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Photocatalytic Degradation of Metronidazole in Aqueous Solution by Niobate $K_6Nb_{10.8}O_{30}$

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Abstract: The photocatalytic degradation of antibiotic metronidazole in aqueous solution by niobate $K_6Nb_{10.8}O_{30}$ photocatalyst that was prepared using a soft-chemical method was studied by Fourier transform infrared spectroscopy and UV-Vis absorption spectrum. Metronidazole is very stable and is difficult to degrade under UV irradiation. $K_6Nb_{10.8}O_{30}$ photocatalyst cannot degrade metronidazole without UV irradiation and shows very high photocatalytic activity for the degradation of metronidazole under UV irradiation. The photocatalytic degradation rate of metronidazole increased with increasing the dosage of $K_6Nb_{10.8}O_{30}$ photocatalyst. The photocatalytic degradation reaction of metronidazole by niobate $K_6Nb_{10.8}O_{30}$ follows the first-order kinetic equation.

Key words: niobate; potassium niobate; metronidazole; photocatalytic; kinetics

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0 Introduction

Antibiotics wastewater as specific pharmaceutical industrial wastewater is difficult to degrade because of complicated components and limited biodegradability. The biological technology is a common method to treat antibiotics wastewater but cannot achieve high removal efficiency. The physical methods, such as flocculation and centrifugal separation, always cause secondary contamination[1]. It is reported that advanced oxidation processes can be used to treat antibiotics-contaminated wastewaters[2,3]. The photocatalytic oxidation technology shows a wide application prospect in treating refractory wastewater for energy conservation and without secondary pollution[4-7]. In recent years, in addition to the use of TiO_2, many attempts have been made to prepare some new photocatalysts, such as niobate photocatalysts, $NiNb_2O_6$ [8], KNb_3O_8[9], $InNbO_4$[10], $InMO_4$ ($M = Nb^{5+}$, Ta^{5+})[11], $K_4Nb_6O_{17}$[12], and Bi-based catalysts, Bi_2MNbO_7 ($M = Al^{3+}$, $Ga^{3+}$and In^{3+})[13], Bi_2WO_6[14], $Bi_{12}GeO_{20}$[15], $BiVO_4$[16].

In this paper, we reported the degradation of metronidazole over $K_6Nb_{10.8}O_{30}$ photocatalyst, which is prepared by a soft-chemical method reported in our previous study[17]. The result indicates that $K_6Nb_{10.8}O_{30}$ photocatalyst exhibited excellent efficiency for the degradation of metronidazole.

1 Experimental

1.1 Preparation

Niobium pentoxide (Nb_2O_5, SCRC, China), potassium hydroxide (KOH, Sinopharm Chemical Reagent ev.Ltd., SCRC, China), citric acid (CA, SCRC, China), hydrochloric acid (HCl, SCRC, China), oxalic acid (OA, SCRC, China), and potassium nitrate (KNO_3, SCRC, China) were used as starting chemical reagents. All of the reagents were of analytical grade without further purification. Metronidazole was commercially available grade. Deionized water was used in the whole experiment. The $K_6Nb_{10.8}O_{30}$ photocatalyst was prepared using the method described previously[17].

1.2 Characterization

The structure and crystallinity of the as-prepared samples were characterized by powder X-ray diffraction (XRD) on a D/MAX-RB powder X-ray diffractometer (Rigaku, Japan) using CuKα radiation. The chemical bonds on the surface of the catalysts were detected by the Fourier transform infrared (FT-IR) spectroscopy (Nexus, Thermo Nicolet, U.S.A.).

1.3 Photocatalytic Activity

An amount of the as-prepared catalyst was added to each 100 mL of metronidazole aqueous solution. Prior to UV illumination, the suspension was magnetically stirred in the dark for 10 min to disperse the catalyst. The reactor was then irradiated with UV light emitted by an 18 W UV light lamp (λ = 253.7 nm). At defined intervals, analytical samples were taken from the reaction suspensions during the reaction and then were centrifuged to remove the suspended particulates. The concentration of metronidazole solution was determined by measuring the absorbance at 318 nm with a UV-Vis spectroscopy (UV-2102/PC, China).

