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TiO_2-mediated photocatalytic degradation of Orange II with the presence of Mn^{2+} in solution

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Abstract

The photocatalytic degradation of Orange II was investigated in aqueous dispersions of titanium dioxide (TiO_2) using UV light as irradiation source. The experimental results demonstrated that the photocatalytic decolorization of Orange II was feasible. The optimum pH value was found to be 7.00. The presence of Mn^{2+} did not alter its degradation pathways, but it reduced the dye degradation efficiency. Mn^{2+} at an elevated level had a more significant detrimental effect on the dye degradation efficiency. The atomic absorption spectrometry and X-ray photoelectron spectroscopy (XPS) analyses showed that Mn^{2+} was adsorbed on the surface of TiO_2. This was the reason for the reduced catalytic efficiency of TiO_2 with the presence of Mn^{2+}. A modified Langmuir–Hinshelwood model was able to describe the TiO_2-mediated photocatalytic kinetics of Orange II appropriately with and without the presence of Mn^{2+} in solution.

Keywords: Mn^{2+}; Orange II; Photocatalytic degradation; TiO_2

1. Introduction

Azo dyes, which are widely used in textile and dyestuff industries, are produced annually in quantities that exceed 6.35×10^5 t [1]. In China, more than 1.8×10^9 m^3 of dye-containing wastewater is discharged annually into natural water systems without treatment [2]. The electron-deficient character of the azo linkage prevents mineralization of these dyes by bacteria [3]. Because of their resistance to biological degradation, biological treatment processes, such as activated sludge and anaerobic processes are ineffective for the removal of these dyes from wastewater [3].

During the last two decades titanium dioxide (TiO_2)-mediated photocatalytic oxidation has been applied for the removal of dyes [4–6]. The optical absorption of TiO_2 near UV region is the major advantage of the photocatalytic method over the UV-driven oxidation methods (e.g. O_3/UV and H_2O_2/UV), that require light of shorter wavelengths ($\lambda < 300$ nm) and hence cannot make use of solar irradiation [4,5]. This method has been successfully tested to deal with wastewaters containing aniline, alcohols and organochlorides [5,6].

The addition of a low percentage of metals was often proposed to improve the photocatalytic activity of TiO_2 through doping, metallization, or impregnation [7–10]. Several metals were used for doping, especially Pt^0, Li^+, Zn^{2+}, Cd^{2+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Al^{3+}. The presence of transition metals may increase the photocatalytic activity either by scavenging e^- that reduces the recombination of charges and therefore favors the formation of OH, or by the intermediate of Fenton type reactions [7]. However, high concentration of metals may have a detrimental effect either by a competitive trapping of oxidizing species H^+ and OH, or by filter effect, when salts are significantly absorbed in UV range [8,9]. The presence of Mn^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+} and Al^{3+} ions in TiO_2 layer supported on glass fibers had a detrimental effect on the photoactivity [8]. The presence of Pt^0 did not change the degradation rate of phenol [10].

On the other hand, metals are often found to be present in some textile wastewaters [11]. Presence of ions in the wastewaters subject to TiO_2-mediated photocatalysis have some influence on the degradation efficiency of dyes, but information about the photocatalytic degradation of dyes in the presence of metals is still sparse. In China, groundwater is often used as water source by textile industries. However, groundwater in the north of China is rich in manganese [12]. As a result, a significant level of Mn^{2+} is present in these textile wastewaters. Therefore, in this study, Mn^{2+} was selected to be a model ion to investigate such influences on

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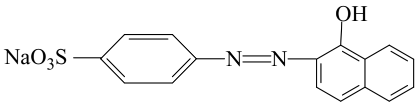

Fig. 1. The chemical structure of Orange II.

the photodegradation of Orange II, an azo dye widely present in textile wastewaters [13,14]. The chemical structure of Orange II is illustrated in Fig. 1. The present study focused on the photocatalytic degradation of Orange II with and without presence of Mn^{2+}. Furthermore, the effect of pH and kinetics of the photocatalytic reactions were evaluated.

2. Experimental

2.1. Chemicals

Tetrabutyl titanate [$Ti(OC_4H_9)_4$], Orange II, and $MnCl_2{\cdot}4H_2O$, all purchased from Shanghai Chemical Reagent Company, were of chemical reagent grade and used without further purification. Doubly distilled water was used throughout the experiments.

