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Oxidative Mineralization and Characterization of Polyvinyl Alcohol Solutions for Wastewater Treatment

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DISCLAIMER

OXIDATIVE MINERALIZATION AND CHARACTERIZATION OF POLYVINYL ALCOHOL SOLUTIONS FOR WASTEWATER TREATMENT.

ABSTRACT

Polyvinyl alcohol (PVA) fabric has been evaluated for use as an effective substitute for conventional cellulose-based nuclear waste decontamination material that are currently used at commercial nuclear facilities. PVA-based waste has been found to be chemically compatible with nuclear process wastewater treatment facilities only when it is more than 90% mineralized with hydrogen peroxide or potassium permanganate. The presence of oxidized PVA in a typical nuclear process wastewater environment has been found to have little of no effect on the efficiency of ion exchange resins and precipitation agents used for the removal of radionuclids from nuclear process wastewater.

Photochemical and ultrasonic treatment of PVA in the presence of hydrogen peroxide was evaluated as the primary method of PVA mineralization because no solid particles are formed in the mixing, pH adjustments, evaporation and blending of oxidized PVA with other nuclear process liquid waste. The disappearance of PVA in hydrogen peroxide with ultrasonic and ultraviolet irradiation treatment was characterized by pseudo-first order reaction kinetics.

Keywords: Polyvinyl acetate, peroxide oxidation, permanganate oxidation, ultraviolet and ultrasonic treatment, nuclear process wastewater, decontamination.

INTRODUCTION

Cellulose-based mop heads, wipes and disposable personal protection clothing are currently used as "clean up" products at nuclear facilities. These conventional cleaning materials are used for picking up radioactive spills and mixed waste as well as in general decontamination operations. Cellulose and other polymer-based materials, which can not be laundered or incinerated due to high radioactive contamination, organic constituents or mixed waste characteristics are disposed in dry active waste streams as bulky solid waste. Increasing cost of final disposal of these types of solid waste makes it necessary to investigate new ways of decreasing radioactive waste treatment and disposal cost.

Polyvinyl alcohol (PVA) is a synthetic polymer produced by alkali or acidic hydrolysis of polyvinyl acetate. Molecular weight (7,000-186,000) and percent hydrolysis govern the physical properties of PVA such as solubility in hot water. PVA produced from the hydrolysis of polyvinyl acetate, with 88-98 % hydrolysis, dissolves most rapidly in hot water (US patents 5,181,966; 5,507,837 and 5,181,967). Items made from this grade of PVA, especially those without coloring pigments can dissolve in hot water at approximately 90-100 ^{o}C. The resulting organic PVA solution, without chemical modification to simpler organic molecules, is not compatible with nuclear process wastewater storage and processing facilities. The processing problems from unadulterated PVA-based liquid waste, such as "skin" formation, coating of ion exchange materials and poor pumpability stems from the high organic content of PVA solution.

Results from this study could serve as part of the technical basis for accepting PVA waste in nuclear process wastewater storage and processing facilities. The data will also be useful in the modification of Orex® commercial process (Orex® process is currently used in the solubilizing of PVA) to accommodate PVA chemical degradation features or in the design of an entirely different equipment unit to simultaneously handle solubilizing and chemical degradation of PVA. The data will also be useful for pilot plant testing of such new equipment to treat radioactive laden PVA by oxidation, pH adjustments and destruction of excess oxidizing agent (hydrogen peroxide).

The principal objectives of this study are to: (1) Identify an appropriate PVA oxidative mineralization technique; (2) perform compatibility and evaporation fate tests for neat and mineralized PVA; and (3) determine potential for PVA chemical interferences which may affect ion exchange utilization for radioactive wastewater processing in the nuclear industry.

EXPERIMENTAL

PVA was oxidized with potassium permanganate (solid crystals, non-acidified and acidified solutions), and hydrogen peroxide (with and without ultrasonic and ultraviolet treatment). Colorimetric-based measurement technique, at 670 ηm, was used to determine the extent of PVA oxidation, that is, amount of PVA left in solution during and after oxidation.

