Mechanistic and Kinetic Studies of Heterogeneous UV/Fenton Process for the Oxidation of Aqueous Organic Pollutants: Electron Transfer at Catalyst Surface to Initiate the Redox Process

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Abstract

Heterogeneous UV/Fenton process provides an attractive photocatalytic degradation process, owing to its relatively low costs in preparing the catalyst (iron oxide/oxalate) and oxidant (hydrogen peroxide) and high treatment efficiency. A number of lab-scale studies have been reported in this area recently. To foster the lab studies to large-scale applications, this work investigates the mechanism and kinetics of heterogeneous UV/Fenton process in oxidizing non-biodegradable dyes. Prior to model development, the roles of photocatalyst, hydrogen peroxide and UV light have been distinctly presumed as follows. With the assistance of light irradiation, iron oxide serves as the electron provider, which elevates its electrons to conduction band. The thus created 'electron-hole' pairs promote the redox reaction between hydrogen peroxide and water molecules adsorbed at the catalyst surface, resulting in the generation of hydroxyl radicals and commencement of pollutant degradation. On the basis of these assumptions on reaction mechanism, a simplified kinetic model was developed following 'free radical reaction' concept. The model simulation concludes that when hydrogen peroxide is in great excessive amount, hydrogen peroxide consumes in parallel with pollutant degradation, both of which follow first-order reaction. The established model tallies well with experimental observations on the photodegradation of various dyes and can be adopted as a generalized kinetic model for scale up purposes.

Keywords: UV/Fenton process; Mechanism; Kinetics; Electron transfer.

1. Introduction

UV/Fenton is a photo-oxidation process where organic pollutants are degraded using iron and H_2O_2 as photocatalyst and oxidant, respectively. Taking into account the potential pollution caused by homogeneous iron, more recently, studies on photocatalytic oxidation using heterogeneous iron oxide/oxalate have been extensively conducted and promising results are reported [1-5]. In sum, the upsides of such a process lie in:

- Effective degradation of organic pollutants with low biodegradability;
- Little catalyst leaching when iron oxide/oxalate was adopted as the catalyst; and
- Saving energy use by conducting the reaction at ambient temperature and utilizing light as the energy source.

Although it has been experimentally confirmed that heterogeneous UV/Fenton process caters such an attractive option in treating refractory wastewater, its further application to actual wastewater treatment still remains many constraints, one of which is attributed to inadequate understanding on the mechanism and kinetics of such process. He et al. [4,5] believed that the oxidation results from hydroxyl radical produced by a photocatalytic process where iron oxalate (α-FeOOH) and H_2O_2 form certain type of compound at the iron catalyst surface. Their proposed mechanism is represented by the below four equations [5]:

$$Fe^{III} + H_2O_2 \rightarrow FeOOH + H_2O_2 \quad (a)$$

$$Fe^{III}OOH + hv \rightarrow Fe^{IV}{=}O + \bullet OH \quad (b)$$

$$Fe^{IV}{=}O + H_2O \rightarrow Fe^{III}OH + \bullet OH \quad (c)$$

$$\text{Organics} + \bullet OH \rightarrow \text{degraded or mineralized products} \quad (d)$$

Obviously, this mechanism assumes that the interaction between iron oxalate, H_2O_2 and H_2O at the catalyst surface accounts for the eventual production of hydroxyl radical. They have also exhibited some experimental observations advocating the proposed mechanism.

However, so far no kinetic model has been established to completely address the roles of: a) light; b) catalyst, including the active element and supporting material; and c) H_2O_2 in a typical heterogeneous UV/Fenton process. We believe that better understanding of the reaction mechanism and development of kinetic model will benefit the application of proved heterogeneous UV/Fenton process to large scale.

This study attempts to understand the reaction mechanism involved in the UV/Fenton process and accordingly develop a kinetic model. Relevant published experimental data are cited to validate the model's prediction.

