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Heterogeneous Fenton-like degradation of methylene blue (MB) by magnetic nanoparticles Fe_3O_4@TiO_2 in neutral condition

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Abstract. The traditional Fenton system (Fe^{2+}–H_2O_2) only works in an acidic environment and produces a large quantity of sludge. In this study, magnetic nanoparticles Fe_3O_4@TiO_2 were used as a high-performance Fenton-like catalyst for the degradation of MB. The surface morphology was characterized by Transmission Electron Microscopy (TEM). And the Fenton-like catalytic activity of Fe_3O_4@TiO_2 was evaluated under different pH condition and various H_2O_2 in feed concentration, respectively. The results indicated that nanoparticles Fe_3O_4@TiO_2 show high efficiency for methylene blue (MB) degradation under the reaction condition of H_2O_2 40mM, Fe_3O_4@TiO_2 20mM, MB 300mg/L, pH 7 and 30℃, the mineralization of persistent MB can achieve 72% COD removal ratio.

1. Introduction

Wastewater produced by chemical industry, textile industry and leather manufacturing, often contains considerable amounts of organic pollutants, which can cause negative impacts for ecosystems and humans for their toxicity, carcinogenic or mutagenic properties. Therefore, it is significant to degrade the organics in wastewater before discharge [1]. Fenton oxidation is one of the simplest and most efficient AOPs in environment remediation. However, one disadvantage of this method is that the reaction achieves its high activity at relatively low pH range, usually at approximate pH=3, which is not beneficial for the chemical equipment and operation. In addition, the wastewater after treatment is preferred to be neutralized before discharge, so a large amount of slurry will be produced, which causes the problem of solid waste for further treatment and greatly increasing the running cost.

In recent years, heterogeneous Fenton-like catalysts, such as iron-based clays and zeolites, and iron oxide minerals [2, 3], have received considerable interests due to their advantages of facile recovery and recycling as well as dramatically decreased slurry. And among these catalysts, Fe_3O_4 nanoparticles not only have unique characteristic of magnetic feature but also showed higher reactivity in neutral condition. For example, when the concentrations of Fe_3O_4 and H_2O_2 were 5g/L and 1.2M, phenol and aniline could be removed completely after 6h at 308K. However, it is found that the total organic carbon abatement efficiency for phenol and aniline were only 42.79% and 40.38%, respectively [4].

Recently, TiO_2 coupled with iron oxide has been reported to have a good magnetic response and displayed high photocatalytic efficiency [5-7]. In this work, we have successfully synthesized the Fe_3O_4@TiO_2 NPs, which were applied to the Fenton-like degradation of methylene blue (MB) as a model of recalcitrant contaminants. The effects of operational parameters as concentrations of catalyst and H_2O_2, and pH value on the degradation efficiency of TC were systematically evaluated.

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Extraordinarily high and stable catalytic activity has been achieved on Fe_3O_4@TiO_2 with a wide working pH range of 5–9.

2. Materials and methods

2.1. Reagents
All reagents used in the experiments were of chemical reagent grade and used without further purification. 30% (w/w) hydrogen peroxide, ferrous sulfate ($FeSO_4$•$7H_2O$), titanium tetrachloride ($TiCl_4$), NH_3•H_2O (25%, w/w), H_2SO_4 and NaOH were obtained from Beijing Chemicals Corporation (Beijing, China).

2.2. Fe_3O_4@TiO_2 MNPs preparation
Fe_3O_4@TiO_2 MNPs were prepared by coprecipitation of Fe^{2+} and Ti^{4+} in aqueous solutions. In a typical procedure, 0.06mol/L $FeCl_3$ and $TiCl_4$ solutions were mixed uniformly, and then dilute alkaline solution was added drop wise to the solution. After 2h vigorous stirring under an Ar stream, the black particles were deposited and separated from solution by a powerful magnet, washed with de-ionized water and ethanol to neutral pH. Then Fe_3O_4@TiO_2 MNPs were dried under vacuum and stored in the desiccator for further experiments.

2.3. Experimental procedure
Fe_3O_4@TiO_2 MNPs was dispersed in 100mL MB solution. And the specific pH of MB solution was adjusted with solutions of H_2SO_4 or NaOH. Degradation of MB was initiated by adding a desired dosage of H_2O_2. Then the mixture was vibrated 250rpm at 30℃. At selected time intervals, Ailquots were collected and sediment were separated by magnetic separation. The concentration of MB was determined after Na_2SO_3 was added to quench excess H_2O_2.

2.4. Characterization of Fe_3O_4@TiO_2 MNPs
TEM images were conducted with a CM200 transmission electron microscope.

3. Results and discussion

3.1. Characterization of Fe_3O_4@TiO_2 MNPs

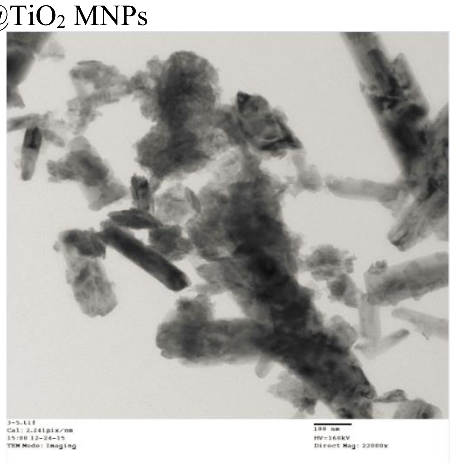

Fig.1. TEM image of synthesized Fe_3O_4@TiO_2 MNPs

Fig. 1 displays TEM images of Fe_3O_4@TiO_2 MNPs samples. It can be seen that the obtained Fe_3O_4@TiO_2 MNPs are plane particles, which show great difference from uniform spherical of Fe_3O_4 MNPs. And the particle size is about 20nm, which has good consistency with samples' XRD results.