Both unadulterated 5% PVA and oxidized PVA solutions (<90% oxidation) were mixed with a typical nuclear process wastewater simulant at room temperature and at temperatures greater than 100 °C to characterize the mixture for precipitation, "skin" formation and reverse dissolution of PVA. The viscosity and pH of neat PVA and oxidized PVA solutions were also monitored for comparison. Absolute viscosity measurements were based on forced-piston principle where electromagnetic coils drive an internal piston up and down inside a measurement chamber filled with oxidized PVA or neat unadulterated PVA solution

The effect of oxidized PVA solution on ion exchange process for the uptake of radionuclides was evaluated with two ion exchange materials (crystalline silicotitanate (CST) and monosodium titanate (MST)) for cesium, strontium and plutonium removal and one precipitation agent (tetraphenyl borate(TPB)) for cesium removal.

Chemicals and materials.

The experimental set up for the oxidation and measurement of rheological properties of oxidized 5% PVA solutions included the following: model 2000 Labsonic 20 kHz ultrasonic generator (B. Braun, Allentown, PA), model DR/300 UV-VIS spectrophotometer (Hach cooperation, Loveland, CO), multiple wavelength mercury UV lamp (UVP, Upland CA), model TCV 300 forced-piston viscometer (Cambridge Applied System Inc., Medford, Ma), orbital shaker (New Brunswick scientific, Edison, NJ). The H_2O_2/UV/ ultrasonic oxidation set up consisted of a multi-wavelength mercury UV lamp (254, 302 and 366 ηm), suspended at 10 mm above pyrex® glass petri dishes or 150-mL

Teflon® beaker reaction vessels. The principal chemicals and reagents used included potassium permanganate, 50 % hydrogen peroxide (Hach, Loveland CO), 5% PVA solution prepared directly from white woven PVA fabric (Isolyser company, Norcross GA), nitric and boric acids, iodine, potassium iodide, milli-Q water, CST (UOP (Ionsive IE-911 lot # 999096810002), MST (Allied Signal, Des Plaines, IL) and TPB (Savannah River Plant).

Preparation of PVA solutions and colorimetric determination of percent PVA in solution

About 200 grams of PVA fabric pieces was dried in a vacuum oven overnight at 75 °C The five percent PVA solution was prepared by slowly dissolving 50.000 ± 0.0001 grams of the oven dried PVA fabric in about 700 mL milli-Q (distilled and de-ionized water) water on a hot plate. The temperature of the hot water was maintained between 90-100 °C. After the complete dissolution of the PVA in about 700 mL of hot water the solution was quantitatively transferred into a 1000-mL volumetric flask and the solution volume brought to mark with milli-Q water. This PVA preparation approach requires continuous stirring of the mixture to prevent the formations of small hydrated PVA balls. These small hydrated balls are not soluble in hot water. It is, however, easier to prepare a 4 or 3% PVA solution to prevent the formation of these PVA ball suspensions.

PVA Calibration standards

4% boric acid solution (40 g boric acid per Liter of distilled water) and

Iodine solution (12.7 g of iodine, and 25 g of potassium iodide, per Liter of distilled water) are the principal reagents for the colorimetric determination of percent PVA in solution.

PVA calibration standards, 0.5% PVA by weight stock solution, was quantitatively prepared by dissolving 0.1000 g of the oven dried PVA fabric in 20-mL of hot distilled water at 100 °C. 10-mL of this PVA solution was quantitatively transferred to a 1000-mL volumetric flask and brought to volume with hot distilled water (0.0050 % PVA intermediate stock solution). Based on aliquot intermediate stock solutions, the calibration standards were prepared by quantitatively transferring the aliquot samples to a 100-mL volumetric flask and adding 20 mL of 4% boric acid solution and 6 mL of iodine solution to each 100-mL flask. The flask volume was brought to the 100-mL mark with distilled water. Table 1 shows ten calibration standards, which were obtained by diluting various aliquot samples of the intermediate stock solution to the 100-mL mark in a 100 mL volumetric flask.

This method for determining percent PVA in solution, before or after oxidation, was adapted from an Air Product procedure for determination of PVA concentration in dilute aqueous matrices such as those obtained from the extraction of paper (Hanson 1998). This colorimetric technique is based on the formation of stable PVA green colored complexes with iodine in the presence of boric acid. By performing a wavelength scan with one of the calibration standards from 500 to 800 ηm, the maximum absorption band (λ max) of the iodine/PVA complex was determined to be around 670 ηm. Results of the wavelength scan and absorption profile are plotted in Figure 1. The calibration curve,

Figure 2, was derived from the absorbance values plotted against the percent PVA per 100-mL at λ max. During or after the oxidation of PVA the percent mount of PVA left in solution was determined by transferring 0.1 ml of the solution to 100-mL flask already containing 20 mL of 4% boric acid solution and 6 mL of iodine solution. The 100-mL flask was brought to volume with distilled water (dilution factor of 1000). After shaking the contents of the flask to ensure uniformity, the absorbance of the sample was taken at λ max and the result compared to the calibration curve. During the mixing or shaking of the flask the sample was discarded if blue/green precipitates were observed.

