

Degradation of methyl orange by Zn(0) assisted with silica gel

Jing Guo, Danjun Jiang, Yong Wu, Pei Zhou, Yeqing Lan*

College of Sciences, Nanjing Agricultural University, Nanjing 210095, PR China

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ABSTRACT

The degradation of methyl orange (MO) by Zn(0) assisted with silica gel was investigated under different conditions. The results show that the degradation of MO by Zn(0) alone was slow and incomplete due to the rapid corrosion of Zn(0) particles on surface. However, the degradation of MO can be markedly enhanced when Zn(0) and silica gel coexist, even under neutral and alkaline conditions. MO removal was improved with a pH decrease, an increase of the initial amount of silica gel and Zn(0), and specific surface area of silica gel. The degradation of MO by Zn(0) assisted with silica gel can be described by a pseudo-first-order kinetic. And the surface of Zn(0) before and after the reaction was characterized by the microscopic analysis of morphology, revealing the potential mechanism responsible for the enhanced reactivity of silica gel.

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1. Introduction

Azo dyes, which contain one or more nitrogen to nitrogen double bonds ($-N=N-$) linking substituted aromatic structures, contribute to about 70% of all used dyes in industries such as textiles, food-stuffs and leather [1]. It is of particular concern considering that they are known to have mutagenic and carcinogenic effects [2]. Over 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents as industrial wastewater into the environment [3]. Due to the aromatic character of most dye molecules and the stability of π conjugated system formed with benzene rings and nitrogen to nitrogen double bonds, the release of these colored wastewaters poses a serious threat to the environment [4,5]. Therefore, the degradation of azo dyes for environmental treatment is receiving increasing attention. Many treatment methods including biological, physical and chemical techniques enhance the removal of dyes to varying degrees [6–9].

The use of zero-valent metals (ZVMs) for removal of contaminants from environment has been well studied for a long time, and the most significant use of ZVMs is permeable reactive barrier (PRB) containing granular zero-valent iron (ZVI), which relies on reduction to degrade chlorinated solvents and other groundwater contaminants [10,11]. Extensive studies on the environmental

applications of reduction by ZVMs have focused on remediation of wastewater and soil contaminated with chlorinated organic compounds (COCs) [12–17], nitrate and nitrite [18,19], nitro aromatic compounds [20], and various metals [21–23]. And in recent years, it has been suggested that ZVMs showed reduction of critical functional groups in complex organic compounds including pesticides [24,25], herbicides [26], and azo dyes [27–29]. Although most research on contaminant degradation by ZVMs has been focused on iron [22–29], other metals have been studied, especially zero-valent zinc (ZVZ) [13,17], which is a stronger reductant than iron [30]. Treated by ZVZ, dye waste waters can be decoloured, and the products (aromatic amine) are easily degraded by microorganisms [27].

However, since waste removal by ZVZ is a corrosive process, the formation of passivating scales such as Zn(II)(hydr)oxides on the surface of Zn(0) particles over time with the rise of pH may limit its long-term reduction potential by blocking the active sites on Zn(0) surface, which causes a rapid decrease in reduction activity by inhibiting access of targets to Zn(0) surface, especially at a high pH [13]. In order to enhance the extent and rate of degradation, some new methods have been exploited. Nano-scale zero-valent metals have been used to treat organic pollutants in the environment [23,29], because of their large surface area-to-volume ratio and high reactivity. Bimetallic reductants have been developed recently, which incorporate a second zero-valent metal such as Al, Ni, Pt, Cu or Pd onto the zinc surface as a catalyst [31–33]. In addition, some other researches perform in the presence of ultrasound [34,35], some electroenhancement, photoenhancement etc. [10].

