

# Reaction and Mass Transfer Kinetics Model of Hydrogen Peroxide Oxidation of Starch under Influence of Ultraviolet Irradiation

Andri Cahyo Kumoro<sup>1\*</sup>, Ratnawati Ratnawati<sup>1</sup>,  
Diah Susetyo Retnowati<sup>1</sup>

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## Abstract

The coupled hydrogen peroxide/ultraviolet irradiation ( $H_2O_2/UV$ ) process as one of environmentally friendly advanced oxidation processes (AOPs) has been successfully applied in the oxidation of corn starch. The aim of this work was to develop a simplified model for the describing of reaction kinetics and mass transfer phenomena of starch oxidation using hydrogen peroxide under influence of UV irradiation. The model development involved the elementary chemical and photochemical reactions as well as pseudo-steady state mass transfer of hydroxyl radicals from bulk liquid to the surface of starch particles. Effects of initial  $H_2O_2$  concentration and pH were investigated. The results show that  $H_2O_2/UV$  starch oxidation follows the first order reaction with respect to  $H_2O_2$  and starch concentrations. The proposed model satisfactorily describes the  $H_2O_2/UV$  starch oxidation phenomena, where very good agreement with experimental data was obtained. Hydroxyl radical's mass transfer from bulk liquid to the surface of starch particles was found to be the rate controlling step for coupled  $H_2O_2/UV$  starch oxidation.

## Keywords

kinetics, mass transfer, modeling, starch, rate controlling step, photo-oxidation

## 1 Introduction

With regard to their low viscosity, high stability, clarity, film forming and binding properties, oxidised starches have been considered as one of multipurpose biomaterials. Oxidised starches with high degree oxidation are used widely in the paper, textile, laundry finishing and binding materials for decades [1]. In the food industries, oxidised starch with carboxyl content up to 1.1% [2] is used as a coating and sealing agent in confectionary, as an emulsifier [3], as a dough conditioner for bread [4], as a replacer for gum Arabic, as a binding agent in batter applications and many more [5].

A number of techniques have been used to prepare oxidised starch, which include the use of oxidising agent such as hypochlorite, air oxygen, ozone, bromine, chromic acid, permanganate, nitrogen dioxide and hydrogen peroxide ( $H_2O_2$ ) [6]. Oxidised starch is produced by reacting starch with oxidising agent under controlled temperature and pH [7], type and amount of catalyst [8], oxidant concentration, starch slurry consistency, reaction time [9] and starch physicochemical properties [1].

In the oxidation process, the hydroxyl groups of the anhydroglucose (AGU) units of the starch molecules are oxidised to carbonyl and carboxyl groups [8]. The carboxyl groups of the starch molecules play important roles in the enhancement of starch paste stability, whereas the carbonyl groups play a minor role in the prevention of retrogradation of starches [10]. Oxidation also causes degradation of the starch molecules by which a modified starch with low viscosity is produced. These advantageous properties allow the uses of oxidised starch in various applications, mainly when high solid concentration is needed [10].

Thanks to its high efficiency, hypochlorite oxidation is thus far the most popular process for commercial scale production of oxidised starches. However, this oxidising agent is highly potential to generate toxic chlorinated by-products. Coupled  $H_2O_2/UV$  starch oxidation has been reported to successfully produce oxidised starches containing significant amounts of carboxyl and carbonyl contents [11]. Oxidised starches with higher carbonyl content were obtained under acidic rather than alkaline conditions, increasing  $H_2O_2$  concentrations and

<sup>1</sup> Department of Chemical Engineering, Faculty of Engineering, Diponegoro University

Prof. H. Soedarto, SH Road-Semarang, Indonesia

\* Corresponding author, e-mail: [andrewkomoro@undip.ac.id](mailto:andrewkomoro@undip.ac.id)

absence of oxygen [12]. In  $\text{H}_2\text{O}_2/\text{UV}$  starch oxidation, self-decomposition and photolysis of  $\text{H}_2\text{O}_2$  generate radicals to oxidise the starch, leaving water and free oxygen as by-products. Thus, this oxidation process is considered as a more environmentally friendly and preferred starch oxidation process, specifically when a chlorine-free process is obliged [8, 10].

Unfortunately, no studies on the kinetics of starch oxidation by coupled  $\text{H}_2\text{O}_2/\text{UV}$  irradiation have been reported in the literature. All available literatures reported the study of starch oxidation by coupled  $\text{H}_2\text{O}_2/\text{UV}$  in batch reactors and followed by analysis of the physicochemical properties of the final products [9, 11, 12]. Later, El-Sheikh et al. suggested that three reactions may occur simultaneously during starch oxidation: (a) oxidation which is followed by the formation of carboxyl and carbonyl groups, (b) further oxidation of the carbonyl to carboxyl groups and (c) decarboxylation, which primarily occurs at C-2, C-3, and C-6 [9]. This would indicate that the reaction path is consecutive with carbonyl groups as intermediates, which react further to carboxyl groups after prolonged reaction times. Therefore, to obtain a clear understanding of the reaction kinetics of starch oxidation using coupled  $\text{H}_2\text{O}_2/\text{UV}$  irradiation, a set of experiments on the effect of initial  $\text{H}_2\text{O}_2$  concentration and pH were performed in a well-mixed batch system and followed by a simple mathematical modelling.

## 2 Materials and Methods

### 2.1 Materials

The common corn starch (Cargill Gel 03420) used for oxidation experiments in this study was purchased from Cargill Food and Pharma Specialties North America (Cedar Rapids, IA, USA). Hydrogen peroxide stock solution was a reagent-grade 35-wt. % solution used as received from Sigma-Aldrich without further treatment. Other chemicals are of analytical grade with purity  $\geq 98\%$  were purchased from Sigma-Aldrich Pte.Ltd, Singapore. Distilled water, which was further purified with a Barnstead Ultrapure mixed-bed cartridge, was used in cleaning and experimentation.

### 2.2 Microstructure characterisation of starch

Low-temperature nitrogen adsorption was performed to determine the specific surface area, mesopore volume and average pore diameter using an apparatus ASAP 2405 (Micromeritics Inc., USA). While observation on shape, surface structure and size of starch particles was performed by scanning electron microscopy (SEM) using a Leica Cambridge S360 (Leica, Wetzlar, Germany) scanning electron microscope at  $5000\times$  magnifications with accelerating voltage of 10 kV.