2.2. Preparation and characterization of TiO_2

The photocatalyst, TiO_2, was prepared by using sol-gel method, following the procedures reported by Yuan and Zhang [15]. The prepared TiO_2 particles were analyzed by X-ray diffraction patterns. The X-ray diffraction pattern analysis, as illustrated in Fig. 2, showed that the prepared TiO_2 was mainly of anatase and that the average crystal grain size was 22 nm.

2.3. Photocatalytic experiments

The photoreactor used was a 500 ml cylindrical glass equipped with a magnetic agitator. A 160 W high-pressure mercury lamp was located in the center of the reactor.

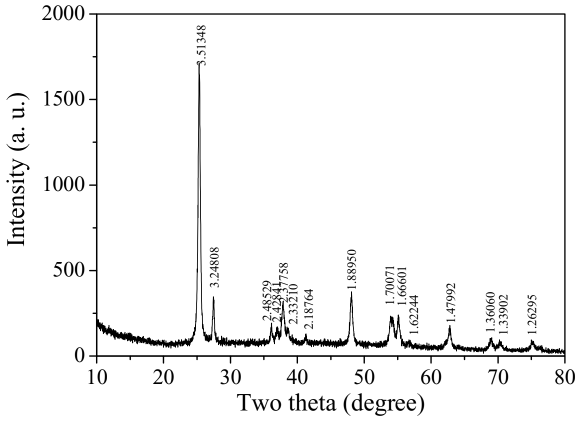

Fig. 2. X-ray diffraction pattern of TiO_2.

The photocatalytic activity of the catalyst with and without the presence of Mn^{2+} was evaluated by measuring the concentrations of Orange II. In typical experiments, TiO_2 particles of 0.2 g were suspended in 400 ml of 20 mg l^{-1} Orange II aqueous solution. Dosage of Mn^{2+} varied from 0 to 2.78 mg l^{-1}. The magnetic stirring was used to maintain the TiO_2 in suspension.

In all experiments, prior to irradiation, the suspended aqueous solution was mixed continuously in dark for 30 min to ensure sorption/desorption equilibrium. The concentration of substrate in bulk solution at this point was used as the initial value for further kinetic determination. A 20 ml sample was withdrawn at given time interval and filtered through a 0.22 μm Millipore filter prior to analysis. The pH was adjusted with HCl or NaOH as required.

2.4. Analyses

The disappearance of Orange II was monitored by an UV-Vis spectrophotometer (UV-2401PC, Shimadzu Co.). The concentration of the dye was measured by using an HPLC (HPLC-1100, Agilent Co.) equipped with a Hypersll-ODS column. An eluent of methanol–water (70:30) was used for the HPLC analysis. The concentrations of Mn^{2+} were determined by using an atomic absorption spectrometer (WFX-120, Beijing Rayleigh Analytical Instrument Corp., Beijing), and its distribution was analyzed by using X-ray photoelectron spectroscopy (XPS) (Escalab Mkii, VG Co.). The total organic carbon (TOC) concentration was measured by a TOC analyzer (TOC-VCPN, Shimadzu Co.).

3. Results and discussion

3.1. UV-Vis spectra of dye solutions

Fig. 3 illustrates the UV-Vis absorption spectra of the initial solutions and the samples after 10 and 15 min irradiation with and without the presence of Mn^{2+}. There were three characteristic absorbance peaks at 228, 310 and 484 nm. The former two peaks derived from aromatic rings, and the latter peak from conjugated structure formed by azo bond.

As shown in Fig. 3a, without the presence of Mn^{2+}, the absorbance peaks in both UV and visible regions reduced after 10 min of UV irradiation, suggesting that Orange II was sensitive to TiO_2-mediated photocatalysis. A further increase in irradiation time from 10 to 15 min resulted in a further decrease in the height of the absorbance peaks at 228, 310 and 484 nm, respectively.

With the presence of Mn^{2+}, the UV-Vis spectra of the solutions after irradiation were changed in the same way as those without the presence of Mn^{2+} (shown in Fig. 3b), but the absorbance reduction was much lower. This suggests that the presence of Mn^{2+} did not alter the photodegradation pathways of Orange II, but reduced the degradation efficiency.