The application of nano-scale zero-valent metal, bimetallic and ultrasound systems are capable of removing organic pollutants, but may be costly or difficult to operate in many situations. The

* Corresponding author. Tel.: +86 25 84396697; fax: +86 25 84395255.
E-mail address: lanyq102@njau.edu.cn (Y. Lan).

aim of this study is to investigate the reductive degradation process of methyl orange (MO) by low-cost micro-scale zinc powder in the presence of micro-scale silica gel at the pHs ranging from 4 to 10 at 25 °C. MO was selected as the model pollutant since it is a typical azo dye with a mono-azo group that is widely used in the textile industry. Silica gel powder, whose principal component is $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, is environmentally benign and costs low, and widely used for chromatography or as catalyst supporter [36,37]. The effects of the Zn(0), silica gel and MO dosage or initial concentration also will be studied; the surface of Zn(0) before and after the reaction will be characterized by the microscopic analysis of morphology, revealing the potential mechanism responsible for the enhanced reactivity of micro-scale silica gel. The enhancement effects of silica gel in reductive degradation of azo dye by Zn(0) have never been reported.

2. Materials and methods

2.1. Materials

Methyl orange (industrial grade) was purchased from Beijing Chemical Reagents Company. The stock solution (1000 mg/L) of methyl orange was prepared in deionized water. Micro-scale zinc particles (analytical grade) were obtained from the Development Center of Kemiou Chemical Reagent, Tianjin, China. And silica gel (reagent grade) was supplied from Jiyida Silica Reagent Company.

All the stock solutions were stored in a refrigerator at 4 °C in the dark prior to use. And all glassware used in the experiments was cleaned by soaking in 1 M HCl for 12 h and thoroughly rinsed with tap water and then deionized water.

2.2. Pretreatment of Zn particles

To remove oil film and oxides on the Zn surface that may affect the removal of MO, the Zn particles were treated with 0.4% H_2SO_4 , and then rinsed with deionized water for five times to remove residual H_2SO_4 . The cleaned Zn particles were dried in a vacuum oven at 60 °C for 2 h and then stored in a desiccator, kept sealed.

2.3. Characterization of Zn particles

The specific surface area of zinc particles, measured using Brunauer–Emmet–Teller gas adsorption isotherm with N_2 gas on a JW-004 surface area analyzer (Beijing Jing Wei Gao Bo), was 2.3 m^2/g . The surface morphological analysis of Zn particles before and after reaction was performed on a scanning electron microscope with a JEOLJSM-6380LV microscope at a 30 kV beam potential.

2.4. MO removal experiments

All batch experiments for MO degradation were conducted in 100 mL glass bottles. The solution was adjusted with diluted NaOH and H_2SO_4 to desired pH, and the final volume was 50 mL (with 50 mg/L MO). Then, the desired amount of silica gel and pre-cleaned ZVZ was added into the reaction solution immediately. The reaction bottles were sealed with rubber plugs and placed in a shaking water bath (BS-31, SIM Company) at 25 ± 0.1 °C and 180 rpm. Control experiments (no silica gel) were also performed under the same conditions. To investigate the influence of the passive film of Zn(II)(hydr)oxide on MO degradation in the presence of dissolved O_2 , the reaction systems had about 50 mL headspace occupied by air, and none of the solutions was degassed with N_2 .

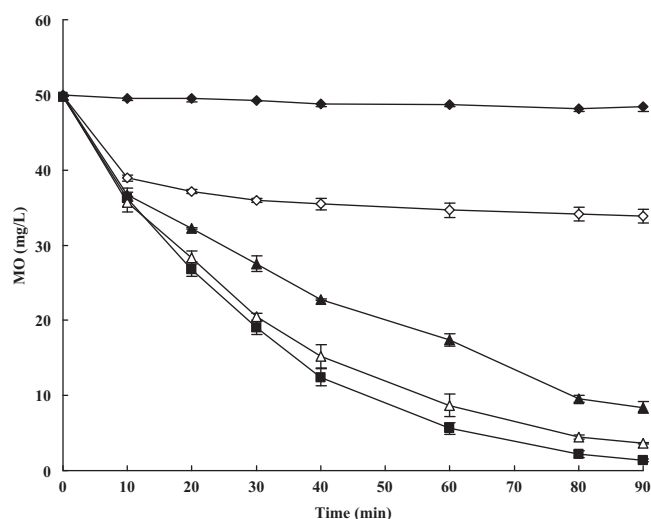


Fig. 1. Degradation of MO in different systems. Initial conditions: $T = 25$ °C, $\text{pH} = 4$, $c(\text{MO}) = 50$ mg/L, $\text{Zn}(0)$ loading = 0.5 g/L, silica gel loading = 5 g/L. (◆) MO + silica gel; (◇) MO + Zn(0); (▲) MO + Zn(0) + silica gel (60–100 mesh); (△) MO + Zn(0) + silica gel (200–300 mesh); (■) MO + Zn(0) + silica gel (300–400 mesh).