2 Results and Discussion

2.1 XRD Analysis

The phase composition and crystallinity of the as-prepared $K_6Nb_{10.8}O_{30}$ powders were analyzed using powder X-ray diffraction. As shown in Fig. 1, the XRD pattern can be identified and indexed using the standard XRD data of $K_6Nb_{10.8}O_{30}$ (JCPDS 87-1856), which crystallizes in the cubic system, space group P4/mbm (127).

2.2 Standard Curve

The absorbance of metronidazole aqueous solution with different concentrations at the absorption maximum 318 nm is given in Fig. 2. In Fig. 2, the relationship between the absorbance and the concentration of metronidazole aqueous solution fits with good linearity within the whole experimental concentration range.

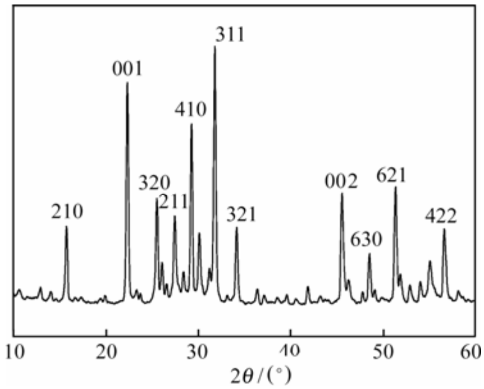

Fig. 1 XRD pattern of the as-prepared $K_6Nb_{10.8}O_{30}$ catalyst

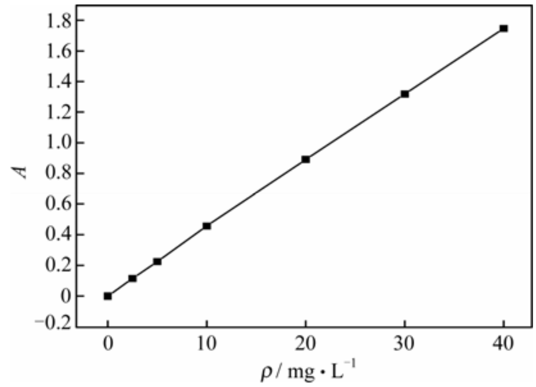

Fig. 2 The relationship between the absorbance and the concentration of metronidazole aqueous solution

2.3 Degradation of Metronidazole

Figure 3 shows the photodegradation of metronidazole solution (10 mg/L) over the $K_6Nb_{10.8}O_{30}$ catalyst under different conditions. As shown in Fig. 3, a blank experiment in the absence of the photocatalyst under UV light irradiation within 180 min showed that the photolysis of metronidazole was negligible, which indicated that metronidazole is stable under UV light irradiation. In the dark, the degradation rate of metronidazole over the $K_6Nb_{10.8}O_{30}$ catalyst did not increase but decrease, which can be attributed to that the photocatalytic particles in the suspension were not totally separated. With $K_6Nb_{10.8}O_{30}$

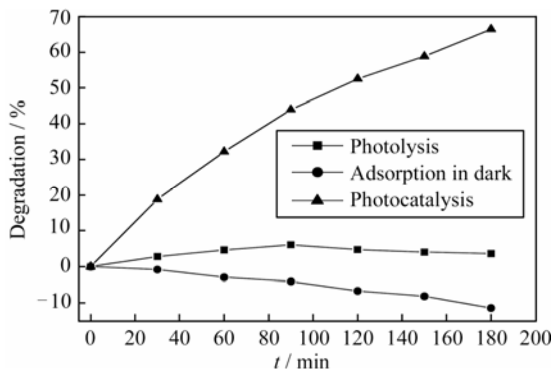

Fig. 3 Photocatalytic degradation of metronidazole aqueous solution (10 mg/L) by $K_6Nb_{10.8}O_{30}$ (1.0 g/L) under different conditions

as the photocatalyst, nearly 70% of metronidazole was removed after 180 min of irradiation. The results indicate that the degradation of metronidazole is not caused by photolysis or adsorption but by the photocatalytic reaction over the $K_6Nb_{10.8}O_{30}$ under the UV light irradiation.

