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Photocatalytic reaction kinetics model based on electrical double layer theory

Ⅲ. Surface complexation model of methyl orange adsorption on TiO_2 surface①

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Abstract: Based on the infrared characterization of methyl orange adsorption on TiO_2 surface and the titration of TiO_2, the triple layer model of methyl orange adsorption on TiO_2 was established according to electric double theory. The software FITEQL3.1 was applied to calculate the distribution of organic adsorption on TiO_2 surface by introducing dummy components to help to overcome mathematical difficulties. It is shown that the chem.-adsorption species of methyl orange have a great adsorption amount. The adsorption constants of three kinds of surface complexation expressed as $SOH^+ org^-$, SOH_2org_2 and $SOHorg^-$ are 5.98, 17.57 and − 4.2, respectively.

Key words: adsorption; methyl orange; TiO_2; surface complexation; photocatalysis
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1 INTRODUCTION

TiO_2 heterogeneous photocatalysis is a relatively innovative technology for the degradation of gaseous or aqueous organic pollutants. There were a number of literatures related to the effect of photocatalyst, reactor design, solution composition, the organic substrate, light intensity on the reaction rate and kinetics[1-6]. The investigation of intermediates and products had been focused on by means of GC-MS, ESR, FTIR and ion chromatography[7, 8]. However, only few papers related to the interactions between organic matter and metal oxides. In fact, the relationship between surface complexation and its effects on the intermediates or products is a very important factor to disclose the adsorption mechanisms of organic matter/TiO_2 surface[9, 10]. In our previous study, we demonstrated that methyl orange is oxidized more quickly at low pH due to electrostatic attraction between the negatively charged anion and the positively charged surface, based on the physical absorption mechanisms. However, organic matter may be attacked directly by hole when it is adsorbed to TiO_2 surface owing to chemisorption mechanisms. And we found the photocatalytic degradation process of methyl orange does not rule out the first-class kinetics or Langmuir-Hinshelwood (L-H) kinetics.

It has been documented that many photocatalytic reactions follow the L-H rate form as shown below:

$$-r_i = -\mathrm{d}c_i/\mathrm{d}t = k_i K_i c_i/(1+K_i c_i)$$

where $-r_i$ is the reaction rate of the component i being degraded, c_i is the concentration of the component i, k_i is the reaction rate constant, and K_i is the binding constant.

This method has serious drawbacks, primarily related to the subjectivity in estimating initial rates from experimental data[11]. In most cases, the above equation can be simply abbreviated as pseudo-first reaction kinetics form, $\ln(c/c_0) = Kt$, where K is apparent rate constant. The method cannot properly characterize the activity of photocatalyst when chemisorption happens on the TiO_2 surface. For the purpose to identify effect of the adsorption of organic on TiO_2 surface on the reaction kinetics, the farther study on the relationship between adsorption and photocatalytic reaction is needed. In this paper, we try to

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describe the distribution of organic adsorption on TiO_2 surface and the photocatalytic kinetics to establish the mathematic model of adsorption. And the triple layer model of methyl orange adsorption on TiO_2 will be established according to electric double theory, based on the infrared characterization of methyl orange adsorption on TiO_2 surface and the titration of TiO_2 [12, 13].

2 EXPERIMENTAL

2.1 Materials

All the reagents were analytical grade and used without further purification. TiO_2 was purchased from Japan Titan Kogyokk Co, and its BET surface area was 61 m^2/g. Based on the X-ray diffraction measurement, no other crystal besides anatase was detected.

Methyl orange was chosen as an objective organic matter with different molecular formula, including quinone and azo structure in different pH solution with different colors.

2.2 Methods

TiO_2, weighed by analytical balances, was added into the beaker containing methyl orange solution with 200 mL volume. Then NaOH was added and the solution was stirred for half an hour. The experimental procedure was described as follows: fetching 20 mL suspension into the beakers, respectively; then adding HCl with a mount of concentration to adjust pH; stirring for 24 h in dark. The suspension was separated by centrifugal at 3200 r/min for several times. The solution was adjusted to about pH = 7, then diluted and centrifugalized again. Then, the absorbency of solution was determined by Model 752 spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Methyl orange adsorption on surface of TiO_2 vs pH

The uptake versus pH curves for methyl orange adsorption on the surface of TiO_2 with different initial concentrations of 1.2×10^{-4}, 2.4×10^{-4}, 4.8×10^{-4} mol/L, are shown in Fig. 1. The curves show that methyl orange has great adsorption capacity in acid solutions and less adsorption capacity in basic solutions with different initial concentrations.

