Journal of Hazardous Materials 177 (2010) 750–754

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A novel approach of preparing TiO_2 films at low temperature and its application in photocatalytic degradation of methyl orange

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ARTICLE INFO

Article history:
Received 26 August 2009
Received in revised form
21 December 2009
Accepted 22 December 2009
Available online 4 January 2010

Keywords:
Non-calcinated TiO_2 film
Electrophoretic deposition
Photocatalytic activity
Methyl orange degradation

ABSTRACT

Here we introduce a novel approach of preparing TiO_2 films on conductive substrates at low temperature by electrophoretic deposition method without successive calcinate treatment. The photocatalytic activity of the non-calcinated TiO_2 film was evaluated by degradation rate of methyl orange (MO). We found that the degradation rate of MO increased with the amount of TiO_2, and it was higher in both acidic and alkaline media than under neural condition. In addition, lower pH was more favorable for the degradation of MO. The photocatalytic degradation of MO could be described as pseudo-first order reactions. When the initial concentration of MO increased from 1 mg/L to 10 mg/L, the highest degradation rate was achieved at 5 mg/L. The apparent reaction rate constant was calculated to be 0.0098 min^{-1}.

1. Introduction

In 1972, the publication about photocatalytic degradation of water on the titanium oxide (TiO_2) electrode by Japanese scholars Fujishima and Honda [1] raised the curtain on the study of photocatalysis. In 1976, Carey et al. [2] found that after irradiated by UV light, TiO_2 was capable to catalyze the dechloridization of polychlorobiphenyl (a group of organic pollutants) in water, which initiated the application of the photocatalytic technology on environmental remediation. In the past decades, TiO_2 has been applied in decomposition and mineralization of some persistent organic pollutants (POPs) such as phenols, chlorophenols, pestcides, herbicides, benzenes, humic acids and others [3–7], as well as water and air purification [8–12].

However, for the particulate TiO_2 suspension, removal of the catalyst after use is expensive and technologically difficult. Recently, the use of TiO_2 thin films for the purpose of solving environmental issue has emerged. Compared to powder TiO_2 particles, immobilized TiO_2 films are more promising in practical applications, especially in water treatment [13,14].

Conventional methods to prepare TiO_2 thin films can be classified into three categories: gas-phase preparation [15], liquid-phase preparation [15] and electrochemical preparation [15–17]. The first two methods require expensive equipments, high temperature treatment, as well as complicated procedures, and are consequently energy-consuming. The electrochemical preparation method is relatively simple, the size and shape of TiO_2 nano-particles can be well controlled [15,16]. Therefore, it has been widely used in recent years.

Different methods have been investigated to produce semiconducting TiO_2 films with different functions. Electrochemical anodization of metal Ti followed by calcination can be used to fabricate TiO_2 nanowires, nanorods and nanotubes [18–20]. The preparation of TiO_2 films with photocatalytic function is conventionally accomplished through electrophoretic deposition followed by calcination at high temperature [21,22]. By using the TiO_2 film prepared on the stainless steel substrate, successful photodegradation of formaldehyde gas [23] had been demonstrated.

Here, our laboratory developed a novel method to prepare TiO_2 films with photocatalytic function at low temperature by an electrochemical method. We prepared TiO_2 films on different conductive substrates such as nickel network, aluminium plates and conductive glass plates. The experiments were conducted at low temperature, and the calcination step is not required. The photocatalytic treatment of wastewater by our TiO_2 films was demonstrated with a model pollutant methyl orange (MO).

2. Experimental

2.1. Chemicals and instruments

High-purity (99.99%) nickel network and aluminum plates were purchased from Beijing Non-ferrous Metal Co., Ltd., China. Tetrabutyl titanate (Tianjin Fuchen Chemical Reagent Co., Ltd.), isopropyl

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doi:10.1016/j.jhazmat.2009.12.095

