

Research article

A simplified kinetics model of natural and iron complex catalysed hydrogen peroxide oxidation of starch

Andri Cahyo Kumoro,* R. Ratnawati and Diah Susetyo Retnowati

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Prof. H. Soedarto, SH Road, Tembalang, Semarang, 50275, Indonesia

Received 7 December 2014; Revised 23 March 2015; Accepted 31 March 2015

ABSTRACT: Hydrogen peroxide is well known as one of environmentally benign reagents for the oxidation of starch. The aim of this work was to develop a simplified model for the describing of mass transfer and reaction kinetics phenomena of non-catalytic and iron complex catalysed starch oxidation using hydrogen peroxide under alkaline condition. The model was composed based on hydrogen peroxide consumptions for its decomposition and reaction with starch molecules as well as mass transfer between liquid–solid reactants. Effects of starch-water ratio (S/L), catalyst concentration and pH were evaluated. The results show that both non-catalytic and iron complex catalysed hydrogen peroxide starch oxidation follows pseudo-first-order reaction with respect to hydrogen peroxide concentration. The proposed model satisfactorily describes the overall reaction, where very good agreement with experimental data was obtained. Mass transfer between liquid–solid reactants was likely to be the controlling step for the iron complex catalysed starch oxidation using hydrogen peroxide. © 2015 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: kinetics; modeling; carbohydrate; controlling rate; solid-liquid reaction

INTRODUCTION

Although oxidised starch is primarily used as surface sizing agents and coating binders in the paper industry as well as to provide water holdout for superior printing properties,^[1] its applications in any industries where film formation and adhesion properties are desired steadily increase.^[2] Oxidised starch is commonly manufactured by oxidation of starch using a specific oxidising agent under controlled pH and temperature. Hydroxyl groups on the starch molecules are oxidised to carbonyl and carboxyl groups during the oxidation process, which contribute to the improvement of starch paste stability.^[1] In addition, the reaction also causes degradation of the starch molecules producing a modified starch with low viscosity. This allows the use of oxidised starch in various applications where high solid concentration is needed.^[3]

A number of oxidising agents have been used in the starch oxidation process including sodium hypochlorite, bromine, periodate, permanganate, hydrogen peroxide and ammonium persulfate.^[2] Due to its high efficiency, hypochlorite oxidation is the most common technique for the commercial production of oxidised starch.

Unfortunately, this oxidant may lead to a formation of toxic chlorinated by-products. Alternatively, hydrogen peroxide has also been used as oxidant in a commercial practice to a much lesser extent. Unlike sodium hypochlorite, this oxidant does not generate harmful by-product. During oxidation reaction, decomposition of hydrogen peroxide produces an oxygen atom to oxidise the starch, leaving water as a by-product. For that reason, hydrogen peroxide is therefore considered as a more environmentally benign and preferred oxidant especially when a chlorine-free process is obliged.^[1,4]

Unfortunately, only few studies on the kinetics of starch oxidation by hydrogen peroxide are reported in the literature.^[1,5] Most reported studies were performed in batch reactors and followed by analysing only the final products.^[6,7] It is reported that hydroxyl groups in starch molecules are first oxidised to carbonyl groups and then to carboxyl groups, which primarily occurs at C-2, C-3 and C-6.^[4] This would indicate that the reaction path is consecutive with carbonyl groups as intermediates, which react further to carboxyl groups after prolonged reaction times. Depending on the type of oxidant used, parallel reaction paths are also reported. An oxidant may promote selective formation of carbonyl groups by oxidation of the hydroxyl groups at the positions C-2 and C-3, whereas another oxidant may trigger the hydroxyl groups at the position C-6 to form carboxyl groups.^[8] A study by Tolvanen *et al.*

*Correspondence to: Andri Cahyo Kumoro, Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Professor Haji Soedarto, SH Road, Tembalang, Semarang 50275, Indonesia. E-mail: andrewkomoro@undip.ac.id

on the catalytic system FePcS/H₂O₂ concluded that oxidation reactions take place mainly on the outer surface of the starch granules. As a result, partial surface oxidation of the granules allows further oxidation in the inner part of the granules that becomes more accessible.^[51] Therefore, to obtain a clear understanding of the reaction kinetics of starch oxidation using H₂O₂ and metal complex catalyst, a set of experiments was performed in a batch mode (all components were added at the beginning of the experiments) followed by a simple mathematical modelling.

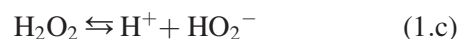
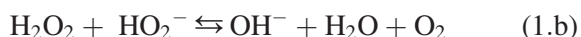
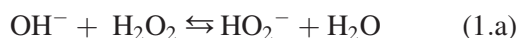
REACTION KINETIC MODEL DEVELOPMENT

A simple kinetic model was proposed to explain the reaction rate of starch oxidation using hydrogen peroxide with or without the presence of water soluble iron complex catalyst. Because the residual concentration of free hydrogen peroxide in the bulk liquid is the easiest parameter to measure, then the overall oxidation reaction rate was simply expressed as the rate of hydrogen peroxide consumption rather than the rate of carbonyl and carboxyl group formations in the starch molecules. To adequately describe the real phenomena of the system, the following assumptions were taken: (1) oxidation reactions occur mainly on the outer surface of the starch granules and followed by further oxidation in the inner part of the granules,^[51] (2) no accumulation of substances in the combined film on the solid film region, (3) reaction temperatures are set to be below the gelatinization temperature of the starch; therefore, changes in the surface area and volume of starch granules are negligible and (4) reaction rate is temperature, hydrogen peroxide concentration, pH and impurities dependent.

Decomposition of hydrogen peroxide with or without catalyst

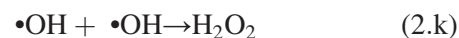
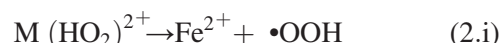
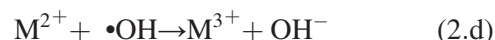
Under alkaline condition, hydrogen peroxide spontaneously decomposes to oxygen and water, and the rate of this natural decomposition is dependent on the temperature, concentration and impurities. The overall reaction of natural decomposition of hydrogen peroxide [Eqn (1.d)] was proposed to be a sequential reaction comprising Eqn (1.a) and Eqn (1.b).^[51] Ionisation of hydrogen peroxide to form a proton and a hydroperoxide anion also simultaneously occurs as expressed by Eqn (1.c).^[9]

Natural decomposition:



In the presence of metal catalyst however, hydrogen peroxide is decomposed more rapidly, forming a hydroxide ion (OH⁻), hydroxyl radicals (•OH) and hydroperoxide radical (•OOH) [Eqns (2.a) and (2.b)].^[4] The metal catalyst is regenerated according to Eqn (2.e). Moreover, radical interactions can lead to recombination at rate constant of 5 × 10⁹ (1/M.s) to form hydrogen peroxide according to Eqn (2.k).^[10] However, the steady-state concentration of hydroxyl radicals is only about 10⁻¹⁰ M at best; therefore, under normal circumstances, recombination of OH radicals to form hydrogen peroxide can be totally neglected. The metal-catalysed decomposition of hydrogen peroxide takes place via the following mechanisms^[11]:

Catalytic decomposition:



It is difficult to measure the concentration of radicals (C_{•OOH} and C_{•OH}) in the reaction system experimentally. Therefore, they should be calculated using the correlations between them and hydrogen peroxide concentration (C_{HPI}) when only the M²⁺ is considered. The aforementioned correlations are expressed by the following equations^[12]:

$$C_{\bullet\text{OH}} = C_{\text{HR}\bullet} = \frac{k_{2a}}{k_{2d}} C_{\text{HPI}} \quad (3.a)$$

$$C_{\bullet\text{OOH}} = \frac{k_{2a} k_{2b}}{k_{2c} k_{2d}} C_{\text{HPI}} \quad (3.b)$$

k_{2a}, k_{2b}, k_{2c} and k_{2d} are the reaction rate constants for reactions (2.a), (2.b), (2.c) and (2.d), respectively.

Brooks and Moore^[13] and Tolvanen *et al.*^[11] reported that the decomposition of hydrogen peroxide under alkaline condition either without or with the presence of metal catalyst obeys second-order reaction with respect to hydrogen peroxide concentration. With the absence of metal ion, Brooks and Moore^[13] assumed a non-chain process occurs when one mole of hydrogen peroxide and one mole of perhydroxyl anion form an intermediate complex, which decomposes to molecular oxygen. Tolvanen *et al.*^[11] analyse their own hydrogen peroxide decomposition data empirically using power law to come out with conclusion of second-order reaction with respect to hydrogen peroxide concentration. To obtain better theoretical reason, we applied the integral method to analyse the kinetics of natural and metal ion catalysed decompositions of hydrogen peroxide using the data reported by Tolvanen *et al.*^[11] That effort revealed that both natural and metal-catalysed decompositions of hydrogen peroxide are pseudo-first-order reactions with regard to hydrogen peroxide concentration. Our results agree well with Abbot and Brown^[14] and Lin and Gurol,^[15] who reported that the hydrogen peroxide reactions using Fe(III) are first order with respect to hydrogen peroxide concentration, and Tolvanen *et al.*,^[16] who investigate the decomposition of hydrogen peroxide with the presence of iron tetrasulphothalocyanine. In addition, Lin *et al.*^[17] also reported first-order kinetics of natural decomposition of hydrogen peroxide. Therefore, hydrogen peroxide decomposition rates can be simply written as

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

$$r_{\text{CatDecHP}} = - = -k_{\text{Cat}}C_{\text{HPI}} \quad (4.b)$$

k_{Nat} and k_{Cat} are the natural and catalytic decomposition rate constants. To facilitate further study on the effect of temperature (T) on the reaction rate, the reaction rate constant ($k = k_{\text{Nat}}$ or k_{Cat}) was assumed to follow the Arrhenius correlation:

$$k = A.e^{-E/RT} \quad (5)$$

with A , E and R are the Arrhenius (collision) constant, activation energy and ideal gas constant, respectively.

Diffusion of hydrogen peroxide and hydroxyl radical from the bulk liquid to the surface of starch particles

As oxidation reactions take place mainly on the outer surface of the starch granules and followed by further oxidation in the inner part of the granules, hydrogen peroxide should diffuse from bulk of liquid to the active surface of solid granules.^[5] Because the

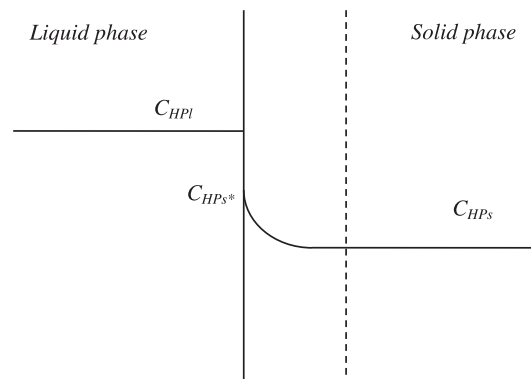


Figure 1. Schematic diagram of concentration gradient for mass transfer through combined film in the solid phase for hydrogen peroxide and hydroxyl radical.

diffusion resistance of fluid through the solid film is greater than the resistance of fluid diffusion through the fluid film, it is plausible to make simplification by assuming the existence of a combined film on the solid film region. Then, the concentration gradient can be approximated as shown in Fig. 1, and the mass transfer rate can be written as

$$\begin{aligned} r_{\text{DifHP}} &= -\left(\frac{dC_{\text{HPI}}}{dt}\right)_{3a} \\ &= K_{\text{cs}} \frac{S_{\text{pt}}}{V_{\text{pt}}} (C_{\text{HPs}^*} - C_{\text{HPs}}) \end{aligned} \quad (6.a)$$

$$\begin{aligned} r_{\text{DifHR}} &= -\left(\frac{dC_{\text{HRl}}}{dt}\right)_{3b} \\ &= K_{\text{cs}} \frac{S_{\text{pt}}}{V_{\text{pt}}} (C_{\text{HRs}^*} - C_{\text{HRs}}) \end{aligned} \quad (6.b)$$

with $\frac{S_{\text{pt}}}{V_{\text{pt}}}$ and K_{cs} are, respectively, the specific surface area of the starch and combined mass transfer coefficient in the solid phase. In this case, C_{HPs^*} exists in equilibrium with C_{HPI} . Similarly, C_{HRs^*} presents equilibrium with C_{HRl} and can be represented by the following Henry-like correlations:

$$C_{\text{HPs}^*} = H \times C_{\text{HPI}} \quad (7.a)$$

$$C_{\text{HRs}^*} = H \times C_{\text{HRl}} \quad (7.b)$$

Substituting Eqn (7.a) to Eqn (6.a) gives

$$\begin{aligned} r_{\text{DifHP}} &= -\left(\frac{dC_{\text{HPI}}}{dt}\right)_{3a} \\ &= K_{\text{cs}} \frac{S_{\text{pt}}}{V_{\text{pt}}} (H \times C_{\text{HPI}} - C_{\text{HPs}}) \end{aligned} \quad (8.a)$$