### 2.3 Oxidation of starch

The reactor used in this work was a 5 L three-necked rounded bottom glass flask equipped with a quartz immersion well containing a 450 watt Heraeus monochromatic UV lamp,

which generates UV light at a wavelength of 254 nm. In order to prevent any leakages of UV light, the whole parts of the reactor was covered with aluminium foil. Prior to oxidation, a pre-determined mass of native corn starch was dispersed in 3.5 L of distilled water in the reactor by vigorous agitation using a magnetic stirrer to obtain starch-water slurry with starch-water ratio (S/L) = 1/20. Then, a pre-determined amount of  $\text{H}_2\text{O}_2$  was added drop wise to the slurry under continuous stirring to obtain certain  $\text{H}_2\text{O}_2$  concentration (0.25 M, 0.5 M, 0.75 M and 1 M). The oxidation of the starch-slurry was initiated by switching on the UV lamp and the whole contents were kept at ambient temperature for 10 hours under continuous stirring at studied pH (3, 5, 7 and 9). At every 2 hours interval, a slurry sample was withdrawn from the reactor through the sampling ports using a long hypodermic stainless steel needle for analyses. The slurry samples were filtered in vacuo by which a creamy solid cake was obtained from each sample. After washing with distilled water and followed by appropriate drying, the oxidised starch was obtained as a white solid. The oxidised starch was then subjected to carbonyl and carboxyl content determinations, while the filtrates obtained from filtration of the slurry samples were subjected to  $\text{H}_2\text{O}_2$  concentrations determination. The carboxyl contents of the oxidised starch were determined by the paste titration method of Chattopadhyay et al. [5]. The hydroxylamine hydrochloride method of Smith [13] was used to estimate the total carbonyl contents of the sample. The  $\text{H}_2\text{O}_2$  concentration in the slurry before, during and after the oxidation reaction was determined according to colorimetric methods previously used by Nicole et al. [14].

## 3 Model Development

A mathematics model was proposed to describe the reaction and mass transfer kinetics of starch oxidation using  $\text{H}_2\text{O}_2$  under influence of UV light. To adequately describe the realistic phenomena of the system, the following assumptions were taken into consideration: (i) oxidation begins from the external surface of the starch granules and followed by further oxidation in the internal part of the granules [15], (ii) steady state mass transfer of substances occurs in the combined film on the solid film region, (iii) oxidation occurs at temperatures below the gelatinization temperature of the starch, so that no significant changes in the surface area and volume of starch granules are observed, (iv) no reaction between starch and its by-products to form higher molecular weight intermediates, (v) two mechanisms are responsible for the oxidation of starch/AGU, namely, the hydroxyl radical attack and direct photolysis, while oxidation by other intermediate radicals such as  $\text{HO}_2\cdot$  and  $\cdot\text{O}_2^-$  is neglected because their reactivity to organic compounds is very low [16], (vi) UV radiation is competitively absorbed by  $\text{H}_2\text{O}_2$  and starch molecules, (vii) hydroxyl radicals are only consumed by starch and intermediate free radicals, (viii)  $\text{H}_2\text{O}_2$  and its conjugate base ( $\text{H}_2\text{O}_2/\text{HO}_2^-$ ) are only decomposed by

direct photolysis and their reaction with free radicals, (ix) the kinetics is assumed to follow first order rate with respect to the organic species (starch/AGU, carbonyl and carboxyl groups) concentration and hydroxyl radical concentration [17] and (x) the steady state approximation can be applied for the concentration of radicals.

### 3.1 Decomposition of H<sub>2</sub>O<sub>2</sub> with/without UV irradiation

Hydrogen peroxide may decompose spontaneously to oxygen and water, and the rate of this self decomposition depends on the temperature, concentration and impurities. Table 1 presents selected reactions occurred in starch oxidation H<sub>2</sub>O<sub>2</sub>/UV system.

**Table 1** Selected reactions in H<sub>2</sub>O<sub>2</sub>/UV starch oxidation

Reaction	Reaction rate constant	Ref.	Equation
<b>H<sub>2</sub>O<sub>2</sub> self-decomposition</b>			
H <sub>2</sub> O <sub>2</sub> ⇌ HO <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	$K_1 = 2.51 \times 10^{-12}$	[17]	(1.a)
H <sub>2</sub> O <sub>2</sub> + HO <sub>2</sub> <sup>-</sup> ⇌ OH <sup>-</sup> + H <sub>2</sub> O + O <sub>2</sub>	$k_2 = 3.7 \times 10^{-8}$ (1/M.s)	[18]	(1.b)
2H <sub>2</sub> O <sub>2</sub> → 2H <sub>2</sub> O + O <sub>2</sub>	$k_3 = 3.82 \times 10^{-4}$ (1/M.s)	[19]	(1.c)
<b>H<sub>2</sub>O<sub>2</sub> photolysis</b>			
H <sub>2</sub> O <sub>2</sub> + hv (< 254 nm) ⇌ 2HO <sup>•</sup>	$r_{uv,H} = 3.07 \times 10^{-5}$ (M/s)	[20]	(2.a)
HO <sup>•</sup> + H <sub>2</sub> O <sub>2</sub> → HO <sub>2</sub> <sup>•</sup> + H <sub>2</sub> O	$k_4 = 2.7 \times 10^7$ (1/M.s)	[21]	(2.b)
HO <sub>2</sub> <sup>•</sup> + H <sub>2</sub> O <sub>2</sub> → HO <sup>•</sup> + H <sub>2</sub> O + O <sub>2</sub>	$k_5 = 5.0 \times 10^{-1}$ (1/M.s)	[22]	(2.c)
HO <sub>2</sub> <sup>•</sup> + HO <sub>2</sub> <sup>•</sup> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	$k_6 = 8.3 \times 10^5$ (1/M.s)	[21]	(2.d)
HO + HO <sub>2</sub> <sup>•</sup> → H <sub>2</sub> O + O <sub>2</sub>	$k_7 = 8.0 \times 10^9$ (1/M.s)	[23]	(2.e)
HO <sup>•</sup> + HO <sup>•</sup> → H <sub>2</sub> O <sub>2</sub>	$k_8 = 5.2 \times 10^9$ (1/M.s)	[24]	(2.f)
HO <sup>•</sup> + HO <sup>•</sup> → H <sub>2</sub> O + O <sub>2</sub>	$k_9 = 4.7 \times 10^9$ (1/M.s)	[25]	(2.g)
<b>Starch oxidation</b>			
HO <sup>•</sup> + Starch → Carbonyl	$k_{10} = \dots\dots\dots$ (1/M.s)		(3.a)
hv + Starch → Carbonyl	$r_{uv,S} = \dots\dots\dots$ (M/s)		(3.b)
HO <sup>•</sup> + Carbonyl → Carboxyl	$k_{11} = \dots\dots\dots$ (1/M.s)		(3.c)
HO <sup>•</sup> + Carboxyl → CO <sub>2</sub> + H <sub>2</sub> O	$k_{12} = \dots\dots\dots$ (1/M.s)		(3.d)

