Degradation of Oxytetracycline by the Iron Wire/H$_2$O$_2$ System

Jian ZHOU
Shanghai Institute of Technology
Ecological comprehensive laboratory
Shanghai, 201418, China
e-mail: ayhgxzj@163.com

Meifang HOU
Shanghai Institute of Technology
Ecological comprehensive laboratory
Shanghai, 201418, China
e-mail: mfhou@sit.edu.cn

Dongyu PAN
Shanghai Institute of Technology
Ecological comprehensive laboratory
Shanghai, 201418, China
e-mail: dongyu_pan@foxmail.com

Abstract—**The degradation of oxytetracycline (OTC) by the iron wire/H$_2$O$_2$ system was investigated. The effects of initial concentration of OTC, H$_2$O$_2$ dosage, initial pH value, iron wire dose and reused times of iron wire on the degradation of OTC were examined. The results showed that iron wire exhibited high catalytic activity and stability on the activation of H$_2$O$_2$ for the degradation of OTC. The degradation kinetic of OTC could be well described by the pseudo first-order kinetic model. The reactive oxygen species (·OH) produced in the iron wire/H$_2$O$_2$ system is significant key to the degradation of OTC. The mechanism of oxidative degradation of OTC was discussed by the UV-Vis spectra analysis and monitoring the iron ions dose and pH value of the reaction solution.**
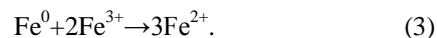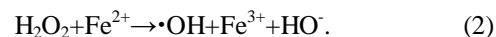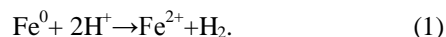
Keywords-iron wire; H$_2$O$_2$; Fenton; oxytetracycline

I. INTRODUCTION

Antibiotics are widely used in large quantities not only for the treatment of bacterial diseases in both humans and animals but also for the feed supplement in agricultural livestock production [1,2]. However, antibiotics have received increasing public concern and scientific interest in the recent years because of their adverse effects on human health and aquatic ecosystems [3,4]. As broad spectrum bacteriostatic agent, the tetracyclines such as oxytetracycline (OTC) have been the most widely used veterinary antibiotics in the USA and elsewhere [5,6]. Most OTC is excreted without undergoing metabolism and the conventional treatment technologies, such as biodegradation, adsorption, filtration and chlorination [7,8,9,10], cannot remove OTC efficiently leading to its frequent detection in various aquatic environments [1,11,12,13]. The presence of OTC in aquatic environments can affect the selection of genetic variants of microorganisms resulting in the development of drug resistant bacteria or pathogens, which may threaten the ecosystem and human health [1,14,15]. Therefore, the development of environmentally friendly technologies that effectively remove OTC is very important.

The Fe^0-based Fenton process, which is the Fe^0/H$_2$O$_2$ system, has been considered as a promising technique to remove different pollutants in wastewater [16,17,18,19,20]. Fe^0 as the potent source for Fe^{2+} could pseudo-activate H$_2$O$_2$ to produce hydroxyl radical (·OH, E_0=2.72V) which is a nonselective oxidant in the Fe^0-based Fenton reactions (Eqs. 1-3) [21,22,23].

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2. \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + Fe^{3+} + HO^-. \tag{2}$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+}. \tag{3}$$

The several works of degradation of OTC on account of ·OH oxidation have been reported in the recent years [24,25,26,27,28]. There is certain feasibility for the degradation of OTC by Fe^0-based Fenton process. Generally, the zero-valent iron powder, nanoscale zero-valent iron and metal iron are used as source of Fe^0 in the Fe^0-based Fenton reaction [21,23,29,30,31]. However, the zero-valent iron powder and nanoscale zero-valent iron are difficult to be collected and recycled after reaction. Therefore, the more cheaper and easy recyclable metal iron wire was chosen as pseudo-catalytic of H$_2$O$_2$ for the degradation of OTC in this work. The degradation kinetics and mechanism of OTC were also discussed.