Substituting Eqn (3.a) and Eqn (7.b) to Eqn (6.b) results

$$r_{\text{DiffHR}} = -\frac{k_2}{k_5} \left(\frac{dC_{\text{HPI}}}{dt} \right)_{3b} \\ = K_{\text{cs}} \frac{S_{\text{pt}}}{V_{\text{pt}}} \left(H \cdot \frac{k_{2a}}{k_{2d}} \cdot C_{\text{HPI}} - C_{\text{HR}\cdot\text{s}} \right) \quad (8.b)$$

Reaction of atmospheric oxygen and hydroxyl radicals from hydrogen peroxide decomposition with starch molecules at the reaction surface

The reaction mechanisms of hydrogen peroxide with starch are very complex and may change depending on the reaction conditions. Carbohydrates with lacking of carbonyl group are almost inert to aqueous hydrogen peroxide.^[18] Tolvanen *et al.*^[5] observed no or hardly formation of new carboxyl groups during un-catalysed hydrogen peroxide oxidation of potato and corn starches. Direct oxidation of organic contaminants by atmospheric oxygen from decomposition of hydrogen peroxide [Eqn (1.a)] is slow, often considered too slow to be of significance.^[19] On the other hand, depending on pH of the system, the highly reactive hydroxyl radical generated from hydrogen peroxide decomposition may react with carbohydrate exceedingly rapidly.^[20] This free radical oxidises the glucose unit by subtracting hydrogen from a C–H group on the sugar ring, forming a radical (R•CHOH) that further reacts with metal ion or hydrogen peroxide yielding a carbonyl groups or oxidises hydroxyl groups in glucose units to carbonyl and/or carboxyl groups.^[2,6] Generally, though, the reaction follows a mechanism similar to the one listed as follows:



Based on their experiments on the influence of alkali on the decomposition of hydrogen peroxide in the presence of starch, Tolvanen *et al.*^[16] concluded that the decomposition is first order with respect to hydrogen peroxide. Therefore, the rate of reaction of starch oxidation using hydrogen peroxide on the starch surface without catalyst can be written as

$$-r_{\text{OxHP}} = -\left(\frac{dC_{\text{HPI}}}{dt} \right)_4 = k_{\text{ox,Nat}} \frac{S_{\text{pt}}}{V_{\text{pt}}} C_{\text{Ag}} C_{\text{HPs}} \quad (10)$$

C_{HPs} is the concentration of hydrogen peroxide in the starch surface, while $k_{\text{ox,Nat}}$ is the reaction rate constant. Assumption (2) suggests an equimolar rate between hydrogen peroxide diffusion through the combined film and the reaction of hydrogen peroxide

on the starch surface. Rearrangement of Eqns (8.a) and (10) will obtain

$$-r_{\text{OxHP}} = -r_{\text{DiffHP}} = \frac{S_{\text{pt}}}{V_{\text{pt}}} \frac{H \cdot C_{\text{HPI}}}{\left(\frac{1}{K_{\text{Cs}}} + \frac{1}{k_{\text{ox,Nat}} \cdot C_{\text{Ag}}} \right)} \quad (11)$$

Because the concentration of starch molecules in the starch granules (C_{Ag}) is very much higher than the concentration of hydrogen peroxide on the starch surface suggesting a nearly constant value of C_{Ag} , and the oxidation reaction is very slow,^[5] then $\frac{1}{K_{\text{Cs}}} + \frac{1}{k_{\text{ox,Nat}} \cdot C_{\text{Ag}}} \approx c$. This simplification results in a pseudo-first-order reaction with respect to hydrogen peroxide concentration as follows:

$$-r_{\text{OxHP}} = -r_{\text{DiffHP}} = \frac{S_{\text{pt}}}{V_{\text{pt}}} \cdot \frac{H}{c} \cdot C_{\text{HPI}} \quad (12)$$

Assumption (3) suggests that no starch fragmentation occurs during the oxidation process, therefore, the value of $\frac{S_{\text{pt}}}{V_{\text{pt}}} \cdot \frac{H}{c} = k_{\text{r,Nat}}$ will be constant. As a result, Eqn (12) becomes

$$-r_{\text{OxHP}} = -r_{\text{DiffHP}} = k_{\text{r,Nat}} \cdot C_{\text{HPI}} \quad (13)$$

The rate of reaction of starch oxidation using hydrogen peroxide on the starch surface using metal ion catalyst can be expressed as

$$-r_{\text{OxHR}} = -\left(\frac{dC_{\text{HRI}}}{dt} \right)_5 = k_{\text{ox,Cat}} \frac{S_{\text{pt}}}{V_{\text{pt}}} C_{\text{Ag}} C_{\text{HR}\cdot\text{s}} \quad (14.a)$$

Substituting of Eqn (3.a) to Eqn (14.a) results in

$$-r_{\text{OxHR}} = -\left(\frac{dC_{\text{HPI}}}{dt} \right)_5 = k_{\text{ox,Cat}} \frac{S_{\text{pt}} k_5}{V_{\text{pt}} k_2} C_{\text{Ag}} C_{\text{HR}\cdot\text{s}} \quad (14.b)$$

$C_{\text{HR}\cdot\text{s}}$ is the concentration of hydroxyl radical in the starch surface, while $k_{\text{ox,Cat}}$ is the catalytic reaction rate constant. Taking advantage of the assumption (2), the rate of hydroxyl radical diffusion through the combined film should be equal to the reaction rate of hydroxyl radical on the starch surface. Rearrangement Eqns (4.b), (8.b) and (14.b) will obtain

$$-r_{\text{OxHR}} = -r_{\text{CatDecHP}} = -r_{\text{DiffHR}} \\ = \frac{\left(1 + H \cdot \frac{k_{2a}}{k_{2d}} \right) \cdot C_{\text{HPI}}}{\left(\frac{1}{k_{\text{Cat}}} + \frac{V_{\text{pt}}}{S_{\text{pt}}} \frac{1}{K_{\text{Cs}}} + \frac{1}{k_{\text{ox,Cat}} \cdot C_{\text{Ag}}} \right)} \quad (15)$$

k_{2a} and k_{2d} are the reaction rate constants for reaction (2.a) and (2.d), and their value are 6.3×10^1 (1/M.s)

and 3.2×10^8 (1/M.s), respectively.^[11] Therefore, the value of $1 + H \cdot \frac{k_{2a}}{k_{2d}}$ will be reasonably approximated to be 1. Because the concentration of carbohydrate molecules in the starch granules (C_{Ag}) is very much higher than the concentration of hydrogen peroxide, and the reaction with hydroxyl radical is very fast,^[20] then $\frac{1}{k_{Ox,Cat} \cdot C_{Ag}} \approx 0$. This simplification results in a pseudo-first-order reaction with respect to hydrogen peroxide concentration as follows:

$$-r_{OxHR} = -r_{CatDecHP} = -r_{DiffHR} = \frac{C_{HPI}}{\left(\frac{1}{k_{Cat}} + \frac{V_{pt}}{S_{pt}} \frac{1}{K_{Cs}}\right)} \quad (16)$$