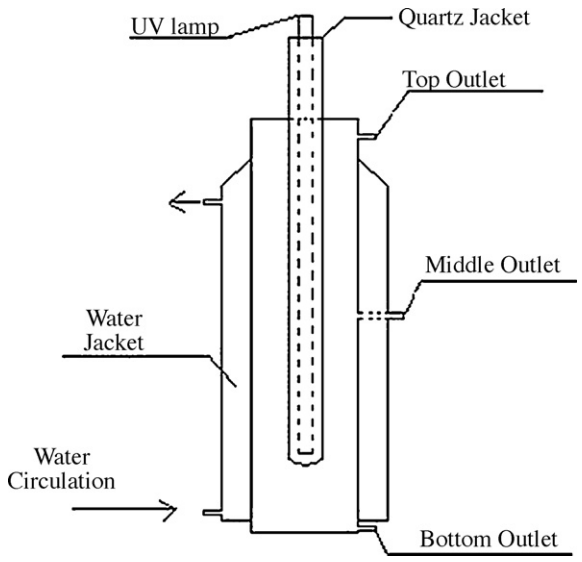

Fig. 1. Schematic diagram of the photocatalysis reactor.

alcohol (Shanghai Experimental Reagent Co., Ltd.), methyl orange (Tianjin Kemiou Chemical Reagent Co., Ltd.) and all other reagents were of analytical grade and used without further purification. Deionized water (18.0 MΩ cm) was made from Barnstead system (Barnstead).

The pH buffer solutions used in the experiments were the mixture of Na_2HPO_4 (0.2 M) and NaH_2PO_4 (0.2 M), adjusted by H_3PO_4 or NaOH to obtain the desired pH.

Cary-50 ultraviolet spectrophotometer (Varian), field emission scanning electron microscope (FESEM, SIRION 200, FEI, Netherlands) were used in the experiments. X-ray diffraction (XRD) patterns obtained on a X-ray diffractometer (PANalytical B.V.) using Cu Kα radiation at a scan rate (2θ) of 0.05° s^{-1}. The zeta potential of catalysts was determined by Zetasizer (Malvern ZS90).

2.2. Preparation of the non-calcinated TiO_2

The non-calcinated TiO_2 films were prepared as follows. The plating solution contained 17% (wt%) tetrabutyl titanate, 3% isopropyl alcohol, 3% concentrated nitric acid and 77% deionized water. The solution was first cultured for 12 h at room temperature, and then diluted 10 times before use. A constant potential (30 V) was applied between the nickel network (or aluminium plate) and a Pt electrode for 20 min. Both electrodes were immersed in the plating solution with ice/water bath.

2.3. Photocatalytic degradation of MO

The photocatalytic activity of the non-calcinated TiO_2 films was evaluated by measuring degradation rate of MO, a compound used here as a model pollutant. The experiments were carried out in a 1000 mL cylindrical glass reactor filled with 950 mL MO aqueous solution. The reactor was equipped with an ultraviolet (UV) lamp (power – 28 W with wavelength of 254 nm). The temperature of reactor was controlled by circulation of tap water inside the water jacket during degradation experiments (Fig. 1). The nickel network pieces coated with TiO_2 (8 cm × 4 cm/piece) were put into the reactor. The nickel network was first pre-saturated in the MO aqueous solution at dark for 30 min in order to reach adsorption/desorption equilibrium, then the UV lamp and water circulation were turned on to initiate degradation process. Every degradation experiment lasted 2 h, and a small sample was taken out every 15 min from the middle outlet (see Fig. 1). UV spectrometer was used to determine the absorbance (A) of the samples (λ_{max} = 460 nm to λ_{max} = 465 nm with pH 2–10). Every experiment was repeated at least three times, and the average (with RSD less than 5% for three repeated results) was used as the final results. The concentration of MO was calculated from an absorbance vs. concentration calibration curve. The degradation rate (%) was evaluated by the following equation:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where D is degradation rate, C_0 and C_t are the concentrations of the MO solution at UV irradiation time 0 and t, respectively.

3. Results and discussion

3.1. Morphology of the non-calcinated TiO_2 film

Fig. 2 illustrates the different morphologies of the nickel network before (Fig. 2(a)) and after (Fig. 2(b–d)) electroplating, respectively. It is obvious that the TiO_2 particles were successfully deposited on the nickel network (Fig. 2(b and c)). The magnified image in Fig. 2(c) showed the heterogeneity of the deposited TiO_2 on the substrate Ni network. The left and top parts of the deposited TiO_2 film in Fig. 2(c) were composed of nano-particles, while the center part had more dense structure with nanometer scale holes. Additionally, a long crack was also observed. The heterogeneous morphology of the deposited TiO_2 film might be attributed to the uneven substrate Ni network, which showed islands, alleys and cracks from the SEM image (Fig. 2(a)). The image with a higher magnification (Fig. 2(d)) shows the size of particles ranged from 30 nm to 40 nm. Heated at 450 °C for 1 h did not significantly affect the morphology of coated TiO_2 particles from SEM image (not shown here).

