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Preparation and characterization of NZVI–MCM-48 mesoporous molecular sieves and its mechanism for treatment of methylene blue wastewater

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ABSTRACT

The nanoscale zero valent iron (NZVI) and ordered mesoporous molecular sieve Mobil Composition of Matter No. 48 (MCM-48) composite material (NZVI–MCM-48) were prepared by the hydrothermal treatment at 120°C for 36 h and then drying at 100°C of synthetic solution with a mole ratio of silica, cobalt, cetyltrimethylammonium bromide (CTAB), sodium hydroxide, sodium fluoride, and water is l:0.01:0.65:0.5:0.1:71 to get the NZVI–MCM-48 raw powder which was then treated by roasting in a nitrogen atmosphere to release the surfactant and by high temperature carbonization and reduction. The existence of NZVI in the composite material and its orderliness, form, and element composition were analyzed by characterization means such as X-ray diffractometer (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM), and energy dispersive spectrometer (EDS). The orthogonal degradation experiment for treating methylene blue (MB) wastewater by the composite material led to a 853 mg/g decolorization rate of MB and a 821 mg/g chemical oxygen demand (COD) removal rate under the optimal conditions including an initial concentration of wastewater of 10 mg/L, an initial pH of 6, a concentration of the added sample of 0.8 g/L, and a reaction time of 60 min. The degradation mechanism for MB wastewater is also discussed.

Keywords: NZVI–MCM-48 mesoporous molecular sieve; Hydrothermal synthesis; Methylene blue; Degradation mechanism

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1. Introduction

In recent years, nanoscale zero valent iron (NZVI) particles have been widely used in the treatment of organic wastewater for their excellent adsorption performance and very high reduction activity, thanks to their small particle size, large specific surface area, and surface energy [1–4]. However, it was reported in some literatures that there were some deficiencies in the process of removing the pollutants from water using nano iron particles. Sun et al. [5] reported that nano iron particles were apt for aggregation due to

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their large specific surface area and for oxidization due to their high surface energy, and would even spontaneously ignite when directly exposed in air. Elliott and Zhang [6] also pointed out that nano iron could be used only under an anaerobic condition.

Presently, nano iron particles can be prepared by various methods such as evaporation condensation, thermal plasma, high energy ball milling, solid phase reduction, and liquid phase reduction. Of them, liquid phase reduction has been much favored for its relatively simple process. However, this method requires the protection by inertia gas in the process, greatly increasing the difficulty and cost of preparation. The preparation of NZVI for water treatment mostly adopts the liquid phase reduction method, where the metallic iron salts (mainly Fe(II) and Fe(III) salts) are reduced to single element particles of iron under the function of a strong reductant (such as KBH_4 and $NaBH_4$) [7].

$$\text{For } Fe^{2+}: 2Fe^{2+} + BH_{4r}^{-} + 3H_2O \rightarrow 2Fe\downarrow \\ + H_2BO_3^{-} + 4H^{+} + 2H_2\uparrow$$

$$\text{For } Fe^{3+}: 4Fe^{3+} + 3BH_4^{-} + 9H_2O \rightarrow 4Fe\downarrow \\ 3H_2BO_3^{-} + 12H^{+} + 6H_2\uparrow$$

However, when these traditional materials are used to disperse NZVI particles, only a composite material with random particle size distribution can be obtained due to their inherent defect of wide pore size distribution. In this study, NZVI-loading ordered mesoporous molecular sieve, NZVI–MCM-48, was prepared by high temperature carbonization and reduction method, and was characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM) energy dispersive spectrometer (EDS), and transmission electron microscope (TEM) methods [8]. Its removal effect of methylene blue (MB) from water under different conditions was investigated and the reaction mechanism of MB under the function of NZVI–MCM-48 was studied.

