We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS

BOOK CITATION INDEX

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Kinetic Modeling of Photodegradation of Water-Soluble Polymers in Batch Photochemical Reactor

Dina Hamad, Mehrab Mehrvar and Ramdhane Dhib

Abstract

Synthetic water-soluble polymers, well-known refractory pollutants, are abundant in wastewater effluents since they are extensively used in industry in a wide range of applications. These polymers can be effectively degraded by advanced oxidation processes (AOPs). This entry thoroughly covers the development of the photochemical kinetic model of the polyvinyl alcohol (PVA) degradation in UV/H_2O_2 advanced oxidation batch process that describes the disintegration of the polymer chains in which the statistical moment approach is considered. The reaction mechanism used to describe the photo-degradation of polymers comprises photolysis, polymer chain scission, and mineralization reactions. The impact of operating conditions on the process performance is evaluated. Characterization of the polymer average molecular weights, total organic carbon, and hydrogen peroxide concentrations as essential factors in developing a reliable photochemical model of the UV/H_2O_2 process is discussed. The statistical moment approach is applied to model the molar population balance of live and dead polymer chains taking into account the probabilistic chain scissions of the polymer. The photochemical kinetic model provides a comprehensive understanding of the impact of the design and operational variables.

Keywords: kinetic modeling, population balance, free radical-induced degradation, advanced oxidation process, water-soluble polymer

1. Introduction

The growing turnover and consumption of synthetic water-soluble polymers generate a huge amount of wastes during production, use, and disposal off. After usage, water-soluble polymers are expected to end up in rivers, lakes, oceans and even in wastewater treatment plants, thus creating a potential pollution hazard. In contrast to biopolymers, water-soluble polymers are resistant to microorganisms-mediated biodegradation [1–3]. Synthetic water-soluble polymers cover a wide range of highly varied families of products and have numerous interesting applications.

One of the concerns is the accumulation of such non-biodegradable water-soluble polymers in the environment. Particularly, polyvinyl alcohol (PVA) is one

of the most commercially important water-soluble synthetic polymers with an annual worldwide production of 650,000 tons. PVA polymers are abundant in wastewater effluents due to the extensive usage in paper and textile industries that accordingly generates significant amounts of PVA in wastewater streams [4, 5]. The PVA polymers are used in industry as paper and textile coatings, and also as laundry packing materials [6]. Its iodine complexes are widely used as polarization layers in liquid crystal displays (LCDs) [7]. As the production of PVA finds new markets, its consumption grows and the volume of wastewater containing PVA increases during its production and consumption. Moreover, PVA is highly soluble in water, and it leaches readily from soil into groundwater creating environmental issues. PVA polymers act as collector reagents that can be either chemisorbed or physically adsorbed since these polymer compounds have oxygen hetero-atoms capable of binding to different metal ions effectively and increase the mobilization of heavy metals from sediments of lakes and oceans which results in accumulation of hazardous materials. [6, 8–11]. Besides, The PVA solutions exhibit high surface activity supporting the formation of foams which can hinder the transport of oxygen into water streams. Therefore, the removal of PVA from wastewater systems is essential.

Conventional biological technologies are not efficient to breakdown PVA polymer chains since the degradation capacity of most microorganisms towards PVA is very limited and requires specially adapted bacteria strains [1]. In addition, wastewaters containing PVA can cause foam formation in biological equipment which inhibits the activity of aerobic microorganisms due to oxygen absence that results in unstable operation with low performance [9]. As a result, the advanced oxidation processes are utilized as alternative treatment techniques for the treatment of polymeric wastewater systems. The advanced oxidation technologies are proven to be effective in treating industrial wastewater [10, 11]. AOPs involve the formation of strong oxidants such as hydroxyl radicals and the reaction of these oxidants with pollutants in wastewater. In wastewater treatment applications, AOPs usually refer to a specific subset of processes that involve H_2O_2, O_3, and UV light as shown in the schematic diagram in **Figure 1**.

The degradation of water-soluble polymers by different AOPs is studied in the open literature whether those polymers are refractory, toxic, hazardous or recalcitrant compounds. Recent studies on the removal of PVA have focused on radiation-induced oxidation process such as photo-Fenton [7], photocatalytic processes [7, 12], radiation-induced electrochemical process [13], and UV/H_2O_2 process [14–17]. Even though the degradation of a polymer component must be assessed by the reduction and analysis of its molecular weights, there are only a few studies in the open literature on the devolution of the molecular weight size distributions of water-soluble polymers [9, 17]. Also, the residual hydrogen peroxide is still a challenging issue in the UV/H_2O_2 process which has been overlooked in some studies.

Furthermore, there is little information on the photochemical mechanism of the photo-oxidative degradation of PVA polymer solutions in a UV/H_2O_2 process. Recently, several attempts have been made to comprehend the chemical kinetics dominating thermal degradation of water-soluble polymers and assuming constant pH [18, 19]. Besides, no data is available on the distribution of the molecular weights of the polymer being degraded.

Under UV radiation, polymer chains are broken down into oligomers (short-chain polymers), dimers and monomers. Enhanced photo-degradation of polymer can lead to a broader distribution of molecular weights, indicating that the degraded polymer becomes less and less uniform. This behavior is expected for degraded polymers, as irradiation promotes an increase in the number of polymer chains, lowering the molecular weight, and consequently increasing the polydispersity. Hence, polymer degradation is a fragmentation process in which population balance
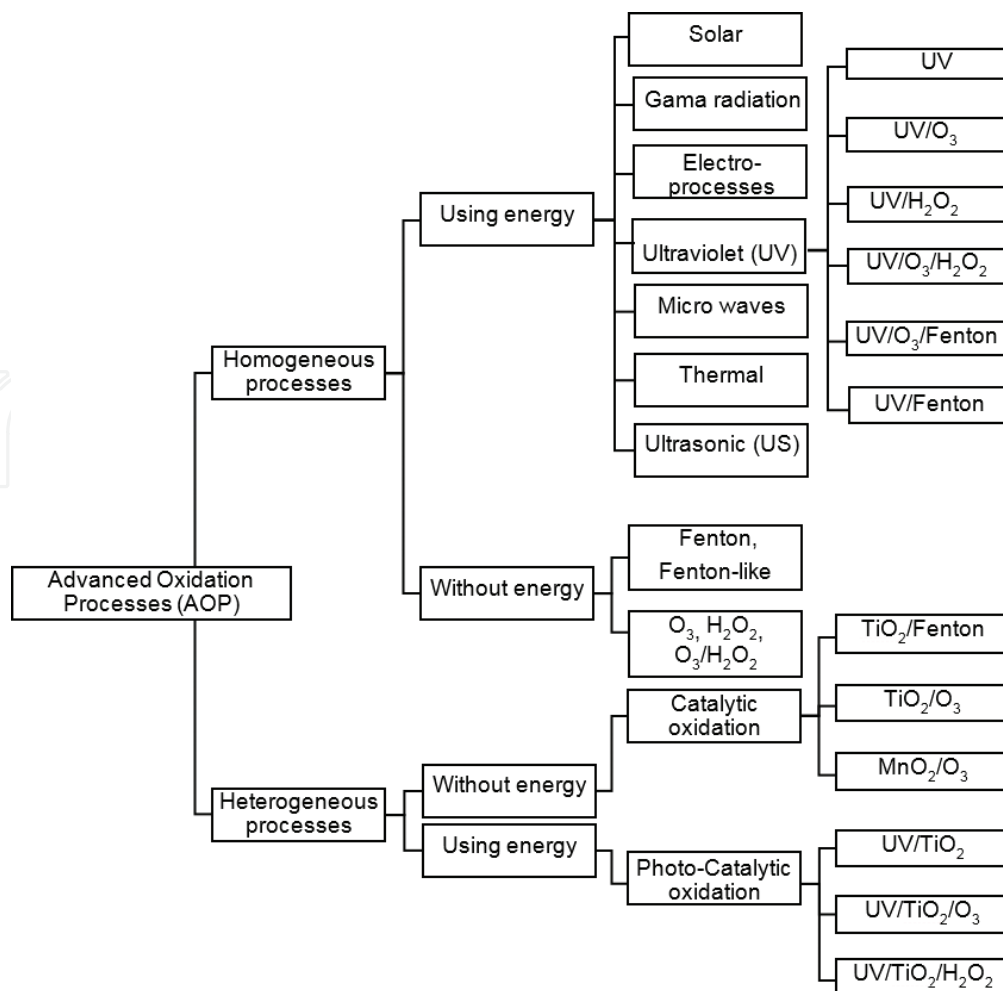
Figure 1.
Schematic classification of the advanced oxidation processes.

concepts is often applied in fragmentation models to describe how the distributions of different size entities evolve over the time of reaction.