Under influence of UV irradiation, H<sub>2</sub>O<sub>2</sub> is decomposed more rapidly, forming hydroxyl radicals (HO<sup>•</sup>) and hydroperoxide radical (HO<sub>2</sub><sup>•</sup>). However, radical interactions may lead to recombination to form H<sub>2</sub>O<sub>2</sub> at rate constant of  $5 \times 10^9$  (1/M.s) according to Eqs. (2.d) and (2.f) [26]. Since the steady-state concentration of hydroxyl radicals is only about  $10^{-8}$  -  $10^{-12}$  M at best, therefore recombination of HO<sup>•</sup> radicals to form H<sub>2</sub>O<sub>2</sub> can be totally omitted [27].

Kumoro et al. reported a pseudo-first-order kinetics of natural decomposition of H<sub>2</sub>O<sub>2</sub> [28]:

$$r_{NatDecHP} = -\left(\frac{dC_{HPI}}{dt}\right)_1 = -k_{Nat} \cdot C_{HPI} \quad (4)$$

with  $k_{Nat}$  is the self decomposition rate constant. The rate of direct photolysis of H<sub>2</sub>O<sub>2</sub> is described as [16]:

$$r_{UVDecHP} = -\left(\frac{dC_{HPI}}{dt}\right)_2 = \phi_{H_2O_2} f_{H_2O_2} I_o (1 - e^{-At}) \quad (5)$$

where  $\phi_{H_2O_2}$  is the H<sub>2</sub>O<sub>2</sub> quantum yield,  $I_o$  is the UV irradiation intensity, and  $\phi_{H_2O_2}$  is the fraction of radiation that is absorbed by H<sub>2</sub>O<sub>2</sub> which, based on assumption (vi) equals unity. The primary quantum yield of H<sub>2</sub>O<sub>2</sub> is 0.49, while solution total absorbance ( $At$ ) at the UV radiation with wavelength  $\lambda$  is [29]:

$$A_t = 2.303 \cdot l \cdot \epsilon_{H_2O_2} C_{HPI} \quad (6)$$

where  $At$ ,  $l$ ,  $\epsilon_{H_2O_2}$  and  $C_{HPI}$  are the absorbance, the effective reactor light path (annular), molar extinction coefficient (43.6 (1/M.cm)) [30] and H<sub>2</sub>O<sub>2</sub> concentration, respectively. The initial concentrations of H<sub>2</sub>O<sub>2</sub> and starch were known. The values of  $I_o$  and  $l$  were  $3.07 \times 10^{-5}$  (M/s) and 6.35 cm, respectively. Because H<sub>2</sub>O<sub>2</sub> and its conjugate base (HO<sub>2</sub><sup>-</sup>) are decomposed or produced by free-radical reactions, the overall kinetic expression for H<sub>2</sub>O<sub>2</sub> is then obtained by combining its decomposition and production through free-radical reactions:

$$r_{HPI} = \left(\frac{dC_{HPI}}{dt}\right) = -k_{Nat} C_{HPI} - \phi_{H_2O_2} f_{H_2O_2} I_o (1 - e^{-At}) - k_4 C_{HPI} C_{HO^{\bullet}} - k_5 C_{HO_2^{\bullet}} C_{HPI} + k_6 \cdot C_{HO_2^{\bullet}}^2 + k_8 \cdot C_{HO^{\bullet}}^2 \quad (7)$$

### 3.2 Diffusion of hydroxyl radicals

As oxidation is assumed to begin from the outer surface of the starch granules, hydroxyl radicals must firstly diffuse from bulk of liquid solution to the active surface of the starch granules [15]. Since the starch granules are porous and very small in size, the hydroxyl radicals mass transfer rate is not likely to be controlled by the intraparticle diffusion inside the starch pores. Thus, the boundary layer diffusion is supposed to be the rate controlling step in the systems [31]. The diffusion resistance of fluid through the solid film is generally higher than that of the fluid film. Therefore, a simplification by assuming the existence of a combined film on the solid film region is adequate. Then, the hydroxyl radical's concentration gradient can be approximated as shown in Fig. 1.

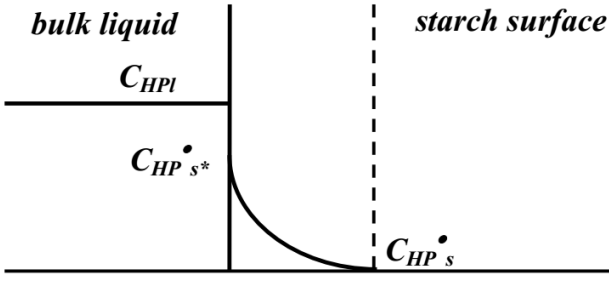


Fig. 1 Hydroxyl radical's concentration gradient at combined film.