2. Experiment

2.1. Test agents

Silica sol (SiO_2 25%, $\rho = 1.15$, Shanghai No. 2 Chemical Reagent Factory), cetyltrimethylammonium bromide (CTAB) (AR, Shanghai Qingxi Chemical Technology Co., Ltd.), sodium hydroxide (AR, Shanghai Jiuyi Chemical Reagent Co., Ltd.), hydrochloric acid (AR, Shanghai Jiuyi Chemical Reagent Co., Ltd.), cobalt sulfate (AR, Guangdong Jieshan Chemical Factory) sodium fluoride (AR, Tianjin Damao Chemical Reagent Factory), absolute ethyl alcohol (AR, Shanghai Jiuyi Chemical Reagent Co., Ltd.), MB (Shanghai Sansi Chemical Reagent Co., Ltd.), $Fe(NO_3)\cdot 9H_2O$ (AR, Shanghai Jiuyi Chemical Reagent Co., Ltd.), and N_2 (99.99%, Shanghai Gas Company).

2.2. Preparation of composite material

0.45 g NaOH and 0.095 g NaF were dissolved in 25 mL deionized water and 5.31 g CTAB was then added; the system was kept at 35°C temperature and agitated for 0.5 h; 4.7 mL silica sol was added drop by drop under strong agitation and finally, 0.0631 g cobalt sulfate and $Fe(NO_3)\cdot 9H_2O$ solution of certain amount that is fully dissolved in absolute ethyl alcohol were added; the resultant solution was agitated for 1 h, put into an reactor, and underwent hydrothermal treatment at 120°C for 36 h. The reaction substance had a quantity ratio of $n(SiO_2):n(Co):n(CTAB):n(NaOH):n(NaF):n(H_2O) = 1:0.01:0.65:0.5:0.1:71$. The resultant substance was taken out, filtered, washed, and dried at 100°C to get the NZVI–MCM-48 raw powder.

2.3. Characterization of composite material

The XRD analysis of the sample was made using German Bruker D8-ADVANCE X-ray analyzer with Cu target, K_α radiant source, 40 kV tube voltage, 100 mA tube current, 0.2°/s scanning step length, and 0–70° scanning scope. The TEM analysis adopted a JEOL JEM-2010 TEM to directly observe the form, structure, and particle size of the sample at an accelerated voltage of 200 kV. The sample was pulverized as fine as possible and treated by ultrasonic dispersion in absolute ethyl alcohol. The dispersed liquid drops were deposited on carbon-plated copper sieve, sampled, dried, and observed by HREM. A JSM-6700F SEM was used to observe the sample form and element contents.

2.4. Orthogonal experiment of MB treatment by NZVI–MCM-48

The optimal conditions for MB treatment by NZVI–MCM-48 were determined by orthogonal method. The experiment-related four main factors were determined according to the literature without considering their mutual interaction. On this basis, a four-factor three-level orthogonal experiment table was prepared to find out about the optimal preparation conditions of

NZVI–MCM-48 for MB treatment. The decolorization rate of MB and chemical oxygen demand (COD) removal rate were chosen as observation indexes. The design of the levels and orthogonal experiments of the factors through single-factor preparatory experiments is shown in Table 1.

3. Results of analysis and discussion

3.1. XRD analysis of NZVI–MCM-48 composite materials

The small-angle and wide-angle XRD results of the NZVI-carrying ordered mesoporous molecular sieve NZVI–MCM-48 with different Fe/Si molar ratios roasted at 800°C in a nitrogen atmosphere for 3 h are shown in Fig. 1. It can be seen from the small-angle XRD pattern that the samples with a Fe/Si molar ratio of 0.15 and 0.20 have the typical characteristic diffraction peak of MCM-48 mesoporous molecular sieves, which is basically consistent to the pure silicon MCM-48 pattern illustrating that such samples have an extremely good cubic structure and order. When the Fe/Si molar ratio is greater than 0.20, the diffraction peak continuously weakens with the increase of iron load mesoporous MCM-48 can prevent NZVI from oxidization by air at the ambient temperature.