The degradation of high molecular weight polydisperse materials results in the formation of a large number of polymeric chains with different chain lengths and various chemical compositions, i.e., the number of branches. Population balance based models have been developed to study the molecular weight decrease of polymers in a fragmentation process [5, 13, 20–22]. Population balance approach is generally employed to model the size distribution of the macromolecular compound during polymerization, depolymerization, and chain breakage. The population balance model is a balance equation of species of different sizes, and it is similar to the mass, energy, and momentum balances, to track the changes in the size distribution.

Few important studies have been done to understand the chemical kinetics that dominates the degradation of water-soluble polymers with UV radiation. Even though encouraging results on the degradation of polymers were obtained, data on the molecular weight distribution of the treated polymer need to be collected. Hence, it is worthwhile to investigate further the degradation process of synthetic polymer and the devolution of their molecular weight distributions. Other studies have theoretically analyzed the thermal degradation of synthetic polymers and provided a mathematical interpretation of the polymer chain scissions. The photochemical mechanism and kinetic modeling of the photo-oxidative degradation of water-soluble polymers have been investigated in several studies. Nevertheless, the proposed mechanisms may be complex and not well-established. The majority of mathematical approaches to polymer degradation consider only the polymer

molecular-weight distribution (MWD) or chain-length distribution. The treatment of the wastewater streams contaminated with PVA polymers is studied using different processes [7, 12, 13, 16]. The kinetics models proposed in these studies were validated using total organic carbon (TOC) data instead of polymer concentrations or polymer molecular weights, and a constant pH was assumed.

The photo-oxidative degradation of water-soluble polymers in laboratory scale photochemical reactors is the focus of this chapter. The photochemical kinetic model of the polymer degradation in UV/H_2O_2 process that describes the polymer chain scission is discussed in which the statistical moment approach is presented. The development of a photochemical kinetic model incorporates the population balance of all chemical species. Considering the probabilistic nature of the polymer fragments, the statistical moment approach is applied for modeling the population balance of live and dead polymer chains, which allows estimating the polymer average molecular weights as a function of radiation time. The model also considered the effect of process parameters on the decrease of polymer molecular weight, hydrogen peroxide residual, and the acidity of the treated solution.

2. UV/H_2O_2 system description

The critical design parameters in the UV/H_2O_2 process include the H_2O_2 dose, the UV lamp type and intensity, and the reactor contact time. Basic UV reactor design configurations used for the removal of polymers from wastewater depend mainly on the flow rate. The tower design is typically utilized for large-scale applications. In the tower configuration, multiple UV lamps are arranged horizontally within a single large reactor vessel with the contaminated water flowing perpendicularly past the UV lamps [23]. For small-scale systems, a single UV lamp per reactor vessel is arranged vertically. For example, a small-scale system may consist of three individual reactor vessels in series, each containing one UV lamp in a vertical position.

A typical laboratory-scale batch recirculation UV/H_2O_2 system consists of an annular photoreactor, a large volume reservoir tank, centrifugal pump, and heat exchanger. The circulation tank contains the polymer solution for treatment. The hydrogen peroxide is injected into the circulation tank. A centrifugal magnet pump is placed on the circulation line to maintain a steady flow of the aqueous polymer solution between the tank and photoreactor. A flow meter is used to measure the circulation rate. The cylindrical photoreactor is made of steel vessel of annual shape and is connected to the circulation tank. The reactor is equipped with an internal quartz glass in which a low-pressure mercury UV lamp is mounted at its centerline of the cylinder with stainless steel housing. The annular photoreactor should have a very small annular space to assure a uniform light distribution in the photoreactor. Most AOPs are modular processes. Therefore, more than one reactor can be employed in series mode to obtain higher retention times or in parallel mode to process larger volumes to achieve the desired effluent for a given flow rate.

3. Characterization of polymeric wastewater

Determination of the polymer molecular weight, TOC content, and residual hydrogen peroxide are crucial parameters to assess the performance of the photodegradation process. The treated samples are analyzed using gel permeation chromatography (GPC) to determine the molecular weights of the degraded polymer samples. The GPC theory depends on the principle of size exclusion; therefore, when a polymer solution is passed through a column of porous particles, large

molecules cannot enter the pores of the packing and hence, they elute first. However, smaller molecules that can penetrate or diffuse into the pores are retained for a while in the column and then elute at a later time. Thus, a sample is fractionated by molecular hydrodynamic volume, and the resulting profile describes the molecular weight distribution. A concentration detector (e.g., differential refractometer (RI) or UV detector) is placed downstream of the columns to measure the concentration of each fraction as a function of time. The actual method for determining the molecular weight averages and the MWD depends upon the attached detectors. GPC provides a convenient, quick, and relatively easy method which can be used on a routine basis for determining the various moments of molecular weight.

The extent of degradation reactions to CO_2 is monitored by measuring the total organic carbon content of the samples. TOC analyzer is based on the oxidation of organic compounds to carbon dioxide and water, with subsequent quantities of carbon dioxide. The TOC analyzer subtracts the inorganic carbon (CO and CO_2) and reports the total organic carbon, which is a close approximation of organic content. The amount of carbon dioxide generated upon oxidation of the organic carbon in the sample was determined by the non-dispersive infra-red (NDIR) detector, which is sensitive to low levels of TOC.

The reduction of hydrogen peroxide concentration during the degradation reaction is determined using spectrophotometer method using 9-dimethyl-1, 10-phenanthroline (DMP) method. The most common way of measuring hydrogen peroxide residual in wastewater is DMP-spectrophotometer method. 9-Dimethyl-1,10-phenanthroline (DMP) method is based on the chemical reduction of copper (II) by hydrogen peroxide in the presence of DMP, thus forming a bright yellow (copper (II) – DMP) complex that is directly determined by UV–vis spectrophotometer [24]. The DMP method appears to be simple, robust, and rather insensitive to interference. Intermediate compounds such as acetic and formic acids, formaldehyde, and acetaldehyde, which are formed by the decomposition of organic matter exposed to AOPs, do not interfere with the DMP method.

4. Polymer chain scission mechanism

The degradation of polymers by advanced oxidation processes is mainly due to free-radical-induced chain scission that led to successive oxidation reactions which result in lower molecular weight polymer fragments. The chain scission reaction is a chemical reaction between the macromolecular compounds (polymers) and end/mid-chain radicals. As the reaction progresses, the large polymer molecules eventually break down into live and dead polymer chains of lower molecular weights. A further molecular disintegration can ultimately lead to carbon dioxide and water as final products in case of complete mineralization.

In other words, the chain scission reaction can be defined as a bond scission that takes place in the backbone of the polymer chain. The chain scission reaction increases the number of polymer chains and reduces the polymer molecular weight [25]. Consequently, the chain scission results in an increase in the polydispersity of the polymer sample which represents the breadth of the distribution curve.

The concept of polymer degradation may be explained by chain-end scission or random chain scission mechanisms where chain breaking occurs at a random location along the chain. Therefore the molecular weight decreases continuously with the extent of reaction. Chain-end scission is considered as a special case of random chain scission where the chain scission reactions are occurring most likely at the polymer chain end that results in a release of a single monomer molecule. Random chain scission is the reverse of step-growth polymerization while chain-end scission

is the reverse of chain growth polymerization [26]. Aarthi et al. [14] studied the photodegradation of water-soluble polymers by combined ultrasonic and ultraviolet radiation and found that the degradation process is controlled by random and midpoint scission. On the other hand, Konaganti and Madras [27] investigated the photocatalytic degradation of polymethyl methacrylate, polybutyl acrylate, and their copolymers by random and chain-end scissions.

In the photodegradation of PVA polymer, the random chain scission mechanism initially dominates which experimentally proved by the rapid decrease in the polymer molecular weights. In random chain scission, all bonds may have an equal probability of being cleaved along the polymer chain. Apparently, the degradation process leads to a steep decrease in molecular weights. The chain cleavage occurs and effectively shortens the polymer chains [17]. It can be concluded that PVA degradation occurs mostly by random chain scission which explains the drastic decrease in the polymer concentration.

4.1 Polymer average molecular weights

Polymer molecules are made of repeat monomer units that chemically bonded into long chains. The chain length is often expressed in terms of the molecular weight of the polymer chain, related to the relative molecular weight of the monomer and the number of monomer units connected in the chain.