The pHs during the process of the reaction were measured with a CyberScan pH2100 Bench Meter (Eutech Instruments), after three-point calibration.

All the experiments in this section were performed in triplicate.

2.5. Analytical methods

At given time intervals, 3 mL aliquot of sample was removed with a syringe and immediately filtered through a 0.45 μm membrane filter to a clean and dry glass tube to determine MO concentration. Samples were analyzed by the UV–vis spectrometer (Beijing Ruili Corp, UV-9100) immediately at the characteristic λ_{max} of 460 nm at pH 4–10 and the λ_{max} remains stable in this pH range. UV–vis spectra showing MO degradation in a 1-cm quartz cell were also recorded by a spectrophotometer (Shimadzu 1700). Total organic carbon (TOC) was monitored using a Shimadzu-5000 TOC analyzer.

3. Results and discussion

3.1. Effect of silica gel on degradation of MO

The reductive degradation of MO was conducted under different conditions. The results presented in Fig. 1 showed no noticeable change in MO concentration in the system containing MO and silica gel, indicating that the loss of MO resulted from the adsorption onto silica gel could be ignored.

The degradation efficiency of MO by Zn(0) in 90 min was 32.09%. The reductive degradation of MO by Zn(0) was suggested to the following two pathways [38]. According to Eq. (1), MO molecule was adsorbed on the surface of Zn(0) particles, and two electrons were transferred from Zn(0) to the refractory organic molecule, the nitrogen to nitrogen double bonds ($-\text{N}=\text{N}-$) were broken. In Eq. (2), zero-valent zinc first reacts with water molecules in the reaction system and generates atomic hydrogen which is able to reduce MO to aromatic amine in the presence of ZVZ as a catalyst.

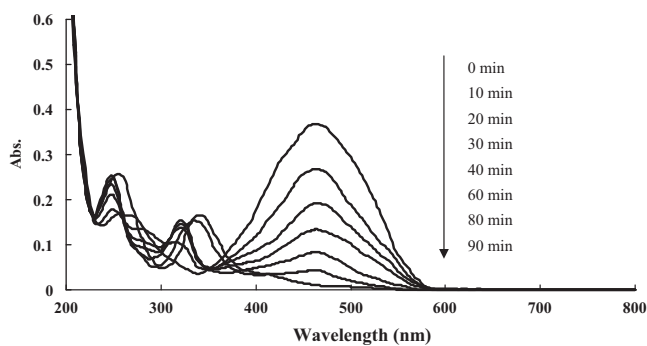
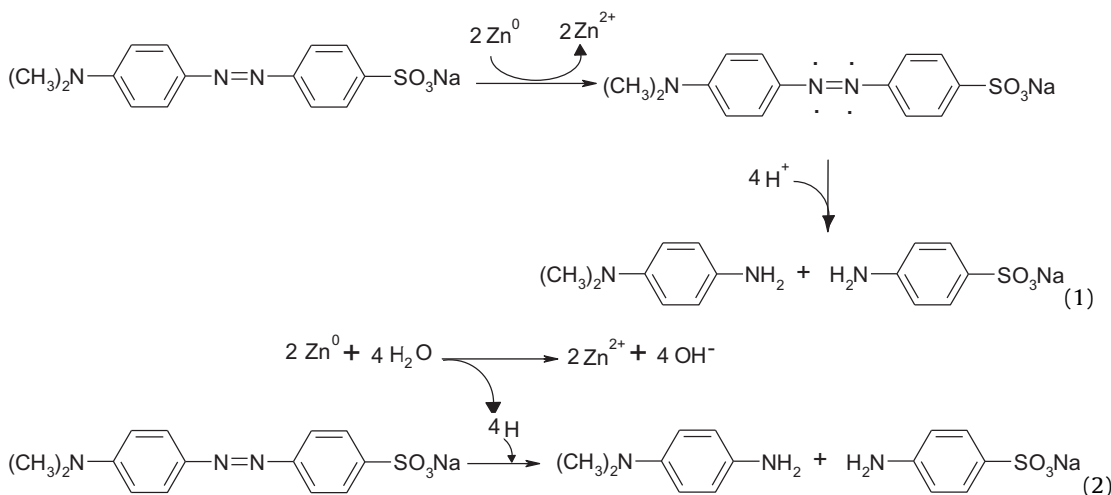