Taking the benefit of assumption (3), no starch fragmentation occurs during the oxidation process; therefore, the value of $\frac{V_{pt}}{S_{pt}} \frac{1}{K_{Cs}} = \frac{1}{K_{Cs}}$ will be constant. As a result, Eqn (16) becomes

$$\begin{aligned} -r_{OxHR} &= -r_{CatDecHP} = -r_{DiffHR} \\ &= \frac{C_{HPI}}{\left(\frac{1}{k_{Cat}} + \frac{1}{K_{Cs}}\right)} \end{aligned} \quad (17)$$

The overall reaction rate

The overall reaction rate (r_{ox}) during natural oxidation of starch using hydrogen peroxide can be regarded as the overall consumptions of hydrogen peroxide, which include the decomposition of hydrogen peroxide and oxidation of the starch. Because all hydroxyl radicals generated from catalytic decomposition of hydrogen peroxide will oxidise starch molecules, then the overall reaction rate of catalytic decomposition of hydrogen peroxide to hydroxyl radical should be equal to the observed rate of reaction between hydroxyl radicals and starch molecules. For non-catalytic and catalytic oxidations of starch, this definition can be written as

$$\begin{aligned} -r_{ox,Nat} &= -\left(\frac{dC_{HPI}}{dt}\right) = -(r_{DecHP} + r_{oxHP}) \\ &= (k_{Nat} + k_{r,Nat}) \cdot C_{HPI} \end{aligned} \quad (18.a)$$

$$\begin{aligned} -r_{ox,Cat} &= -\left(\frac{dC_{HPI}}{dt}\right) = -r_{OxHR} = -r_{CatDecHP} \\ &= -r_{DiffHR} = \frac{C_{HPI}}{\left(\frac{1}{k_{Cat}} + \frac{1}{K_{Cs}}\right)} \end{aligned} \quad (18.b)$$

Under a specific condition, the values of $k_{Nat} + k_{r,Nat}$ and $\frac{1}{\left(\frac{1}{k_{Cat}} + \frac{1}{K_{Cs}}\right)}$ are constant, therefore they can be written as $k_{obs, Nat}$ and $k_{obs, Cat}$, respectively. Then,

the introduction of these new terms to either Eqn (18.a) or (18.b) and followed by integration from $t=0$ to $t=t$ with boundary condition $C_{HPI}=C_{HPI0}$ and $C_{HPI}=C_{HPI}$ should result

$$C_{HPI} = C_{HPI0} \cdot e^{-(k_{obs,Nat}) \cdot t} \quad (19.a)$$

$$C_{HPI} = C_{HPI0} \cdot e^{-(k_{obs,Cat}) \cdot t} \quad (19.b)$$

The optimum value of $k_{obs, Nat}$ and $k_{obs, Cat}$ in Eqns (19.a) and (19.b) can be obtained through minimisation of the average of absolute relative errors (AARD) between the calculated hydrogen peroxide concentration and that of experimental data reported by Tolvanen *et al.*^[11] and Tolvanen *et al.*^[16] for hydrogen peroxide oxidation of starch with or without iron tetrasulfophthalocyanine catalyst (FePcS).

$$AARD = \frac{1}{N} \sum_1^n ABS \left(\frac{C_{HPI,exp} - C_{HPI,calc}}{C_{HPI,calc}} \right) \times 100\% \quad (20)$$

MATERIALS AND METHODS

Materials

Native potato starch and high amylose corn starch for oxidation experiments were purchased from Sigma-Aldrich Inc. (ST. Louis, MO, USA). All chemicals used were of analytical grade purity and purchased from Sigma-Aldrich Pte Ltd. (Singapore). Water soluble iron tetrasulfophthalocyanine (FePcS) was prepared by a modified Weber-Busch procedure as described previously by Hadasch *et al.*^[21] The molecular structures of the FePcS catalyst and anhydroglucose unit of starch are illustrated in Fig. 2 (a) and 2(b).

Methods

Microstructure characterization of starches

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). Measurements involved determining the isotherms of adsorption of high-purity nitrogen at temperature of 77.3 K. The monolayer capacity was calculated on the basis of Brunauer-Emmett-Teller adsorption isotherm from five measurement points in the relative pressure range p/p_0 0.006–0.2.^[22] Prior to the measurements, starch samples were dried for 24 h in vacuum at 100 °C, automatically desorbed and flushed with pure helium. Pore characteristic was determined according to

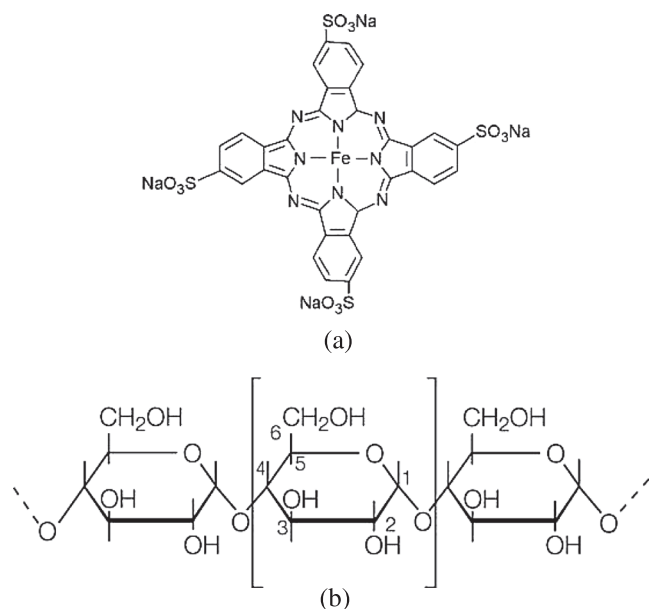


Figure 2. The molecular structure of iron complex catalyst (a) and anhydroglucose unit (b).

Barrett-Joyner-Halenda method.^[23] Samples were analysed in triplicate.