The molecular weight of a polymer is described by the average values of the molecular weights of the polymer chains. The molecular weight distribution (MWD) is the distribution of sizes in a polymer sample while the polydispersity index (PDI) represents the breadth of the distribution curve. Thus, the polydispersity index is used as a measure of the broadness of molecular weight distribution of a polymer sample. Most synthetic water-soluble polymers are polydisperse since they contain polymer chains of unequal lengths. The increase in the polydispersity index results in broader molecular weight distribution. The PDI is defined as the ratio of weight average molecular weight (M_w) to the number average molecular weights (M_n). The molecular weight of a polymer is not a single value since polymer molecules even those of the same type, have different sizes, so the method of averaging mainly determines the average molecular weight. The number average molecular weight is considered as the ordinary arithmetic average of the molecular weights of the polymer while the weight average molecular weight is determined by measuring the weight of each species in the sample, rather than the number of molecules of each size.

Enhanced photodegradation of polymer by UV radiation can lead to a wider distribution of molecular weights because the polymer chains are broken down into short-chain polymers such as oligomers, dimers, and monomers [28]. The irradiation promotes the decrease in the polymer molecular weights and the increase in the polydispersity of the molecular weight distribution of the degraded polymer as shown in **Figure 2**.

The shape of the molecular weight distribution changes as a function of the treatment time. The untreated PVA has a uniform narrow distribution with a polydispersity index (PDI) close to unity. During the degradation process, the distribution shifts to the left as the polymer molecular weight was considerably lowered. Song and Hyuan [29] confirmed the shifting of MWD and the generation of monomer by chain-end scission at the thermal degradation of polystyrene in a batch reactor. The broadness of the molecular weight distribution which is expressed by an increase in polydispersity is due to the fragmentation and chain-scission mechanism of the polymer degradation during the UV/H_2O_2 process.
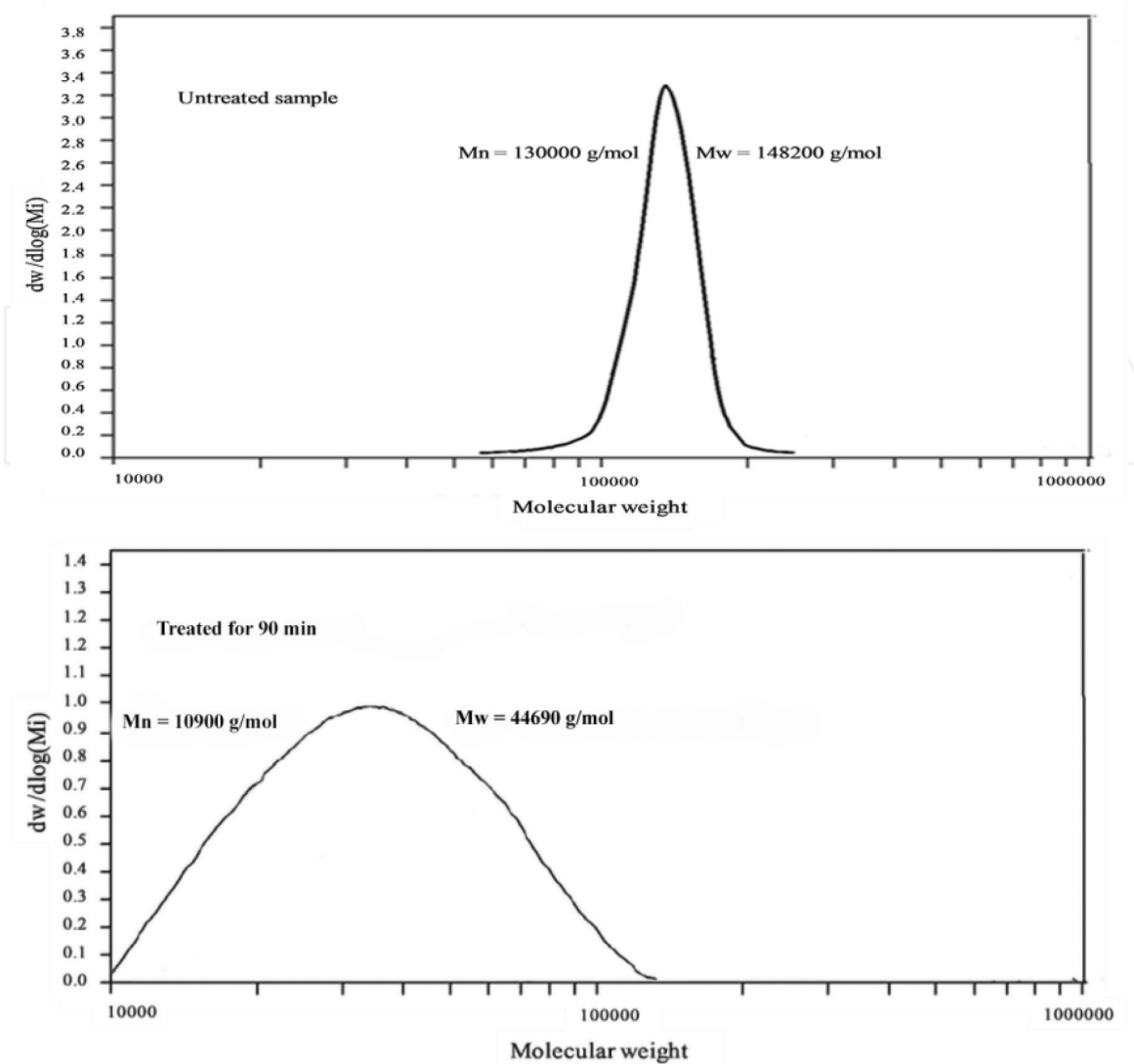
Figure 2.
Effect of radiation time on MWD of the degraded PVA polymer by UV/H₂O₂ process (data from [17]).

5. Photodegradation kinetic model development

The principle in the AOP process is the formation of hydroxyl radicals which react immediately with organic contaminants in the wastewater streams. The hydroxyl radicals are highly reactive because of the presence of unpaired electrons. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and the intermediate products until thermodynamically stable oxidation products are formed at complete mineralization of the pollutant.

Usually, the mineralization starts directly with pollutant degradation, however, for PVA polymers it occurs at a later stage of the reaction. In this case, it is desired to model a specific polymer degradation as the TOC is not the right parameter to choose for the development of an adequate model for polymer disintegration in a photo-oxidation process. It is plausible to develop a model that takes into account the polymer molecular weights.

Under the effect of UV light of a specific wavelength and using an oxidant such as hydrogen peroxide, water-soluble polymer chains can break down into smaller chains. Under the effect of radiation energy, chemical bonds of polymer chains are destabilized and weakened. The chain scission reaction is, therefore, initiated and it is defined as a bond scission that takes place in the backbone of the polymer chain.

As the reaction progresses, the large polymer molecules P_r eventually break down into live and dead polymer chains of lower molecular weights, and consequently, new intermediate polymeric components are formed. A further molecular disintegration can ultimately lead to carbon dioxide and water as final products in case of complete mineralization according to the following reaction:

$$P_r + H_2O_2 \xrightarrow{hv} intermediates \rightarrow CO_2 + H_2O \tag{1}$$
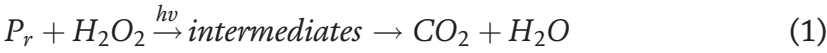
Under the UV irradiation, the photolysis of hydrogen peroxide generates hydroxyl radicals as follows:

$$H_2O_2 \xrightarrow{hv} 2HO^{\bullet} \tag{2}$$

The highly reactive hydroxyl radical can undergo a series of promoted dissociation reactions. Several authors [30, 33, 40, 41] have proposed a detailed chemical kinetic mechanism of hydrogen peroxide decomposition. Photolysis reactions of hydrogen peroxide (Reactions (3)–(15)) and the rate constants are provided in **Table 1**.