Fig. 2. UV-vis spectra record for MO degraded by Zn(0) assisted with silica gel. Initial conditions: $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 4$, $c(\text{MO}) = 50\text{ mg/L}$, $\text{Zn}(0)$ loading = 0.5 g/L , silica gel loading = 5 g/L .

And the biodegradability of the main product aromatic amine has been greatly improved as compared with that of MO [27].

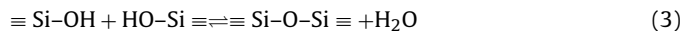


Both Eqs. (1) and (2) indicate that H^+ was consumed. And it can be seen from Fig. 1 that the degradation rate decreased dramatically as precipitates such as Zn(II)(hydr)oxides form and coat on the surface of Zn(0) particles with the rise of pH, inhibiting access of targets to active sites on Zn(0) surface. Therefore, micro-scale zinc powder alone was insufficient to decompose this dye.

In the MO/Zn(0)/silica gel ternary system, the color removal is much more efficient, and the degradation efficiency reached 83.16, 92.65 and 97.04%, respectively in 90 min with 60–100, 200–300 and 300–400 mesh silica gel, whose specific surface area was 289.36, 403.59 and 495.27 m^2/g , correspondingly. The removal rate of MO was obviously enhanced with the increased specific surface area of silica gel, and the 300–400 mesh silica gel was selected for the following studies.

In Fig. 2, we observed that the visible absorbance of degradation solution becomes lower, and that the characteristic UV absorption wavelengths shift to the longer wavelength. The absorbance at 460 nm decreased from 0.370 to near zero, and the characteristic wavelength shifts from 230 to 246 nm with the continuing of the reaction because of the destruction of nitrogen to nitrogen double bonds ($-\text{N}=\text{N}-$) and the generation of aromatic amine. When the azo dye is reduced, the azo double bond is destroyed, and the absorbance caused by the azo group (460 nm) becomes lower. Products (substituted aromatic amine) form and increase in quantity with the reaction. Consequently, the characteristic absorption of the products appeared and became significant. As an auxochrome, the amino-group caused the wavelength to shift to the longer area.

Silica gel has been used as an alternative of polysilicic acid particles [39]. Polysilicic acid consists of silica tetrahedrons that are linked via silicon–oxygen–silicon bonds. Its formation can be described according to the equation [40]:



In natural river and seawater, polysilicic acid decomposes to monomer within a few hours or days, and at equilibrium with amorphous silica polysilicic acid become stable beginning with pH 10 and monomeric species dominates over a wide range of pH, especially at low pH [41].

The enhancement of MO degradation by Zn(0) in the presence of silica gel is ascribed to the formation of polysilicic acid sol in aqueous system and then depolymerized to silicic acid, which is a weak acid gradually discharged into the reaction system to prevent forming passive films of Zn(II)(hydr)oxides on the Zn(0) surfaces. The assumption was confirmed by the analysis of the surface morphology of the zinc particles before and after the reaction. It is observed from the SEM images (Fig. 3) that there is an obvious difference between un-reacted and reacted zinc powder. Fig. 3 shows that

the pristine zinc particles were uniformly distributed in size and shape. The residual zinc particles collected at the end of 90-min-reaction in the absence of silica gel were aggregated and coated with Zn(II)(hydr)oxides on the surface. However, the residual zinc particles in the presence of silica gel exhibited stratiform structure, which means they were effectively consumed along their edges and a passive film of Zn(II)(hydr)oxides did not form on the surface of ZVZ during the reaction.