Scanning electron microscopy was performed to obtain the shape, surface structure and size of starch particles. Starch samples were dehydrated in 99.6% ethanol, dried and directly mounted on circular aluminum stubs with silver paste. They were then coated with gold using Sputter Coater CS 100 (Poland). Starch samples were observed and photographed in a Leica Cambridge S360 (Leica, Wetzlar, Germany) scanning electron microscope at 1500 times (potato starch) and 5000 times (corn starch) magnifications with accelerating voltage of 10 kV.^[24]

Oxidation of starch

A set of experiments was performed in a 250 mL glass reactor immersed in a waterbath heater to maintain the temperature at 52 °C. A specific amount of starch (3.10 to 24.76 g) was suspended in 120 mL deionized water at room temperature to obtain solid to liquid ratio (S/L between 1/12 to 2/3). The suspension was introduced into the reactor and continuously agitated using a glass stirrer at 700 rpm. The suspension system

was heated up, and the temperature was maintained at 52 °C. The pH was adjusted manually to the desired level (7.8 or 8.4) by addition of 2 M NaOH. All H₂O₂ was added instantaneously, and the initial concentration of H₂O₂ was determined by titration prior to the catalyst addition. The catalyst was added by dissolving it (10, 20 or 40 g) in 10 mL of water and poured into the reactor. During the experiments, samples were collected at certain time intervals, and the H₂O₂ concentration was immediately analysed by iodometric titration. The experiments were terminated when the H₂O₂ concentration was close to zero (or alternatively until the concentration did not decrease significantly). To ensure the reproducibility of the data, the experiments were carried out in triplicate.

RESULTS AND DISCUSSION

Non-catalytic starch oxidation using hydrogen peroxide

The non-catalytic oxidation of corn and potato starches using hydrogen peroxide was carried out at 52 °C, which is below the gelatinization temperature of both starches. The gelatinization temperatures of the starch are 61.1 °C for potato starch^[25] and 65.5 °C for corn starch.^[26] The results of non-catalytic starch oxidation modelling are presented in Table 1 and Fig. 3. The profile of hydrogen peroxide concentrations during the oxidation of high amylopectin starch (potato starch) in comparison with high amylose starch (corn starch), both at pH=8.4 and temperature of 52 °C is shown in Fig. 3. For comparison purposes, the profile of hydrogen peroxide concentration during its natural decomposition is also included in that figure. Obviously, the difference of the hydrogen peroxide consumption rates is evident. In the presence of low amylose, hydrogen peroxide consumption rate was very slow, which the value almost the same with hydrogen peroxide decomposition rate. Starches with lack of carbonyl group or low amylose content are mostly inert to aqueous hydrogen peroxide as indicated by no or little formation of new carboxyl groups during potato starch oxidation by Tolvanen *et al.*^[5] Petri *et al.*^[19] also suggest that direct oxidation of organic contaminants by atmospheric oxygen from

Table 1. Observed reaction rate constants ($k_{\text{obs,Nat}}$) of non-catalytic hydrogen peroxide oxidation of corn and potato starches at 52 °C and pH 8.4.

System	$k_{\text{obs,Nat}}$ (1/min)	K_s (1/min)	AARD (%)	Remark
H ₂ O ₂	1.68×10^{-4}	—	3.16	—
Corn starch + H ₂ O ₂	9.27×10^{-4}	7.59×10^{-4}	8.21	High amylose
Potato starch + H ₂ O ₂	1.81×10^{-4}	1.30×10^{-5}	3.37	High amylopectin

AARD, average of absolute relative errors.

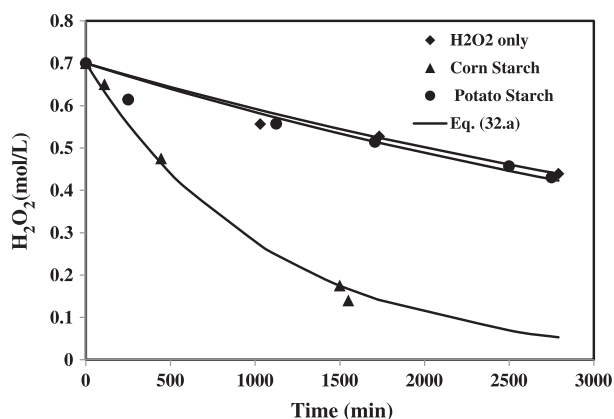


Figure 3. Non-catalytic hydrogen peroxide oxidation of corn and potato starch at 52 °C and pH 8.4.

decomposition of hydrogen peroxide is slow, often considered too slow to be of significance. For system with the presence of high amylose starch however, hydrogen peroxide consumption rate was much more rapid, and the reaction rate constant was about five times of that of low amylose starch. Because most amylose is residing mostly within the amorphous region of the starch granule, then it is logical that hydrogen peroxide will diffuse more easily in the pores and reacts with corn starch.^[27] In both cases, the reaction is well suited by the simple first-order kinetics. Based on the hydrogen peroxide concentration curve, Tolvanen *et al.* concluded that in the absence of the catalyst, the hydrogen peroxide decomposition follows zero-order kinetics.^[16] However, our analysis revealed that a first-order kinetic gives better estimation of hydrogen peroxide decomposition rate. The AARD of hydrogen peroxide concentrations calculated using Eqn (19.a) during corn and potato starch oxidations were 8.21% and 3.37%, respectively.

The model reveals that instead of only experiencing decomposition, some hydrogen peroxide molecules also simultaneously undergo reaction with starch. This

fact is indicated by lower hydrogen peroxide concentration at any time when starch is present in the system. In addition, the observed reaction rate constants of hydrogen peroxide-starch systems as tabulated in Table 1 are higher than that of hydrogen peroxide alone. Table 1 also discloses the fact that non-catalytic starch oxidation using hydrogen peroxide is controlled by mass transfer resistance. Amylose-rich corn starch, which is more porous, has higher mass transfer coefficient or less mass transfer resistance than amylopectin rich potato starch, which is less porous. The scanning electron microscope images of potato and corn starches are presented in Fig. 4(a) and Fig. 4(b), while the pore and specific surface area of both starches obtained from low temperature nitrogen sorption analysis are presented in Table 2.

Iron complex catalysed starch oxidation using hydrogen peroxide

The catalytic starch oxidation investigated in this study employed iron tetrasulfophthalocyanine (FePcS) catalyst with concentration of 70–280 mg/L or about 8.2×10^{-5} – 32.08×10^{-5} m, while the initial hydrogen peroxide concentration was 2.1 m. The pseudo-first-order reaction rate constant for decomposition of hydrogen peroxide using that water soluble iron complex catalyst in the absence of starch was 25.80×10^{-4} (1/min). This value is lower than that of reported by Lin and Gurol for the decomposition of hydrogen peroxide with goethite (α -FeOOH) catalyst, which is 9.80×10^{-3} (1/min).^[15] However, the observed rate constant value is still higher than that of extrapolated value for decomposition of hydrogen peroxide using ferric perchlorate ($\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$) catalyst reported by De Laat and Gallard,^[11] which is 7.80×10^{-4} (1/min). The difference of iron sources is likely to be the cause of the variation of apparently observed pseudo-first-order reaction rate constant values.

