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The oxidation kinetics of reduction intermediate product of methyl red with hydrogen peroxide

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Abstract

The reduction of methyl red and oxidation of intermediate product of its reduction in the presence of molecular oxygen and hydrogen peroxide in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4) were studied at carbon paste electrode by voltammetry. The pseudo-reversible reduction of methyl red in red quinonoid form in a $2e^-$, $2H^+$ addition ended to the colorless corresponding hydrazo compound without any following reaction. When dissolved oxygen or hydrogen peroxide were present, the intermediate product of methyl red reduction was oxidized to re-form the original. The apparent rate constant k_f of the oxidation reaction of intermediate product by hydrogen peroxide was 744 mol^{-1} L s^{-1}.

Keywords: Methyl red; Hydrogen peroxide; Carbon paste electrode

1. Introduction

A lot of azo dyes, one of the oldest synthetic chemicals, are released into the environment during manufacture and usage, which pollutes the environment and cause harm to organisms. Therefore, the degradation of azo dyes for environmental treatment has been paid attention intensively. The two kinds of degradation pathways have been mainly studied. One pathway is oxidation degradation of azo dyes, such as photocatalytic oxidation by ultraviolet or solar light in the presence of oxidant hydrogen peroxide and catalyst such as TiO_2 and its mixture with nanoparticles of other metal oxides [1–5], electro-generated active agent oxidation [6,7] and others [8]. The mechanism for oxidation degradation was studied in detail, and kinetic parameters were determined in most cases. The other is reduction degradation including electroreduction [9–11] and bioreduction with enzyme [12–14] and microbes [15–20], which is preferred because of easy availability, cheap cost and high efficiency. The reduction degradation process consists of the decolorization of azo dye by reduction of azo bond under anaerobic condition and the sequent full mineralization by oxidation of amine under aerobic condition. For this, a series of sequential anaerobic/aerobic operation systems for enzyme and microbial reduction degradation of azo dye were designed [21,22].

As far as the decolorization is concerned, although the reduction processes from azo bond to two amines for azo dyes are dependent on substituents, substitution pattern and medium environment, it goes through two stages as given in following equation:

$$\mathrm{R{-}N{=}N{-}R' + 2e + 2H^+ \rightarrow R{-}NH{-}NH{-}R' + 2e + 2H^+ \rightarrow R{-}NH_2 + R'{-}NH_2}$$

Because intermediate hydrazo compound is unstable, different reactions arising from the intermediate product could take place, such as disproportionation, oxidation and subsequent reduction. The decolorization rate either was reduced by molecular oxygen as azo dyes were re-formed via the oxidation of the hydrazo compound, or was accelerated by some enzymes and redox mediators as the reduction of the hydrazo compound was catalyzed [12–14,23]. Therefore, the kinetic data of these reactions are required for the design of the operation systems and for the optimization of the operation conditions for the reduction decolorization.

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Voltammetry due to its simplicity and high sensitivity has been often employed to study the reduction mechanism of azo dyes under deaeration condition and to study the kinetics of the forward reaction from hydrazo bond to amine for azo dyes [24–26]. However, few attempts have been made to study the kinetics of backward reaction from hydrazo bond to azo one via oxidation, especially in the presence of molecular oxygen. It is known that a catalytic voltammetry in the presence of an oxidant, due to a redox cycle of reactant of interest including the electrochemical reduction of the reactant simultaneous with the chemical regeneration through oxidation of its reduction product by oxidant, allows to determine the rate constant of the oxidation reaction [27,28]. This work seeks the kinetics for oxidation reaction of the intermediate product hydrazo compound with active oxygen species for reduction decolorization of azo dyes by using catalytic voltammetry. For this, the voltammetric behavior of methyl red (4′-dimethyl amino azobenzene-2-carboxylic acid), a monoazo compound with electron donating substituent, at carbon paste electrode (CPE) with stronger affinity to reactant and hydrophobic electrode surface in the absence and the presence of hydrogen peroxide, one of active oxygen species, was studied.