The calibration equation for the percent PVA versus absorbance profile in Figure 2 is linear. Where,

$$Y\ (\%PVA) = 0.0022\ X\ (absorbance) - 0.000003$$

PVA OXIDATION WITH POTASSIUM PERMANGANTE

Three approaches were used in the oxidation of 5% PVA solution with potassium permanganate. In the first approach, PVA oxidation reactions were carried out with solid crystals of potassium permanganate directly introduced into known volumes of 5% PVA solutions. This non aqueous-based permanganate oxidation of PVA if found to be equally efficient as oxidation with aqueous-based permanganate will result in minimizing final waste volume generated from oxidative mineralization of PVA.

In the second and third approaches of permanganate oxidation of PVA, non-acidified and acidified potassium permanganate solutions were used. Concentrated nitric acid was used for acidification of the oxidizing solutions.

Solid permanganate crystal and non-acidified permanganate oxidation of PVA solution.

Oxidation of PVA with potassium permanganate was carried out with known amounts of potassium permanganate crystals directly added to polyethylene vials containing 10-ml portions of 5% PVA solution at room temperature. The vials were put into an orbital shaker for agitation to ensure uniform mixing and dissolution of the oxidizing crystals. After mixing of the PVA with the oxidizing crystals the oxidation was almost instantaneous. Ten minutes after mixing the content of each vial was analyzed colorimetrically for percent PVA left in solution (a measure of extent of oxidation). Figure 3 shows a typical plot of extent of oxidation versus weight in grams of potassium permanganate per 10 mL 5% PVA solution. For a better than 90% conversion of PVA 0.24 grams of the solid potassium permanganate crystals per 10 ml portion of 5% PVA was needed (24 grams per liter of 5% PVA solution). Using this amount of solid potassium permanganate ensured there were no precipitation of black manganese particles. A higher concentration of potassium permanganate than 24 gm/liter yielded almost a 100% oxidation of PVA at room temperature. However, black manganese dioxide precipitates were formed and the resulting mixture turned into an unpumpable jelly-like paste. After 24 hours on bench top, it was observed that all the samples in vials containing greater than or equal to 0.25 grams of potassium permanganate per 10-ml portion of oxidized 5% PVA had turned into a solid paste.

In the oxidation of PVA a better than 90% degradation is considered an acceptable extent of mineralization of PVA, because the remaining PVA in solution is denatured up to the point where it does not posses neat PVA solution characteristics. This 90% benchmark

was selected by mixing different levels of oxidized PVA with nuclear wastewater simulant and observing for reverse dissolution or precipitation of PVA.

Oxidation of 5% PVA with non-acidified potassium permanganate solution was relatively faster than solid permanganate oxidation because in the latter case all the permanganate crystals did not dissolve with ease during the course of the reaction.

Acidified potassium permanganate oxidation of PVA

Acidified 0.35 molar potassium permanganate solution was used for the oxidation of 5% PVA (5-mL conc. HNO_3 per liter of 0.35 M solution of $KMnO_4$). Varying volumes of the permanganate solution (0.5 to 5 ml of 3.5M $KMnO_4$) were mixed with 10-ml portions of 5% PVA solutions, and after shaking for 10 minutes the amount of PVA left in each solution was determined colorimetrically as earlier described.

The time needed for a better than 90% conversion of PVA was relatively shorter for acidified permanganate solution in comparison with non-acidified or solid permanganate oxidation of PVA. In addition, there were relatively no manganese dioxide (MnO_2) precipitates. Smaller volumes of acidified KMnO4 solutions(0.35M) were required for a better than 90% oxidation of PVA (5%) and oxidized PVA solutions were clear and colorless due to the absence of MnO_2 precipitates. To obtain a better than 97% oxidation of PVA (5%) only about 2-mL portions of acidified $KMnO_4$ (0.35 M) per 10-ml of 5%PVA were required (Figure 4). Thus, acidified PVA solutions require less potassium permanganate for complete mineralization (11.5 g $KMnO_4$/L).

