_4, ATP, Fe_3O_4/ATP and Fe_3O_4/ATP/H_2O_2 separately. The results were shown in Fig. 10. It shows that the degradation ratio of MB is not very fast and high when only H_2O_2 exists and obtains 80% degradation ratio after 60 min, which means that MB can be *oxidised* by H_2O_2 gradually at high temperature. When only Fe_3O_4, ATP, or Fe_3O_4/ATP exists, the degradation ratios of MB are all very low (under 20%) after 60min due to the poor *adsorptive* ability at temperature of 60°C.The adsorptive ability of Fe_3O_4 is lowest of the three because Fe_3O_4 is a kind of ores which have no high surface area. It also can be seen that after

loading Fe_3O_4 on ATP surface, the adsorption ability of ATP dropped a lot contrast with its original form. When both Fe_3O_4/ATP (after 4 times recycle) and H_2O_2 exist, the degradation ratio of MB can reach 99% within 60 min. It means that in Fe_3O_4/ATP/H_2O_2 system, the *catalysis* is the main reaction in MB degradation process other than directly oxidation by H_2O_2 or adsorption by Fe_3O_4/ATP.

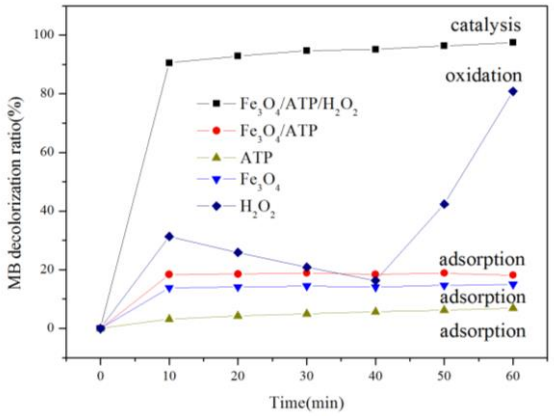


Fig. 10. Comparison experiments.

IV. Conclusions

In this study attapulgite was used as the carrier to prepare heterogeneous catalyst Fe_3O_4/ATP successfully which demonstrated higher efficiency in MB degradation. Systematic experiments under various factors during the preparation of the catalyst were performed to optimize the catalyst performance and preparation methods. Ethanol solvent is superior to oil amine solvent for leading better catalytic performance and less pollution to the environment when used in Fe_3O_4/ATP catalyst preparing. Low temperature and moderate concentration of the predecessor solution will benefit the catalytic performance. Ultrasonic treatment can effectively shorten the dipping time of the catalyst in predecessor solution and improve the load capacity of the active components on catalyst supporter at the same time. As a result, the optimal preparing conditions of Fe_3O_4/ATP catalyst are: ethanol is as solvent, n-hexane is as dispersant, predecess or solution temperature is 25 ℃, predecessor solution concentration is 30 mmol/L, ultrasonic time is 30 min, and ultrasonic frequency is 100 KHz. Catalyst dosage, pH value and hydrogen peroxide dosage are all the important factors influencing the removal rate of MB, and BBD coupled with RSM was used to optimize the important parameters of heterogeneous Fenton-like reactions on Fe_3O_4/ATP for MB degradation. The results showed that the order of influence is pH>Fe_3O_4/ATP dosage>H_2O_2 dosage. pH value has crucial effect on MB decolorization ratio in Fe_3O_4/ATP/H_2O_2 system. MB removal ratios are high at acid and alkaline solution but low at neutral solution. The model predicted that the optimal conditions were pH 2, Fe_3O_4/ATP 10g/L and H_2O_2 98mmol/L. Through the recycle experiments of the catalyst, it can be seen that the catalyst has good repeatable performance. The catalysis capacity of the recycled catalyst can be even better than that of initial ones. According to comparison experiments, Fe_3O_4/ATP/H_2O_2 system has strong catalysis effect on MB degradation, rather than adsorption or direct oxidation.

Conflict of Interest

The authors declare no conflicts of interest to this work.

Author Contributions

Chunyuan Qian and Lingyu Dong conducted the research; Ting Zhang and Chunyuan Qian analyzed the data; Ting Zhang wrote the paper; all authors had approved the final version.

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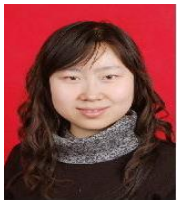

Ting Zhang was born on July 2, 1979. In 2001, she graduated from Wuhan University of Technology (Wuhan, China) and got her B.E. degree in environmental engineering. From 2004 to 2007, she achieved her M.E. degree in Lanzhou University of Technology (Lanzhou, China), majoring in environmental engineering. And in 2016 she graduated from Lanzhou University and got her Ph.D degree in environmental science. Her research field is environmental catalysis.

She has been working in Lanzhou University of Technology for 17 years and now she is an associate professor of the Department of Environmental Engineering. Some previous publications are: (1) Ting Zhang, Zhongren Nan. Decolorization of Methylene Blue and Congo Red by attapulgite-based heterogeneous Fenton catalyst. Desalination and Water Treatment. 2016, 57(10): 4633-4640; (2) Ting Zhang, Minmin Chen, Shu-rong Yu. Decolorization of methylene blueby an attapulgite-based heterogeneous Fenton catalyst: Process optimisation. Desalination and Water Treatment.2017, 63, 275–282; (3) Ting Zhang, Minmin Chen, Yu Zhang, Yi Wang, Microencapsulation of stearic acid with polymethylmethacrylate using iron (III) chloride as photoinitiator for thermal energy storage, Chinese Journal of Chemical Engineering, 2017, 25, 1524-1532. Her current and previous research interests are catalytic desulfurization, environmental catalysis and environmental material.

Dr. Zhang has got two science and technology progress awards of Gansu province.

Lingyu Dong was born in August 1994. She graduated from Lanzhou University of Technology with a bachelor's degree in environmental engineering in June 2017, and became a master degree candidate of College of Petrochemical Technology in Lanzhou University of Technology which is located at No. 36, Pengjiaping Road, Lanzhou Gansu (P.R. China) in the same year. She mainly engaged in the study of environmental catalysis, environmental materials and degradation of organic wastewater.

She has made some progress in her research on environmental catalysis, and she has great interests in making new discoveries in the field of environmental protection.

Ms. Dong was awarded scholarship several times at school, and won the first prize scholarship in 2018 (awarded to the top 10%).

Chunyuan Qian was born in August 1994. She graduated from Zhejiang Ocean University with a bachelor's degree in environmental engineering in June 2017, and became a master degree candidate of College of Petrochemical Technology in Lanzhou University of Technology, which is located at No. 36, Pengjiaping Road, Qilihe District, Lanzhou City, Gansu Province (P.R. China). She is mainly engaged in environmental catalysis, environmental materials and degradation of organic wastewater.

She has some research in environmental catalysis and organic wastewater degradation, and will actively work on wastewater treatment in the future.

Ms. Qian has won several national inspirational scholarships, academic scholarships, etc. during the undergraduate course. At the graduate level, she has obtained first-class scholarships in 2018 (award to the top 10%).