2. Experimental

2.1. Apparatus

Cyclic voltammograms were recorded on a model CHI660 electrochemical workstation (CH Instruments, USA) controlled by CH660 software that operated under Windows 2000 environment. A three-electrode system was equipped with a laboratory-made CPE, an Ag/AgCl reference electrode and a platinum-wire auxiliary electrode; and another three-electrode system was equipped with a hanging mercury drop working electrode (HMDE), an Ag/AgCl reference electrode and a platinum-wire auxiliary electrode.

2.2. Reagents

All chemicals were of analytical-reagent grade, and were used as received without further purification. Double-distilled water was used throughout the experiments. Methyl red (1.0×10^{-5} mol L^{-1}) (The Chemical Reagent Plant, Shanghai, China) solution was prepared in ethanol–water solution (volume ratio of ethanol and water was 4:6). Hydrogen peroxide (0.1 mol L^{-1}) solution was standardized by $KMnO_4$ standard solution. Acetate buffer with various pH values was prepared by mixing 0.2 mol L^{-1} HAc solution with 0.2 mol L^{-1} NaAc solution in different volume ratios.

2.3. Fabrication and activation of CPE

CPE was prepared in conventional fashion [29]. Four milligrams of graphite powder (spectrographic grade, Kelong Chemical Reagent Plant, Chengdu, China) was mixed with 1 mg of silicon oil (chromatographic grade, Kelong Chemical Reagent Plant, Chengdu, China) in a mortar and pestle. A portion of the carbon paste was packed into an end of a plastic tube (4 mm i.d.). A copper wire was inserted from other end of a plastic tube into the carbon paste to provide the electrical contact. The electrode surface was smoothed against a piece of tracing paper. Before the laboratory-made CPE

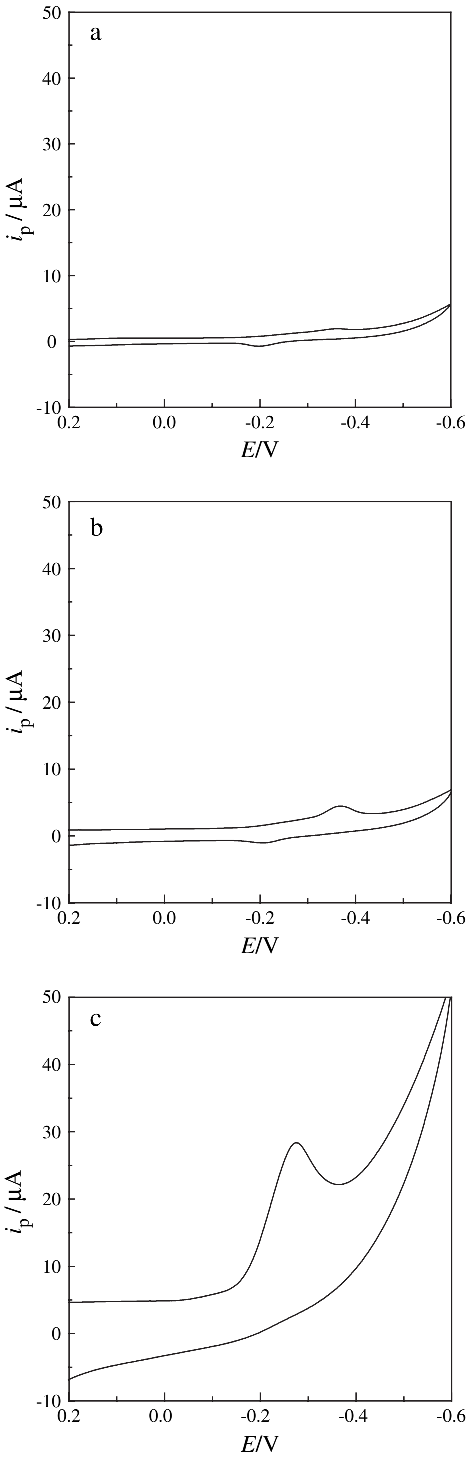


Fig. 1. Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} methyl red in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4). Potential scan rate $v = 0.10$ V s^{-1}. The initial potential 0.2 V; potential of reverse −0.6 V. (a) After deaeration; (b) without deaeration; (c) in the presence of 1.0×10^{-3} mol L^{-1} hydrogen peroxide.

was used, it was at first subjected to a 60 s pre-anodization at +1.5 V and a 60 s pre-cathodization at −1.0 V, and then to cyclic scans between +1.5 V and −1.0 V several times in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4), until the stable background current was obtained.