II. MATERIALS AND METHODS

A. Materials

The iron wire of 2 mm in section diameter was collected from waste recycling station and then cleaned with alcohol cotton. The OTC (>98%) was purchased from Adamas-beta Co., Ltd. The chemicals including H$_2$O$_2$ (30%, v/v), isopropanol, HCl and NaOH were obtained in analytical grade from Sinopharm Chemical Reagent Co., Ltd, China. Deionized water was used for preparing the solutions in the experiments.

B. Procedure and Approach

If specification, batch experiments were carried out in a

150 mL glass flask exposed to air at 298 K in dark and all experimental iron wires were only retained two sections. The degradation of OTC in the presence of iron wire and H_2O_2 was investigated under different factors, including the initial concentration of OTC, the H_2O_2 dosage, the initial pH value, the iron wire dose and the reused times of iron wire. The initial pH value in the solution of OTC was adjusted by 1.0 M HCl and 1.0 M NaOH. For all experiments, the 100 mL solution of OTC with the desired initial pH value was added with the iron wire and H_2O_2 under vigorous stirring. At different time intervals, 5 mL sample was taken and then filtered using 0.45 um filter to get the filtrate for analysis. The concentration of OTC was quantified by monitoring the changes in the main absorption peak of aqueous solutions in UV-Vis spectrometer (TU-1901-PC, Beijing). The pH value was detected by pH meter (pHS-3E, Shanghai, China). The concentration of aqueous iron ions were determined by the ferrozine method [32].

III. RESULTS AND DISCUSSION

A. *Effect of the Initial Concentration of OTC*

The effect of the initial concentration of OTC on the degradation of OTC is shown in Figure 1. The experimental results showed that OTC could be effectively degraded by iron wire/H_2O_2 system. The degradation rate of OTC gradually decreased with the increase of its initial concentration, perhaps because some by-products were formed during the degradation of OTC and their concentrations might gradually increase with the increase of initial OTC concentration, leading to the competition for finite ·OH between the by-products and OTC [33].

Generally, the degradation kinetic of OTC on account of ·OH oxidation conforms to the pseudo first-order kinetic model (Eq. 4) [25,26,27].

$$\ln(C/C_0) = -kt. \quad (4)$$

Where C_0 is the initial concentration of OTC and C is the concentration of OTC at time (t). The k is the first order reaction rate constant. The pseudo first-order kinetic model could well describe the degradation kinetic of OTC. Therefore, kinetic model of all experiments were treated with first-order kinetic in this paper. The pseudo first-order kinetic constant (k) for OTC is listed in Table I under its different initial concentration. The results showed that the degradation kinetic constant for OTC decreased gradually with the increase of its initial concentration.
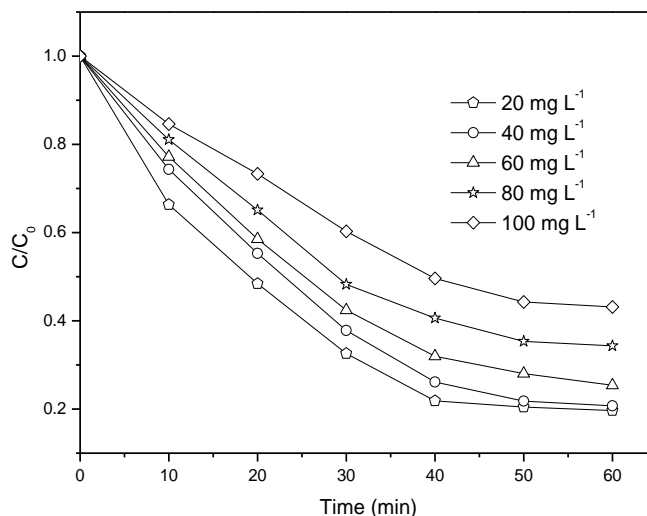