No.	Reaction mechanism	Rate constant		Reference
(3)	$HO^{\bullet} + H_2O_2 \xrightarrow{k_1} HO_2^{\bullet} + H_2O$	2.7×10^7	L/mol s	[30]
(4)	$H_2O_2 + HO_2^{\bullet} \xrightarrow{k_2} HO^{\bullet} + H_2O + O_2$	3.0	L/mol s	[31]
(5)	$H_2O_2 + O_2^{\bullet-} \xrightarrow{k_3} HO^{\bullet} + OH^- + O_2$	13×10^{-2}	L/mol s	[32]
(6)	$HO^{\bullet} + HO_2^- \xrightarrow{k_4} HO_2^{\bullet} + OH^-$	7.5×10^9	L/mol s	[33]
(7)	$O_2^{\bullet-} + H^+ \xrightarrow{k_5} HO_2^{\bullet}$	1.0×10^{10}	L/mol s	[34]
(8)	$HO^{\bullet} + HO^{\bullet} \xrightarrow{k_6} H_2O_2$	5.5×10^9	L/mol s	[30]
(9)	$HO_2^{\bullet} + HO^{\bullet} \xrightarrow{k_7} H_2O + O_2$	6.6×10^9	L/mol s	[35]
(10)	$HO_2^{\bullet} + HO_2^{\bullet} \xrightarrow{k_8} H_2O_2 + O_2$	8.3×10^5	L/mol s	[34]
(11)	$HO_2^{\bullet} \xrightarrow{k_9} O_2^{\bullet-} + H^+$	1.6×10^5	1/s	[34]
(12)	$HO_2^{\bullet} + O_2^{\bullet-} \xrightarrow{k_{10}} O_2 + HO_2^-$	9.7×10^7	L/mol s	[34]
(13)	$HO^{\bullet} + O_2^{\bullet-} \xrightarrow{k_{11}} O_2 + OH^-$	7.0×10^9	L/mol s	[36]
(14)	$H_2O_2 \xrightarrow{k_{12}} HO_2^- + H^+$	4.5×10^{-12}	1/s	[37]
(15)	$HO_2^- + H^+ \xrightarrow{k_{13}} H_2O_2$	2.0×10^{10}	L/mol s	[37]
(16)	$P_r + HO^{\bullet} \xrightarrow{k_{p_1}} P_r^{\bullet} + H_2O$	8.06×10^6	L/mol s	[38]
(17)	$P_r + HO_2^{\bullet} \xrightarrow{k_{p_2}} P_r^{\bullet} + H_2O_2$	4.69×10^{-1}	L/mol s	[38]
(18)	$P_r^{\bullet} \xrightarrow{k_p} P_{r-1}^{\bullet} + P_1$	3.66×10^2	1/s	[38]
(19)	$P_{r-s}^{\bullet} + P_s^{\bullet} \xrightarrow{k_{tc}} P_r$	4.44×10^2	L/mol s	[38]
(20)	$P_1 + HO_2^{\bullet} + O_2^{\bullet-} \xrightarrow{k_{d_1}} 2HCOOH + HO^-$	1.89×10^6	L/mol s	[38]
(21)	$P_1 + HO_2^{\bullet} \xrightarrow{k_{d_2}} CH_3COOH + HO^{\bullet}$	1.35×10^2	L/mol s	[38]
(22)	$HCOOH \overset{K_{a1}}{\leftrightarrows} HCOO^- + H^+$	1.77×10^{-4}		[39]

No.	Reaction mechanism	Rate constant		Reference
(23)	$CH_3COOH \overset{K_{a2}}{\leftrightarrow} CH_3COO^- + H^+$	1.76×10^{-5}		[39]
(24)	$CH_3COOH + 2HO_2^\bullet \overset{k_{14}}{\rightarrow} 2HCOOH + H_2O_2$	1.60×10^7	L/mol s	[39]
(25)	$HO^\bullet + CH_3COO^- \overset{k_{15}}{\rightarrow} {}^\bullet CH_2COO^- + H_2O$	3.20×10^9	L/mol s	[39]
(26)	$HCOOH + 2HO^\bullet \overset{k_{17}}{\rightarrow} CO_2 + 2H_2O$	1.30×10^8	L/mol s	[39]

Table 1.
Photolysis reactions of hydrogen peroxide and the rate constants.

The mechanism of degradation polymer solution using UV irradiation using hydrogen peroxide as an oxidant results in the generation of polymeric hydroxyl radicals, which undergo degradation reactions. The live polymer radicals $P_r^\bullet$ are the precursor of subsequent polymer chain breakage (Reactions (16)–(19)). The polymer radical may combine with another polymer radical to terminate the reaction (Reactions (21)). The scission products are radical and non-radical fragments (monomer or polymer with lower molecular weight) as follows:

$$P_r^\bullet \overset{k_p}{\rightarrow} P_s + P_{r-s}^\bullet \tag{27}$$

where $s = 1$ f0r chain-end scission and $2 \leq s \leq r$.

Reactions (20)–(26) represent the complete mineralization of polymer compounds. It has been experimentally proven that the acidity of the treated solution varies during the degradation reaction by the UV/H$_2$O$_2$ process [17, 39]. The pH decreases at the beginning of the reaction, and the solution becomes more acidic due to the formation of intermediate oxidation products such as carboxylic acids [42]. A regain in the pH of the solution is expected in case of complete mineralization as a result of the degradation of acidic compounds that are oxidized to carbon dioxide that escapes the system and water at the end of the reaction. The experimental findings indicate that there is evidence of the formation of acetic and formic acids associated with the degradation of the monomer (vinyl alcohol) produced at the complete degradation of PVA polymer. Therefore, the photochemical kinetic mechanism incorporates the acidity aspect of the solution as the polymer degradation progresses. The complete mineralization of polymer compounds and the production of by-products with no hazard to the environment (Reactions (20)–(26)) are considered as remarkable advantages of the advanced oxidation processes. A photochemical kinetic model was developed based on the mechanism presented in Reactions (1) to (27).

The polymer degradation reactions are assumed to be irreversible. Binary fragmentation is also considered to explain kinetics fragmentation in which a polymer of chain length r splits into two polymer units. The reaction rate constants are assumed independent of polymer chain length. The degradation reaction is carried out at a constant temperature with a good mixing condition. For a batch reactor with recirculation, negligible degradation of the polymer per pass and good mixing condition are assumed. Direct photolysis of the polymer without the presence of hydrogen peroxide is neglected.

The photochemical kinetic model describing the PVA polymer degradation by photo-oxidation comprises a radiation energy balance coupled with a molar balance of the chemical species participating in the degradation reactions of the polymer. The quantum yield of PVA is usually negligible since there is no measurable change in PVA molecular weight under UV radiation alone [17]. The molar absorptivity of PVA polymer is determined using spectrophotometer by measuring the absorbance of different concentrations of PVA aqueous solutions at a wavelength of 254 nm.

For the kinetics, the general molar balance equation (Eq. 28) [43] must be applied to the recirculating batch photoreactor.

$$\frac{\partial c_i}{\partial t} + \nabla.N_i = R_i \qquad (28)$$

Assuming that the system works under the well-stirred conditions ($\nabla.N_i = 0$), the ratio of the photoreactor volume to the total volume $\ll 1$, and high recirculating flow rate to ensure small conversion per pass, the rate of the change of the concentration in the tank could be written as follows [44]

$$\frac{dC_i}{dt} = \frac{V_{ph}}{V_T} \sum_{j=1}^{m} R_{ij}, \qquad C_i(0) = C_{i0} \qquad (29)$$

In which $C_i(t)$ is the ith component concentration, V_{ph} is the volume of the photoreactor, V_T is the volume of the whole system, $C_i(0)$ is the initial molar concentration of species i, and R_{ij} is the chemical reaction rate of component i in reaction j (j = 1,2,.,m).

According to the basic photochemical mechanism given in **Table 1**, the mole balance of small molecule species gives the following reaction rate equations:

$$\frac{1}{\alpha}\frac{d[H_2O_2]}{dt} = -R_{UV, H_2O_2} - k_1[HO^\bullet][H_2O_2] - k_2[HO_2^\bullet][H_2O_2] - k_3[O_2^{\bullet-}][H_2O_2]$$
$$+ k_6[HO^\bullet]^2 + k_8[HO_2^\bullet]^2 + k_{p2}[HO_2^\bullet][P_r] - k_{12}[H_2O_2] + k_{13}[HO_2^-][H^+]$$
$$+ k_{14}[CH_3COOH][HO_2^\bullet] - k_{15}[HCOO^-][H_2O_2]$$
$$(30)$$

$$\frac{1}{\alpha}\frac{d[HO^\bullet]}{dt} = 2R_{UV, H_2O_2} - k_1[HO^\bullet][H_2O_2] + k_2[HO_2^\bullet][H_2O_2] + k_3[O_2^{\bullet-}][H_2O_2]$$
$$- k_4[HO_2^-][HO^\bullet] - 2k_6[HO^\bullet]^2 - k_7[HO^\bullet][HO_2^\bullet] - k_{p1}[HO^\bullet][P_r]$$
$$- k_{11}[HO^\bullet][O_2^{\bullet-}] - k_{d1}[HO^\bullet][P_1] + k_{d2}[HO_2^\bullet][P_1] - 2k_{16}[HO^\bullet]^2[HCOOH]$$
$$(31)$$