Figure 4 shows the effect of the initial concentration of metronidazole solution on the photocatalytic degradation rate of the metronidazole under the UV light irradiation within 180 min. As shown in Fig. 4, the metronidazole could be removed effectively by the $K_6Nb_{10.8}O_{30}$ catalyst. The removal rate of metronidazole reached nearly 70%, while the metronidazole concentrations were 5 mg/L and 10 mg/L, respectively. While the metronidazole concentration increased to 20 mg/L, the degradation rate decreased significantly but still reached nearly 53%.

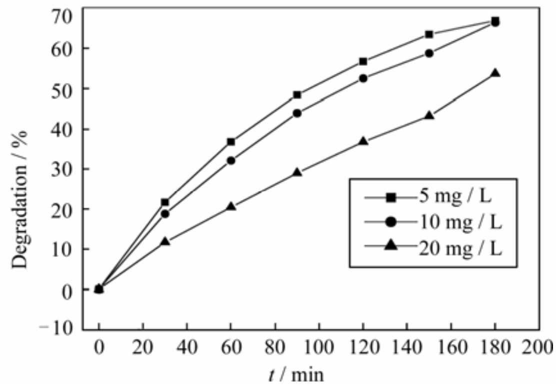

Fig. 4 The photocatalytic degradation of metronidazole solution with various initial concentrations over the $K_6Nb_{10.8}O_{30}$ catalyst

Figure 5 shows the effect of the dosage of the photocatalyst on the photocatalytic degradation rate of metronidazole (10 mg/L). As shown in Fig. 5, an increase in $K_6Nb_{10.8}O_{30}$ catalyst dosage leads to an increase in the degradation rate of metronidazole significantly. While the catalyst dosage increased to 1.5 g/L, the adsorption rate of metronidazole reached nearly 75%.

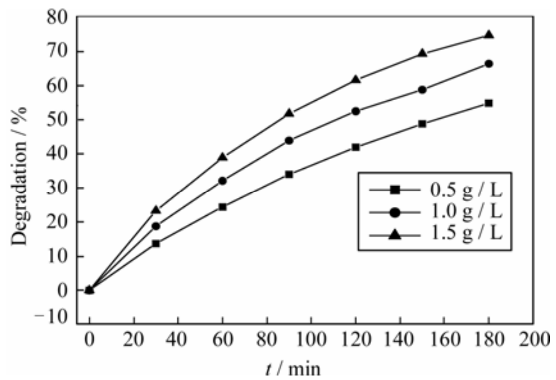

Fig. 5 The effect of the catalyst dosage on the photocatalytic degradation of metronidazole

Figure 6 displays the temporal evolution of the spectral changes of metronidazole (10 mg/L) aqueous solution during the photocatalytic reaction over the $K_6Nb_{10.8}O_{30}$ catalyst. It can be seen that the distinctive peak at 318 nm decreased gradually with the increase in reaction time, which indicated that the structure of metronidazole was destroyed during the photocatalytic reaction. It is worth noting that the intensity of the absorption peak of metronidazole solution at about 220 nm increased with increasing reaction time, which indicated that the nitro group and nitrogen existing in metronidazole were degraded to become nitrite ion. The results confirm that the metronidazole can be completely degraded by $K_6Nb_{10.8}O_{30}$ catalyst under UV light irradiation.

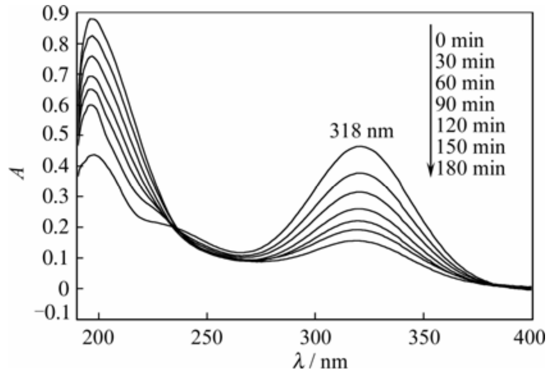

Fig. 6 UV-Vis absorption spectra of metronidazole solution (10 mg/L) during photocatalytic reaction

Figure 7 shows the FT-IR spectra of the $K_6Nb_{10.8}O_{30}$ catalyst before and after the photocatalytic reaction of metronidazole. As compared with the original catalyst, before and after the photocatalytic reaction, there are no significant differences and no characteristic peaks of metronidazole in the spectrum of the recovered catalyst, which further confirm that the removal of metronidazole is mainly caused by the photocatalytic degradation instead of adsorption. The FT-IR analysis indicates that the structure of the as-prepared catalyst is stable.