3.2. Effect of Fe_3O_4@TiO_2 MNPs amounts

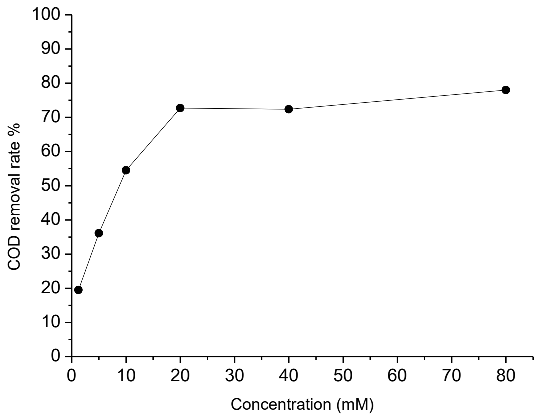

Fig.2. Effect of Fe_3O_4@TiO_2 MNPs on COD removal efficiency at pH7.

Fig. 2 illustrates the effect of Fe_3O_4@TiO_2 MNPs amounts on the COD removal rate with initial MB 300mg/L and H_2O_2 dosage 40mM at pH=7 and T=30℃. It is found that with the increased addition of Fe_3O_4@TiO_2 MNPs from 1.25mM to 80mM, COD abatement efficiency also increased from 20% to 78%. The extra catalytic activity by Fe_3O_4 MNPs is related to the increased amount of active sites on Fe_3O_4@TiO_2 surface. Because more active sites in reaction system can accelerate more production of HO•, MB can be degraded with improved efficiency.

3.3. Effect of H_2O_2 concentration

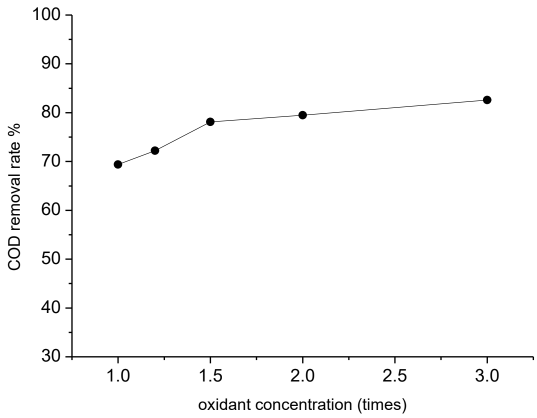

Fig.3. Effect of H_2O_2 dosage on COD removal efficiency at pH7

Fig. 3 indicates that the optimal H_2O_2 concentration is about 40 mM for the MB degradation on Fe_3O_4@TiO_2 MNPs at pH=7 and T=30 ℃. It is clear that COD removal rate changed slowly from 69% to 83% with increased H_2O_2 concentration in the range of 40-120mM. And the existence of optimum H_2O_2 concentration is related to the effect of excessive H_2O_2. Because of its scavenging effect on OH radicals, efficiency of OH radicals decreased in the solution so that H_2O_2 oxidation efficiency also decreased.

3.4. Effect of pH

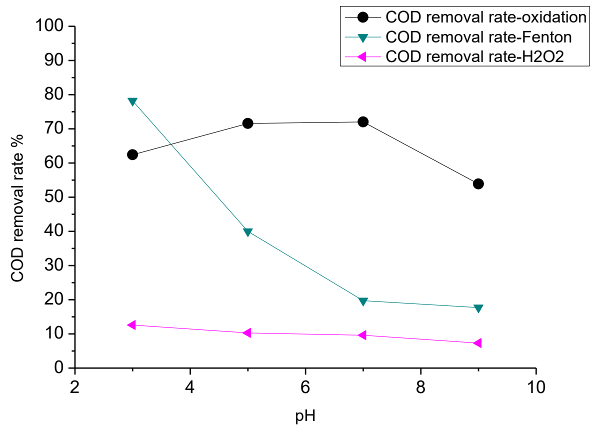

Fig.4. Catalytic oxidation effect of MB analogues at different pH

The degradation of MB under different pH values was evaluated as shown in Fig.4. It is found that the COD abatement efficiency was less than 10% with only 40mM H_2O_2, which is ascribed to the weak oxidation potential of H_2O_2 compared with hydroxyl radicals. In the typical Fenton reaction, the maximum78% COD removal rate was observed with the initial parameters of pH=3. But the efficiency decreased with the increased pH, which is consistent with the usual Fenton reaction. However, the highest degradation of MB, about 72% COD removal rate, was achieved in the Fenton-like system catalyzed by Fe_3O_4@TiO_2 MNPs at pH=7. Therefore, it is reasonable to consider that SiO_2 coated on Fe_3O_4 could effectively enhance the catalytic activity of Fe_3O_4.

4. Conclusion

Highly active Fe_3O_4@TiO_2 MNPs were successfully synthesized by co-precipitation method, and used as heterogeneous Fenton-like catalysts that can degrade MB from aqueous solution efficiently. Unlike the traditional Fenton process, the COD removal efficiency remained relatively high at a wide pH range from 5~9 for MB.

Acknowledgements

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