$$\frac{1}{\alpha}\frac{d[H^+]}{dt} = -k_5[O_2^{\bullet-}][H^+] + k_9[HO_2^\bullet] + k_{12}[H_2O_2] - k_{13}[H^+][HO_2^-] + k_{a1}[HCOOH]/$$
$$[HCOO^-] + k_{a2}[CH_3COOH]/[CH_3COO^-]$$
$$(32)$$

$$\frac{1}{\alpha}\frac{d[HCOOH]}{dt} = k_{d1}[HO^\bullet][P_1] + k_{a1}^{-1}[H^+][HCOO^-] + k_{14}[HO_2^\bullet]^2[CH_3COOH]$$
$$- k_{16}[HO^\bullet]^2[HCOOH]$$
$$(33)$$

$$\frac{1}{\alpha}\frac{d[CH_3COOH]}{dt} = k_{d2}[HO_2^\bullet][P_1] + k_{a2}^{-1}[H^+][CH_3COO^-] - k_{14}[HO^\bullet]^2[CH_3COOH]$$
$$(34)$$

$$\frac{1}{\alpha}\frac{d[HO_2^\bullet]}{dt} = k_1[HO^\bullet][H_2O_2] - k_2[HO_2^\bullet][H_2O_2] + k_4[HO_2^-][HO^\bullet] + k_5[O_2^{\bullet-}][H^+]$$
$$- k_7[HO^\bullet][HO_2^\bullet] - 2k_8[HO_2^\bullet]^2 - k_9[HO_2^\bullet] - k_{p2}[HO_2^\bullet][P_r]$$
$$- k_{10}[HO_2^\bullet][O_2^{\bullet-}] + k_{d1}[HO^\bullet][P_1] - k_{d2}[HO_2^\bullet][P_1] - 2k_{14}[HO_2^\bullet]^2[CH_3COOH]$$
$$(35)$$

$$\frac{1}{\alpha}\frac{d[HO_2^-]}{dt} = -k_4[HO_2^-][HO^\bullet] + k_{10}[HO_2^\bullet][O_2^{\bullet-}] + k_{12}[H_2O_2] - k_{13}[HO_2^-][H^+]$$

(36)

$$\frac{1}{\alpha}\frac{d[O_2^{\bullet-}]}{dt} = -k_3[O_2^{\bullet-}][H_2O_2] - k_5[O_2^{\bullet-}][H^+] + k_9[HO_2^\bullet] - k_{10}[HO_2^\bullet][O_2^{\bullet-}]$$
$$- k_{11}[HO^\bullet][O_2^{\bullet-}]$$

(37)

$$\frac{1}{\alpha}\frac{d[P_1]}{dt} = k_p p_r^\bullet - k_{d1}[HO_2^\bullet][O_2^{\bullet-}][P_1] - k_{d2}[HO_2^\bullet][P_1]$$

(38)

$$R_{UV,i} = -\emptyset_i f_i I_o \left(-\exp\left(-2.303\,b\sum_{i=1}^{N}\varepsilon_i.C_i \right) \right)$$

(39)

where α is defined as the ratio of photoreactor volume V_{ph} to the total volume of the system V_T, $\emptyset_i$ is the number of moles of the pollutant transformed per number of photons of wavelength λ absorbed by the pollutant, b is the path length of the ray through the medium, ε is the molar absorptivity, f_i is the fraction of the UV irradiation absorbed by the ith chemical species, I_o is the incident light intensity emitted at the source, and the C_i is the ith species concentration.

The molar balance of the macromolecules P_r and $P_r^\bullet$ in Reactions (16) to (21) requires special modeling approach as the PVA polymer is randomly broken down, polymer chains species of different sizes are subsequently generated, and they are expected to degrade further. The concept of the population species is considered to express the variations of the photochemical degradation of PVA. The random degradation of polymer chains of length r can be described using breakage population balance of all polymer species.

Generally, the moment operation is introduced as an easier method to transform the integro-differential equations in the continuous kinetics model or the sum in the discrete model to ordinary differential equations. McCoy and Madras [45] and Stickle and Griggs [46] provided simple mathematical expressions for the discrete model. The macromolecular reactions show that the polymer consists of degrading active polymer radicals $P_r^\bullet$ and dead polymer P_r. Polymer degradation is described by a discrete approach so that a mass balance provides a difference-differential equations. The net accumulation rate of dead polymer chains of chain length r is given as follows [38]:

$$\frac{1}{\alpha}\frac{d[p_r]}{dt} = -R_{UV,PVA} - k_{p_1}[HO^\bullet][p_r] - k_{p_2}\left[HO_2^\bullet[p_r] + k_p\sum_{s=1}^{r}\Omega(r,s)p_s^\bullet + k_{tc}\sum_{s=1}^{r}p_r^\bullet p_{r-s}^\bullet \right]$$

(40)

Similarly, the net accumulation rate of live polymer radicals of chain length r is expressed as:

$$\frac{1}{\alpha}\frac{d[p_r^\bullet]}{dt} = R_{UV,PVA} + k_{p_1}[HO^\bullet][p_r] + k_{p_2}[HO_2^\bullet][p_r] - k_p[p_r^\bullet] + k_p\sum_{s=1}^{r}\Omega(r,s)p_s^\bullet$$
$$- 2k_{tc}\sum_{s=1}^{r}p_s^\bullet p_{r-s}^\bullet$$

(41)

Using statistical mechanics, the concept of moments was applied to determine the molecular weight distribution of a polymer population. This reaction requires the production of a specified scission product from any of a range of macromolecules, so a stoichiometric kernel $\Omega(r,s)$ is employed for a polymer chain of length r to represent

the probability of getting shorter polymer chain lengths r-s and s [47]. In general, polymer degradation occurs most likely by random chain scission. Therefore, it is postulated that there is a low probability of the occurrence of chain-end scission reactions. For random chain scission, the distribution of shorter polymer chains is given as follows [45, 46]:

$$\Omega(r,s) = 1/r \tag{42}$$

5.1 Polymer population balance

Polymer degradation is a fragmentation process in which population balance concepts is often applied in fragmentation models to describe how the distributions of different size entities evolve over the time of reaction. The degradation of high molecular weight polydisperse materials results in the formation of a large number of polymeric chains with different chain lengths and various chemical compositions. Population balance approach is generally employed to model the size distribution of the macromolecular compound during polymerization, polymer degradation, depolymerization, and chain breakage.

In 1971, Randolph and Larson [48] proposed a solution for the population balance equation (PBE) in a well-mixed batch system. They used the concept of moment transform to convert the population balance equations into ordinary differential equations. Population balance based models have been developed to study the molecular weight decrease of polymers in a fragmentation process by advanced oxidation processes [18, 20, 22, 49]. Microwave-assisted oxidative degradation as an emerging advanced oxidation technology was used for poly(alkyl methacrylate) degradation. Random chain scission and Continuous distribution kinetics were employed to determine the degradation rate of the polymer [50]. Photocatalytic degradation of polyacrylamide co-acrylic acid by random chain scission has been investigated by Vinu and Madras [51]. The rate coefficients were determined as a linear function of the composition of co-monomer. Madras and McCoy [52] studied the kinetics of oxidative degradation of polystyrene by di-tert-butyl peroxide provided the ratio of the rate parameters for both oxidizer and polymer decomposition by moment analysis assuming random chain scission mechanism. Population balance and moment equations are solved for rate parameters [21, 53]. The model proposed by McCoy and Wang [21] is sufficiently applicable to a variety of degradation processes. Moment equations can be applied in batch and continuous stirred tank reactor (CSTR) reactors for binary or ternary fragmentation.