The hydroxyl radicals mass transfer rate through the combined film can be written as:

$$r_{DfHR} = \left( \frac{dC_{HO^*}}{dt} \right)_s = k_{cs} \cdot W_s \cdot S_s (C_{HO^*s}^* - C_{HO^*s}) \quad (8)$$

with  $k_{cs}$ ,  $W_s$ ,  $S_s$  and  $C_{HO^*s}$  are respectively the combined mass transfer coefficient in the solid phase, mass concentration of starch, specific surface area of the starch and hydroxyl radical concentration in the starch surface. In this case,  $C_{HO^*s}^*$  presents in equilibrium with  $C_{HO^*}$ , which can be represented by the following Henry-like correlation:

$$C_{HO^*s}^* = H \times C_{HO^*} \quad (9)$$

Substitution Eq. (9) to Eq. (8) results:

$$r_{DfHR} = \left( \frac{dC_{HO^*}}{dt} \right)_s = k_{cs} \cdot W_s \cdot S_s (H \cdot C_{HO^*} - C_{HO^*s}) \quad (10)$$

Mass transfer coefficient for a spherical particle in stirred solution can be estimated by the following equation [32]:

$$Sh = \frac{d_p \cdot k_{cs}}{D_{HO^*}} = 2 + Re_p^{1/2} \cdot Sc_c^{1/3} \quad (11)$$

$$Re_p = \frac{\rho_{liq} \cdot N \cdot d_p^2}{\mu_{liq}} \quad Sc_c = \frac{\mu_{liq}}{\rho_{liq} D_{HO^*}}$$

where  $Re_p$  and  $Sc_c$  are the Reynold's and the Schmidt numbers. In addition,  $D_{HO^*}$ ,  $r_{liq}$ ,  $\mu_{liq}$ ,  $d_p$  and  $N$  are the diffusivity of hydroxyl radical in water ( $7.1 \times 10^{-9}$  m<sup>2</sup>/s) [33], density and viscosity of the solution, actual diameter of the starch particle and agitation speed, respectively.

### 3.3 Reaction of starch with hydroxyl radicals

The reaction between  $H_2O_2$  and starches take places via complex mechanisms and may differ depending upon the reaction conditions. Direct oxidation of organic compounds by atmospheric oxygen from decomposition of  $H_2O_2$  is very slow and often ignorable [34]. In contrast, depending on pH of the system, the highly reactive hydroxyl radical ( $HO^*$ ) generated from  $H_2O_2$  decomposition and photolysis may react with AGU in the starch molecules exceedingly rapidly [35]. Although the real starch oxidation reaction mechanism is very complicated, it can

be simplified by Eqs. (3.a) to (3.c) in Table 1. The concentration of carbonyl ( $C_{CHO}$ ) and carboxyl ( $C_{COOH}$ ) groups are easily measured throughout the experiments, while the concentration of hydroxyl radicals  $C_{HO^*}$  is not. Therefore, the kinetic of starch oxidation using  $H_2O_2$  under influence of UV irradiation is analysed based on the changes of  $H_2O_2$ , carbonyl and carboxyl group's concentrations.

De Laat et al. [36] proposed that the rate of direct photolysis of starch molecules by UV irradiation can be represented by:

$$r_{OxUV} = \left( \frac{dC_{AGU}}{dt} \right)_1 = -\phi_{AGU} f_{AGU} I_o (1 - e^{-A t}) \quad (12)$$

The value of the quantum yield of photolysis of AGU ( $f_{AGU}$ ) can be obtained from starch photolysis experiments without  $H_2O_2$  at  $e_{AGU} = 14822$  (1/M.cm),  $I_o = 3.07 \times 10^{-5}$  (Einstein/s),  $V = 4$  L and  $l = 6.35$  cm as suggested by De Laat et al. [36]. As a result, a mean value of ( $f_{AGU}$ ) =  $0.035 \pm 0.003$  was obtained at 30°C.

The rate of starch oxidation using  $H_2O_2$  on the starch surface under influence of UV light can be expressed as [37]:

$$r_{OxHR} = \left( \frac{dC_{AGU}}{dt} \right)_2 = -k_{ox,UV} \cdot S_s \cdot C_{AGU} C_{HO^*s} \quad (13)$$

$C_{HO^*s}$  is the concentration of hydroxyl radical in the starch surface, while  $k_{ox,UV}$  is the starch oxidation rate constant. Assuming steady state mass transfer in the combined film on the solid film region, the mass transfer coefficient of hydroxyl radicals from bulk solution to the starch active surface can be calculated as:

$$k_{cs} = \frac{k_{ox,UV} \cdot C_{AGU} \cdot C_{HO^*s}}{W_s \cdot S_s (H \cdot C_{HO^*} - C_{HO^*s})} \quad (14)$$

As the value of  $S_s$  and  $k_{ox,UV}$  are constants, then Eq. (13) can be simplified and combined with Eq. (12) to obtain total starch oxidation reaction rate:

$$\frac{dC_{AGU}}{dt} = -k_{10} C_{AGU} C_{HO^*s} - \phi_{AGU} f_{AGU} I_o (1 - e^{-A_{AGU} t}) \quad (15.a)$$

At low value of  $C_{AGU}$  Eq. (15.a) becomes

$$\frac{dC_{AGU}}{dt} = -\left( k_{10} C_{HO^*s} + 2.303 \cdot \varepsilon \cdot l \cdot \phi_{AGU} f_{AGU} I_o \right) \cdot C_{AGU} \quad (15.b)$$

On the other hand, at high value of  $C_{AGU}$  Eq. (15.a) can be written as

$$\frac{dC_{AGU}}{dt} = -k_{10} C_{AGU} C_{HO^*s} - 2.303 \cdot \varepsilon \cdot l \cdot \phi_{AGU} f_{AGU} I_o \quad (15.c)$$

Carbonyl and carboxyl groups reside in the inner parts of starch granules, therefore they are assumed to be free from direct

photolysis by UV irradiation. However, since carbonyl and carboxyl groups may react further with hydroxyl radicals, then the mass balances for these groups are:

$$\frac{dC_{\text{Carbonyl}}}{dt} = k_{10} \cdot C_{\text{AGU}} \cdot C_{\text{HO}^\bullet_s} - k_{11} \cdot C_{\text{Carbonyl}} \cdot C_{\text{HO}^\bullet_s} + \varphi_{\text{AGU}} f_{\text{AGU}} I_o \cdot (1 - e^{-A_{\text{AGU}} t}) \quad (16)$$

$$\frac{dC_{\text{Carboxyl}}}{dt} = k_{11} C_{\text{Carbonyl}} C_{\text{HO}^\bullet_s} - k_{12} C_{\text{Carboxyl}} C_{\text{HO}^\bullet_s} \quad (17)$$

$$\left( \frac{dC_{\text{AGU}}}{dt} \right) = - \left( \frac{dC_{\text{Carbonyl}}}{dt} \right) - k_{11} C_{\text{Carbonyl}} C_{\text{HO}^\bullet_s} \quad (18)$$