Oxidized PVA samples from acidified permanganate oxidation with pH values less than 3 were put into small glass vials and the pH of the samples adjusted with 1.0 molar solution

of sodium hydroxide to pH 12. After pH adjustments black precipitates of MnO_2 was observed along with some amounts of salt in the sample matrix.

Based on above information (2-mL of acidified $KMnO_4$ (0.35 M) per 10-ml of 5%PVA required for a better than 97% oxidation of PVA.) one can construct a table showing the volume of acidified $KMnO_4$ (0.35 M) solution required to obtain about 97% PVA mineralization for any given percent PVA solution. The experimentally verified data are summarized in Table 2 and Figure 5 below. All five samples of PVA solution, with different percent PVA compositions, showed an average of 97 ± 1 % extent of PVA oxidation with their respective calculated amounts of acidified $KMnO_4$ (0.35M).

From the linear equation in Figure 5, the grams of potassium permanganate per mL of a given percent PVA solution (acidified) required for a better than 97% oxidation of PVA can be calculated:

$$Y\ (g\ KMnO_4\ /mL\ PVA) = 0.0018(\%PVA) + 0.0002.$$

PHOTOCHEMICAL OXIDATION OF PVA IN HYDROGEN PEROXIDE.

Kinetics of PVA Oxidation with hydrogen peroxide under UV light.

Hydrogen peroxide acting as an oxidizing agent is added to the PVA solution and its decomposition to form peroxides, for example hydroxyl radicals, is activated by UV light. The peroxides (hydroxyl radicals) then react with the PVA, initiating a rapid cascade of oxidation reactions that ultimately mineralize the PVA (Jaeger et al. 1979).

$$H_2O_2 + h\nu\ (UV) \rightarrow \text{peroxides } (OH^{\cdot}, (O_2H)^{\cdot}, (H_2OOH)^{+}) \quad (1)$$

$$\text{Peroxides} + \text{PVA} \rightarrow \text{products} \quad (2)$$

In equation 1 above the photo-dissociation of hydrogen peroxide results in the production of powerful oxidizing radicals (hydroxyl, hydroperoxide, peroxonium and peroxide ions). The peroxides are the principle agents responsible for the oxidative mineralization of PVA (equation 2). Per equation 1 and 2 the oxidation of PVA is a complex and irreversible consecutive set of reactions.

A Pyrex® glass sample receptacle was used for all the UV studies because it shows a greater than 90% UV transmission above 300 ηm (Winer 1979). For the UV lamps, the corresponding energies per mole are, respectively, 327 kJ/mole (longer wave UV energy source at 366 ηm), 396 kJ/mole (intermediate long wave at 302 ηm), and 471 kJ/mole (short wave at 254 ηm). The energy data are obtained by converting wavelength in ηm to energy units E (kJ/mole), that is, E = 1.1962E05/λ kJ/mole.

The rate of decomposition of hydrogen peroxide with the absorption of photon energy (equation 1) is given by

$$(-d[H_2O_2])/dt = \Phi\ ([H_2O_2]\ d[h\nu]_{abs})/dt \qquad (3)$$

Where Φ is the quantum yield for hydrogen peroxide degradation with the absorption of photon energy, and $d[h\nu]_{abs}/dt$ is the photon flux. Per equation 3, the steady state concentration of H_2O_2 in the aqueous media is assumed to be dependent on the absorbed photon flux. However, in excess of micro-mole quantities of H_2O_2 concentration this may not be the case (Korman et al. 1988). Therefore, the solution to equation 3 becomes extremely difficult to solve for unique values. Since the quantitative kinetic calculation for this complex photo-dissociation of H_2O_2 is not straightforward, the apparent reaction

rate constant for the mineralization of PVA in the presence of H_2O_2 will be based on initial PVA concentration and its concentration changes with time only.

Hence, from equation 2 above,

$$\text{Peroxides} + \text{PVA} \xrightarrow{K_1} \text{Products.}$$

$$-d[PVA]/dt = K_1[\text{peroxides}]\,[PVA] \qquad (4)$$

If equation (4) is integrated, noting that at time, t =0, concentration of products = 0, then

$$\text{Ln}\,[PVA]_0/[PVA]_t = K_1[\text{Peroxides}]\tau \qquad (5)$$

If it is assumed that $K_1[Peroxides] =$ constant, K_2, (where τ is time), then

$$\text{Ln}\,[PVA]_0/[PVA]_t = K_2\tau \qquad (6)$$

A plot of the left-hand side of equation 6 versus τ should yield a straight line with the slope equal to K_2. Here, we have assumed that K_2 represents the apparent reaction rate constant for the oxidative mineralization of PVA.