The population balance model is a balance equation of species of different sizes, and it is similar to the mass, energy, and momentum balances, to track the changes in the size distribution. The benefit of the population models is that they provide a straightforward technique to derive expressions for the moments of the polymer distributions during the degradation reaction. Hulburt and Katz [54] applied the concept of moments to determine the molecular weight distribution of a polymer population for a dead and live polymer moments as follow:

$$\mu_n = \sum_{r=1}^{\infty} r^n p_r \tag{43}$$

$$\lambda_n = \sum_{r=1}^{\infty} r^n p_r^{\bullet} \tag{44}$$

where p_r and $p_r^{\bullet}$ are the polymer and the polymer radical concentrations with chain length r, μ_n and λ_n are the nth moment of the quantities p_r and $p_r^{\bullet}$ and n having

values of 0, 1, or 2 stands for zeroth, first, and second moments, respectively. The application of the moment method allows converting the discrete differential population balance equations into ordinary differential ones. The moments of dead polymer P_r and live polymer radical $P_r^\bullet$ are used to determine the average molecular weights of the polymer. Applying the statistical moment concept to Eqs. (43, 44) gives the following model of dead and live polymer moments for n = 0, 1, and 2, respectively:

$$\frac{1}{\alpha}\frac{d[\mu_0]}{dt} = -R_{UV,PVA} - k_{p1}[HO^\bullet]\mu_0 - k_{p2}[HO_2^\bullet]\mu_0 + k_{tc}\lambda_0^2 + k_p\lambda_0 \tag{45}$$

$$\frac{1}{\alpha}\frac{d[\mu_1]}{dt} = -R_{UV,PVA} - k_{p1}[HO^\bullet]\mu_1 - k_{p2}[HO_2^\bullet]\mu_1 + 1/2k_p\lambda_1 + k_{tc}\lambda_1\lambda_1 \tag{46}$$

$$\frac{1}{\alpha}\frac{d[\mu_2]}{dt} = -R_{UV,PVA} - k_{p1}[HO^\bullet]\mu_2 - k_{p2}[HO_2^\bullet]\mu_2 + 1/3k_p\lambda_2 + k_{tc}\lambda_2\lambda_2 \tag{47}$$

$$\frac{1}{\alpha}\frac{d[\lambda_0]}{dt} = R_{UV,PVA} + k_{p1}[HO^\bullet]\mu_0 + k_{p2}[HO_2^\bullet]\mu_0 - 2k_{tc}\lambda_0^2 \tag{48}$$

$$\frac{1}{\alpha}\frac{d[\lambda_1]}{dt} = R_{UV,PVA} + k_{p1}[HO^\bullet]\mu_1 + k_{p2}[HO_2^\bullet]\mu_1 - 1/2k_p\lambda_1 - 2k_{tc}\lambda_0\lambda_1 \tag{49}$$

$$\frac{1}{\alpha}\frac{d[\lambda_2]}{dt} = R_{UV,PVA} + k_{p1}[HO^\bullet]\mu_2 + k_{p2}[HO_2^\bullet]\mu_2 - 2/3k_p\lambda_2 - 2k_{tc}\lambda_0\lambda_2 \tag{50}$$

Using statistical mechanics, the concept of moments is applied to determine the molecular weight distribution of a polymer population. The number average molecular weight M_n and the weight average molecular weight M_w are calculated according to:

$$M_n = NACL \cdot M_o \tag{51}$$

$$M_w = WACL \cdot M_o \tag{52}$$

where M_o is the molecular weight of the monomer unit. The number average chain length (NACL) and the weight average chain length (WACL) are given by:

$$NACL = \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} \tag{53}$$

$$WACL = \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1} \tag{54}$$

A parameter estimation scheme is typically performed for the polymer photodegradation model equations to estimate the rate constants that are not available in the open literature. The objective function is the summation of squared errors between the model predictions and experimental data for selected process variables. The parameter estimation scheme is formulated to determine the estimates of the rate constants by minimizing the objective function which is subjected to the kinetic model equations.

The validity of the kinetic model is examined by direct comparison of model predictions with experimental data of the process parameters such as polymer molecular weights, polymer concentration, hydrogen peroxide residual, and pH of the solution. The goodness-of-fit between experimental y_{exp} and predicted y_m data for each variable are then determined by calculating the root mean square error (RMSE) for n' data points. The good agreement between the model predictions and the experimental results confirms the adequacy of the developed photochemical kinetic model.

5.2 Model predictions of the process variables

The polymer average molecular weights decrease with irradiation time due to the chain cleavage that effectively shortens the polymer chains which supports the success of the degradation process. The profile of the polymer molecular weight with time during the degradation process can indicate the type and mechanism of the chain scission. For instance, the steep reduction in the molecular weights of the PVA polymer at the beginning of the degradation reaction under UV irradiation is caused by the random chain scission mechanism that dominates initially in the photo-oxidative degradation of polyvinyl alcohol. At the end of the degradation reaction, the chain scission reactions occur most likely at the polymer chain end releasing a single monomer molecule when the polymer has considerably degraded. Whereas, the PVA degradation occurs mostly by random chain scission at the beginning of the reaction which explains the drastic reduction in the polymer concentration as clearly shown in **Figure 3** for initial PVA concentration of 50 mg/L. For water-soluble polymers, it is common to use a different approach, based on discrete population balance equations, to model polymer degradation involving
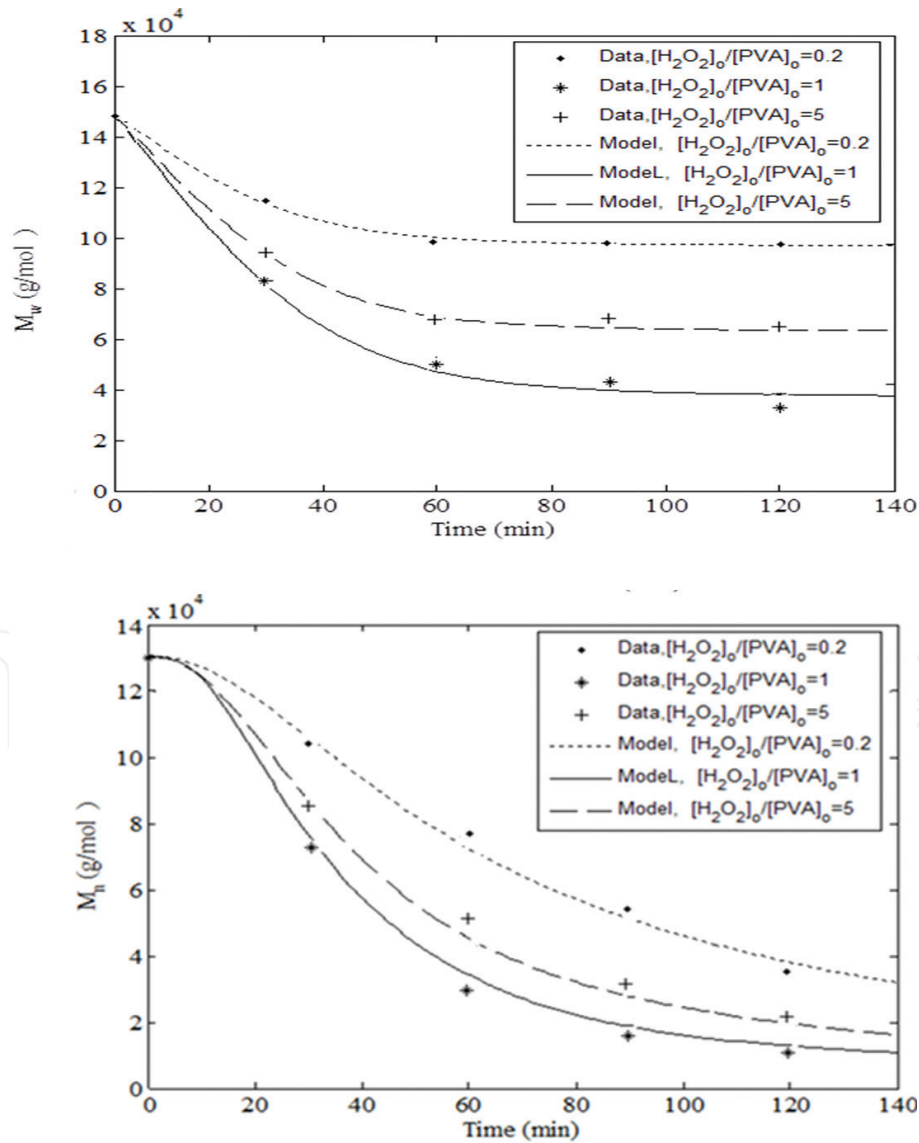

Figure 3.
Variation of the weight average M_w and number average M_n molecular weights of PVA at different [H_2O_2]/[PVA] mass ratios in a batch UV/H_2O_2 photoreactor (data from [38]).

random scission and end-chain scission in order to predict the evolution of a population of molecules undergoing different scission mechanisms.