3.2. Tem analysis of NZVI–MCM-48 composite materials

The TEM images of NZVI-carrying–MCM-48 indicating that the increase of iron load can damage the order structure of material to a certain extent. The corresponding wide-angle XRD characterization result shows that when the Fe/Si molar ratio is 0.15 and 0.20, there is only a weak, wide diffraction peak at 44.68° indicating that many small crystals of iron are formed in the ordered mesoporous silicon oxide pore canal. With the increase of iron load, more diffraction peaks occur. In the wide-angle XRD pattern of the samples with a Fe/Si molar ratio greater than 0.20, there is a sharp diffraction peak at 44.68°. It is found from the comparison with the standard iron PDF card that it rightly corresponds to the crystal plane diffraction (44.68) of NZVI (110), and the sharp and regular peak form indicates that ZVI has a high crystallization degree. No evident diffraction peak of iron oxide is observed in the figure, illustrating that the existence of ordered composite materials which underwent carbon heat treatment with different Fe/Si molar ratios of 0.15 (a), 0.2 (b), and 0.3 (c) are shown in Fig. 2 (50,000×; a: 20 nm; b: 20 nm; c: 50 nm). Compared with the small-angle XRD results as is shown in Fig. 1 and it is obvious that an ordered structure occurs when the Fe/Si molar ratio is 0.15 and 0.2. With the increase of iron load, the orderliness of the composite materials decreases. When the iron load is raised to enable a Fe/Si molar ratio to be 0.3, the structure is destructed. Meanwhile, it can be observed that black nano iron particles disperse widely in MCM-48 in image (a) and image (b), and in image (c), due to the destructed molecular sieve structure, the nano iron particles are cladded.

Table 1
Orthogonal experiment design table.

Factor level	Initial concentration (A)	pH (B)	Sample addition (g/L) (C)	Reaction time (min) (D)
1	20	4	0.4	60
2	15	5	0.6	120
3	10	6	0.8	180

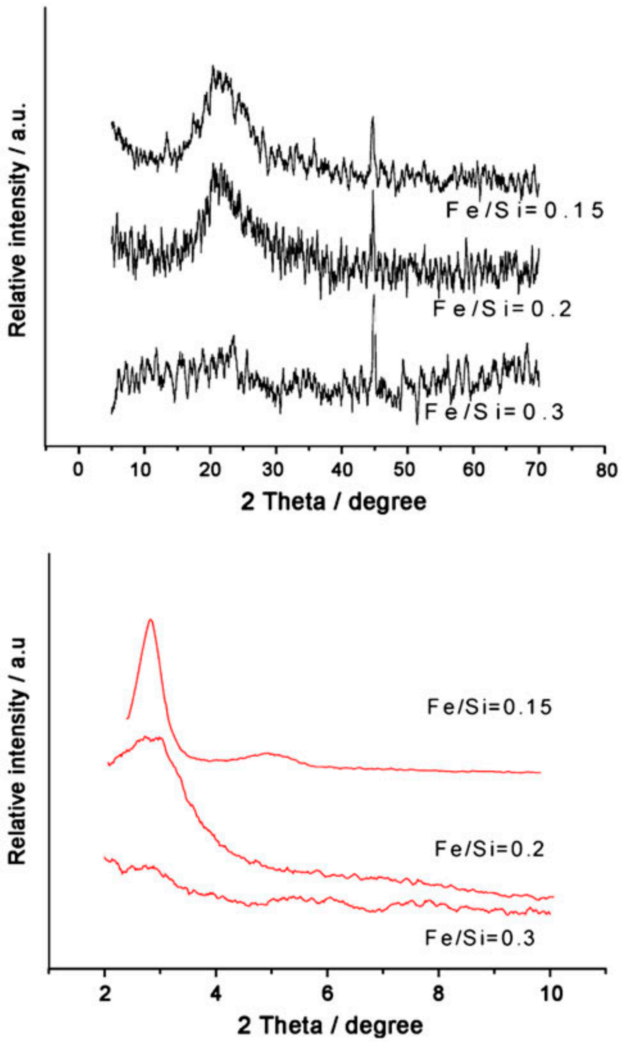

Fig. 1. XRD patterns of NZVI–MCM-48 with different Fe/Si molar ratios.