Fig. 3 shows XRD patterns of the as-prepared film (Fig. 3(a)) and the film (Fig. 3(b)) calcinated at 450 °C for 1 h. Both films are mainly in well-crystallized anatase phase (peaked at *ca.* 25.2 nm (1 0 1) and 37.6 nm (0 0 4)), but small rutile peaks were also observed at *ca.* 27.3 nm and 36.0 nm. Both anatase and rutile peak intensities increased slightly after calcination, which had been reported before [24,25].

The average crystallite size of anatase in the samples can be calculated with the Scherrer formula using the anatase (1 0 1) diffraction peaks:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where D is the average crystallite size, K is a constant (0.89 here), λ is the wavelength of the X-ray radiation (0.154 nm), β is the band broadening (full width at half-maximum) and θ is the diffraction angle. The particle sizes are calculated to be 31.3 nm and 47.0 nm for the non-calcinated and calcinated samples, respectively, which agrees well with SEM results. The particles in the calcinated samples are slightly larger than those in the non-calcinated ones, which is similar to the previous observation [23].

The TiO_2 films coated on aluminium and conductive glass plates were demonstrated to be in anatase phase as well (data not shown). The coated films were denser compared to that on the nickel network and their color was light gray.

3.2. Photocatalytic degradation by the non-calcinated TiO_2 film

3.2.1. Photocatalytic activity

In order to verify the photocatalytic activity of the non-calcinated TiO_2 film, two experiments were conducted at pH 7.0 and pH 2 (maximal photocatalytic activity, see Section 3.2.2) simultaneously, one with bare nickel network and the other with TiO_2 coated nickel network (four pieces). The initial MO concentrations