It is worth mentioning that hydrogen peroxide has a significant effect on the performance of the degradation process. The polymer molecular weight averages decrease with an increase of hydrogen peroxide concentration up to a certain limit. Therefore, a higher level of hydrogen peroxide has an adverse effect on the molecular weight reduction which can be interpreted by the scavenging effect of H_2O_2 over hydroxyl radicals which hinders the radical degradation since the amount of H_2O_2 added to the system is proportionally high [55]. The excess amount of hydrogen peroxide acts as a scavenger of hydroxyl radicals (Reaction (3) in **Table 1**) thus forming hydroperoxyl radicals. As shown earlier in the photochemical kinetics mechanism, the hydroperoxyl radical reacts with the PVA polymer (Reaction (17) in **Table 1**) [38]. Therefore, the probability of hydroxyl radicals attacking the polymer can be significantly reduced. The hydroperoxyl radicals are less reactive than hydroxyl radicals that subsequently suppress the degradation reaction. The photochemical model takes into account the scavenging effect of hydrogen peroxide by incorporating reaction rate equations of all radicals in order to enhance the reliability of the model.

The PVA polymers are effectively degraded in a UV/H_2O_2 photochemical reactor. In fact, the rates of polymer degradation and TOC removal did not match with each other. In fact, the TOC accounts for the carbon content of all chemical species, including PVA polymers. The difference between TOC and PVA removal efficiencies as shown in **Figure 4** is due to the presence of intermediate oxidation products and the non-degraded polymer residuals towards the end of reaction which can slightly increase the TOC content of the treated solution.

Figure 4 clearly illustrates the thresholds of the mass ratio of H_2O_2 and the polymer at which both the TOC removal and PVA degradation efficiencies at maximum values. In the advanced oxidation process, the amount of oxidant has to be experimentally determined according to the specified operating conditions for each pollutant so that the photochemical reaction performs at its best. Using excess hydrogen peroxide in the treatment process not only impedes the removal rate of the organic pollutants but also increase the hydrogen peroxide residual in the treated solution which can negatively affect the operating cost of the photoreactor system.
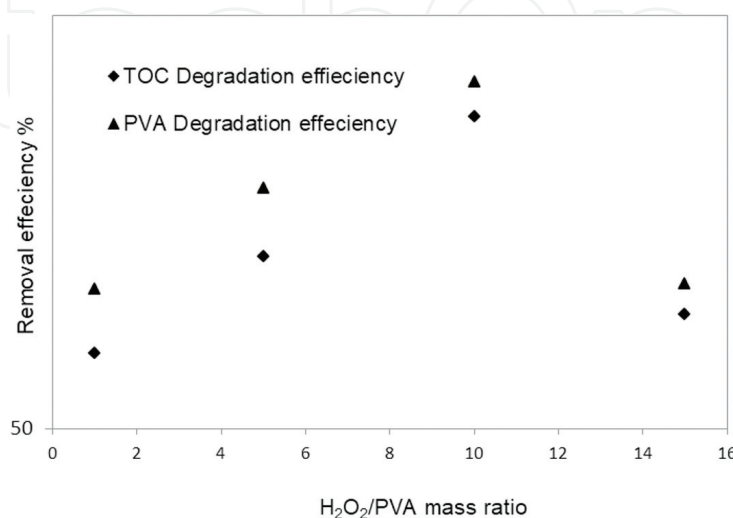

Figure 4.
PVA degradation and TOC removal efficiency for PVA (500 mg/L) degradation in UV/ H_2O_2 photoreactor [data from [17]].

6. Conclusions

The performance of the UV/H$_2$O$_2$ advanced oxidation process was evaluated for the degradation of polymeric wastewater in the batch photoreactor. The UV/H$_2$O$_2$ process can significantly modify the structure of the PVA polymer and be a potential practice for the degradation of water-soluble polymers in wastewater. Under the effect of UV light, hydrogen peroxide is readily decomposed into hydroxyl radicals of high reactivity which become oxidizing agents and can immediately attack the chains resulting in polymer disintegration.

A theoretical description of the UV/H$_2$O$_2$ process incorporates a population balance of polymer system and a molar balance of all chemical species to adequately represent the degradation of PVA polymer in a UV/H$_2$O$_2$ batch recirculating process. Modeling the photochemical degradation of the polymers represents a new approach to investigate the variations in polymer molecular weights. Considering the importance of oxidant in the advanced oxidation process performance, the dosage of hydrogen peroxide has to be experimentally determined for each polymer in order to achieve a better photochemical degradation of water-soluble polymers in wastewater. Incorporating the scavenging effect of hydrogen peroxide and the variation of the solution acidity is essential for the predictive quality and reliability of the photochemical model for degradation of polymers by UV/H$_2$O$_2$ process.

The photochemical mechanism and the photochemical kinetic model provide a framework for understanding the real characterization of the UV/H$_2$O$_2$ process and contribute to enhancing the design of industrial UV/H$_2$O$_2$ processes for the treatment of wastewaters contaminated with water-soluble polymers.

Acknowledgements

Nomenclature

C	molar concentration, mol/L
i	number of species
kp	rate constant of propagation, 1/s
kp$_1$	rate constant of propagation, L/mol s
kp$_2$	rate constant of propagation, L/mol s
kt$_c$	rate constant of termination by coupling, L/mol s
M$_n$	number average molecular weight of the polymer, g/mol
M$_w$	weight average molecular weight of the polymer, g/mol
P$_1$	monomer
P_r	dead polymer of chain length r
P_{r-s}	dead polymer of chain length r-s, where $1 \leq s < r$
$P_r^\bullet$	live radical of chain length r
$P_{r-s}^\bullet$	live radical of chain length r-s, where $1 \leq s < r$
R	rate of reaction, mol/L s
AOP	advanced oxidation process
DMP	9-dimethyl-1,10-phenanthroline

GPC	gel permeation chromatography
MWD	molecular weight distribution
NDIR	non-dispersive infra-red
PBE	population balance equation
PDI	polydispersity index
PVA	polyvinyl alcohol
TOC	total organic carbon
US	ultrasound
UV	ultraviolet

Author details

Dina Hamad[1]*, Mehrab Mehrvar[2] and Ramdhane Dhib[2]

1 Chemical Engineering and Pilot Plant Department, National Research Center, Cairo, Egypt

2 Department of Chemical Engineering, Ryerson University, Toronto, Ontario, Canada

*Address all correspondence to: dhamad@ryerson.ca

IntechOpen

References

[1] Vitale P, Ramos P, Colasurdo V, Fernandez M, Eyler Y. Treatment of real wastewater from the graphic industry using advanced oxidation technologies: Degradation models and feasibility analysis. Journal of Cleaner Production. 2018. DOI: 10.1016/j.jclepro. 2018.09.105

[2] Shonberger H, Baumann A, Keller W. Study of microbial degradation of polyvinyl alcohol (PVA) in wastewater treatment plants. American Dyestuff Reporter. 1997;**86**:9-18

[3] Solaro A, Corti A, Chillini E. Biodegradation of polyvinyl alcohol with different molecular weights and degree of hydrolysis. Polymers for Advanced Technologies. 2000;**11**:873-878

[4] Hamad D, Dhib R, Mehrvar M. Photochemical degradation of aqueous polyvinyl alcohol in a continuous UV/ H_2O_2 process: Experimental and statistical analysis. Journal of Polymers and the Environment. 2016;**24**:72-83

[5] Ghafoori S, Mehrvar M, Chan P. Free-radical-induced degradation of aqueous polyethylene oxide by UV/ H_2O_2: Experimental design, reaction mechanisms, and kinetic modeling. Industrial & Engineering Chemistry Research. 2012;**51**:14980-14993

[6] Sun W, Tian J, Chen L, He S, Wang J. Improvement of biodegradability of PVA-containing wastewater by ionizing radiation pre-treatment. Environmental Science and Pollution Research. 2012;**19**: 3178-3184

[7] Zhang Y, Rong W, Fu Y, Ma X. Photocatalytic degradation of polyvinyl alcohol on Pt/TiO_2 with Fenton reagent. Journal of Polymers and the Environment. 2011;**19**:966-970

[8] Ciner F, Akal Solmaz SK, Yonar T, Ustun GE. Treatability studies on wastewater from textile dyeing factories in Bursa, Turkey. International Journal of Environment and Pollution. 2003;**19**: 403-407

[9] Zhang SJ, Yu HQ. Radiation-induced degradation of polyvinyl alcohol in aqueous solutions. Water Research. 2004;**38**:309-316

[10] Rosario-Ortiz FL, Wert EC, Snyder SA. Evaluation of UV/H2O2 treatment for the oxidation of pharmaceuticals in wastewater. Water Research. 2010;**44**: 1440-1448