$$\begin{aligned} \frac{dC_{\text{HO}^\bullet}}{dt} = & 2 \cdot \varphi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_o (1 - e^{-At}) \\ & - k_4 C_{\text{HPI}} C_{\text{HO}^\bullet} + k_5 C_{\text{HO}_2^\bullet} C_{\text{HPI}} \\ & - k_7 C_{\text{HO}_2^\bullet} C_{\text{HO}^\bullet} - k_8 C_{\text{HO}^\bullet}^2 \\ & - k_9 C_{\text{HO}^\bullet}^2 - k_{10} C_{\text{AGU}} C_{\text{HO}^\bullet_s} \\ & - k_{11} \cdot C_{\text{Carbonyl}} \cdot C_{\text{HO}^\bullet_s} \\ & - k_{12} C_{\text{Carboxyl}} C_{\text{HO}^\bullet_s} \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{dC_{\text{HO}_2^\bullet}}{dt} = & k_4 C_{\text{HPI}} \cdot C_{\text{HO}^\bullet} - k_5 C_{\text{HO}_2^\bullet} C_{\text{HPI}} \\ & - k_6 C_{\text{HO}_2^\bullet} C_{\text{HO}_2^\bullet} - k_7 C_{\text{HO}_2^\bullet} C_{\text{HO}^\bullet} \end{aligned} \quad (20)$$

Being a highly reactive species, hydroxyl radical may react with carbohydrate nearly instantaneously [35]. Therefore, its concentration can be assumed remains low throughout the reaction in vigorously oxidising systems [34]. Then, the absolute slope of its concentration will be small compared to other time dependences in the reaction system. As a consequence, steady-state approximation (SSA) for hydroxyl radical concentration, where concentrations of radical species are assumed to be constant at the initial concentrations (i.e.,  $t = 0$ ) during the experiments can be implemented [37].

$$\frac{dC_{\text{HO}^\bullet}}{dt} \approx 0 \quad \text{and} \quad \frac{dC_{\text{HO}_2^\bullet}}{dt} \approx 0$$

This assumption is very beneficial to eliminate  $\text{CHO}^\bullet$  from the expression of carbonyl and carboxyl groups' formation rate. The steady-state concentration of hydroxyl radical ( $C_{\text{HO}^\bullet}$ ) and perhydroxy radical ( $C_{\text{HO}_2^\bullet}$ ) can be expressed as:

$$C_{\text{HO}^\bullet_{\text{SSA}}} \approx \frac{k_5 C_{\text{HO}_2^\bullet} C_{\text{HPI}} + 2 \cdot \varphi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_o (1 - e^{-At})}{k_4 C_{\text{HPI}} + k_7 C_{\text{HO}_2^\bullet} + k_{10} C_{\text{AGU}} + k_{11} C_{\text{Carbonyl}} + k_{12} C_{\text{Carboxyl}}} \quad (21)$$

$$C_{\text{HO}_2^\bullet_{\text{SSA}}} \approx \frac{k_4 C_{\text{HO}^\bullet} C_{\text{HPI}}}{k_5 C_{\text{HPI}} + k_6 C_{\text{HO}_2^\bullet} + k_7 C_{\text{HO}^\bullet}} \quad (22)$$

where  $k_4, k_5, k_6, k_7, k_{10}, k_{11}$  and  $k_{12}$  are reaction rate constants, where hydroxyl and perhydroxyl radicals are consumed in starch (AGU) and reaction intermediates. Initial concentrations of the hydroxyl radical were assumed to be zero. However, as the oxidation was carried out at low pH, it is not necessary to consider the hydroperoxide and ion superoxide radicals, because their concentrations are not significant at this pH [38] and their reactivity to organic compounds is very low [16]. The term  $k_5 C_{\text{HO}_2^\bullet} C_{\text{HPI}}$  in the numerator and  $k_7 C_{\text{HO}_2^\bullet}$  in the denominator of Eq. (21) is negligible compared to the other terms. Then the steady state concentration of hydroxyl radical can be simplified to:

$$C_{\text{HO}^\bullet_{\text{SSA}}} \approx \frac{2 \cdot \varphi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_o (1 - e^{-At})}{k_4 C_{\text{HPI}} + k_{10} C_{\text{AGU}} + k_{11} C_{\text{Carbonyl}} + k_{12} C_{\text{Carboxyl}}} \quad (23)$$

This approach and the fact that self decomposition of  $\text{H}_2\text{O}_2$  is very low lead to simplification of Eq. (7) to become:

$$\begin{aligned} \frac{dC_{\text{HPI}}}{dt} = & -\varphi_{\text{H}_2\text{O}_2} f_{\text{H}_2\text{O}_2} I_o (1 - e^{-At}) \\ & - k_4 C_{\text{HPI}} C_{\text{HO}^\bullet_{\text{SSA}}} + k_8 \cdot C_{\text{HO}^\bullet_{\text{SSA}}}^2 \end{aligned} \quad (24)$$

$$\begin{aligned} \frac{dC_{\text{Carbonyl}}}{dt} = & \varphi_{\text{AGU}} f_{\text{AGU}} I_o \cdot (1 - e^{-A_{\text{AGU}} t}) \\ & + k_{10} C_{\text{AGU}} C_{\text{HO}^\bullet_{\text{SSA}}} \\ & - k_{11} C_{\text{Carbonyl}} C_{\text{HO}^\bullet_{\text{SSA}}} \end{aligned} \quad (25)$$

$$\begin{aligned} \frac{dC_{\text{Carboxyl}}}{dt} = & k_{11} C_{\text{Carbonyl}} C_{\text{HO}^\bullet_{\text{SSA}}} \\ & - k_{12} C_{\text{Carboxyl}} C_{\text{HO}^\bullet_{\text{SSA}}} \end{aligned} \quad (26)$$

$$\left( \frac{dC_{\text{AGU}}}{dt} \right) = - \left( \frac{dC_{\text{Carbonyl}}}{dt} \right) - k_{11} C_{\text{Carbonyl}} C_{\text{HO}^\bullet_{\text{SSA}}} \quad (27)$$

The optimum value of  $k_{10}, k_{11}$  and  $k_{12}$  in Eqs. (25), (26) and (27) can be obtained through minimization of the average of absolute relative errors (AARD) between the calculated  $\text{H}_2\text{O}_2$ , carbonyl group and carboxyl group concentrations and those of experimental data.