Figure 1. The degradation of OTC at pH 3.0 under its different initial concentration with 4 g L^{-1} iron wire and 30 mmol L^{-1} H_2O_2.
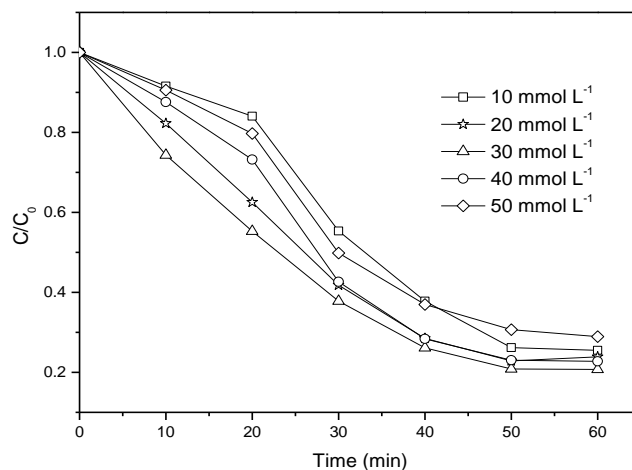

Figure 2. The degradation of 40 mg L^{-1}OTC at pH 3.0 under different dosage of H_2O_2 with 4 g L^{-1} iron wire.

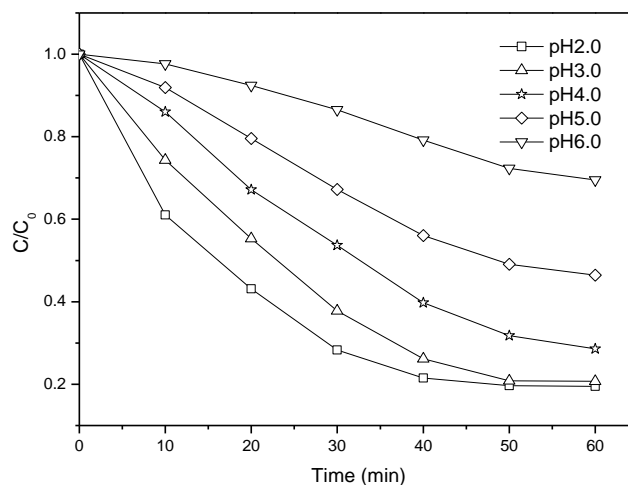
Figure 3. The degradation of 40 mg L^{-1} OTC under different initial pH value with 30 mmol L^{-1} H_2O_2 and 4 g L^{-1} iron wire.
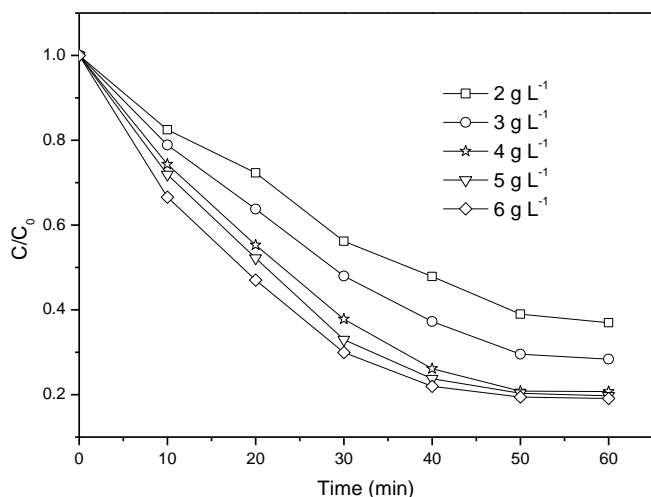
Figure 4. The degradation of 40 mg L^{-1} OTC at pH 3.0 under different dose of iron wire with 30 mmol L^{-1} H_2O_2.
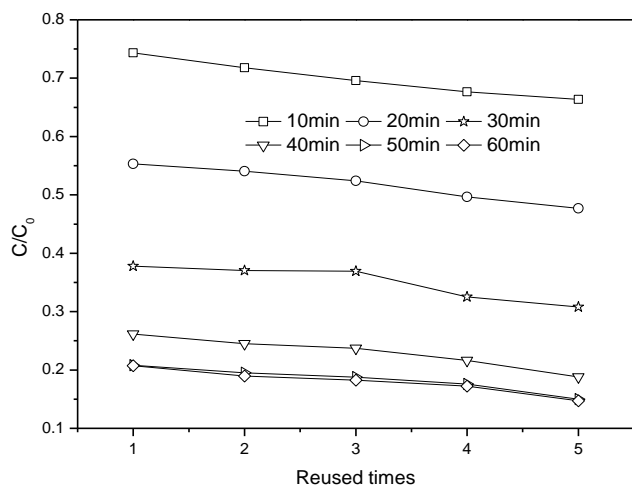