2. Mechanism

It is broadly concurred by physicians and chemists that, when light illuminates a semiconductor and the photon absorbed has energy at least equal to the bandgap of the semiconductor, electrons are elevated to the conduction band from valence band, causing electron-hole pairs [6]. When the irradiated semiconductor is in contact with a redox couple, electron transfer occurs and a redox reaction is initiated.

Fe_2O_3 is one of the typical semiconductor materials having a bandgap of 2.0 eV. In view of this, in an UV/Fenton process Fe_2O_3 plays the role an electron-hole provider. This assumption can be represented by the following equations:

$$Fe_2O_3 + hv \rightarrow h^+ + e^- \quad (1)$$

In absence of O_2, the role of H_2O_2 in the UV/Fenton process is to accelerate the electron scavenge process and prevent the combination of electron-hole pairs [7]. Meanwhile H_2O also produces hydroxyl radical by accepting the created holes. The above mechanism can be represented by the following two half reactions:

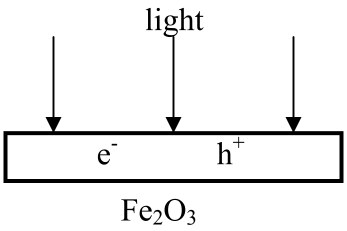
$$H_2O_2 + e^- + H^+ \rightarrow OH\bullet + H_2O \quad (2)$$

$$H_2O + h^+ \rightarrow OH\bullet + H^+ \quad (3)$$

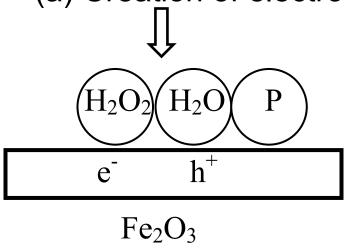
The overall reaction is thus

$$H_2O_2 + hv \rightarrow 2OH\bullet \quad (4)$$

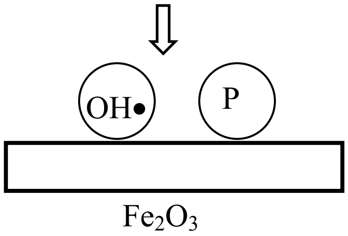
The generated hydroxyl radical will further attack pollutant to commence the degradation process. Although it appears in Eq.(4) that hydroxyl radical is the product of H_2O_2 cleavage, the actual redox reaction is actually completed due to the contact between H_2O_2 and H_2O at the catalyst surface. Light, iron oxide and H_2O_2 and H_2O all play important roles in this step. The above-assumed mechanism is in general agreement with He et al.'s proposal [4-5] and demonstrated in Fig. 1.



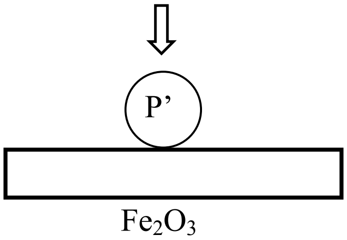
(a) Creation of electron-hole pair.



(b) Adsorption of H_2O_2, H_2O and pollutant onto Fe_2O_3 surface.



(c) Production of hydroxyl radical and start of pollutant degradation.



(d) Production of reaction intermediates.

Fig. 1 Schematic diagram of the proposed reaction mechanism.

Based on the proposed reaction mechanism, we outlined the pathway of a certain pollutant degradation process as below:

Production of Electron-Hole Pairs:

$$Fe_2O_3 + hv \rightarrow h^+ + e^- \tag{1}$$

Rapid Adsorption of H_2O_2 and Pollutant (denoted as P) by Catalyst Support

$$H_2O_2 \Leftrightarrow [H_2O_2] \tag{5}$$

$$P \Leftrightarrow [P] \tag{6}$$

Generation of Hydroxyl Radical: Initiation Period

$$[H_2O_2] \xrightarrow{k_1} 2[OH\bullet] \tag{7}$$

Propagation Period:

OH• consumed due to oxidizing pollutant

$$[OH\bullet] + [P] \xrightarrow{k_2} [P'\bullet] \tag{8}$$

OH• scavenged by H_2O_2

$$[OH\bullet] + [H_2O_2] \xrightarrow{k_3} [HO_2\bullet] + [H_2O] \tag{9}$$

$$[OH\bullet] + [HO_2\bullet] \xrightarrow{k_4} [H_2O] + [O_2] \tag{10}$$

The intermediate P'• will subsequently transform/decompose to produce other types of intermediates/products. It is also very likely that OH• will further attack P'• to form other intermediates. For simplicity, in this model we assume that the further oxidation by OH• is very slow and can be ignored.

Termination Period

$$[OH\bullet] + [OH\bullet] \xrightarrow{k_5} [H_2O_2] \tag{11}$$

$$[HO_2\bullet] + [HO_2\bullet] \xrightarrow{k_6} [H_2O_2] + [O_2] \tag{12}$$

There are two more reactions possibly involved in the photo-Fenton process as well, namely the cleavages of H_2O_2 and $HO_2\bullet$ expressed by Eq.s (13) and (14).

$$[H_2O_2] \xrightarrow{k_7} [H^+] + [HO_2^-] \tag{13}$$

$$[HO_2\bullet] \xrightarrow{k_8} [H^+] + [O_2^-\bullet] \tag{14}$$

$[O_2^-\bullet]$ also serves as an important oxidant to degrade pollutant.

Apparently, k_1 is closely associated with the light intensity of UV lamp and the ability of absorbing photons by the prepared catalyst, whereas k_2 is primarily dependent on the type of pollutant to be degraded. Table 1 lists the rate constants of all the rest reactions.

Table 1. Rate constant of reaction involved in heterogeneous UV/Fenton process

Constant	k_3[a]	k_4[b]	K_5[a]	k_6[a]	k_7[b]	k_8[b]
Value, $M^{-1}s^{-1}$	2.7×10^7	7.6×10^{10}	5.3×10^9	8.5×10^5	0.46	1.9×10^5

a: Han et al. [8], all data were measured at 25 °C;
b: Domae et al. [9], all data were measured at 288 °C.

3. Simplified Kinetic Model

According to the proposed mechanism we can derive a mathematically simplified kinetic model for the heterogeneous UV/Fenton process. For simplicity, reactions represented by Eq.s (13) and (14) are ignored due to their relatively slow reaction rates shown in Table 1 (at room temperature k_7 and k_8 will approximately decrease by 10 times).

The changes of [P], [H_2O_2], [OH•] and [HO_2•] radicals as functions of time are:

$$\frac{dC_P}{W_{CAT}dt} = -k_2[OH\bullet][P] \tag{15}$$

$$\frac{dC_{H_2O_2}}{W_{CAT}dt} = -k_1[H_2O_2] - k_3[OH\bullet][H_2O_2] + k_5[OH\bullet]^2 + k_6[HO_2\bullet]^2 \tag{16}$$

$$\frac{dC_{OH\bullet}}{W_{CAT}dt} = 2k_1[H_2O_2] - k_2[OH\bullet][P] - k_3[OH\bullet][H_2O_2] - k_4[OH\bullet][HO_2\bullet] - k_5[OH\bullet]^2 \tag{17}$$

$$\frac{dC_{HO_2\bullet}}{W_{CAT}dt} = k_3[OH\bullet][H_2O_2] - k_4[OH\bullet][HO_2\bullet] - k_6[HO_2\bullet]^2 \tag{18}$$