$$AARD = \frac{1}{N} \sum_1^n ABS \left( \frac{C_{i,\text{exp}} - C_{i,\text{calc}}}{C_{i,\text{calc}}} \right) \times 100\% \quad (28)$$

## 4 Results and Discussion

### 4.1 Effect of initial hydrogen peroxide concentration

The oxidation of corn starch using  $H_2O_2$  solution was carried out at  $30^\circ C$ , which is below the gelatinisation temperature of the starch [39]. The native corn starches have  $12 \mu m$  average diameter,  $0.57 m^2/g$  specific surface area,  $1210 cm^3/g$  mesopore volume,  $7.95 nm$  average pore diameter and  $0.56$  porosity. Those microstructure properties reveal that corn starches are highly porous and very small in diameter. The water diffusion coefficient of the starch particles is  $23.125 \times 10^{-10} m^2/s$  [40]. Figure 2 illustrates no significant changes in granules size and surface characteristics of native and oxidised corn starches.

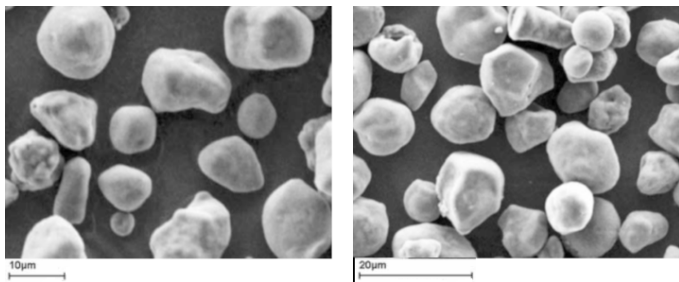


Fig. 2 Microstructure of native and oxidised corn starch

The modelling results of corn starch oxidation under influence of UV irradiation at  $pH = 3$ , temperature of  $30^\circ C$  and various initial  $H_2O_2$  concentrations are presented in Fig. 3, 4 and 5 and Table 2.

Table 2 Rate constants at various  $H_2O_2$  concentration

$[H_2O_2]$ (M)	$k_{10} \times 10^{-8}$ (1/M.s)	$k_{11} \times 10^{-6}$ (1/M.s)	$k_{12} \times 10^{-5}$ (1/M.s)	$k_{CS} \times 10^3$ (m/s)	AARD (%)
0.25	2.3096	7.0615	1.7512	3.1836	2.33
0.50	3.3297	7.1998	2.0833	3.2323	3.87
0.75	7.4401	11.190	2.0874	3.3020	2.99
1.00	14.673	31.431	2.6842	3.6016	2.71

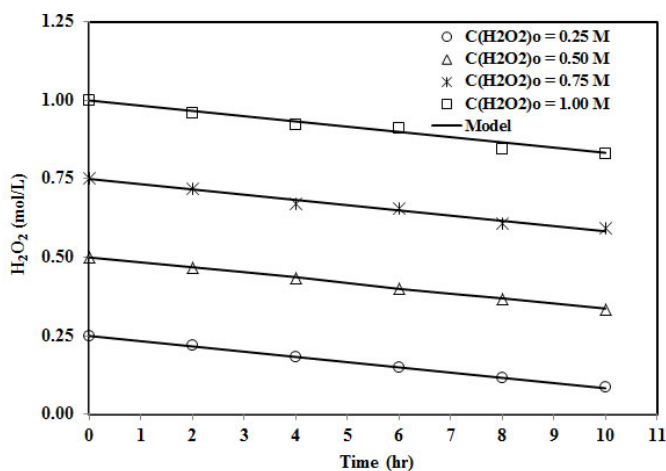


Fig. 3 Profile of  $H_2O_2$  concentration during oxidation of corn starch at  $30^\circ C$ ,  $pH 3$ , starch-water ratio (S/L) = 1/20

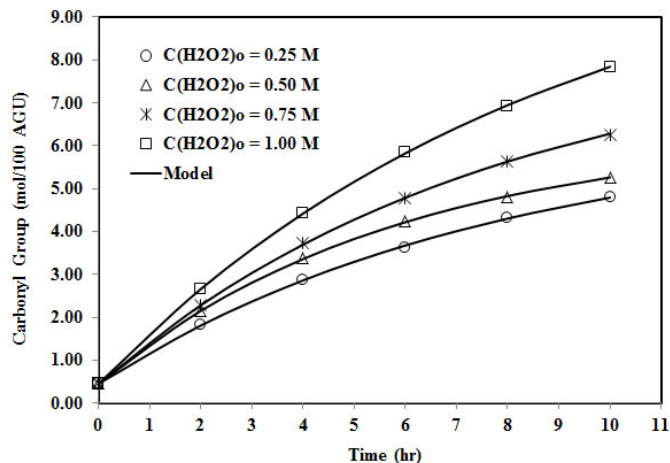


Fig. 4 Profiles of carbonyl group concentration during oxidation of corn starch at  $30^\circ C$ ,  $pH 3$ , starch-water ratio (S/L) = 1/20

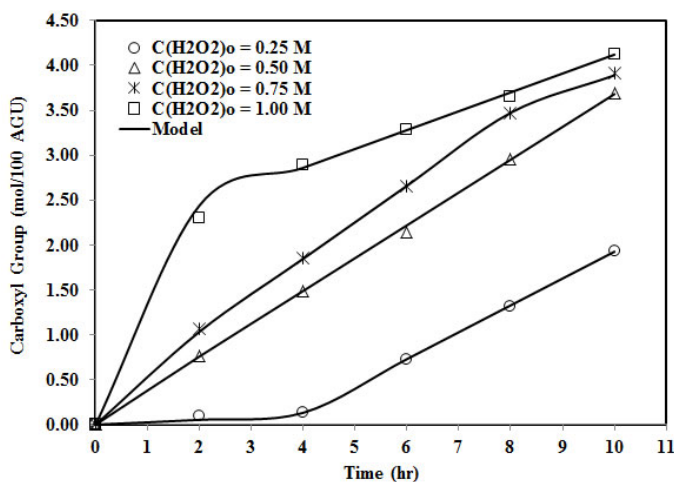


Fig. 5 Profile of carboxyl group concentration during oxidation of corn starch at  $30^\circ C$ ,  $pH 3$ , starch-water ratio (S/L) = 1/20