2.4. Procedure

Voltammetric behavior of 1.0 mL 1.0×10^{-5} mol L^{-1} methyl red in 0.2 mol L^{-1} acetate buffer (pH 4.4) in the absence and the presence of dissolved oxygen or hydrogen peroxide was examined on a model CHI660 electrochemical workstation, respectively. All experiments were performed at room temperature.

3. Results and discussion

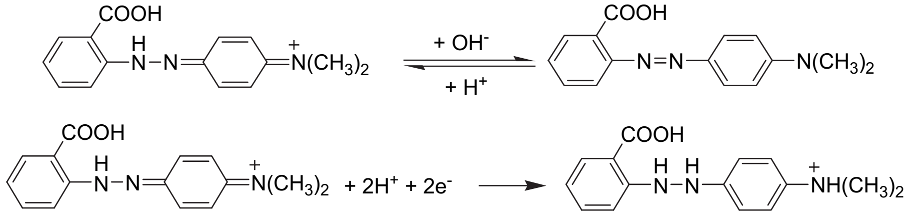
3.1. Reduction behavior of methyl red at CPE

The voltammetric behavior of methyl red at HMDE has been studied in detail [24–26]. The voltammetric behavior of methyl red at HMDE was examined again to compare with that at CPE in the absence and the presence of dissolved oxygen or hydrogen peroxide. Under deaeration with pumping oxygen-free nitrogen for 10 min, methyl red showed a single reduction wave at −0.460 V in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4), two waves at −0.486 V and −1.216 V in 0.1 mol L^{-1} NH_4–NH_4Cl buffer (pH 9.0), and the first reduction wave at −0.486 V was about 25 times higher than that at −1.216 V in peak current intensity. These results were identical with that of Xu et al. [24], and indicated that the two-electron addition step for the reduction of azo bond followed other chemical reactions of its intermediate product by catalysis of proton in most cases. Additionally, it is still observed that all the peak currents of these reduction waves of methyl red were not influenced by oxidant, even by hydrogen peroxide. Based on these reasons, it is difficult to estimate the kinetic parameter of oxidation reaction for intermediate product with voltammetric results of methyl red at HMDE in the absence and the presence of oxidant.

The voltammetric behavior of methyl red at CPE was further examined in various supporting electrolytes after deaeration. Experiments showed that no wave appeared at pH > 4.8, a reduction wave at pH < 4.8. The character of the reduction wave of methyl red in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4) was examined in the potential range of 0.2 V to −1.0 V. As showed in Fig. 1(a), only a reduction wave appeared with peak potential $E_{p,c}$ −0.368 V on cathodic scan and an oxidation wave with peak potential $E_{p,a}$ −0.203 V on reverse scan. The difference ΔE_p ($E_{p,a} - E_{p,c}$) of the peak potential of oxidation and reduction peaks was 165 mV, and the ratio $i_{p,a}/i_{p,c}$ of the peak currents was about 1.1. With the potential scan rate v increasing from 0.1 to 1.0 V s^{-1}, the peak current $i_{p,c}$ of the reduction wave increased linearly, with the linear regression equation $i_{p,c}$ (μA) = 1.31 + 4.30v (V s^{-1}) (r = 0.9981, n = 9). These indicated that the reduction of methyl red was pseudo-reversible process with adsorption character, and did not accompany with other following chemical reactions.