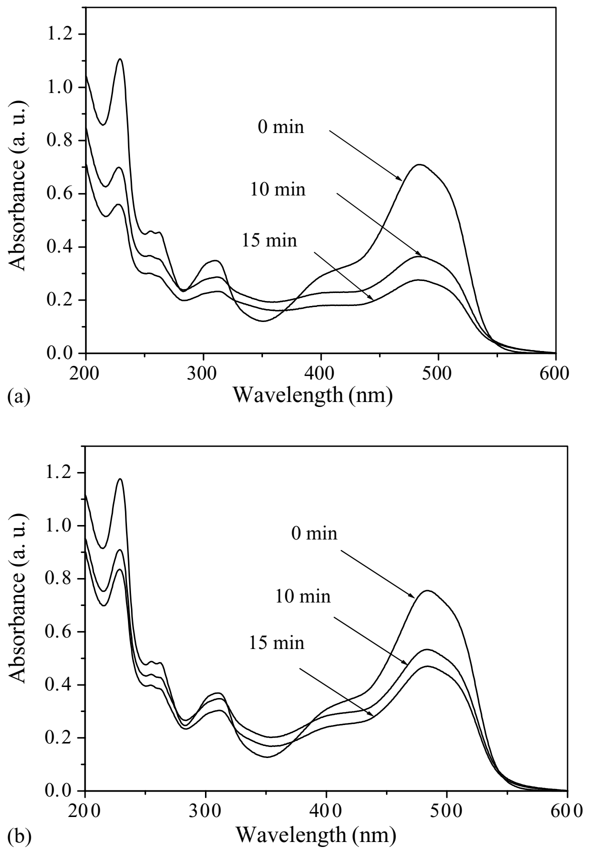

Fig. 3. UV-Vis absorption spectra of the initial Orange II solutions and the samples after irradiation: (a) without the presence of Mn^{2+} and (b) with the presence of Mn^{2+}.

3.2. Effect of pH

The effect of the pH on the degradation of Orange II was examined in the pH range of 3.00–10.85 and the results are presented in Fig. 4. It is observed that photodegradation of Orange II was strongly favored at pH 7.00, where dye degradation efficiency was greater than 90% after 30 min irradiation, while at other pH values, the degradation was much slower and the degradation efficiency was less than 75%. Thus, 7.00 was the optimum pH value for the TiO_2-mediated photocatalysis of Orange II in this study. The following experiments were thus conducted at pH 7.00.

The results presented in Fig. 4 clearly show that pH had a significant influence on the degradation efficiency of Orange II. The variation of solution pH might change the surface charge of the TiO_2 particles and 'shift the potentials of catalytic reactions. As a result, the adsorption of the dye on the TiO_2 particles was changed and the catalytic reaction rate was also altered [8].

3.3. Effect of Mn^{2+} on degradation of Orange II

Blank experiments show that the disappearance of Orange II was negligible without UV irradiation or in the absence of TiO_2. The degradation of Orange II in the presence of various Mn^{2+} concentrations is illustrated as a function of irradiation time in Fig. 5. Disappearance of Orange II with the presence of Mn^{2+} followed a similar pattern without Mn^{2+}. However, presence of Mn^{2+} substantially reduced the degradation efficiency of Orange II. Furthermore, an elevated Mn^{2+} concentration resulted in a more significant decrease in the degradation efficiency of Orange II.

The above results show that the decolorization of Orange II with photocatalytic methods is feasible. However, from the practical point of view, not only decolorization but also TOC removal is of interest. Fig. 6 presents the degradation efficiencies of Orange II and TOC as a function of irradiation time at pH 7.00. The initial Orange II concentration in this experiment was 20 mg l^{-1}, corresponding to a measured TOC of 11 mg l^{-1}. As shown in Fig. 6, there was a substantial decrease of the TOC of the solution with irradiation time, e.g., the TOC removal reached 77% after 30 min irradiation. However, the TOC removal efficiency was much lower than that of decolorization. This is due to the formation of uncolored products during the degradation of Orange