A slight decrease in  $H_2O_2$  concentrations of each reaction system with time was observed. This fact has suggested some researchers to consider that  $H_2O_2$  concentration almost constant during AOP using coupled  $H_2O_2/UV$  if  $H_2O_2$  presents in excess [29]. The increase in the extent of starch oxidation with increasing  $H_2O_2$  concentration and reaction time is shown by a corresponding increase in the carboxyl and carbonyl group contents of the oxidised starches (Figure 4 and Figure 5). With increasing concentration of  $H_2O_2$  in the solution, the fraction of UV light absorbed for photo-decomposition of  $H_2O_2$  also increases, and, consequently, so does its photolysis rate [41]. Therefore, it is reasonable to say that faster rates of oxidation occurs as more and more hydroxyl radicals as the oxidising species are progressively produced [9].

As seen in Figs. 3, 4 and 5, the calculated  $H_2O_2$ , carbonyl and carboxyl group's concentrations are very close with those obtained from experiments. This result shows that the proposed model satisfactorily predicts the  $H_2O_2$ , carbonyl and carboxyl group's concentrations for coupled  $H_2O_2/UV$  starch oxidation. As reported in Table 2, the proposed model agrees well with the

experimental data for a wide range of initial  $\text{H}_2\text{O}_2$  concentration as indicated by low values of AARD between 2.33% and 3.87%. Table 3 also presents that the reaction rate constants ( $k_{10}$ ,  $k_{11}$  and  $k_{12}$ ) increased with the increase in initial  $\text{H}_2\text{O}_2$  concentration. At low  $\text{H}_2\text{O}_2$  concentrations, the photolysis of  $\text{H}_2\text{O}_2$  was only able to generate less hydroxyl radicals; therefore the oxidation rate was limited. As  $\text{H}_2\text{O}_2$  concentration increased, more hydroxyl radicals were created, and thus led to an increase in the reaction rate. The value of  $k_{10}$ ,  $k_{11}$  and  $k_{12}$  obtained in this work are consistent with the constants reported by several workers with other modes of generation of hydroxyl radicals. The value of reaction rate constant between 1,2-dibromo-3-chloropropane and hydroxyl radicals was  $1.47 \times 10^8$  (1/M.s) [27], while rate constants of phenol degradation to catechol and resorcinol by UV/ $\text{H}_2\text{O}_2$  process were  $9 \times 10^8$  and  $2 \times 10^8$  (1/M.s), respectively [42]. Considering the typical rate constants of organic compounds with hydroxyl radicals vary from  $10^6$  to  $10^{10}$  (1/M.s) [43], corn starch can be considered as fast reacting compounds with hydroxyl radicals.

Table 2 also discloses the fact that starch oxidation using  $\text{H}_2\text{O}_2$  under influence of UV irradiation is controlled by mass transfer resistance. In general, the liquid-solid mass transfer coefficients obtained in this work were between  $3.1836 \times 10^{-3}$  and  $3.6016 \times 10^{-3}$  (m/s), and all were far below the reaction rate constant of the respective  $\text{H}_2\text{O}_2$  concentrations.

#### 4.2 Effect of pH

The optimum pH for coupled  $\text{H}_2\text{O}_2$ /UV degradation of organic substances is strongly dependent on the type of the respective compounds [44]. To investigate the effect of the initial pH of  $\text{H}_2\text{O}_2$  solution on the oxidation of corn starch, oxidation experiments were conducted with an initial pH between 3 and 9 at  $30^\circ\text{C}$ , initial hydrogen peroxide concentration of 0.50 M and starch-water ratio (S/L) = 1/20. The data obtained from experiments and modelling calculation is depicted in Figs. 6, 7 and 8.

Figures 6, 7 and 8 confirm that oxidation of corn starch using  $\text{H}_2\text{O}_2$ /UV process was more efficient at lower pH than at higher pH. The highest carbonyl and carboxyl group's concentrations were obtained at pH 3. This is because under acidic condition, more hydroxyl radicals are being produced compared to that at alkaline condition [45].

However, when the starch oxidations were carried out at higher pH, the oxidation rates as shown by  $\text{H}_2\text{O}_2$  consumptions were found to decrease rapidly when pH increased from 5 to 7. A slight decrease in starch oxidation rate was found when the pH of the system was further increased from 7 to 9. These findings are in good agreement with previous works reported in the literature. During treatment with UV/  $\text{H}_2\text{O}_2$  process, the contribution to the degradation of two hydrophenols by hydroxyl radical destruction was more than 95% in acidic and neutral solutions [44]. De Laat et al. observed that the efficiencies of UV/  $\text{H}_2\text{O}_2$  processes were not affected by pH below 8, while a decrease was observed for higher pH [46].

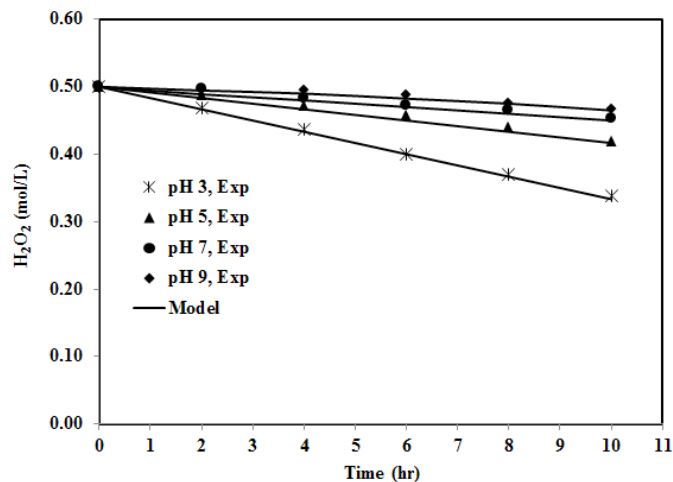


Fig. 6 Profile of  $\text{H}_2\text{O}_2$  concentration during oxidation of corn starch at  $30^\circ\text{C}$ , starch-water ratio (S/L) = 1/20, initial hydrogen peroxide concentration 0.5 M and various pH