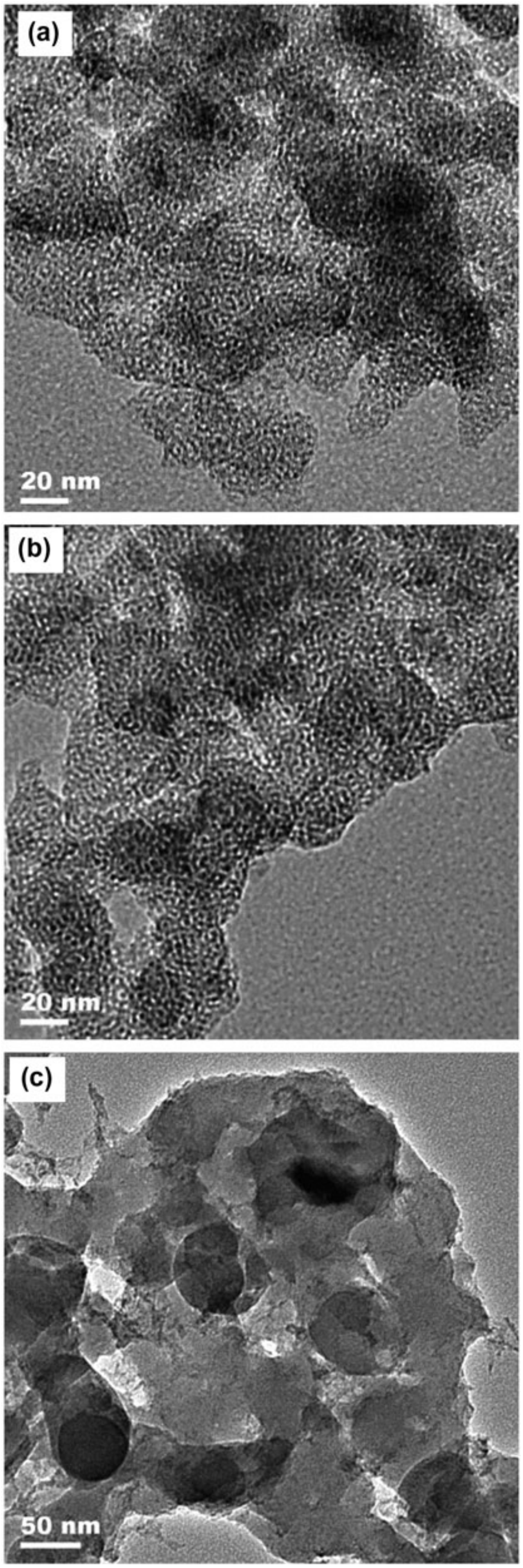

Fig. 2. TEM images of NZVI–MCM-48 with different Fe/Si molar ratios of 0.15 (a), 0.20 (b), and 0.30 (c) (50,000×; a: 20 nm; b: 20 nm; c: 50 nm).

3.3. SEM analysis of NZVI–MCM-48 composite materials

The micro forms of load-type NZVI with a Fe/Si molar ratio of 0.15, 0.20, and 0.30, respectively, under the SEM are shown in Fig. 3(a)–(c) (a: 20,000×; b: 20,000×; c: 20,000×). It can be seen from Fig. 3 that