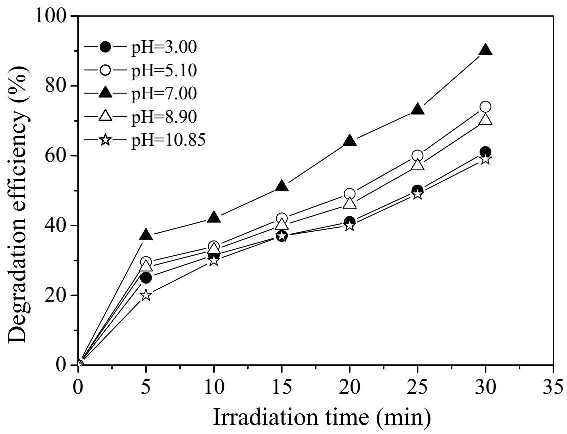

Fig. 4. Degradation efficiency of Orange II vs. irradiation time at various pH values.

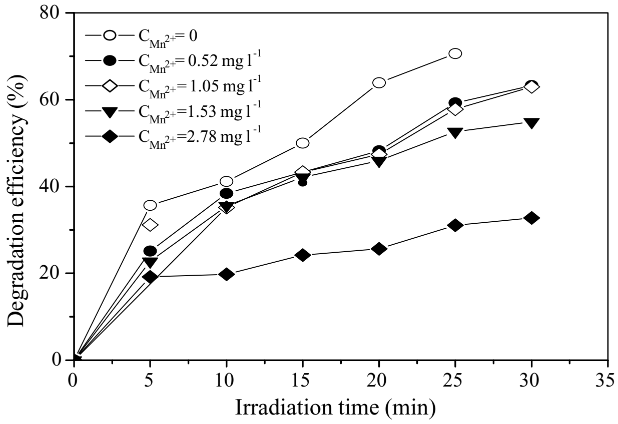

Fig. 5. Degradation efficiency of Orange II vs. irradiation time as a function of Mn^{2+} concentrations.

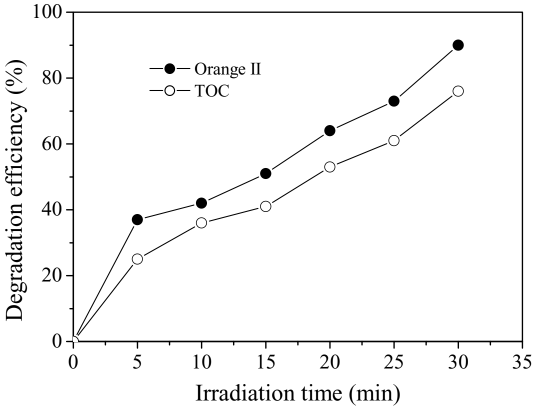

Fig. 6. Degradation efficiencies of Orange II and TOC vs. irradiation time at pH 7.00.

II, which continue to contribute to the TOC of the solution. To achieve complete degradation, longer irradiation time is required.

3.4. Function of Mn^{2+}

The above results demonstrate that the presence of Mn^{2+} in solution did have a negative influence on the TiO_2-mediated photocatalysis of Orange II. The atomic absorption spectrometry and XPS analyses, shown in Table 1 and Fig. 7, respectively, were useful for identifying the reasons for the inhibition of Mn^{2+} on the TiO_2-mediated photocatalysis. At a Mn^{2+} dosage of 0.455 mg l^{-1}, after 10 min irradiation, 0.101 mg Mn^{2+} was found in the solution, but 0.078 mg Mn^{2+} on the surface of TiO_2. After 15 min irradiation, the corresponding values were 0.106 and 0.072 mg. This indicates that over one-third Mn^{2+} was on the surface of catalyst. The XPS analytical results shown in Fig. 7 provide further support that Mn^{2+} was binding on the catalyst.

Table 1
Distribution of Mn^{2+}

Irradiating time (min)	Mn^{2+} in the solution (mg)	Mn^{2+} on the surface of TiO_2 (mg)
0	0.178	0
10	0.101	0.078
15	0.106	0.072

Due to the adsorption of Mn^{2+} on the TiO_2 surface, the amount of Orange II adsorbed on TiO_2 surface decreased. As a consequence, the catalytic efficiency was reduced. As Mn^{2+} concentration increased in the solution, Mn^{2+} adsorbed on the surface of TiO_2 increased accordingly, resulting in a further enhanced inhibition on the Orange II degradation. This assumption warrants further experiments for confirmation.