Oh et al. [42] claimed that the role of silica in the enhanced removal of Cr(VI) by ZVI was a scavenger for reaction precipitates as well as its pH buffering effect. With larger specific surface area, it was presumed that the affinity of silica gel to reaction products including Zn(II)(hydr)oxides was greater.

Furthermore, a small amount of poly-zinc silicate (PZSS) which is a new type of coagulant and has been widely used to purify drinking water and wastewaters in various industries because of its non-toxicity and specific characteristics of the charge-neutralization and the bridging effect may be produced in this system [43,44]. The flocculation of PZSS may contribute to the increased removal of MO.

3.2. TOC analysis

Generally speaking, the mineralization process is incomplete both in the two-component system with MO and Zn(0) and in the MO/Zn(0)/silica gel ternary system, and the possible reason is due to the fact that substituted aromatic amine is the main product.

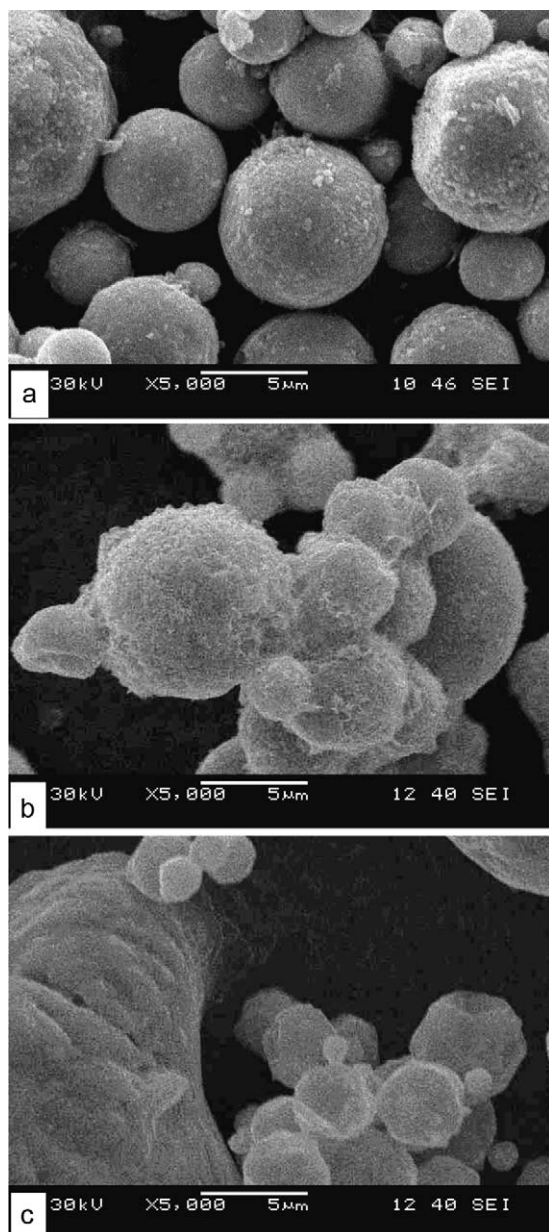


Fig. 3. Surface morphological analysis of Zn particles by scanning electron microscope with a JEOLJSM-6380LV microscope at a 30 kV beam potential: (a) the surface of pristine acid-washed Zn; (b) the surface of residual Zn alone after 90-min reaction; (c) the surface of residual Zn in the presence of silica gel after 90-min reaction.

However, compared with two-component system as shown in Fig. 4, there is a distinct increase in TOC removal with an addition of silica gel. It is enhanced from 12.17% in the absence of silica gel to 29.67% in the presence of silica gel in 90-min-reaction, from 14.28 to 36.49% in 180-min-reaction, and from 17.72 to 44.00% in 360-min-reaction. The increase of TOC removal in MO/Zn(0) system is not significant with reaction time, while in the ternary system it is marked even after the complete decoloration reaction. As previously discussed, it may be due to the fact of a small amount PZSS produced in the system containing polysilicic acid and zinc ions.