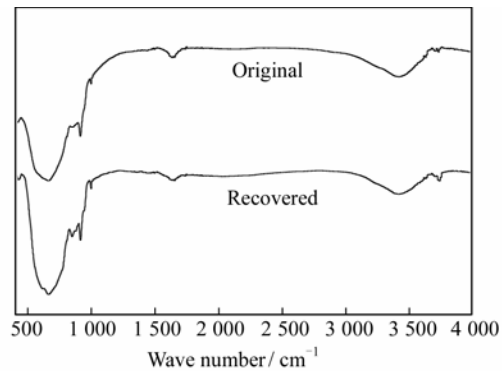

Fig. 7 FT-IR spectra of the $K_6Nb_{10.8}O_{30}$ catalyst before and after the photocatalytic reaction

According to the absorbance of metronidazole aqueous solution, the residual concentration of metronidazole at different reaction time can be obtained via the standard curve in Fig. 2. Figure 8 displays the relationship between $\ln(\rho_0/\rho_t)$ and the degradation time t with different catalyst dosages, where c_0 is the initial concentration of aqueous metronidazole, and c_t is the concentration of aqueous metronidazole at the reaction time t[18-22]. As shown in Fig. 8, the photodegradation $\ln(\rho_0/\rho_t)$ has a linear relationship with reaction time t, suggesting that the photocatalytic degradation of metronidazole on the $K_6Nb_{10.8}O_{30}$ catalyst is well described by the first-order reaction[23-27]. Table 1 lists the kinetic equations and parameters of the photodegradation of metronidazole over $K_6Nb_{10.8}O_{30}$ catalyst with different dosages. It can be seen that all of the correlation coefficients R are larger than 0.99, which show very good fitting results. The rate parameter increased with increasing the catalyst dosage, which agrees well with the experiment results in Fig. 8 and suggests that the photocatalytic efficiency improves greatly with increasing the catalyst dosage.

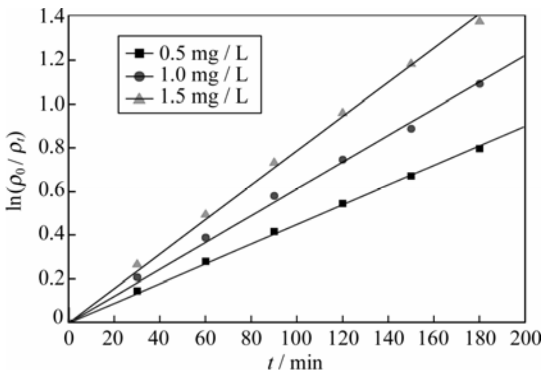

Fig. 8 First-order reaction kinetics for the degradation of metronidazole on $K_6Nb_{10.8}O_{30}$ catalyst

Table 1 First-order reaction kinetics equations and kinetic parameters with different catalyst dosages

$\rho(K_6Nb_{10.8}O_{30})$ /g•L^{-1}	First-order reaction kinetics equation	k / min^{-1}	R
0.5	$\ln(\rho_0/\rho_t) = 0.004\,49\,t$	0.004 49	0.999 66
1.0	$\ln(\rho_0/\rho_t) = 0.006\,11\,t$	0.006 11	0.998 91
1.5	$\ln(\rho_0/\rho_t) = 0.007\,86\,t$	0.007 86	0.999 32

k means the rate constant

3 Conclusion

The $K_6Nb_{10.8}O_{30}$ catalyst that was synthesized by soft-chemical method exhibited high photocatalytic activity for the degradation of metronidazole. The degradation of metronidazole was caused by the combination of the $K_6Nb_{10.8}O_{30}$ catalyst and UV light instead of adsorption. The photodegradation rate of metronidazole decreased with the increase of metronidazole concentration during the reaction time and using the same catalyst dosages. Under the UV light irradiation, the structure of metronidazole can be destroyed by the $K_6Nb_{10.8}O_{30}$ photocatalyst. The photocatalytic degradation reactions follow the first-order reaction law. The FT-IR spectra analysis indicates that the composite structure of the catalyst is stable after the photocatalytic reaction.

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