Quasi-steady state approximation requires:

$$\frac{dC_{OH\bullet}}{dt} = 0 \text{, and} \tag{19}$$

$$\frac{dC_{HO_2\bullet}}{dt} = 0 \tag{20}$$

If we assume that $C_{OH\bullet}$ and $C_{HO2\bullet}$ are very low when compared with C_P and C_{H2O2}, both $[OH\bullet]^2$ and $[HO_2\bullet]^2$ can be treated as zero and the rearrangement of Eq. (17)-(20) yields:

$$k_3[OH\bullet][H_2O_2] - k_4[HO_2\bullet][OH\bullet] \approx 0 \tag{21}$$

$$2k_1[H_2O_2] - (k_2[P] + 2k_3[H_2O_2])[OH\bullet] \approx 0 \tag{22}$$

Thus

$$[HO_2\bullet] \approx \frac{k_3}{k_4}[H_2O_2] \tag{23}$$

$$[OH\bullet] \approx \frac{2k_1[H_2O_2]}{k_2[P] + 2k_3[H_2O_2]} \tag{24}$$

Assuming that k_2 and k_3 are in the same order of magnitude, when H_2O_2 is in great excess (i.e. initial molar ratio of H_2O_2 to P is greater than 10), Eq.(24) will be simplified into:

$$[OH\bullet] \approx \frac{2k_1[H_2O_2]}{2k_3[H_2O_2]} = \frac{k_1}{k_3} = \text{constant} \tag{25}$$

Under such circumstance, Eq.s (15) and (16) will become:

$$\frac{dC_P}{W_{CAT}dt} = -k_2[OH\bullet][P] = -\frac{k_1k_2}{k_3}[P] = -k'[P] \tag{26}$$

$$\frac{dC_{H_2O_2}}{W_{CAT}dt} \approx -k_1[H_2O_2] - k_3[OH\bullet][H_2O_2] = -2k_1[H_2O_2] = -k''[H_2O_2] \tag{27}$$

If the adsorption affinities to catalyst surface and/or the initial concentrations of pollutant and H_2O_2 are low, the relationship between the species at catalyst surface and in bulk liquid can be considered linear, i.e.

$$[P] = K_P C_P \tag{28}$$

$$[H_2O_2] = K_{H_2O_2} C_{H_2O_2} \tag{29}$$

By means of the above equations, when the photooxidation is kinetically controlled, Eq.s (26) and (27) will be

$$\frac{dC_P}{W_{CAT}dt} = -k' C_P \tag{30}$$

$$\frac{dC_{H_2O_2}}{W_{CAT}dt} = -k'' C_{H_2O_2} \tag{31}$$

Eq.s (30) and (31) indicate that during the reaction process both pollutant and H_2O_2 decrease following first order reaction. The pollutant degradation rate constant k'(=k_1k_2/k_3) is the function of reactor configurations (types of UV lamp and phtocatalysts, etc.) and the properties of pollutants, whereas H_2O_2 consumption rate constant k"(=$2k_1$) is dependent on reactor configuration only. In addition, the rate constants of pollutant degradation and H_2O_2 consumption are closely related. It must be emphasized that both Eq.s (30) and (31) are only valid when the initial H_2O_2 concentration is in great excessive amount.

4. Model verification

4.1 Effect of pollutant concentration on degradation rate

Previous studies on the degradation of Orange II [3], Red HE-3B [1] and MY 10 [4] using Fe-based heterogeneous UV/Fenton process have been used to examine the validity of the proposed kinetic model. The quoted operational parameters are summarized in Table 2.

Table 2 Operational parameters for dye degradation

Target Dye	Orange II	Red HE-3B	MY10
Catalyst Loading	Fe-B = 0.5 g	Fe-Lap-RD = 1.8 g	α-FeOOH = 0.025 g
Initial Pollutant	0.2 mM	100 mg/L	0.1 mM
Initial H_2O_2	10 mM	500 mg/L	1.0 mM
pH	3.0	3.0	9.0

In all the cases the initial molar concentration ratios of H_2O_2 to pollutants are greater than 10. The affinities of dye molecules to the catalyst are relatively low. Furthermore, the prepared catalysts in Feng et al.'s work [1-3] are very fine particles (particle size ranged between 20 and 200 nm). He et al. [4] did not start the photocatalytic reaction until the adsorption/desorption of aqueous species by catalyst particles reached equilibrium. Therefore it can be rationally assumed that all the photocatalytic oxidations proceeded within kinetically controlled region.