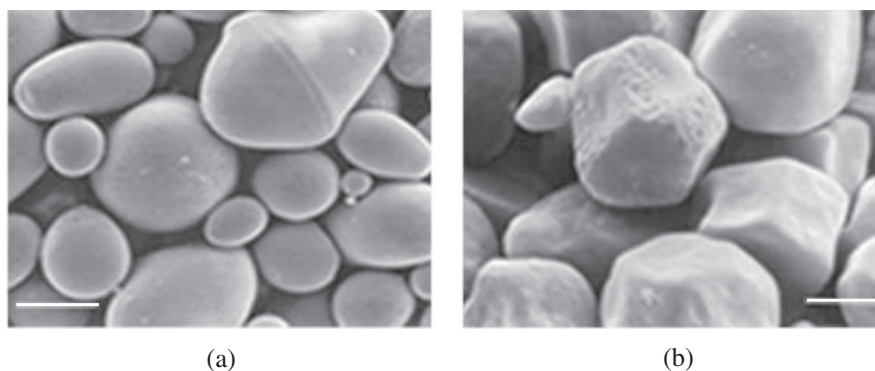


Figure 4. Scanning electron microscope photograph of native potato (a) and corn (b) starches.

Table 2. Microstructure parameters of potato and corn starches.

Material	Specific surface area (m ² /g)	Mesopore volume (cm ³ /g)	Average pore diameter (nm)	Remark
Corn starch	0.57	1 210	8.90	High amylose
Potato starch	0.15	158	6.52	High amylopectin

The reaction between hydrogen peroxide and starch molecules was found to be highly dependent on the S/L ratio; catalyst concentration and pH (Tables 3–5 and Figs 5–7). However, Table 3 and Fig. 5 also show that iron-catalysed hydrogen peroxide decomposition under alkaline condition without starch was faster than that of with the presence of starch. Similar finding was also reported in the literature.^[28] Walling and Goosen

reported that hydrogen peroxide decomposition using complexed Fe (III) catalyst is retarded by several organic substrates. In addition, this hydrogen peroxide decomposition also depends on hydrogen peroxide/substrate ratios, concentration, pH and temperature.^[28] Surprisingly, the hydrogen peroxide decomposition rate was also even faster when higher value of starch–water ratio (S/L) was applied. At higher value of

Table 3. Observed reaction rate constants ($k_{\text{obs,Cat}}$) of hydrogen peroxide oxidation of corn starch at 52 °C, 40 mg iron complex catalyst and pH 8.4 at various starch–water ratio.

Starch–water ratio (S/L)	$k_{\text{obs,Cat}}$ (1/min)	K_s (1/min)	AARD (%)
H ₂ O ₂ without starch	25.80×10^{-4}	—	2.59
2/3	18.73×10^{-4}	3.16×10^{-5}	3.35
1/3	16.03×10^{-4}	2.70×10^{-5}	6.52
1/6	11.03×10^{-4}	1.85×10^{-5}	2.68
1/12	9.84×10^{-4}	1.65×10^{-5}	1.53

AARD, average of absolute relative errors.

Table 4. Observed reaction rate constants ($k_{\text{obs,Cat}}$) of catalytic hydrogen peroxide oxidation of potato starch at (S/L=1/3), 52 °C and pH 8.4 using various concentration iron complex catalyst.

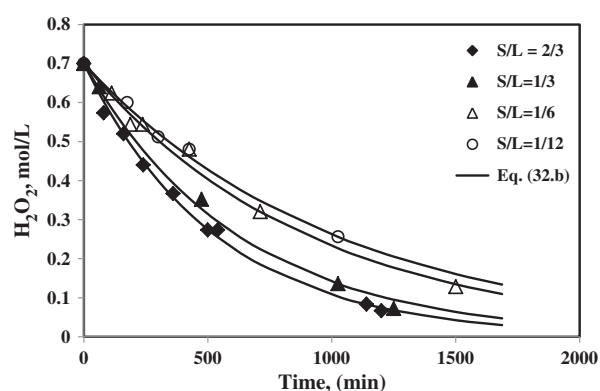
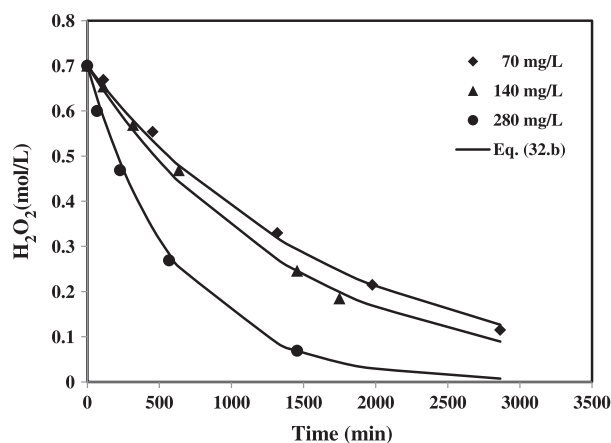
Catalyst concentration (mg/L)	$k_{\text{obs,Cat}}$ (1/min)	K_s (1/min)	AARD (%)
70	5.99×10^{-4}	1.00×10^{-5}	3.13
140	7.21×10^{-4}	1.21×10^{-5}	2.72
280	15.97×10^{-4}	2.69×10^{-5}	2.67

AARD, average of absolute relative errors.

Table 5. Observed reaction rate constants ($k_{\text{obs,Cat}}$) of catalytic hydrogen peroxide oxidation of potato starch using iron complex catalyst at (S/L=1/3), 52 °C and various pH.

pH	$k_{\text{obs,Cat}}$ (1/min)	K_s (1/min)	AARD (%)
8.4	22.00×10^{-4}	8.33×10^{-6}	6.13
7.8	4.98×10^{-4}	3.71×10^{-5}	5.37

AARD, average of absolute relative errors.

**Figure 5. Effect of starch–water ratio (S/L) on iron catalytic hydrogen peroxide oxidation of corn starch at 52 °C and pH 8.4.****Figure 6. Effect of catalyst concentration on catalytic hydrogen peroxide oxidation of potato starch using iron complex catalyst at (S/L=1/3), 52 °C and pH 8.4.**

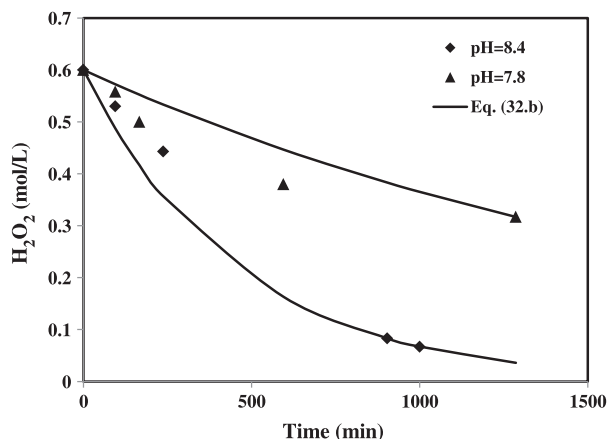


Figure 7. Effect of pH on catalytic hydrogen peroxide oxidation of potato starch using 280 mL iron complex catalyst at S/L=2/3 and 52 °C.