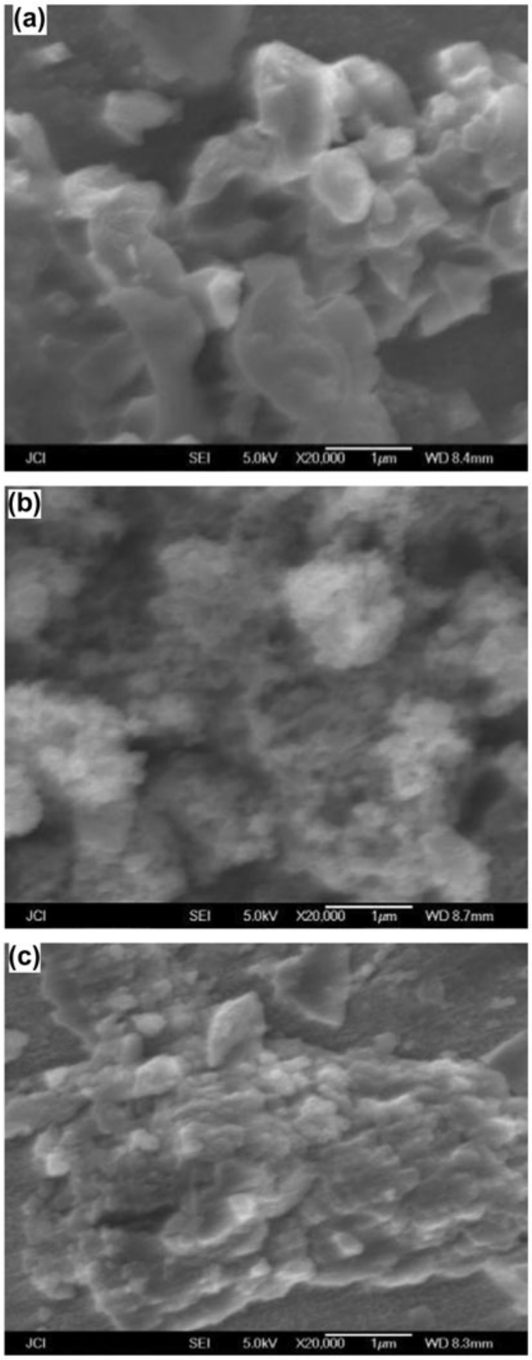

Fig. 3. SEM images of NZVI–MCM-48 samples with different Fe/Si molar ratios of 0.15, 0.20, and 0.30 (a: 20,000×; b: 20,000×; c: 20,000×).

the samples are composed mainly of massive crystals with irregular forms and different sizes. With the increase of NZVI load, the size of the crystals becomes smaller and their dispersity becomes better, with the diameter being 30–50 nm.

3.4. EDS analysis of NZVI–MCM-48 composite materials

It can be seen from Table 2 that the main elements of the composite material are Si, Fe, O, and Na, of which, Si, O, and Na are the main elements of MCM-48 and the Fe content increases with the increase of Fe/Si molar ratio, with the mass percentages being 0.75, 1.26, and 1.95%, respectively.

3.5. Kinetic analysis for the reduction of MB by NZVI–MCM-48 composite material

The kinetics of the reduction of MB by NZVI–MCM-48 were investigated as shown in Fig. 4, the kinetic data obtained for the MB degradative reduction can be fitted to a rate expression of a pseudo-first-order reaction: $\ln(c_t/c_0) = -k_{\mathrm{MB}}t$, where, c_0 and c_t represent the MB concentrations before and after the degradation, t is the degradation time, and k_{MB} is the apparent rate constant of the degradative reduction of MB as a pseudo-first-order reaction.

3.6. Formation mechanism of NZVI–MCM-48 composite material

With respect to the formation mechanism of ordered mesoporous materials, there are the following viewpoints: the liquid crystal template mechanism (LCT) proposed by Beck et al. [9]; the charge density matching mechanism proposed by Monnier et al. [10]; the generalized LCT mechanism proposed by Huo Qisheng et al. [11]; in light of the different interactions between inorganic substances and surfactants; the silicate layering mechanism proposed by Inagaki et al. [12]; and the true LCT mechanism proposed by Attard et al. [13], which is the most representative. However, there had never been attempts to find out about the formation of NZVI particles in ordered mesoporous MCM-48 molecular sieve matrix.

Through some preliminary researches, we have proposed a formation mechanism of NZVI particles in ordered mesoporous MCM-48 molecular sieve matrix. After ferric nitrate is added into the mixture as an iron source, at a certain concentration in water, CTAB surfactant which has amphiphilic groups will form rod-shaped micelles and will arrange regularly to form a liquid crystal structure, with the hydrophobic group pointing inward and the charged hydrophilic group head stretching into the water. When silicon source substance is added, it will bond with surfactant ions and attach to the surface of organic surfactant under the electrostatic function to form the SiO_2 wall of mesoporous organic cylinder surface. In alcohol solution, the hydrolysis of silicon source and iron source will lead to the formation of silicon hydrolytic polymer and iron ion hydrolytic polymer ($[Fe(OH)_x]_n$). Due to the coexistence of silicon hydrolytic polymer and ($[Fe(OH)_x]_n$) in the initial solution, a large amount of surface hydroxyl groups (–OH) may lead to the attachment of ($[Fe(OH)_x]_n$ on the surface of the silicon hydrolytic long chains to form Si–O–Fe bonds. When NZVI–MCM-48 mesoporous molecular sieve composite material is under carbon heat treatment in N_2, the H_2 produced from the composite and carbon material in CTAB will reduce the iron from prevalence status to zero valence at 800°C.