3.5. Kinetic analysis

Langmuir–Hinshelwood expression has been employed to model the kinetics of heterogeneous photocatalysis [8,10,16].

$$r = -\frac{dC}{dt} = \frac{k_r k_a C}{1 + k_a C + k_w C_w + \sum_{i=1}^{n} k_i C_i} \tag{1}$$

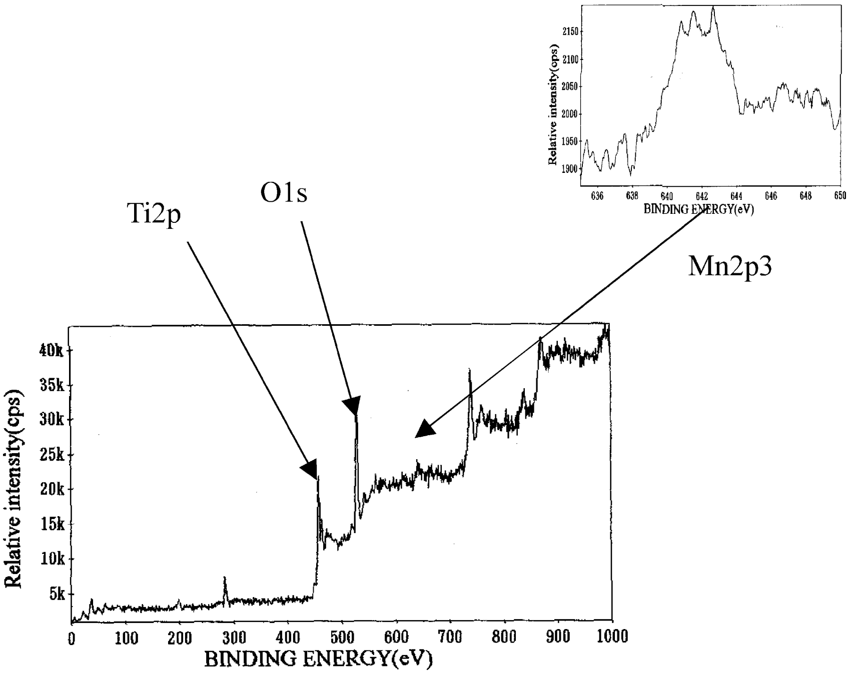

Fig. 7. XPS spectra of Mn^{2+} distribution.

where r is the reaction rate for the oxidation of reactant ($\text{mg}\,\text{l}^{-1}\,\text{min}^{-1}$), k_r is the specific reaction rate constant for the oxidation of reactant ($\text{mg}\,\text{l}^{-1}\,\text{min}^{-1}$), k_a is the equilibrium adsorption constant of reactant ($\text{l}\,\text{mg}^{-1}$), C_w is the concentration of solvent ($\text{mg}\,\text{l}^{-1}$), k_w is the equilibrium adsorption constant of solvent ($\text{l}\,\text{mg}^{-1}$), C_i is the concentration of products ($\text{mg}\,\text{l}^{-1}$), t is the reaction time (min).

If inhibitors, such as Mn^{2+}, are present in the solution, Eq. (1) is modified into the following:

$$r = -\frac{dC}{dt} = \frac{k_r k_a C}{1 + k_a C + k_w C_w + k_{ion} C_{ion} + \sum_{i=1}^{n} k_i C_i} \tag{2}$$

where k_{ion} is the equilibrium adsorption constant of ion ($\text{l}\,\text{mg}^{-1}$), C_{ion} is the concentration of ion ($\text{mg}\,\text{l}^{-1}$).

Under the conditions in this study, it is assumed that there was no competition adsorption between reactant and solvent. Thus,

$$\sum_{i=1}^{n} k_i C_i = 0, \qquad k_w C_w = 0$$

As a result, the following equation arises:

$$r = -\frac{dC}{dt} = \frac{k_r k_a C}{1 + k_a C + k_{ion} C_{ion}} \tag{3}$$

Linearization of Eq. (3) gives the relationship

$$\frac{1}{r} = \frac{1}{k_r} + \frac{(1 + k_{ion} C_{ion})/k_r k_a}{C} \tag{4}$$

When Mn^{2+} was absent, Eqs. (3) and (4) can be simplified as

$$r = -\frac{dC}{dt} = \frac{k_r k_a C}{1 + k_a C} \tag{5}$$

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r k_a C} \tag{6}$$

In the absence of Mn^{2+}, plotting $1/r$ against $1/C$, a straight line was obtained with an intercept of $1/k_r$ and a slope of $1/(k_r k_a)$. This plot is shown in Fig. 8, from which k_r and k_a were estimated as 8.197 ($\text{mg}\,\text{l}^{-1}\,\text{min}^{-1}$) and 0.014 ($\text{l}\,\text{mg}^{-1}$), respectively. The regression line had a correlation coefficient of 0.9907, confirming the applicability of the Eq. (6).