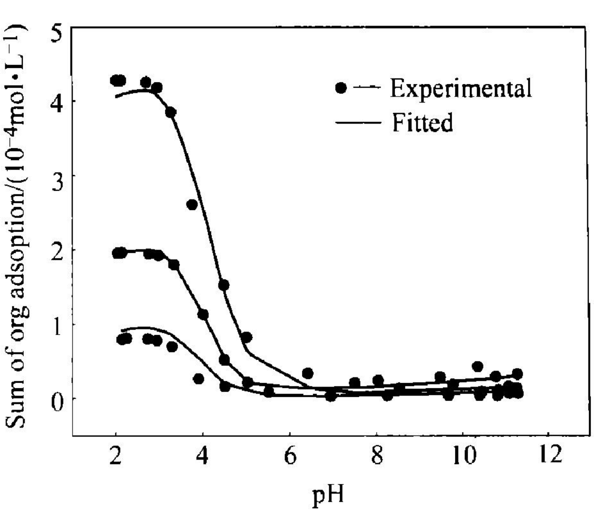

Fig. 1 Methyl orange adsorption on surface of TiO_2 vs pH

3.2 Triple layer adsorption model of methyl orange on TiO_2 surface

The widely used triple-layer model (TLM) of surface complexation model[14] was chosen to describe the effects of methyl orange adsorption on TiO_2 in different pH solutions. According to TLM, we assume that H^+ or OH^- is adsorbed in inner layer (0 plane) and reacts with surface sites of TiO_2, and the methyl orange chem.-adsorbed with surface site is also regarded as binding in 0 plane.

The TiO_2 surface ionization equilibrium can be written as

$-SOH + H^+ = -SOH_2^+$

$pK_{a1} = 5.20$

$-SOH = -SO^- + H^+$

$pK_{a2} = 7.96$

Based on infrared spectra, in acid solution, methyl orange is proven to be partially chem.-adsorbed on the surface of TiO_2, as follows:

$-SOH + 2H^+ + 2org^- = -SOH_2org_2$

In the outer layer, β plane, there exists the adsorption of methyl orange, electrolyte ions. In acid solutions,

$-SOH_2^+ + org^- = -SOH_2^+ \cdots org^-$

$-SOH_2^+ + Cl^- = -SOH_2^+ — Cl^-$

$pK_{Cl^-} = 8.2$

In basic solutions,

$-SO^- + {}^{\delta+}org^- = -SO^- \ldots {}^{\delta+}org^-$

$-SO^- + Na^+ = -SO^- — Na^+$

$pK_{Na^+} = 5.24$

There exist other equilibriums as follows:

$H^+ + OH^- = H_2O$ $pK_w = 14$

$orgH = org^- + H^+$ $pK_{org} = 3.4$

Other parameters are as follows: $c_1 = 4.8$; $c_2 = 0.2$; $N_s = 20.8$ μmol/m^2

3.3 Distribution of organic adsorption on TiO_2 surface

The software FITEQL3.1 was taken to calculate the distribution of organic adsorption on TiO_2 surface and the problem of chemical equilibrium may be solved as the following mathematical approach[15]. Each chemical species can be written as a product of a chemical reaction involving only the components, and no component can be written as a product of chemical reaction involving only other components. The model of chemical equilibrium in the solution is represented by a matrix (**A**) of a_{ij} (stoichiometric coefficients of component j in species i) and by a vector of $\boldsymbol{K}_i$ (stability constants of species i). An experimental data point is represented by a vector of $\boldsymbol{T}_j$ (total concentrations) and by a vector of $\boldsymbol{X}_j$ (free concentration of component j). The components and species representing real chemical entities must obey mass action equations (for each species) and mass balance equation (for each component). Table 1 shows the species represented by stability and matrix **A**, and Table 2 shows the relation of species and component represented by matrix **B**.

Because the concentration of methyl orange measured by the experiment is the sum of two kinds of structure of methyl orange, the each concentration of two kind of structure is not known. The dummy components org, which represent thesum of methyl orange, and ad_{sorg}, which represents the sum of methyl orange adsorption (listed in Tables 1, 2), is introduced. They do not represent real entities but their mathematical treatment is identical to that of real ones. They can help to overcome mathematical difficulties.

By debugging for surface complexation species represented by different components and matrix, it is found that the equations expressed by above tables fit experimental data well as shown in Fig. 1(line). Fig. 2 shows the distribution of surface complexation species vs c_H, the total concentration of H^+ in solution with a different initial methyl orange concentration of 1.2×10^{-4}, 2.4×10^{-4}, 4.8×10^{-4} mol/L. It is shown that chem.-adsorption species of methyl orange has a great adsorption amount. The adsorption constants of three kinds of surface complexation expressed as $SOH^+ org^-$, SOH_2org_2 and $SOHorg^-$ in above tables are 5.98, 17.57 and −4.2, respectively.