Table 2
EDS analysis of Fe^0/MCM-48 with different Fe/Si molar ratios.

Fe/Si molar ratio	Element	O	Na	Si	Fe	Co
0.15	Atomic%	57.32	0.26	42.15	0.34	0.10
	Weight%	70.59	0.31	40.94	0.75	0.24
0.20	Atomic%	57.26	0.28	42.10	0.44	0.09
	Weight%	70.51	0.33	40.89	1.26	0.26
0.25	Atomic%	58.68	0.28	39.03	0.68	0.06
	Weight%	71.84	0.24	27.22	1.95	0.02

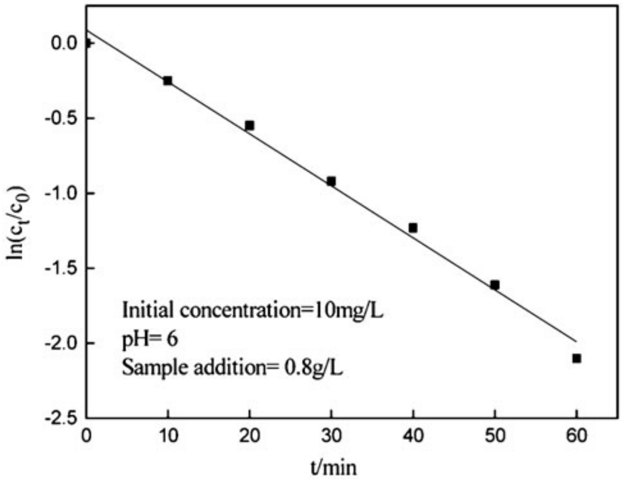

Fig. 4. Kinetic data for the reduction of MB.

3.7. Mechanism study of MB degradation by NZVI–MCM-48 composite material

Iron, which is an active metal and has an electrode potential of E (Fe^{2+}/Fe) = –0.440 V will replace the metals behind it on the metal activity sequence table and get them to deposit on iron surface. It can also reduce ions or compounds and some organic matters with strong oxidability. Fe^{2+} ions have reducibility and an electrode potential of E (Fe^{3+}/Fe^{2+}) = 0.771 V. Therefore, when there is an oxidizer in water, Fe^{2+} can be further oxidized to Fe^{3+}. When the mixed particles of cast iron with impurities or pure iron and carbon are immersed in aqueous solution, countless tiny primary cells will form between iron and carbon, or other elements. The electrode reaction is as follows:

$$\text{Anodic reaction}: \mathrm{Fe} - 2\mathrm{e} \rightarrow \mathrm{Fe}^{2+},$$

$$E^\circ(\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.440\,\mathrm{V};$$

$$\text{Cathodic reaction}: 2\mathrm{H}^+ + 2\mathrm{e} \rightarrow 2[\mathrm{H}] \rightarrow \mathrm{H}_2\uparrow,$$

$$E^\circ E(\mathrm{H}^+/\mathrm{H}_2) = 0.00\,\mathrm{V};$$

When there is dissolved oxygen in water:

$$\mathrm{O}_2 + 4\mathrm{H}^+ + 4\mathrm{e} \rightarrow 2\mathrm{H}_2\mathrm{O}, \quad E^\circ(\mathrm{O}_2) = 1.23\,\mathrm{V},$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e} \rightarrow 4\mathrm{OH}^-, \quad E^\circ(\mathrm{O}_2/\mathrm{OH}^-) = 0.40\,\mathrm{V}$$

As iron is an active metal and has the ability of reduction in a meta-acid aqueous solution, it will directly reduce the dye to amino organic matter. The conjugated system of dye is thus destructed and the chromaticity of wastewater is then decreased.