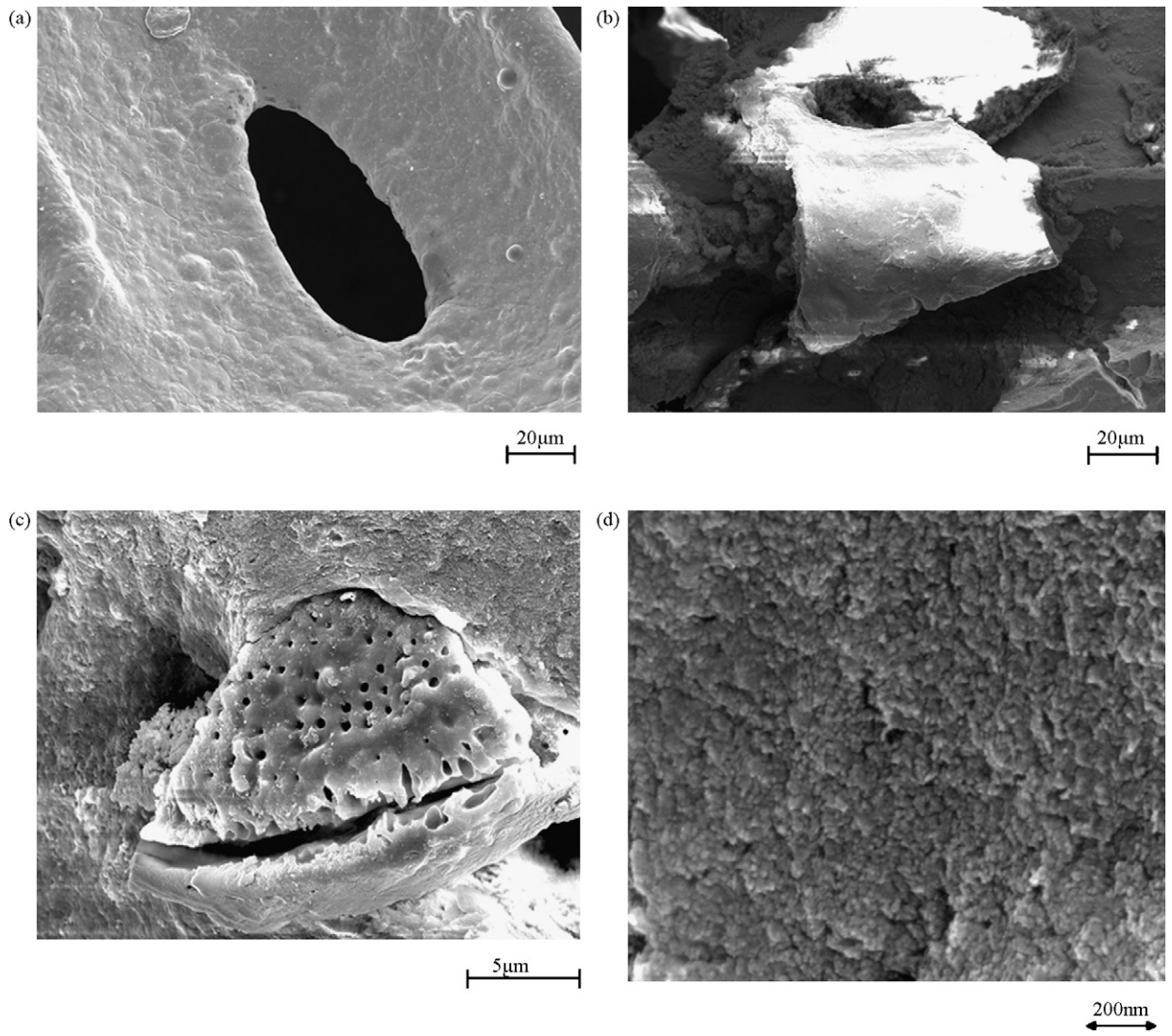

Fig. 2. FESEM images of Ni substrate (a) and TiO_2 particles coated on Ni substrate by electrophoretic deposition with 800× magnification (b), 5000× magnification (c) and 8000× magnification (d).

were 5 mg/L in both experiments. Fig. 4 shows the photocatalytic results (pH 7) after UV lamp illumination for 2 h. It was found that the degradation rate of MO with bare nickel network was $36.5 \pm 0.5\%$ ($n = 3$) at pH 7 and $51.4 \pm 1.1\%$ ($n = 3$) at pH 2, and the non-calcinated TiO_2 film coated nickel network exhibited a much higher degradation rate of $75.2 \pm 1.7\%$ ($n = 3$) at pH 7 and $95.5 \pm 1.5\%$ ($n = 3$) at pH 2.

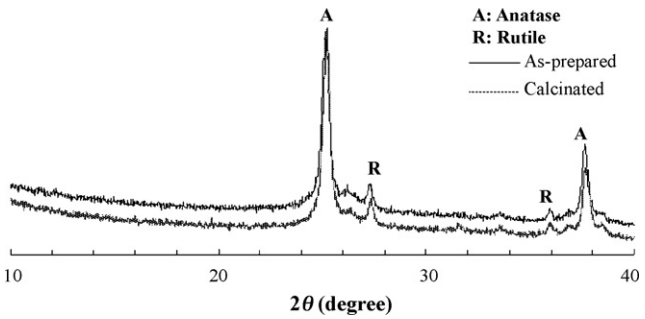

Fig. 3. X-ray patterns for the titania samples prepared by electrophoretic deposition, as-prepared and post-heated at 450 °C for 1 h (calcinated).

The non-calcinated TiO_2 film had the same photocatalytic activity with the TiO_2 film calcinated at 450 °C for 1 h: the former showed a net degradation rate of 38.7% to MO at pH 7, and the latter degraded about 40.0% MO under the same condition.

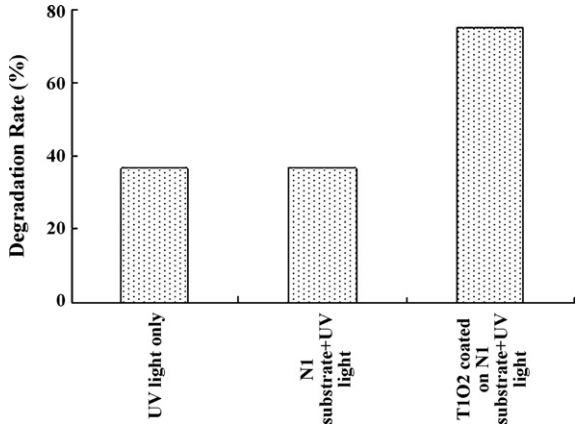

Fig. 4. Comparison of photocatalytic experiments: MO treated by UV only, by UV irradiated Ni substrate and by UV irradiated Ni substrate coated with the as-prepared TiO_2 film.