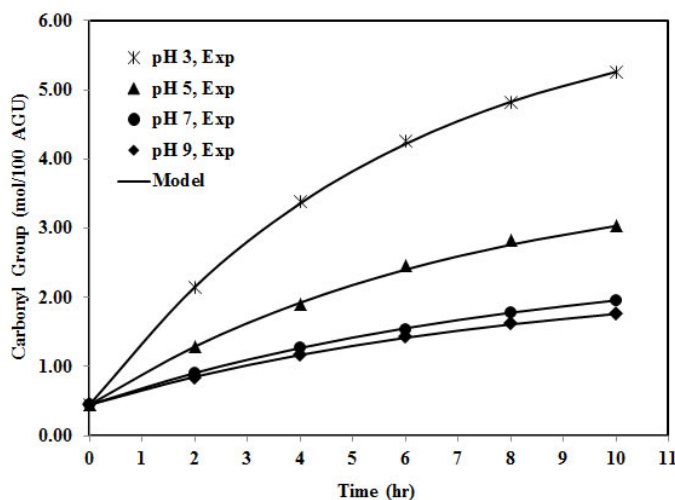


Fig. 7 Profile of carbonyl concentration during oxidation of corn starch at  $30^\circ\text{C}$ , starch-water ratio (S/L) = 1/20, initial hydrogen peroxide concentration 0.5 M and various pH

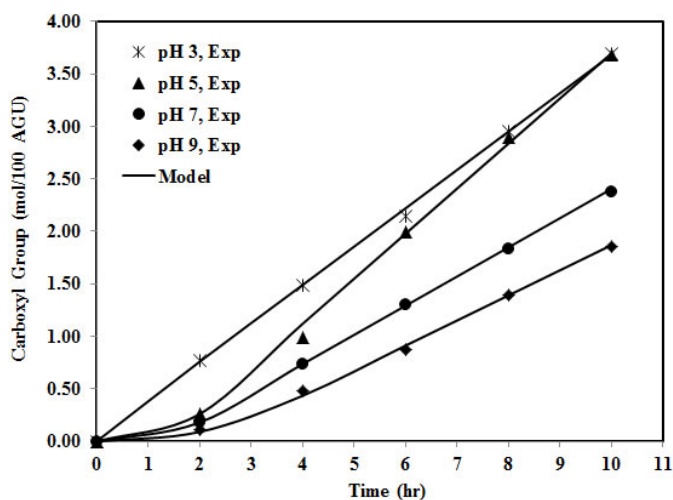


Fig. 8 Profile of carboxyl concentration during oxidation of corn starch at  $30^\circ\text{C}$ , starch-water ratio (S/L) = 1/20, initial hydrogen peroxide concentration 0.5 M and various pH

At high pH conditions  $\text{H}_2\text{O}_2$  tend to ionise to form hydroperoxide anion ( $\text{HO}_2^-$ ), which is a well-known strong scavenger to hydroxyl radical. The reaction between hydroperoxide anion and hydroxyl radical generates a less reactive hydroperoxyl radical ( $\text{HO}_2\bullet$ ) and hence in the reduction in degradation of starch [47]. The self-decomposition rate of  $\text{H}_2\text{O}_2$  to form  $\text{H}_2\text{O}$  and  $\text{O}_2$  at high pH was higher than those at neutral and low pH [48]. Unfortunately,  $\text{O}_2$  has lower oxidising ability compared to that of  $\text{HO}\bullet$  and  $\text{H}_2\text{O}_2$ . This self-decomposition reaction also prohibits the formation of  $\text{HO}\bullet$  radicals in the solution. This phenomenon leads to lower the efficiency of starch oxidation process at alkaline conditions.

Figures 6, 7 and 8 also display the comparison of experimental data and modelling results for  $\text{H}_2\text{O}_2$ , carbonyl and carboxyl group's concentrations as function of pH and reaction time. The proposed model exhibits fairly good predictions as most of the experimental data points fall in the solid lines, which represent the modelling calculation results.

**Table 3** Rate constants at various pH

pH	$k_{10} \times 10^{-8}$ (1/M.s)	$k_{11} \times 10^{-6}$ (1/M.s)	$k_{12} \times 10^{-5}$ (1/M.s)	$k_{cs} \times 10^3$ (m/s)	AARD (%)
3.0	3.3297	7.1998	2.0833	3.2323	3.87
5.0	3.2750	7.1231	1.5258	1.4019	2.48
7.0	1.2725	6.8361	1.7516	1.2215	3.37
9.0	1.2190	6.6288	1.3670	1.1902	2.91

Table 3 shows the agreement between the proposed model with the experimental data as indicated by low values of AARD, which are between 2.48% and 3.87%. Similar to that obtained from the study on the effect of  $\text{H}_2\text{O}_2$ , the value of  $k_{10}$ ,  $k_{11}$  and  $k_{12}$  obtained from the pH study are also consistent with the constants reported by several workers with other modes of generation of hydroxyl radicals [27, 42, 43]. In addition, Table 3 also discloses the fact that starch oxidation using  $\text{H}_2\text{O}_2$  under influence of UV irradiation within the studied range pH is controlled by mass transfer resistance. The liquid-solid mass transfer coefficients obtained from modelling calculations in this work are between  $1.1902 \times 10^{-3}$  and  $3.203 \times 10^{-3}$  (m/s), and all are far below the reaction rate constant of the respective pH.

## 5 Conclusions

A simple model for describing the reaction and mass transfer kinetics of  $\text{H}_2\text{O}_2$ /UV starch oxidation has been successfully developed. The model confirms that the kinetics of starch oxidations using  $\text{H}_2\text{O}_2$  solution under influence of UV irradiation follows first order reaction with respect to  $\text{H}_2\text{O}_2$  and starch concentration. The accuracy of the model in predicting the reaction parameters is reflected by AARD values between 2.33 % to 3.87 %. The observed reaction rate constants for corn starch degradation ranged between  $1.3670 \times 10^5$  to  $1.4673 \times 10^9$  (1/M.s).

On the other hand, the liquid-solid volumetric mass transfer coefficients obtained in this work exist between  $1.1902 \times 10^3$  to  $3.606 \times 10^3$  (m/s). The overall mechanism of corn starch oxidation using  $\text{H}_2\text{O}_2$  under influence of UV irradiation is controlled by mass transfer of hydroxyl radicals to starch granules.

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