When Mn^{2+} was present, e.g. $C_{Mn^{2+}} = 0.26\,\text{mg}\,\text{l}^{-1}$, Eq. (4) was used to estimate the values of the parameters. The reciprocal rate $1/r$ versus the reciprocal dye concentration $1/C$ is plotted in Fig. 9. The high value of correlation coefficient (0.9909) confirms that the TiO_2-mediated photocatalytic kinetics of Orange II in the presence of Mn^{2+} could be described similarly to the kinetics in the absence of Mn^{2+}. From Fig. 9, k_r, k_a and k_{ion} was estimated as 6.897 ($\text{mg}\,\text{l}^{-1}\,\text{min}^{-1}$), 0.017 ($\text{l}\,\text{mg}^{-1}$), and 22.93 ($\text{l}\,\text{mg}^{-1}$), respectively.

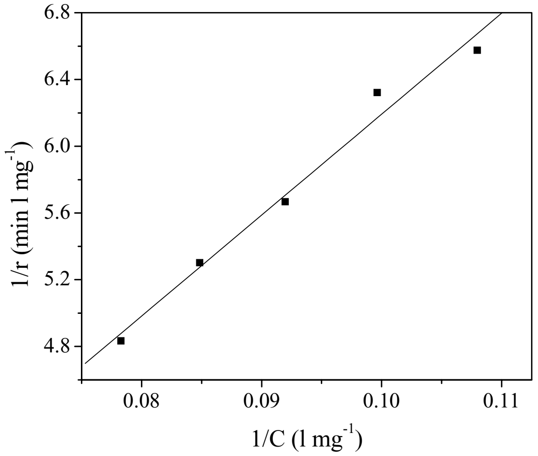

Fig. 8. Langmuir–Hinshelwood model plot without presence of Mn^{2+}.

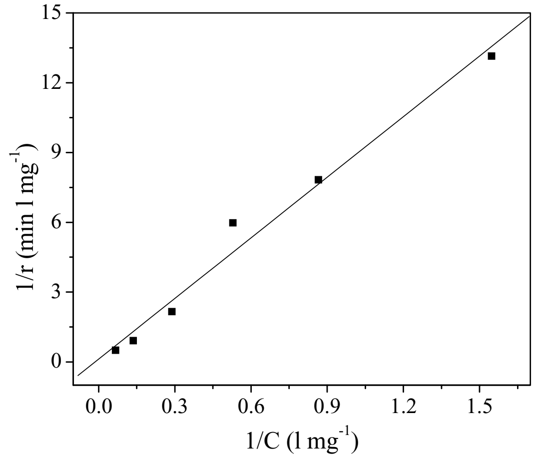

Fig. 9. Modified Langmuir–Hinshelwood model plot with presence of Mn^{2+}.

4. Conclusions

This study demonstrated that the degradation of Orange II with TiO_2-mediated photocatalysis was feasible. The presence of Mn^{2+} did not alter its photodegradation pathways. The optimum pH value was found to be 7.00. Presence of Mn^{2+} substantially reduced the dye degradation efficiency. Furthermore, an elevated Mn^{2+} concentration resulted in a more significant decrease in the degradation efficiency. The TOC removal efficiency was much lower than that of decolorization, attributed to the formation of smaller uncolored products during the degradation of Orange II. The atomic absorption spectrometry and XPS analyses showed that Mn^{2+} was adsorbed on the surface of TiO_2, and thus inhibited the adsorption of Orange II on TiO_2 surface, resulting in a reduced catalytic efficiency. A modified Langmuir–Hinshelwood model was found to be able to describe the TiO_2-mediated photocatalytic kinetics of Orange II appropriately with and without the presence of Mn^{2+}.

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