3.3. Effect of pH on degradation of MO by Zn(0) assisted with silica gel

The degradation of MO was conducted in a pH range of 4–10 with the initial concentrations of MO (50 mg/L), Zn(0) loading (0.5 g/L),

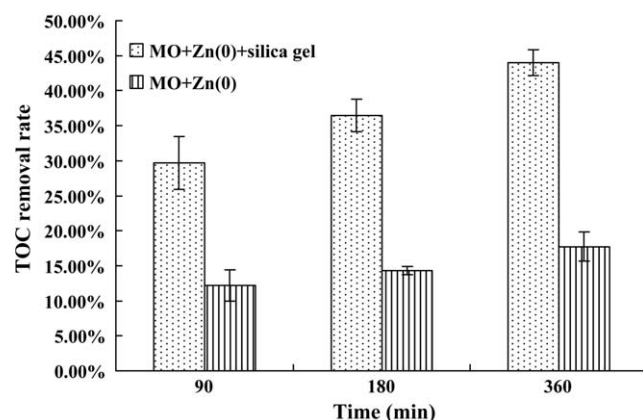


Fig. 4. Comparison of TOC removal in the degradation of MO by Zn(0) particles in the presence and absence of silica gel. Initial conditions: $T=25^{\circ}\text{C}$, $\text{pH}=4$, $c(\text{MO})=50\text{ mg/L}$, $\text{Zn}(0)$ loading = 0.5 g/L, silica gel loading = 5 g/L.

silica gel loading (5 g/L) at 25°C , and the results are illustrated in Fig. 5. It is observed that higher pH leads to lower degradation efficiency. Since the reductive degradation of MO by Zn(0) is a process of consuming H^{+} (Eqs. (1) and (2)), lower pH will benefit the removal of MO. In the presence of silica gel, the removal of MO by Zn(0) can be carried out even in neutral and alkaline initial conditions. However, in the absence of silica gel the removal of MO is negligible at pH 7 and 10.

Table 1 shows the pH change during the reaction. The solution pH increased rapidly in the initial 20-min reaction and then rose slowly under acidic initial conditions. At pH 4 in the absence of silica gel, the pH change during the reaction is closely related to the degradation of MO (see Fig. 1), the solution pH rapidly increased from the initial 4 to 6.47 in 10 min, that is, much H^{+} was consumed in the conversion of Zn(0) to Zn^{2+} during this reaction stage, in correspondence with the relatively high MO degradation rate (Fig. 1). While the solution pH increased slowly during the later reaction stage, and the degradation rate decreased accordingly.

In the presence of silica gel, the production of silicic acid, a weak acid, behaved nearly as a buffer (Eq. (4)) [42], and the measured solution pH, ranging from 6.4 to 7.7, is in good agreement with

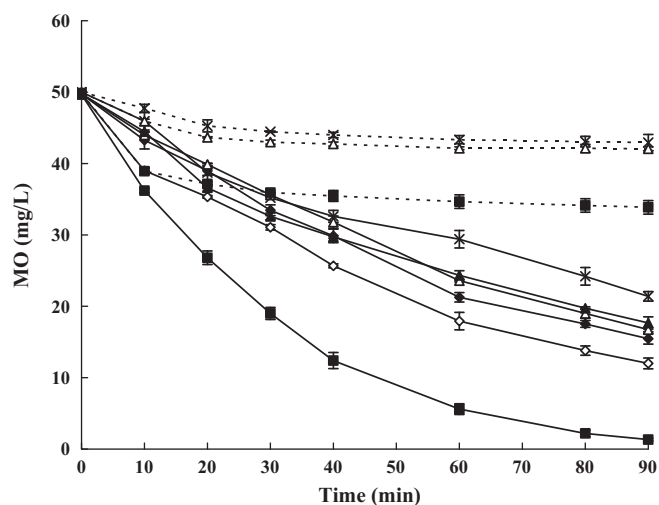


Fig. 5. Effect of pH on the degradation of MO by Zn(0) alone (dotted line) and assisted with silica gel (solid line). Initial conditions: $T=25^{\circ}\text{C}$, $c(\text{MO})=50\text{ mg/L}$, $\text{Zn}(0)$ loading = 0.5 g/L, silica gel loading = 5 g/L. (■) pH 4; (◇) pH 5; (◆) pH 6; (△) pH 7; (▲) pH 8; (×) pH 10.