In wastewater treatment under a meta-acid condition, a great number of Fe^{2+} and Fe^{3+} will be produced. When the pH is adjusted to alkali value and there is oxygen, the flocculent precipitation of $Fe(OH)_2$ and $Fe(OH)_3$ will form and $Fe(OH)_3$ may be hydrolyzed to $Fe(OH)^{2+}$ and $Fe(OH)^+$ ions, which have a very strong flocculation property. The treatment of dye wastewater by NZVI is the joint effect of reduction, coagulation, and adsorption.

The mechanism of decolorization is analyzed as follows. When NZVI particles contact with the dye solution under a proper condition, the conjugated system of dye molecules will break, thus destructing the original chromophoric group or auxochrome group of the dye so as to achieve decolorization. It is inferred that the decolorization reaction proceeds in this way:

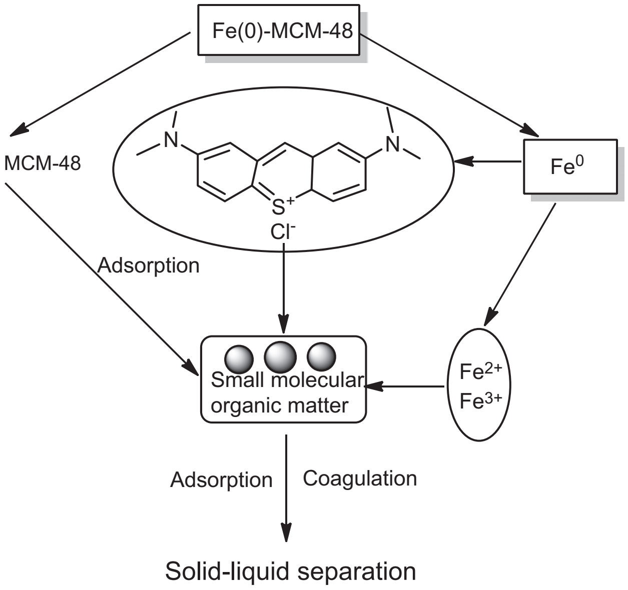

Fig. 5. Molecular structure of MB and the reaction mechanism of catalysis and reduction of NZVI.

1. NZVI adsorbs the dye molecules to the surface and pore cannel of the composite material and transfers two electrons to the hard-to-degrade organic molecule, turning the C=C bond on the benzene ring to –CH and having it reduced and broken [14];
2. NZVI reacts with water molecule to form atomic H, and under the catalysis of NZVI, H reduces MB. Under these two mechanisms, though NZVI is consumed, it plays a role of a catalyst [15]; The decolorization process is shown in Fig. 5. The breaking of C=C bond destructs the integral conjugated chromophoric group of the dye molecule and therefore, the catalyst and reduction technology of NZVI–MCM-48 composite material has a good effect in the decolorization of the dye wastewater.

4. Conclusions

1. This experiment has successfully prepared Fe^0/MCM-48 composite material. It can be known from the XRD result that the sample has an extremely excellent cubic structure. With the increase of iron load, more diffraction peaks occur. The existence of ordered mesoporous MCM-48 can protect NZVI from oxidation by air at the ambient temperature.

(2) It is known from the TEM observation of NZVI–MCM-48 composite material that there is an evident ordered mesoporous structure in the sample. The increase of iron load can lead to a certain degree of destruction of material's ordered structure as well as a lower orderliness of the composite material's mesoporous structure. It also results in many tiny iron crystals in the ordered mesoporous silicon oxide.

(3) The SEM analysis indicates that the composite material has no regular form and size. The EDS analysis shows that the composite material is mainly composed of Si, Fe, O, and Na, of which, Si, O, and Na are the main elements of MCM-48, while the Fe content varies in line with the change in the amount of iron source.

(4) It is known from the orthogonal degradation experiment of MB by NZVI–MCM-48 composite material that the decolorization rate of MB is 853 mg/g and the COD removal rate is 821 mg/g under optimal conditions including an initial concentration of wastewater of 10 mg/L, an initial pH of 6, a concentration of the added sample of 0.8 g/L, and a reaction time of 60 min.

(5) The treatment of dye wastewater by NZVI–MCM-48 composite material is the result of a joint effect of reduction, coagulation, and adsorption. Fe^0/MCM-48 composite material can destruct the conjugation system of the dye molecules through catalysis and reduction functions and thus achieves decolorization.

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