starch–water ratio (S/L), more anhydroglucose units are available in the system for reaction with hydroxyl radicals. Therefore, the reaction occurs at higher speed. Figure 6 depicts that the reaction also goes more rapidly as more catalyst was added to the reaction system. At low catalyst concentration however, only slight differences in the reaction rate constant were observed (Table 4). Increasing of the pH of the reaction system from 7.8 to 8.4 also speeds up the reaction rate 4.4 times (Table 5 and Fig. 7). Similar result was reported by Beltra'n *et al.* that the rates of hydroxyl radical generation by the Fenton's reaction increase with increasing pH.^[29] Tao *et al.* mentioned that the hydroxyl radical formation is faster at pH 8.4, which trigger nucleophilic peroxo complex $\text{PcSFe}^{3+}\text{-OO-}$ to cleave the C–C bond bearing hydroxyl groups to form acids via a Grob-type fragmentation.^[30] Caution should be taken as the catalyst may also undergo deactivation at higher pH via fragmentation of the phthalocyanine ring in the presence of peroxides.^[31] However, at even lower pH (acidic conditions), considerable depolymerisation of the starch may occur.^[32] In this catalytic system, starch oxidation can still proceed at higher rates even under alkaline conditions, distinct from the Fenton reaction, in which iron ions will cause the precipitation of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ at pH greater than 3. In addition, Tachiev *et al.* also reported that pH plays a major role in hydrogen peroxide decomposition rate. For complexed iron (Fe–Ligand and related species), the pH range for significant decomposition extends from 2 to 10, facilitating hydrogen peroxide decomposition in the neutral pH range.^[33]

The slower reaction of iron complex catalysed starch oxidation using hydrogen peroxide compared with the decomposition of hydrogen peroxide under similar condition needs further examination to determine the rate controlling mechanism. Although without giving any evidence, Tolvanen *et al.* suggested that the

oxidation of starch is mainly available at the granule surface, and less oxidation occurs in the centre of the particle.^[5] Collinson and Thielemans also reviewed that the oxidation process begins on the surface of the starch particle before oxidative degradation improves the access of the catalyst to enable oxidation to occur inside the particle.^[34] The hydroxyl radical has been traditionally known as the workhorse of hydrogen peroxide oxidation systems. Hydroxyl radicals generally react with organic compounds via three mechanisms: hydrogen abstraction, addition to multiple bonds and direct electron transfer.^[35] Because hydroxyl radicals are extremely reactive, it is plausible that they will react with hydrogen peroxide and other species on the starch surface nearly instantaneously before being able to diffuse back to the solution. Under these conditions, we may assume that $\cdot\text{OH}$ and $\cdot\text{OOH}$ will be completely consumed on the surface prior to diffusing to the solution. Thus, the reactions of $\cdot\text{OH}$ and $\cdot\text{OOH}$ with solutes in the solution phase are expected to be negligible under the given conditions.^[15] Therefore, a possibility of intrinsic reaction rate on the starch granules as the rate controlling mechanism can now be vanished.

An analysis is then subjected to the rate of decomposition of hydrogen peroxide to form hydroxyl radicals. Hydrogen peroxide concentrations are high in this system because it is introduced at a concentration of approximately 0.7 M. Because of this elevated concentration of hydrogen peroxide, as well as the relatively fast second-order reaction rate for reaction [Eqn (2.a)] (fast for a reaction not involving free radicals as a reactant), the pseudo-first-order rate constant of this reaction may be expected to be very fast. As a result, Fe (II) may be expected to be depleted from solution via Eqn (2.a) at a rapid rate, often within minutes or seconds. Considering that reactions (2.g)–(2.i) that regenerate Fe (II) from Fe (III) with reaction rate constant of 2.7×10^{-3} (1/s) are observed to be considerably slower than Eqn (2.a) with rate constant of 6.3×10^1 (1/M.s).^[11] Thus, the cycling of iron from Fe (III) back to Fe (II) via Eqns (2.g)–(2.i) will generally be the controlling step in the reaction scheme, and the bulk of the iron in the system may be assumed to be Fe (III).^[19] Having known the cycling of iron from Fe (III) back to Fe (II) as the controlling step in the catalytic decomposition of hydrogen peroxide to form hydroxyl radicals, then the controlling step of the overall starch oxidation is necessary to be investigated. The observed reaction rate constants were 4.98×10^{-4} to 22.00×10^{-4} (1/min), whereas the liquid–solid mass transfer coefficients ranged between 8.33×10^{-6} to 3.71×10^{-5} (1/min). It is clear now that mass transfer is the controlling step for the overall iron complex catalysed starch oxidation using hydrogen peroxide.

CONCLUSIONS

The non-catalytic and iron complex catalysed hydrogen peroxide starch oxidations were found to follow pseudo-first-order reaction with respect to hydrogen peroxide concentration. The proposed model is adequately describing the mass transfer and reaction kinetics of both systems as reflected by AARD values between 1.53% and 8.21%. The effect of starch–water ratio (S/L), catalyst concentration and pH on the reaction rate was evaluated. The observed reaction rate constants ranged between 1.81×10^{-4} and 18.73×10^{-4} (1/min). On the other hand, the liquid–solid mass transfer coefficients obtained in this work exist between 8.33×10^{-6} and 7.59×10^{-5} (1/min). The mass transfer of hydroxyl radicals to starch granules was the controlling step for the overall mechanism during iron complex catalysed starch oxidation using hydrogen peroxide.

Acknowledgements

The authors greatly acknowledge Ministry of Education and Culture of the Republic of Indonesia for its financial support through Non-Tax National Revenue-Diponegoro University Budget Execution List Year 2014 under contract No.: 023.04.02.189185/2014.