Table 1
Solution pH change during degradation of MO by Zn(0). Initial conditions: $T = 25\text{ }^{\circ}\text{C}$, $c(\text{MO}) = 50\text{ mg/L}$, $\text{Zn}(0)$ loading = 0.5 g/L, silica gel loading = 5 g/L.

0 min	10 min	20 min	30 min	40 min	60 min	80 min	90 min
4 ^a	6.47	7.11	7.16	7.23	7.25	7.31	7.33
4	6.40	6.52	6.59	6.64	6.75	6.86	6.91
5	6.45	6.58	6.74	6.83	7.03	7.15	7.22
6	6.68	7.16	7.27	7.27	7.34	7.37	7.43
7 ^a	7.28	7.34	7.45	7.49	7.37	7.14	7.05
7	6.94	7.06	7.20	7.21	7.30	7.33	7.45
8	6.90	7.26	7.34	7.43	7.48	7.55	7.56
9	7.30	7.29	7.32	7.42	7.47	7.51	7.63
10 ^a	10.06	10.11	9.86	9.70	9.63	9.47	9.39
10	7.29	7.49	7.55	7.61	7.64	7.66	7.68

^a Without silica gel.

expected buffering capacity ($\text{pK}_a = 6.8$). Under alkaline conditions, the solution pH rapidly decreased at the initial reaction stage and then leveled off, which may result from the simultaneous action of the pH buffering effect of silica gel and the consumption of OH^- according to Eqs. (5) and (6).



As is shown in the supporting information offered by Salter-Blanc and Tratnyek [45] and the analysis of species distribution of Zn(II) obtained by MINEQL + 4.6 [13], the dominant Zn(II) solid

phase is much zincite (ZnO) and some zinc hydroxide ($\text{Zn}(\text{OH})_2$), which is present over a range of relevant pHs under neutral and alkaline conditions. The surface analysis described in Section 3.1 confirms that ZnO is present on the surface. As a result, Eqs. (5) and (6) may also contribute to explain the decreased trend of solution pH during the latter reaction at pH 7 and 10 without silica gel.

It is noticed from Table 1 that all the solution pHs in the presence of silica gel keep near-neutral during the whole reductive degradation of MO, which is of environment-significance.

3.4. Effect of initial amount of silica gel and Zn(0)

The effect of initial amount of silica gel and Zn(0) on degradation of MO by Zn(0) assisted with silica gel was investigated at pH 4 and $25\text{ }^{\circ}\text{C}$. The results shown in Fig. 6 indicate that the increase of initial amount of silica gel and Zn(0) in the ternary system can greatly improve the degradation efficiency. The degradation efficiency increased from 56.42% at 1 g/L silica gel loading to 97.73% at 7 g/L silica gel loading. As previously pointed, a passive film of Zn(II)(hydr)oxides on the surface of Zn(0) will not form when silica gel is in excess, which results in a fast and efficient reduction of MO. The high H^+ buffer capacity at high amount of silica gel is another factor. The enhancement of degradation by the addition of more Zn(0) is due to the increased active sites of the metal surface exposed to targets. In addition, more silica gel and Zn(0) result in increasing production of the flocculant PZSS. Hence, proper amount of silica gel and Zn(0) is a critical factor in establishing optimal efficiency of MO degradation. It is concluded from the results in Fig. 6 that 5 g/L silica gel and 0.5 g/L Zn(0) is suitable to obtain satisfied removal of MO.

Table 2
Pseudo-first-order rate constants (k) of MO degradation by Zn(0) assisted with silica gel.

Initial pH	k (min^{-1})	R^2
<i>(a) At different initial pHs</i>		
4	0.0404	0.9942
5	0.0156	0.9958
6	0.0132	0.9964
7	0.0122	0.9980
8	0.0113	0.9915
10	0.0089	0.9830
<i>(b) With different initial amount of silica gel</i>		
7	0.0408	0.9930
5	0.0404	0.9942
3	0.0261	0.9924
1	0.0087	0.9649
0 ^a	0.0040	0.9892

^a Data from an initial period of 30-min-reaction.