Fig.2 demonstrates good agreement attained between the experimental and simulated results.

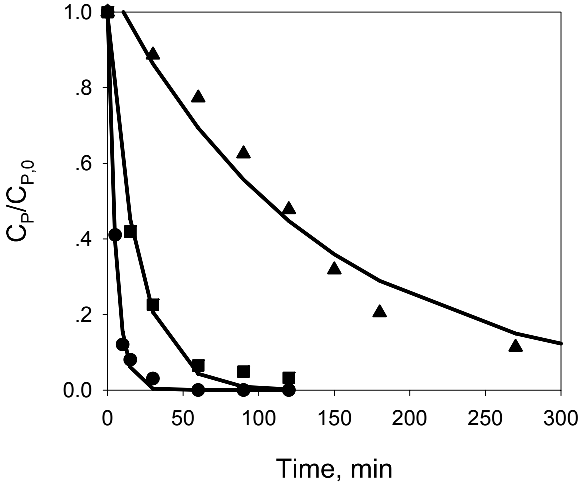


Fig. 2 Simulation of pollutant degradation, ●: Orange II; ■: Red HE-3B; ▲: MY10; ——: simulation by Eq. (30).

Accordingly k’ is estimated to be 0.38 (g·min)$^{-1}$, 0.03 (g·min)$^{-1}$ and 0.28 (g·min)$^{-1}$ for Orange II, Red HE-3B and MY10, respectively. The significance of k’ indicates that the UV/Fenton reaction can be accelerated by improving catalyst’s activity under given light and enhancing the capacity of light absorption by the photo catalysts. In this regard, in addition to the preparation of semiconductor that will be easily activated, efforts should be made to lamp configuration, sound transparency condition in the bulk liquid and even distribution of catalyst particles within the photooxidation reactor.

4.2 Consumption of H_2O_2 against time

It has been previously concluded by the model prediction that the H_2O_2 concentration decreases irrespective of the properties and the concentrations of pollutants. This judgment is confirmed in Fig.3 where the decrease of H_2O_2 concentration exhibits similar patterns against various organics being degraded in the same photooxidation reactor [4,5].

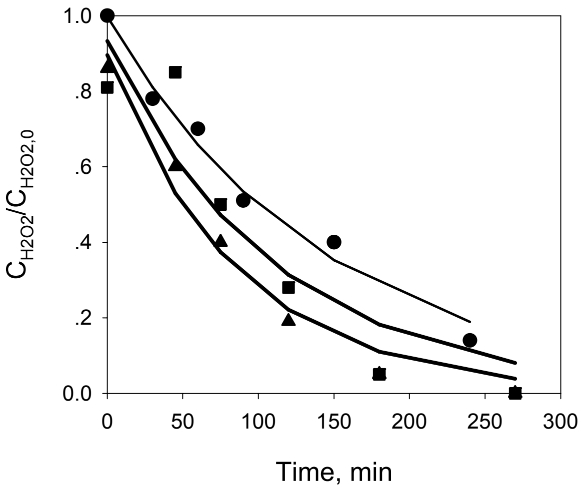


Fig. 3 Simulation of H_2O_2 consumption in oxidizing various pollutants,
●: MY10; ■: salicylic acid; ▲: bezenesulfonic acid; ——: simulation by Eq. (31).

The quoted operational parameters for H_2O_2 measurement are summarized in Table 3.