Figure 5. The degradation of 40 mg L^{-1} OTC at pH 3.0 under different reused times of iron wire with 30 mmol L^{-1} H_2O_2 and 4 g L^{-1} iron wire.
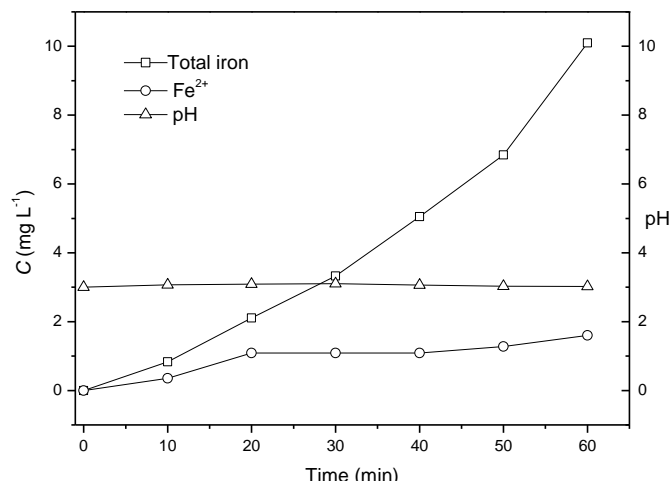

Figure 6. The iron ions dose and pH value during the degradation of 40 mg L^{-1} OTC at pH 3.0 with 4 g L^{-1} iron wire and 30 mmol L^{-1} H_2O_2.

B. *Effect of H_2O_2 Dosage*

In order to analyze the effect of H_2O_2 dosage on the degradation of OTC, the experiments were carried out at different dosage of H_2O_2. The experimental results are shown in Figure 2 and Table II. The degradation rate of OTC and reaction rate constant increased with the increase of H_2O_2 dosage up to 30 mmol L^{-1} and then decreased with H_2O_2 dosage over 30 mmol L^{-1}. Generally, low dosage of H_2O_2 can be easily exhausted, resulting in the difficulty to produce ·OH continuously, and then the removal rate of pollutants was hindered. High concentration of H_2O_2, however, may be the scavenger of ·OH and the competitive radical reactions (Eqs. 5-7), leading to the degradation of OTC was suppressed [25,33,34].
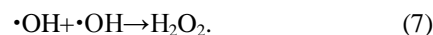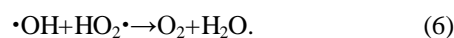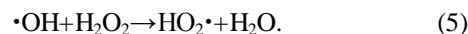
$$·OH+H_2O_2→HO_2·+H_2O. \quad (5)$$

$$·OH+HO_2·→O_2+H_2O. \quad (6)$$

$$·OH+·OH→H_2O_2. \quad (7)$$

TABLE I. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC WITH DIFFERENT INITIAL CONCENTRATION OF OTC.

C_0 (mg L^{-1})	20	40	60	80	100
K ($×10^{-3}$ min^{-1})	37.70	32.55	28.20	22.86	17.03
R	0.9992	0.9981	0.9993	0.9972	0.9981

TABLE II. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC WITH DIFFERENT DOSAGE OF H_2O_2.

H_2O_2 (mmol L^{-1})	10	20	30	40	50
K ($×10^{-3}$ min^{-1})	20.34	29.25	32.55	27.84	22.07
R	0.9483	0.9942	0.9981	0.9675	0.9627

TABLE III. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC AT DIFFERENT INITIAL pH VALUE.

pH	2.0	3.0	4.0	5.0	6.0
K ($×10^{-3}$ min^{-1})	40.36	32.55	21.66	13.51	5.170
R	0.9624	0.9981	0.9749	0.9815	0.9873

TABLE IV. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC WITH DIFFERENT DOSE OF IRON WIRE.

Iron wire (g L^{-1})	2	3	4	5	6
K ($×10^{-3}$ min^{-1})	18.40	24.31	32.55	35.67	38.66
R	0.9963	0.9988	0.9981	0.9980	0.9988

TABLE V. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC AT DIFFERENT REUSED TIMES OF IRON WIRE.