Table 1 Species, lg**K**, and stoichiometry matrix **A**

Name	lg**K**	Ψ(b)	Ψ(0)	Ψ(d)	org	SOH	org^-	ad_{org}	Cl^-	H^+	Na^+
SOH	0	0	0	0	0	1.0	0	0	0	0	0
org^-	0	0	0	0	1.0	0	0	0	0	0	0
orgH	3.4	0	0	0	1.0	0	0	0	0	1.0	0
H^+	0	0	0	0	0	0	0	0	0	1.0	0
SOH^+	5.20	0	1.0	0	0	1.0	0	0	0	1.0	0
SO^-	−7.96	0	−1.0	0	0	1.0	0	0	0	−1.0	0
$SOH+ org^-$	Find	−1.0	1.0	0	1.0	1.0	0	0	0	1.0	0
$SO^- Na^+$	−5.24	1.0	−1.0	0	0	1.0	0	0	0	−1.0	1.0
SOH_2org_2	Find	−2.0	2.0	0	2.0	1.0	0	0	0	2.0	0
Na^+	0	0	0	0	0	0	0	0	0	0	1.0
SOH_2Cl	8.20	−1.0	1.0	0	0	1.0	0	0	1.0	1.0	0
Cl^-	0	0	0	0	0	0	0	0	1.0	0	0
OH^-	−14	0	0	0	0	0	0	0	0	−1.0	0
$SOHorg^-$	Find	1.0	−1.0	0	1.0	1.0	0	0	0	−1.0	0

Table 2 Species, components and stoichiometry matrix **B**

Name	Ψ(b)	Ψ(0)	Ψ(d)	org	SOH	org^-	ad_{org}	Cl^-	H^+	Na^+
SOH	0	0	0	0	1.0	0	0	0	0	0
org^-	0	0	0	1.0	0	1.0	0	0	0	0
orgH	0	0	0	1.0	0	1.0	0	0	1.0	0
H^+	0	0	0	0	0	0	0	0	1.0	0
SOH^+	0	1.0	0	0	1.0	0	0	0	1.0	0
SO^-	0	−1.0	0	0	1.0	0	0	0	−1.0	0
$SOH+ org^-$	−1.0	1.0	0	1.0	1.0	0	1.0	0	1.0	0
$SO^- Na^+$	1.0	−1.0	0	0	1.0	0	0	0	−1.0	1.0
SOH_2org_2	0	0	0	2.0	1.0	0	2.0	0	2.0	0
Na^+	0	0	0	0	0	0	0	0	0	1.0
SOH_2Cl	−1.0	1.0	0	0	1.0	0	0	1.0	1.0	0
Cl^-	0	0	0	0	0	0	0	1.0	0	0
OH^-	0	0	0	0	0	0	0	0	−1.0	0
$SOHorg^-$	1.0	−1.0	0	1.0	1.0	0	1.0	0	−1.0	0

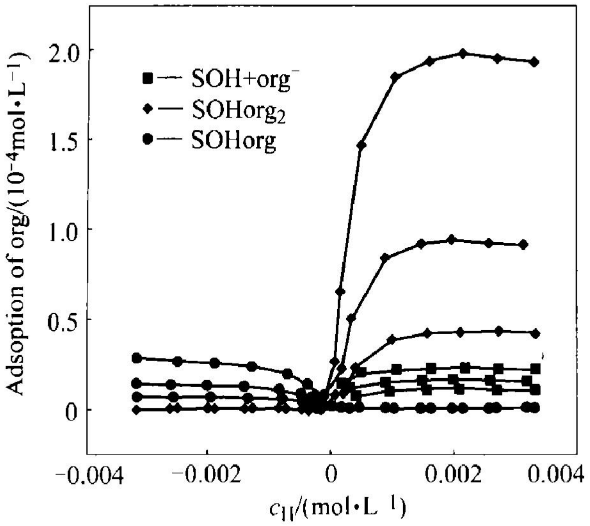

Fig. 2 Distribution of surface complexation species vs c_H in solution

4 CONCLUSION

Based on the infrared characterization of methyl orange adsorption on TiO_2 surface and the titration of TiO_2, the triple layer model of methyl orange adsorption on TiO_2 was established according to the electric double theory. The software FITEQL3.1 was applied to calculate the distribution of organic adsorption on TiO_2 surface. The dummy components were introduced to help to overcome mathematical difficulties. It is shown that chem.-adsorption species of methyl orange has a great adsorption amount. The adsorption constants of three kinds of surface complexation expressed as SOH^+ org^-, SOH_2org_2 and $SOHorg^-$ are 5.98, 17.57 and − 4.2, respectively.

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