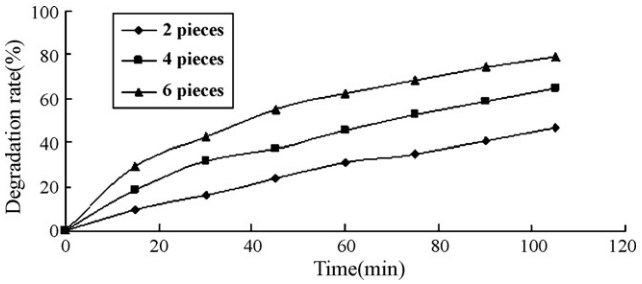

Fig. 5. Dependence of degradation rate of MO on the amount of the as-prepared TiO_2 coated on Ni substrate.

The degradation rate of MO with different amounts of TiO_2 was investigated and the results are shown in Fig. 5. The net degradation rates were $22.0 \pm 0.8\%$ ($n = 3$) for two pieces of the non-calcinated TiO_2 film coated nickel network, $38.7 \pm 1.7\%$ ($n = 3$) for four pieces and $48.7 \pm 1.7\%$ ($n = 3$) for six pieces. The increased degradation rate with the amount of catalyst (TiO_2) further confirmed the photocatalytic activity of the novel non-calcinated TiO_2 film.

3.2.2. pH effect

Four pieces of the non-calcinated TiO_2 film coated nickel network were put into the reactor and the pH of the MO aqueous solution was adjusted by phosphate buffer. The relationship between degradation rate and pH is shown in Fig. 6. The degradation rate was $95.5 \pm 1.5\%$ ($n = 3$) at pH 2.0, $75.2 \pm 1.7\%$ ($n = 3$) at pH 7.0, and $83.3 \pm 1.8\%$ ($n = 3$) at pH 10.0.

To clarify the effect of pH on the degradation rate of MO, we measured zeta potentials of catalysts at different pH values. When pH was lower than 7, the catalyst had positively charged surface, and higher pH (>7) made the surface negatively charged. This is in good agreement with the previous observation [26]. The lower pH produces more H^+ that could adsorb on the surface of TiO_2, making TiO_2 particles positively charged. Positively charged TiO_2 particles assist the migration of photo-induced electrons, which could react with adsorbed O_2 to produce $^{\bullet}O_2^-$ ($e^- + O_2 \rightarrow {}^{\bullet}O_2^-$). In addition, positively charged TiO_2 particles could also inhibit the recombination of electrons and holes, generating more $OH^{\bullet}$ through the reaction between holes and water. Both radical ions $^{\bullet}O_2^-$ and $OH^{\bullet}$ are strong oxidants [27,28] and could be responsible for the enhanced degradation of MO. Similarly, negatively charged in alkaline solutions is favorable for the migration of the hole to TiO_2 surface and generation of $OH^{\bullet}$ [29,30]. At neutral pH, the surface of TiO_2 is not charged, neither $^{\bullet}O_2^-$ nor $OH^{\bullet}$ can be produced from the above pathways.

Acidic solutions were more effective in degrading MO than basic solutions. One possible reason is that sodium ions (dissociated from MO or buffer components) could react with adsorbed OH^- to generate –ONa, which reduced the amount of $OH^{\bullet}$ [31]. The other explanation could be pH increase that change MO from quinoid structure to azo structure [29], and quinoid structure is easier to degrade than azo structure. The validity of the latter was proved by

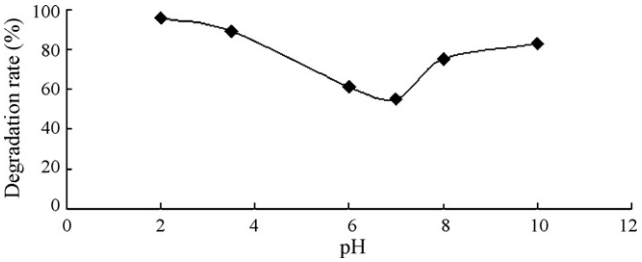

Fig. 6. Dependence of degradation rate of MO on pH. MO was degraded by four pieces of the as-prepared TiO_2 films irradiated by UV lamp.