With the equation on width $\omega_{1/2}$ of the half wave for the adsorption reversible wave in linear sweep voltammetry, $\omega_{1/2} = 90.4/n$, the width of the half wave of the reduction wave of methyl red was 56 mV from the cyclic voltammetric experimental data, the electrons transfer number calculated was 2. In addition, the peak current $i_{p,c}$ increased with pH value increasing from 3.0 to 4.4, and then decreased in the range of 4.4–4.8 (Fig. 2, curve a). On the other hand, the peak potential $E_{p,c}$ shifted linearly to negative direction with pH value increasing in the range of 3.0–4.8. The linear regression equation was $-E_{p,c}$ (V) = 0.24 + 0.056 pH (r = 0.9922, n = 5). The slope $\Delta E_{p,c}/\Delta pH$ indicated that the proton transfer number was also 2.

From the results obtained above, the reduction wave of methyl red should be attributed to the reduction of methyl red in quinonoid form as the red quinonoid form is predominant in pH < 5.1 medium, and the electrode process was a $2e^-$, $2H^+$ addition, that is, the reduction of azo bond ended to hydrazo one, as described below:



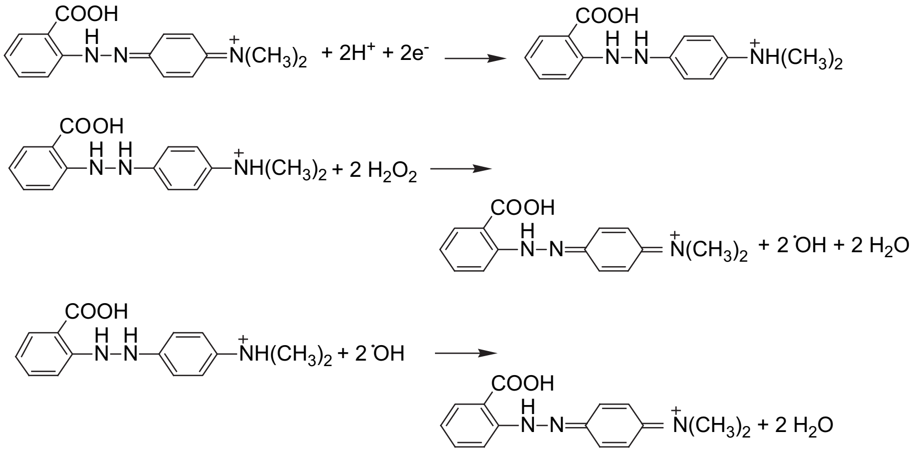
3.2. Catalytic behavior of methyl red in the presence of hydrogen peroxide

When a certain amount of hydrogen peroxide solution was added into 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4), the peak current of the reduction wave of methyl red increased obviously, while the peak potential remained nearly unchanged on cathodic scan, and the oxidation wave disappeared on reverse scan, producing a kinetic wave (Fig. 1(c)). Furthermore, the peak current $i_{p,k}$ of the kinetic wave increased linearly with increasing hydrogen peroxide concentration. When hydrogen peroxide concentration was in the range of 4.0×10^{-4}–1.4×10^{-3} mol L^{-1}, the ratio $i_{p,k}/i_{p,c}$ of the peak current $i_{p,k}$ of the kinetic wave to the peak current $i_{p,c}$ of the corresponding reduction wave was linearly proportional to the square root

$(C_{H_2O_2})^{1/2}$ of hydrogen peroxide concentration. The linear regression equation was $i_{p,k}/i_{p,c} = -0.052 + 58.45(C_{H_2O_2})^{1/2}$ $(\text{mol L}^{-1})^{1/2}$ ($r = 0.9954$, $n = 6$). Moreover, the current function $i_{p,k}\ v^{-1}$ of the kinetic wave decreased sharply with the potential scan rate v increasing from 0.05 to 0.30 V s^{-1}, and then leveled off in the range of 0.30–1.0 V s^{-1} (Fig. 3(c)). Whereas the current function $i_{p,c}\ v^{-1}$ of the corresponding reduction wave was nearly unchanged in the range of 0.05–1.0 V s^{-1} (Fig. 3(a)). These characteristics indicated that the kinetic wave in the presence of hydrogen peroxide was a parallel catalytic one [30].