Reused times	1	2	3	4	5
K ($×10^{-3}$ min^{-1})	32.55	33.89	34.67	37.02	40.36
R	0.9981	0.9975	0.9972	0.9976	0.9976

TABLE VI. THE PSEUDO FIRST-ORDER KINETIC CONSTANTS (K) FOR OTC AT DIFFERENT DOSE OF ISOPROPANOL.

Isopropanol (mmol L^{-1})	0	10	20	30
K ($×10^{-3}$ min^{-1})	32.55	15.22	12.55	2.960
R	0.9981	0.9876	0.9697	0.9707

C. Effect of the Initial pH Value

The experiment of degradation of OTC was carried out at different initial pH value. As shown in Figure 3 and Table III, the degradation rate of OTC and reaction rate constant decreased gradually with the increase of the initial pH value. Obviously, the initial pH value of the reaction solution is important parameter. The lower pH value should be helpful for the corrosion of iron wire to produce Fe^{2+}, and then enhance the decomposition of H_2O_2 to generate $\cdot OH$ on the surface of iron wire (Eqs. 1,2) [35,36].

D. Effect of Iron Wire Dose

The degradation of OTC was studied at different dose of iron wire. According to the results (Figure 4, Table IV), the degradation rate of OTC and reaction rate constant increased gradually and then tend to be gentle with the increase of iron wire dose. The increase of iron wire dose could enlarge the surface area of Fe^0, which was useful for the corrosion of iron wire to produce more Fe^{2+}. However, the excessive Fe^{2+} may be the scavenger of $\cdot OH$ and thus cause adverse effects for the degradation of OTC (Eq. 8) [30].

$$Fe^{2+}+\cdot OH \rightarrow HO^-+Fe^{3+}. \qquad (8)$$
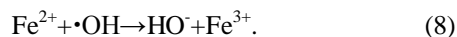
E. Effect of Iron Wire Reused Times

The effect of iron wire reused times for the degradation of OTC was investigated through the five-run reusability experiment. The experimental results were shown in Figure 5 and Table V. It was found that the degradation of OTC in each time period and reaction rate constant increased as the reused times of iron wire increased. It can be derived that iron wire has the high catalytic activity and stability. In the Fe^0-based Fenton process, some iron oxides, mainly magnetite, can be generated on the surface of Fe^0. The magnetite can assist the electron transfer from Fe^0 to magnetite to produce Fe^{2+} by acting as an intermediate /interface in the Fenton reaction [22,23]. Repeated use of iron wire could increase its surface magnetite coverage, which was more favorable to electron transfer for the degradation of OTC.
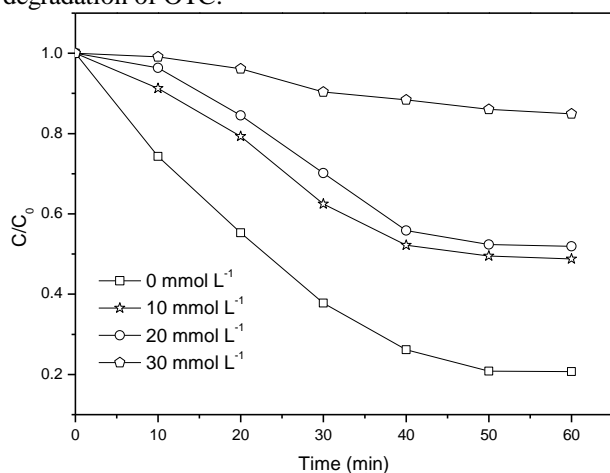