[11] Rozas O, Vidal C, Baeza C, Jardim WF, Rossner A. Organic micropollutants (OMPs) in natural waters: Oxidation by UV/H_2O_2 treatment and toxicity assessment. Water Research. 2016;**98**(554):109-118

[12] Chen Y, Sun Z, Yang Y, Ke Q. Heterogeneous photocatalytic oxidation of polyvinyl alcohol in water. Photochemistry and Photobiology. 2011; **142**(1):85-89

[13] Kaczmarek H, Kaminska A, Swiatek M, Rabek JF. Electrochemical oxidation of polyvinyl alcohol using a RuO_2/Ti anode. Angewandte Makromolekulare Chemie. 1998;**4622**:109-121

[14] Aarthi T, Shaama M, Madras G. Degradation of water-soluble polymers under combined ultrasonic and ultraviolet radiation. Industrial and Engineering Chemistry Research. 2007; **46**:6204-6210

[15] Kim S, Kim T, Park C, Shin E. Photo-oxidative degradation of some water-soluble polymers in the presence of accelerating agents. Desalination. 2003;**155**(1):49-57

[16] Ghafoori S, Mehrvar M, Chan P. Photoreactor scale-up for degradation of polyvinyl alcohol in aqueous solution using UV/H2O2 process. Chemical Engineering Journal. 2014;**245**:133-142

[17] Hamad D, Mehrvar M, Dhib R. Experimental study of polyvinyl alcohol degradation in aqueous solution by UV/ H_2O_2 process. Polymer Degradation and Stability. 2014;**103**:75-82

[18] McCoy B, Madras G. Degradation kinetics of polymers in solution: Dynamics of molecular weight distributions. AIChE Journal. 1997;**43**(3):802-810

[19] Tayal A, Khan S. Degradation of a water-soluble polymer: Molecular weight changes and chain scission characteristics. Macromolecules. 2000;**33**:9488-9493

[20] Madras G, Smith S, McCoy B. Degradation of poly (methyl methacrylate) in solution. Industrial & Engineering Chemistry Research. 1996;**35**(6):1795-1800

[21] McCoy B, Wang M. Continuous-mixture fragmentation kinetics: Particle size reduction and molecular cracking. Chemical Engineering Science. 1994;**49**(22):3773-3785

[22] Kodera Y, McCoy B. Distribution kinetics of radical mechanisms: Reversible polymer decomposition. AIChE Journal. 1997:3205-3214

[23] Kommineni S, Chowdhury Z, Kavanaugh M, Mishra D, Croue J. Advanced oxidation of methyl-tertiary butyl ether: Pilot study findings and full-scale implications. Journal of Water Supply: Research and Technology. 2009;**57**(1):403-418

[24] Kosaka K, Yamada H, Matsui S, Echigo S, Shishida K. Comparison among the methods for hydrogen peroxide measurements to evaluate advanced oxidation processes: Application of a spectrophotometric method using copper (II) ion and 2,9-dimethyl-1,10-phenanthroline. Environmental Science & Technology. 1998;**32**:3821-3824

[25] Ghafoori S, Mehrvar M, Chan P. Kinetic study of photodegradation of water-soluble polymers. Iranian Polymer Journal. 2012;**21**:869-876

[26] Kodera Y, Cha W, McCoy B. Continuous-kinetic analysis for polyethylene degradation. ACS Symposium Series. 1997;**42**(4):1003-1006

[27] Konaganti V, Madras G. Photocatalytic and thermal degradation of poly(methyl methacrylate), poly (butyl acrylate), and their copolymers. Industrial and Engineering Chemistry Research. 2009;**48**(4):1712-1718

[28] Shukla B, Daraboina N, Madras G. Ultrasonic degradation of poly (acrylic acid). Polymer Degradation and Stability. 2009;**94**(8):1238-1244

[29] Song H, Hyun J. An optimization study on the pyrolysis of polystyrene in a batch reactor. Journal of Chemical Engineering. 1999;**16**(3):316-324

[30] Buxton G, Greenstock C, Helman W, Ross A. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O$) in aqueous solution. Journal of Physical and Chemical Reference Data. 1988;**17**:513-886

[31] Koppenol W, Butler J, Van Leeuwen W. The Haber−Weiss cycle. Photochemistry and Photobiology. 1978;**28**:655-658

[32] Weinstein J, Bielski B. Kinetics of the interaction of HO_2 and O^{2-} radicals with hydrogen peroxide: The Haber-Weiss reaction. American Chemical Society. 1979;**101**:58-62

[33] Christensen H, Sehested K, Corfitzen H. Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. Physical Chemistry. 1982;**86**:1588-1590

[34] Bielski B, Cabelli D. Highlights of current research involving superoxide and perhydroxyl radicals in aqueous solutions. International Journal of Radiation Biology. 1991;**59**:291-319

[35] Elliot A, Buxton G. Temperature dependence of the reactions OH + O^{2-} and OH + HO_2 in water up to 200°C. Chemical Society. 1992;**88**:2465-2470

[36] Linden K, Sharpless C, Andrews S, Atasi K, Korategere V, Stefan M, et al. Innovative UV Technologies to Oxidize Organic and Organoleptic Chemicals. London: IWA Publishing; 2005

[37] Whittmann G, Horvath I, Dombi A. UV-induced decomposition of ozone and hydrogen peroxide in the aqueous phase at pH 2-7. Ozone Science and Engineering. 2002;**24**:281-291

[38] Hamad D, Mehrab M, Dhib R. Photochemical kinetic modeling of degradation of aqueous polyvinyl alcohol in a UV/H_2O_2 photoreactor. Journal of Polymers and the Environment. 2018;**26**(8):3283-3293

[39] Taghizadeh M, Yeganeh N, Rezaei M. The investigation of thermal decomposition pathway and products of poly(vinyl alcohol) by TG-FTIR. Applied Polymer Science. 2015;**32**(25): 42117-42129

[40] Liao C, Gurol M. Chemical oxidation by photolytic decomposition of hydrogen peroxide. Environmental Science & Technology. 1995;**29**:3007-3014

[41] Stefan M, Hoy A, Bolton J. Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. Environmental Science & Technology. 1996;**30**:2382-2390

[42] Peng Z, Kong L. A thermal degradation mechanism of polyvinyl alcohol/silica nanocomposites. Polymer Degradation and Stability. 2007;**92**: 1061-1071

[43] Bird R, Stewart W, Lightfoot E. Transport Phenomena. 2nd ed. New York: Wiley & Sons, Inc.; 1960

[44] Labas D, Zalazar S, Brandi J, Martín A, Cassano E. Scaling up of a photoreactor for formic acid degradation employing hydrogen peroxide and UV radiation. Helvetica Chimica Acta. 2002;**85**:82-95

[45] McCoy B, Madras G. Chemical Engineering Science. 2001;**56**:2831-2836

[46] Stickle J, Griggs A. Mathematical modeling of chain-end scission using continuous distribution kinetics. Chemical Engineering Science. 2012;**68**: 656-659

[47] Sterling J, McCoy B. Distribution kinetics of thermolytic macromolecular reactions. AIChE Journal. 2001;**7**:2289-2303

[48] Randolph A, Larson M. Theory of Particulate Processes: Analysis and Techniques of Continuous Crystallization. New York: Academic Press; 1971

[49] Sezgi A, Cha S, Smith J, McCoy B. Polyethylene pyrolysis: Theory and experiments for molecular weight distribution kinetics. Industrial and Engineering Chemistry Research. 1998; **37**(7):2582-2591

[50] Marimuthu A, Madras G. Continuous distribution kinetics for microwave-assisted oxidative degradation of poly(alkyl methacrylates). AIChE Journal. 2008;**54**(8):2164-2173

[51] Vinu R, Madras G. Photocatalytic degradation of polyacrylamide-coacrylic acid. Polymer Degradation and Stability. 2008;**93**(8):1440-1449

[52] Madras J, McCoy B. Oxidative degradation kinetics of polystyrene in solution. Chemical Engineering Science. 1997;**52**(16):2707-2713

[53] Smagala T, McCoy B. Mechanisms and approximations in macromolecular

reactions: Reversible initiation, chain scission, and hydrogen abstraction. Industrial and Engineering Chemistry Research. 2003;**42**:2461-2469

[54] Hulburt H, Katz S. Some problems in particle technology: A statistical mechanical formulation. Chemical Engineering Science. 1964;**19**:555-574

[55] Mehrvar M, Anderson W, Moo-Young M. Photocatalytic degradation of aqueous organic solvents in the presence of hydroxyl radical scavengers. International Journal of Photoenergy. 2001;**3**(4):187-191