Experiments also showed that the effect of pH value on peak current $i_{p,k}$ of the parallel catalytic wave was almost similar to that of the corresponding reduction wave (Fig. 2, curve b). The peak potential shifted to negative direction with pH value increasing from 3.0 to 4.8, and the relation equation was $-E_{p,k}$ (V) $= 0.19 + 0.059$ pH ($r = 0.9913$, $n = 6$). This indicated that the electrode reaction of the parallel catalytic wave was essentially the same as that of the reduction wave, which was still the reduction from the azo bond of methyl red in quinonoid form to hydrazo one.

According to catalytic voltammetry, the production of the parallel catalytic wave of methyl red results from the oxidation of the intermediate product, 4′-dimethyl amino hydrazobenzene-2-carboxylic acid (DAHA), by hydrogen peroxide. The redox cycle coupled the electrochemical reduction with chemical oxidation regeneration of the quinonoid form of methyl red led to the effective increase of the current response. On the other hand, it is known that the reduction of hydrogen peroxide was two successive one-electron processes via a hydroxyl free radical ˙OH. The hydroxyl free radical ˙OH is more active than hydrogen peroxide. One can be sure that the hydroxyl free radical ˙OH took part in the oxidation reaction. Consequently, the production process of the parallel catalytic wave of methyl red was suggested as follows:



In fact, voltammetric behavior of methyl red in the presence of dissolved oxygen was similar to that in the presence of hydrogen peroxide. Fig. 1(b) showed the cyclic voltammogram of methyl red without deaeration in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4). The peak current of the reduction wave increased and that of the oxidation wave decreased in comparison with that in the absence of dissolved oxygen as showed in Fig. 1(a). The ratio $i_{p,a}/i_{p,c}$ of their peak currents was about 0.7. Moreover, Fig. 3(b) showed that the change in the trend of the current function $i_p v^{-1}$ of the reduction wave of methyl red without deaeration was similar to and was less than that in the presence of hydrogen peroxide in Fig. 3(c). Obviously, the enhanced wave in the presence of dissolved oxygen was a parallel catalytic one similar to that in the presence of hydrogen peroxide. Although the catalytic current caused by dissolved oxygen is less than that by hydrogen peroxide, it was assigned to the oxidation of DAHA by molecular oxygen.

3.3. Rate constant of the oxidation reaction of DAHA with hydrogen peroxide

Voltammetric behavior of methyl red at CPE seems to give a very good chance for the determination of kinetic rate constant for the oxidation reaction of intermediate product of azo compound reduction as (1) the reduction from azo bond to hydrazo one in the absence of molecular oxygen did not interfere with other following reactions; and (2) the catalytic wave easily produced in the presence of oxidant and the kinetic parameter based on the current responses was easily obtained.

For this work, as the reaction of hydroxyl free radical ˙OH with DAHA was a free radical one with very high rate constant, the rate of the oxidation reaction was determined by the intermolecular reaction of DAHA with hydrogen peroxide. Furthermore, hydrogen peroxide concentration was far larger than the DAHA concentration under the condition in this work, so the oxidation reaction can be treated as a pseudo-first-order reaction.

According to the current equation for parallel catalytic wave with adsorption character in linear sweep voltammetry [31], which resembles that for parallel catalytic wave without adsorption character in direct current voltammetry in form,