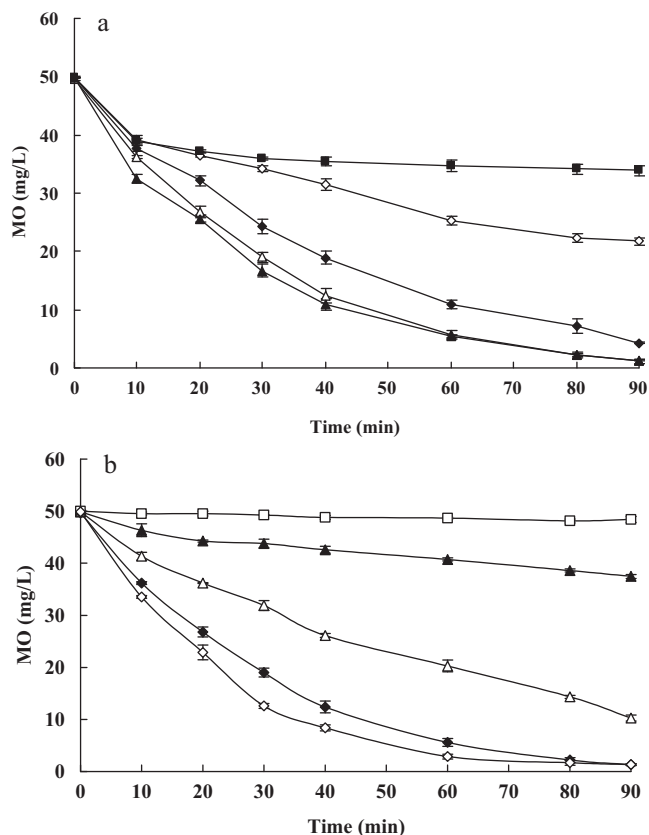


Fig. 6. Effect of initial amount of silica gel (a) and Zn(0) (b) on degradation of MO by Zn(0). Initial conditions: $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 4$, $c(\text{MO}) = 50\text{ mg/L}$. Effect of initial amount of silica gel with an initial amount of 0.5 g/L Zn(0) (a): (■) 0 g/L; (◇) 1 g/L; (◆) 3 g/L; (△) 5 g/L; (▲) 7 g/L. Effect of initial amount of Zn(0) with an initial amount of 5 g/L silica gel (b): (□) 0 g/L; (▲) 0.1 g/L; (△) 0.3 g/L; (◆) 0.5 g/L; (◇) 0.7 g/L.

3.5. Degradation kinetics of MO by Zn(0) assisted with silica gel

In this study, negative natural logarithm of $c(\text{MO})/c_0(\text{MO})$ was used as a function of time to study the degradation kinetics of MO in the presence of Zn(0) and silica gel.

$$-\ln \left[\frac{c(\text{MO})}{c_0(\text{MO})} \right] = kt \quad (7)$$

The rate constants (k) and regression coefficients (R^2) obtained from systems with different initial pHs and different initial amount of silica gel are listed in Table 2. All the curves are linear with fine linear dependence ($R^2 > 0.96$), suggesting that the degradation of MO by Zn(0) assisted with silica gel can be described by a pseudo-first-order kinetic. Decreased pH and more silica gel led to the increased rate constants of degradation of MO.

4. Conclusions

Methyl orange cannot be effectively removed by micro-scale Zn(0) particles alone because of the formation of a passive film on the metal surface in an aqueous system. The degradation rate of methyl orange can be markedly improved when Zn(0) and silica gel coexist, even in neutral and alkaline conditions, and the solution pHs all keep near-neutral during reductive degradation of MO in different initial pH conditions. Such behaviors exert beneficial effects in wastewater treatment. The enhancement of MO degradation in the presence of silica gel was attributed to the good dispersion and supporter role of silica gel, silicic acid produced generally to prevent forming passive films of Zn(II)(hydr)oxides on the Zn(0) surfaces and a small amount PZSS which is a new type of flocculant generated in the reaction system.

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