The UV light intensities (at 1 cm) on the irradiated PVA/H_2O_2 samples in a circular petri-dish are calculated as power per unit area of exposure or Watt per square meter. For the petri-dishes (5.7 cm by 1.2 cm) the intensity is 6 Watt/(0.785)(5.7 cm^2 = 2,352.5 Watt/m^2.

PVA Oxidation with hydrogen peroxide under UV light

The oxidation of a mixture of 5% PVA solution with hydrogen peroxide at room temperature required about 10 to 14 days aging period to obtain a better than 90%

mineralization of 5%PVA solution. This was the case even when the PVA and hydrogen peroxide were in a 1:1 ratio by volume. To enhance the oxidation rate of PVA in the presence of hydrogen peroxide, sonochemical (ultrasonic irradiation) and UV photochemical (ultraviolet light irradiation) techniques were employed.

In runs where ultrasonic energy was used to further enhance the oxidation of PVA, a 20 kHz ultrasonic generator energy output was maintained at 4.58 Watts/cm^2. Here it is assumed that there is a minimum ultrasonic intensity below which there is no enhanced degradation of PVA in the presence of H_2O_2. Based on the work of Mostafa (1958), 3.125 Watts/cm^2 was chosen as this threshold intensity for PVA. The test samples were either put in a 150-ml Teflon® beaker or in a 150-mL Pyrex® glassware. For simultaneous sonication and UV irradiation treatment of the PVA in hydrogen peroxide samples, the UV lamp was aligned along the side of the beaker inside an ultrasonic chamber. In oxidation reactions not involving sonication the PVA/hydrogen peroxide mixtures were put into 5.7 cm by 1.2 cm petri dishes sitting on a small laboratory jack under the mercury UV lamp.

Two principal UV wavelengths (302 and 366 ηm) were evaluated for the photochemical oxidation of PVA in the presence of H_2O_2. There were no appreciable improvements on reaction rate over PVA oxidation with only H_2O_2 when photochemical treatment of PVA at 254 ηm was carried out in the presence of H_2O_2.

No measurable PVA oxidation changes were observed with just treating 5% PVA solutions with ultrasonic energy at 90 Watts for three minutes. Faster oxidation rates for the mineralization of PVA with UV in the presence of H_2O_2 were obtained only with 302

and 366 ηm UV treatments. Here the UV exposure time, in minutes, needed to obtain a better than 90% mineralization of 5% PVA has been designated as T-90.

The oxidation of PVA with hydrogen peroxide with sonochemical treatment showed a small increase in reaction rate over PVA oxidation with H_2O_2 only. The average time required for a better than 90% oxidative mineralization of PVA was reduced by 24%.

PVA oxidation at 366 ηm

Basically two types of PVA oxidation runs were carried out: Oxidation of PVA in H_2O_2 with ultraviolet irradiation and PVA in H_2O_2 oxidation with ultrasonic and ultraviolet treatment.

Oxidation of PVA/H_2O_2 mixtures (5 to 33% H_2O_2 by volume relative to total PVA volume) coupled with UV treatment at 366 ηm, was carried out in petri-dishes. In the second type of oxidation runs, the PVA/H_2O_2 sample mixtures (5 to 33% H_2O_2) were treated with ultraviolet and ultrasonic energy. Here each sample mixture was put into 150-mL Teflon® or Pyrex® glass beaker and sonicated (ultrasonic energy maintained at 4.6 Watts/cm^2) for three minutes initially and then exposed to UV light at 366 ηm. The samples could also be sonicated continuously at a given time interval while it was being treated with UV light. For these runs, at intervals of 20-30 minutes 0.1 mL samples were collected and quantified for percent PVA left in solution. This was carried on until a better than 90% conversion of PVA was attained. Figure 6 shows a typical decay curve for PVA oxidation in H_2O_2 coupled with sonication and UV light at 366 ηm.