$$i_{p,k}/i_{p,c} = 0.81(Zk_f C_{ox} t)^{1/2}$$

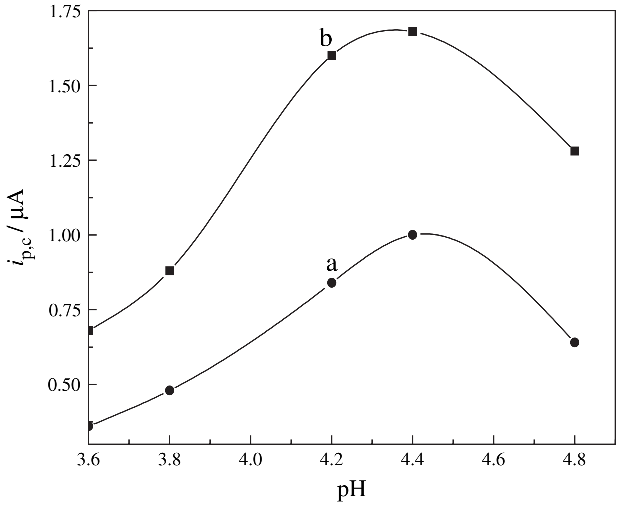


Fig. 2. Dependence of peak current $i_{p,c}$ of the reduction wave of 1.0×10^{-5} mol L^{-1} methyl red on pH value of HAc–NaAc buffer. Potential scan rate $v = 0.10$ V s^{-1}. (a) After deaeration; (b) in the presence of 1.0×10^{-3} mol L^{-1} hydrogen peroxide.

where k_f (mol^{-1} L s^{-1}) is the apparent rate constant and Z is a stoichiometric factor of the oxidation reaction of the reduction product with the oxidant, respectively, t (s) is the sampling time, C_{ox} is oxidant concentration and other symbols possess general meaning. In the case of this work, 1 mol H_2O_2 oxidized 1 mol DAHA, $Z = 1$, and the sampling time t was 7 s. By the slope of the $i_{p,k}/i_{p,c}-(C_{H_2O_2})^{1/2}$ relationship from the experimental data, $0.81(k_f t)^{1/2} = 58.45$ $mol^{-1/2}$ $L^{1/2}$, the apparent rate constant k_f of the oxidation reaction of DAHA with hydrogen peroxide was 744 mol^{-1} L s^{-1}.

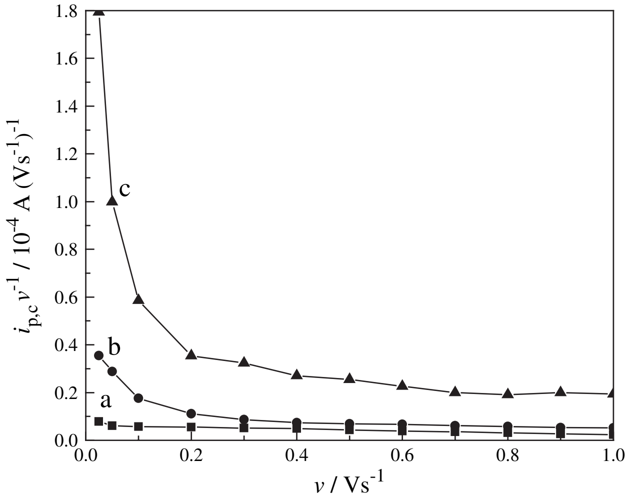


Fig. 3. Dependence of current function $i_{p,c}v^{-1}$ of the reduction wave of 1.0×10^{-5} mol L^{-1} methyl red on potential scan rate v in 0.2 mol L^{-1} HAc–NaAc buffer (pH 4.4). (a) After deaeration; (b) without deaeration; (c) in the presence of 1.0×10^{-3} mol L^{-1} hydrogen peroxide.

4. Conclusions

The voltammetric behavior of methyl red at CPE was different from that at mercury electrode. Methyl red showed only a two-electron, two-proton pseudo-reversible reduction wave, the reduction of azo bond of methyl red ended to hydrazo compound DAHA in weak acidic medium at CPE, which did not accompany any of the following reactions in the absence of oxidant. When dissolved oxygen or hydrogen peroxide was present, a catalytic wave produced as the product DAHA of methyl red reduction was oxidized to the original. With the catalytic responses in the presence of hydrogen peroxide, the apparent rate constant of the oxidation reaction of DAHA with hydrogen peroxide was obtained. The kinetics of oxidation reaction of the intermediate product of azo dyes reduction with active oxygen species may be conveniently estimated by the catalytic voltammetry, which are helpful for both the design of the reduction degradation operation systems and the optimization of the operation conditions under anaerobic conditions.

Acknowledgements

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