Figure 7. The degradation of 40 mg L^{-1} OTC at pH 3.0 under different dose of isopropanol with 30 mmol L^{-1} H_2O_2 and 4 g L^{-1} iron wire.
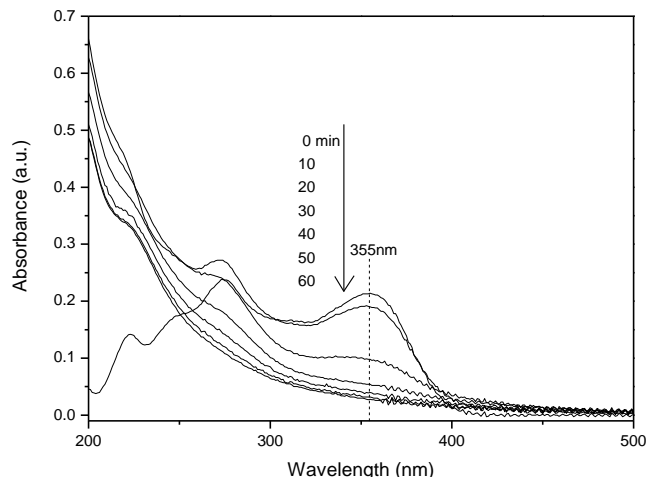

Figure 8. The temporal UV-Vis spectra of reaction solution that was diluted by five times.

F. Mechanism of Degradation of OTC

The iron ions dose and pH value of the reaction solution were determined and the results were depicted in Figure 6. With the degradation time increasing, the concentration of total iron gradually increased which indicated that the iron wire could be continuously corroded to provide iron ions in the reaction. The change of Fe^{2+} dose indicate that the formation rate of Fe^{2+} was not less than its consuming rate in the reaction. The pH value of the reaction solution had barely changed, which suggested that some new H^+ due to the deprotonation of naphthol ring of OTC may be produced in the degradation of OTC [25]. The new created H^+ could neutralize OH^- produced in the decomposition of H_2O_2 and supplement depletion of H^+ due to the corrosion of iron wire (Eqs. 1,2) [22], resulting in the pH value of the reaction solution remained stable.
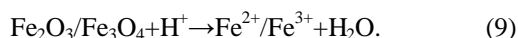
It is well known that the isopropanol is an effective scavenger for $\cdot OH$ [25]. When the different doses of isopropanol were introduced into the iron wire/H_2O_2 system, the experiment results of degradation of OTC were shown in Figure 7 and Table VI. The degradation rate of OTC and kinetic constant (k) obviously decreased with the increase of the initial isopropanol dose, which indicated $\cdot OH$ is the significant key to the degradation of OTC in the iron wire/H_2O_2 system.

Figure 8 illustrates the changes of UV-Vis spectra of reaction solution that was diluted by five times (initial concentration OTC 40 mg L^{-1}, pH 3.0, iron wire dose 4 g L^{-1}, H_2O_2 dosage 30 mmol L^{-1}). The absorption peak at 355 nm is characteristic absorption peak of OTC due to its main structure of naphthol ring [28,37]. It can be seen that the strong absorbance peak at 355 nm decreased gradually with the reaction which indicated that the naphthol ring of OTC was effectively decomposed. However, the absorption peak at 274 nm increased and then disappeared, which suggested the formation of very unstable intermediates during the degradation of OTC.

Based on the above results, a possible oxidation degradation mechanism for OTC by iron wire/H_2O_2 system

was proposed. At first, the surface of iron wire is corroded to produce soluble Fe^{2+} in the acidic solution (Eq. 1,9) [23]. In the thermodynamics, Iron wire corrosion is a spontaneous process under acidic conditions unless its surface is strongly passivated [30]. The generated Fe^{2+} is able to react with H_2O_2 to produce $\cdot OH$ and Fe^{3+} (Eq. 2) [22]. Following the strong oxidizing $\cdot OH$ radicals attack the naphthol ring structure of OTC to form unstable intermediates and H^+, even CO_2 and H_2O (Eq. 10). Meanwhile, the Fe^{3+} could be also reduced to Fe^{2+} by Fe^0 on the surface of iron wire (Eq. 3) [23,31].

$$Fe_2O_3/Fe_3O_4+H^+\rightarrow Fe^{2+}/Fe^{3+}+H_2O. \qquad (9)$$

$$\cdot OH+OTC\rightarrow unstable\ intermediates+H^+\rightarrow CO_2+H_2O. (10)$$

IV. CONCLUSIONS

The iron wire could effectively activate H_2O_2 to degraded OTC in water. Repeated use of iron wire exhibited higher activity and stability in the experiments. The reactive oxygen species ($\cdot OH$) is the significant key to the degradation of OTC by the iron wire/H_2O_2 system.

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