In theory T-90 time can be obtained by solving equation 6. However, because of the assumption that $K_2 = K_1$ [peroxide] T-90 values obtained by solving equation 6 are in error since the concentration of the peroxides are unknown. As a result, T-90 values were determined experimentally by extrapolating from decay curves as in Figure 6. Figure 7 shows an overlay plot for data obtained with PVA oxidation at 366 ηm, with and without sonication, in the presence of H_2O_2. Slopes in Figure 7, which are the reaction rate constants, are respectively, 0.0219 min^{-1} for oxidation with initial sonication for three minutes before exposure to UV at 366 ηm and 0.0176 min^{-1} without sonication. Based on the magnitude of the reaction rate constants the conclusion can be made that PVA oxidation in the presence of hydrogen peroxide and UV light coupled with sonication is faster.

In continuous sonicated and UV treated runs, samples under UV lights were sonicated for three minutes at intervals of 30 minutes, with ultrasonic energy maintained at 90 Watts. (Care must be exercised in the use of 100-mL Pyrex® beaker as sample container for the sonication. The beaker must contain enough sample, at least 50 mL, to prevent the shattering of the beaker due to ultrasonic energy.) At intervals of 20 minutes aliquot samples (0.1 mL) were collected for analysis and determination of percent of PVA left in solution. This was carried out until a better than 90% oxidation was attained. With this continuous sonication/UV treatment of PVA /H_2O_2 mixtures the entire reaction time, the T-90 time, was further reduced from hours to minutes for both oxidation at 366 and 302 ηm (see ahead).

Table 3 is a summary of PVA oxidation data with UV/H_2O_2 coupled with sonication treatment for various proportions of H_2O_2 in 5% PVA. This table also contains the

calculated average reaction rate constants, the average UV illumination time (T-90) needed to obtain a better than 90% oxidation of 5% PVA and corresponding proportions of H_2O_2 in 5% PVA. The UV illumination time required to obtain a better than 90% mineralization of 5% PVA was extrapolated from each decay curve. The first part of Table 3 (column 2 through 5 for oxidation with 17.6% H_2O_2) shows only a single set of data for oxidation without sonication treatment for comparison.

PVA oxidation at 302 ηm

The same procedure, as described above, for oxidation of PVA at 366 ηm was repeated with the UV lamp wavelength changed to 302 ηm.

In Figure 8, overlay plot A is a typical PVA oxidation profile per equation 6 for PVA oxidation at 302 ηm with sonication. The reaction rate constant per equation 6 for this PVA oxidation at 302 ηm is 0.0996 min^{-1}. The magnitude of the reaction rate at 302 ηm is almost a factor of 2 larger than the reaction rate at 366 ηm (overlay plot B Figure 8) indicating a faster reaction rate at 302 ηm.

The first four columns in Table 4 contain a summary of 5 % PVA/H_2O_2/UV oxidation data at 302 ηm with and without sonication. The last four columns in Table 4 show a summary of the average data obtained for 5% PVA oxidation with UV at 302 ηm coupled with continuous sonication of the reacting mixtures of PVA and H_2O_2. Based on the magnitude of the reaction rate constant data the reaction rate for the sonicated PVA/H_2O_2 treatment at 302 ηm is about a factor of 3 better than runs without sonication.

Plots in Figures 9, overlays (A) and (B), are respectively, T-90 illumination time (Time required for a better than 90% mineralization of 5 %PVA) for oxidation at 302 ηm without ultrasonic treatment and 302 ηm with ultrasonic treatment on H_2O_2/PVA reaction mixtures versus percent H_2O_2. Similarly, plots in Figure 10 show overlay plots of reaction rate constant versus percent hydrogen peroxide used in the oxidative mineralization of 5% polyvinyl alcohol solution at 302 ηm with (plot (A)) and without (plot (B)) ultrasonic treatment of H_2O_2/PVA reaction mixtures.

Based on information in these Figures 9 and 10, for any chosen percent hydrogen peroxide used in the oxidation of 5% PVA, the corresponding reaction rate constant and time required for a better than 90% mineralization of PVA can be determined by extrapolation. It is worth noting that parameters obtained from these plots are only valid for oxidation at that specific UV wavelength with ultrasonic energy at 4.6 Watt/cm^2 for sonicated runs. Another method for obtaining the minimum percent by volume of H_2O_2 for the oxidation of 5% PVA may involve solving the equations of the best-fit curve for both the T-90 illumination time and the reaction rate versus percent by volume of H_2O_2 in an overlay plot. From the solution of these two equations the appropriate minimum volume of percent H_2O_2, reaction rate constant and T-90 illumination time can be determined. For example in Figures 9 and 10, for PVA mineralization at 302 ηm with sonication (overlay B Figure 9 and overlay A Figure 10), the following equations are used:

$Y = 209.03\ (\%\ H_2O_2)^{-0.6341}$ and

$Y = 0.00582\ (\%\ H_2O_2) + 0.00631$.