Table 3 Operational parameters for H_2O_2 consumption

Target Pollutant	MY10	Salicylic Acid	Benzenesulfonic Acid
Catalyst Loading	α-FeOOH = 0.025 g		
Initial Pollutant	0.1 mM	0.2 mM	0.2 mM
Initial H_2O_2	1 mM	4 mM	4 mM
pH	9.0	7.0	7.0

The regressed k” is 0.28, 0.36 and 0.48 $(g\cdot min)^{-1}$ for MY10, salicylic acid and benzenesulfonic acid, respectively. The discrepancies on k” may be attributed to the induction period at the start of the reaction (e.g. 0-50 min for salicylic acid) where steady-state approximation is not valid. This relatively long period may cause calculation errors in regressing k”.

Given the proportional relationship between k’ and k”, it is worthy of noting that efforts made to increase the pollutant degradation rate will be at the risks of consuming H_2O_2 very rapidly and therefore hindering the pollutant degradation process. In practice, when the concentration of H_2O_2 has been reduced to a critical value, the pollutant degradation will come to an end. In He et al.’s work [4], it was observed that when the concentration of H_2O_2 decreased from 1.0 mM to 0.14 mM, MY10 concentration profile became flat, implying the degradation of MY10 ceased and 0.14 mM might well be the threshold value of H_2O_2 for degrading MY10.

There might be two ways to solve this problem. First, the initial concentration of H_2O_2 has to be increased to the extent by which the complete degradation of pollutant can be accomplished before H_2O_2 concentration reduces to the threshold value. In Feng et al.’s work [3], complete TOC (total organic carbon) removal was obtained when the initial H_2O_2

concentration was set at 10 mM. The downside of this method will be in the treatment costs. Another alternative is to further add low concentration H_2O_2 when the reaction is about to halt. In the process of dye degradation by H_2O_2 with initial concentration of 1 mM [4], the decrease of TOC stopped after 1 hour of reaction with about 60% initial TOC removed. The removal process was then resumed by injecting 1 mM of H_2O_2 into the reaction system and ultimately 100% mineralization was achieved. Such fact gives rise to the innovations on process operation that deserves investigation in future studies.

5. Conclusions

The effects of light, heterogeneous iron and H_2O_2 in a typical UV/Fenton process have been mathematically simulated and discussed in this study. When light irradiates a semiconductor material, i.e. Fe_2O_3, its accompanied energy elevates the electrons to conduction band, which become readily available for initiating a redox reaction. Apart from absorbing photons and providing electrons, the porous iron catalyst also adsorbs reactants to be in contact with the electron-hole pairs. Once H_2O_2 and H_2O have been adsorbed by catalyst, they accept electrons and holes and produces hydroxyl radical, which acts as the oxidant to degrade pollutants.

A free radical-based kinetic model has been proposed to describe the proposed reaction mechanism. It is concluded that, given the excessive amounts of H_2O_2,

- Both pollutant degradation and H_2O_2 consumption are first-order reactions; and
- The reaction rate of H_2O_2 consumption is independent on the properties of the pollutants to be degraded.

The previous experiments by various researchers using iron catalysts have proved the validity of the proposed kinetic model. It is recommended that in addition to the improvement on reactor configurations and catalyst preparations, efforts should also be made on process operation, taking into account the resultant rapid consumption of H_2O_2.

Notation

C_X	concentration of a certain substance in bulk liquid, mg/L or mM;
$C_{X,0}$	initial concentration of a certain substance in bulk liquid, mg/L or mM;
e^-	electron;
h^+	hole;
K_P	adsorption constant of pollutant, L/mg or L/mmol;
K_{H2O2}	adsorption constant of H_2O_2, L/mg or L/mmol;
k_1~ k_8	reaction rate constant corresponding to the free radical reactions depicted in Eq.s (7) - (14), respectively;
k', k"	first order reaction rate constant corresponding to Eq.s (26) and (27), respectively, s^{-1} or min^{-1};
P	pollutant;
P'	intermediate of photodegradation process;
t	reaction time, s or min;
[x]	concentration of a certain adsorbed species, mg specie/mg adsorbate.

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