REFERENCES

- [1] Tolvanen P, Sorokin A, Ma'ki-Arvela P, Leveneur S, Murzin DY, Salmi T. Batch and semibatch partial oxidation of starch by hydrogen peroxide in the presence of an iron tetrasulfophthalocyanine catalyst: The effect of ultrasound and the catalyst addition policy. *Ind. Eng. Chem. Res.* **2011**; *50*: 749–757.
- [2] Sangseethong K, Termvejsayanon N, Sriroth K. Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches. *Carbohydr. Polym.* **2010**; *82*: 446–453.
- [3] Wurzburg OB. *Modified Starches: Properties and Uses*, Wurzburg OB (eds.). CRC Press: Boca Raton, FL, **1986**; 17–40.
- [4] Isbell HS, Frush HL. Mechanisms for hydroperoxide degradation of disaccharides and related compounds. *Carbohydr. Res.* **1987**; *161*: 181–193.
- [5] Tolvanen P, Ma'ki-Arvela P, Sorokin AB, Salmi T, Murzin DY. Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst. *Chem. Eng. J.* **2009**; *154*(1-3): 52–59.
- [6] Parovuori P, Hamunen A, Forssell P, Autio K, Poutanen K. Oxidation of potato starch by hydrogen peroxide. *Starch/Stärke* **1995**; *47*: 19–23.
- [7] Sorokin AB, Kachkarova-Sorokina SL, Donz  C, Pinel C, Gallezot P. From native starch to hydrophilic and hydrophobic products: a catalytic approach. *Topics Catal.* **2004**; *27*: 67–76.
- [8] Butrim SM, Bil'dyukevich TD, Yurkshtovich TL. Kinetics of starch oxidation in the system nitrogen (IV) oxide-tetrachloromethane. *Russ. J. Appl. Chem.* **2001**; *74*: 2106–2110.
- [9] Duke FR, Haas TW. The homogeneous base-catalyzed decomposition of hydrogen peroxide. *J. Phys. Chem.* **1961**; *65*: 304–306.
- [10] Han SK, Nam SN, Kang JW. OH radical monitoring technologies for AOP advanced oxidation process. *Water Sci. Technol.* **2002**; *46*(11–12): 7–12.
- [11] De Laat J, Gallard H. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environ. Sci. Technol.* **1999**; *33*: 2726–2732.
- [12] Haber F, Weiss J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. Roy. Soc. A* **1934**; *147*: 332–351.
- [13] Brooks RE, Moore SB. Alkaline hydrogen peroxide bleaching of cellulose. *Cellulose* **2000**; *7*: 263–286.
- [14] Abbot J, Brown DG. Kinetics of iron-catalyzed decomposition of hydrogen peroxide in alkaline solution. *Int. J. Chem. Kin.* **1990**; *22*(9): 963–974.
- [15] Lin SS, Gurol MD. Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanism, and implications. *Environ. Sci. Technol.* **1998**; *32*: 1417–1423.
- [16] Tolvanen P, Sorokin A, Mäki-Arvela P, Murzin DY, Salmi T. Oxidation of starch by H₂O₂ in the presence of iron tetrasulfophthalocyanine catalyst: the effect of catalyst concentration, pH, solid-liquid ratio, and origin of starch. *Ind. Eng. Chem. Res.* **2013**; *52*: 9351–9358.
- [17] Lin CC, Smith ER, Ichikawa N, Baba T, Itow M. Decomposition of hydrogen peroxide in aqueous solutions at elevated temperatures. *Int. J. Chem. Kin.* **1991**; *23*: 971–987.
- [18] Kürti L, Barbara C. *Strategic Applications of Named Reactions in Organic Synthesis: Background and Detailed Mechanisms*. Elsevier Academic Press: London, UK, **2005**; 28.
- [19] Petri BG, Watts RJ, Teel AL, Huling SG, Brown RA. *Fundamentals of ISCO using hydrogen peroxide*. In *In situ* chemical oxidation for ground water remediation, Siegrist RL, Crimi M, Simpkin Th J (eds.). Springer Science + Business Media: LLC, **2011**; 33–87.
- [20] Fry SC. Oxidative scission of plant cell wall polysaccharides by ascorbate-induced hydroxyl radicals. *Biochem. J.* **1998**; *332*: 507–515.
- [21] Hadasch A, Sorokin A, Rabion A, Fraisse L, Meunier B. Oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by iron tetrasulfophthalocyanine (FePcS) supported on a cationic ion-exchange resin. *Bull. Soc. Chim. Fr.* **1997**; *134*: 1025–1032.
- [22] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**; *60*: 309–319.
- [23] Barret EP, Joyner LG, Hallenda PP. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**; *73*: 373–380.
- [24] Uthumporn U, Wahidah N, Karim AA. Physicochemical properties of starch from sago (*Metroxylon sago*) palm grown in mineral soil at different growth stages. *IOP Conf. Ser.: Mater. Sci. Eng.* **2014**; *62*(012026): 1–11.
- [25] Shiotsubo T. Gelatinization temperature of potato starch at the equilibrium state. *Agric. Biol. Chem.* **1984**; *48*(1): 1–7.
- [26] Sandhu KS, Singh N. Some properties of corn starches II: physicochemical, gelatinization, retrogradation, pasting and gel textural properties. *Food Chem.* **2007**; *101*: 1499–1507.
- [27] Smith AM, Denyer K, Zeeman SC, Edwards A, Martin C. The synthesis of the starch granule. In *Plant Carbohydrate Biochemistry*, Bryant JA, Burrell MM, Kruger NJ (eds.). BIOS Scientific Publishers Ltd.: Oxford, UK, **1999**; 79–89.
- [28] Walling C, Goosen A. Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide. Effect of organic substrates. *J. Am. Chem. Soc.* **1973**; *95*(9): 2987–2991.
- [29] Beltra'n FJ, Gonzalez M, Rivas FJ, Alvarez P. Fenton reagent advanced oxidation of polynuclear aromatic hydrocarbons in water. *Water Air Soil Pollution* **1998**; *105*: 685–700.
- [30] Tao X, Ma W, Zhang T, Zhao J. A novel approach for the oxidative degradation of organic pollutants in aqueous

- solutions mediated by iron tetrasulfophthalocyanine under visible light radiation. *Chem. Eur. J.* **2002**; *8*: 1321–1326.
- [31] d'Alessandro N, Tonucci L, Bressan M, Dragani LK, Morvillo A. Rapid and selective oxidation of metallosulfo phthalocyanines prior to their usefulness as precatalysts in oxidation reactions. *Eur. J. Inorg. Chem.* **2003**; *9*: 1807–1814.
- [32] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **2005**; *30*(1): 38–70.
- [33] Tachiev G, Roth JA, Bowers AR. Kinetics of hydrogen peroxide decomposition with complexed and “free” iron catalysts. *Int. J. Chem. Kin.* **2000**; *32*(1): 24–35.
- [34] Collinson SR, Thielemans W. The catalytic oxidation of biomass to new materials focusing on starch, cellulose and lignin. *Coord. Chem. Rev.* **2000**; *254*: 1854–1870.
- [35] Bossmann SH, Oliveros E, Gob S, Siegwart S, Dahlen EP, Payawan L, Straub M, Worner M, Braun AM. New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced fenton reactions. *J. Phys. Chem. A* **1998**; *102*: 5542–5550.