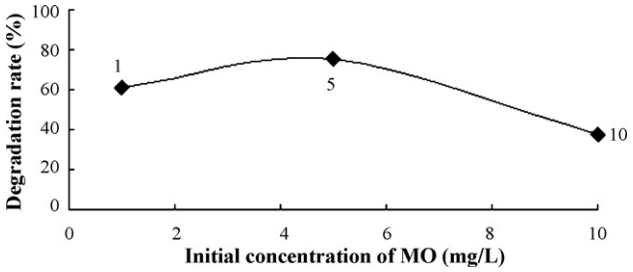

Fig. 7. Effects of MO solution initial concentrations on its photocatalytic degradation rate. Four pieces of the as-prepared TiO_2 films were used for the photocatalytic degradation of MO.

that the degradation rate of MO by UV lamp only increased from 36.5% to 51.4% with decreasing pH from 7 to 2.

3.2.3. The effects of MO initial concentration

The MO degradation by TiO_2 films was also investigated by changing the initial concentration of MO and the results are shown in Fig. 7. The degradation rate was $61.0 \pm 1.2\%$ ($n = 3$) when MO initial concentration was 1 mg/L. It increased to $75.2 \pm 1.7\%$ ($n = 3$) with 5 mg/L MO but decreased to $37.9 \pm 0.9\%$ ($n = 3$) with 10 mg/L MO.

The degradation rate of MO was low at both higher and lower concentrations. Because the benzene ring on MO can absorb UV light at wavelength around 300 nm, when MO concentration is increased, the proportion of UV light absorbed by TiO_2 particles will decrease and result in the drop of the degradation rate. On the other hand, the chances of reaction of MO with electrons, holes and $OH^{\bullet}$ are less with the decrease in MO concentration, therefore the degradation of MO in a low concentration could not be effective by using photocatalyst. The phenomenon was also found in the photocatalytic treatment of other pollutants [32]. Too high pollutant concentration can cost more time and catalyst, and also produces lower degradation rate. However, if the pollutant concentration is very low, it is also difficult to be completely removed.

3.2.4. Kinetics analysis

The kinetic of photocatalytic degradation of MO solution was investigated when MO initial concentrations are 1 mg/L, 5 mg/L and 10 mg/L, respectively. The linear relationship between $\ln(C_0/C)$ and time (see Fig. 8) demonstrated that the photocatalytic degradation of MO followed a pseudo-first-order kinetics:

$$\ln \frac{C_0}{C} = kt \tag{3}$$

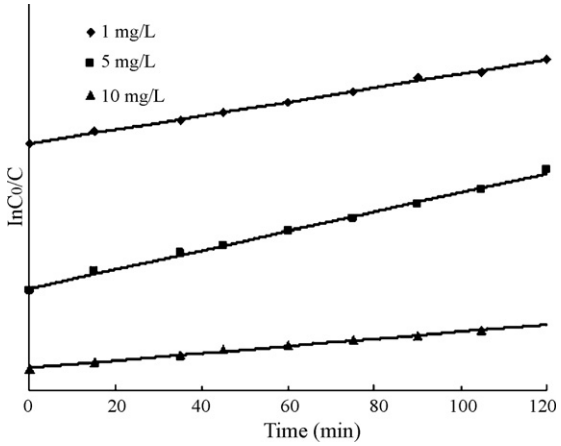

Fig. 8. $\ln(C_0/C)$–time curves with different MO initial concentrations. Four pieces of the as-prepared TiO_2 films were used for the photocatalytic degradation of MO.

where C_0/C is the normalized MO concentration, t is the reaction time, and k is the reaction rate constant (min^{-1}). When MO initial concentration was 5 mg/L, the degradation rate was the highest among the three investigated concentrations, and the rate constant was calculated to be 0.0098 min^{-1}.

4. Conclusions

TiO_2 films were successfully prepared by a novel approach of electrophoretic deposition method without successive heat treatment. The non-calcinated TiO_2 films coated on nickel network exhibited a high photocatalytic activity to the degradation of MO. The photocatalytic degradation rate was improved with the increasing amount of TiO_2. Acidic solutions produced highest degradation rate and neutral pH was demonstrated to be least effective. The photocatalytic degradation of MO can be described with pseudo-first order reaction kinetics.

Acknowledgements

This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, the key project of Natural Science Foundation of Hubei Province (No. 2008CDA041) and the National Science Foundation of Huazhong University of Science and Technology.

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