From the above equations, % H_2O_2 = 8.3%, T-90 = 55 minutes and reaction rate = 0.055 1/minutes.

Figure 11 is a plot of changes in pH of a typical 5% PVA/H_2O_2 reaction mixture with extent of oxidation. By the time the oxidation of 5% PVA is almost 100% the pH has dropped to less than 2.5.

PVA activation energy at 302 ηm oxidation

Three different oxidation reactions of 5% PVA were carried out at temperatures of 28 °C, 45.6 °C and 58.6 °C. The length of ultrasonic treatment was used as a means of increasing the reaction temperature of the mixtures. That is, the longer the sonication time the higher the reaction temperature of the PVA/H_2O_2 reaction mixture (17.6 % H_2O_2 and 82.4% PVA). Table 5 contains a summary of the reaction rates at different temperatures. The reaction rates increased with increasing reaction temperatures. Figure 12 is a plot of the natural log of the reaction rate constants versus the reciprocal of the reaction temperatures in degrees Kelvin. The slope of the line in Figure 12 is -3138.

The slope of the line = -Ea (activation energy)/R (gas constant).

$$Ea = 3138\ (8.3144)\ JK^{-1}\ Mole^{-1} = 26{,}091\ JK^{-1}\ Mole^{-1}$$

The calculated activation energy under these conditions is therefore approximately 26,000 JK^{-1} $Mole^{-1}$.

Oxidation products from Photochemical and sonochemical degradation of PVA.

The oxidation products from the mineralization of PVA in hydrogen peroxide with only ultraviolet irradiation at both 302 and 366 ηm gave a colorless solution, which was chromatographically identified as mainly acetic acid (Finch 1992). With pH adjustment to alkaline conditions, using sodium hydroxide one expects the formation of the corresponding sodium salt (sodium acetate). However, the oxidation products from combined ultraviolet irradiation and ultrasonic treatment of PVA in hydrogen peroxide gave a colored solution with yellow tinge. From chromatographic data the main product is a mixture of acetic and formic acids (Ikada et al. 1977 and Mino et al. 1959). The color difference seems to indicate that there exists an intrinsic difference in reactivity between radicals formed by photolysis and those formed by ultrasonic treatment (Takahide et al. 1998), which would result in the formation of different end products for the oxidation of PVA. The oxidation of PVA with potassium permanganate has been reported to produce mainly oxalic acid and carbon dioxide (Finch 1992).

Estimation of amount of salt produced from pH adjustment of oxidized PVA.

In a nuclear process wastewater treatment facility, in addition to the stringent high alkaline pH requirement (pH > 10) for corrosion and organo-nitrate controls, the wastewater solid content, salts in particular, is of prime importance for meeting wastewater processing requirements.

The main products from hydrogen peroxide-based oxidative mineralization of PVA have been identified mainly as acetic and formic acids:

$$[\text{-}CH_2\text{-}CHOH\text{-}]_n \text{ ----H2O2/UV/ultrasonic-----}\rightarrow CH_3CO_2H + CH_2O_2 \quad (7)$$

The pH of the resulting solutions is 2.9 ± 0.2. To estimate the amount of organic salt formed from pH adjustment to 13.5 with sodium hydroxide 50 mL of the oxidized PVA solution was titrated with 1.0 molar solution of sodium hydroxide. 15 mL of 1.0 molar solution of sodium hydroxide was required to bring the pH of the oxidized PVA solution to about 13.5. This is equivalent to 12 g of sodium hydroxide per liter of 100% oxidized 5% PVA solution. The pH adjustment was carried out while the excess hydrogen peroxide in the oxidized PVA solution was being decomposed in alkaline conditions by heating the mixture. If one assumes that the pH adjustment results in the conversion of all the acids in solution to their corresponding acetate and formate salts of sodium per equation below, then the amount of salt formed can be estimated:

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O \quad (8)$$

$$NaOH + CHOOH \rightarrow CHOONa + H_2O \quad (9)$$

From equation 8 above, stoicheiometrically, 82 g of sodium acetate salt is produce from the neutralization reaction per 40 grams of sodium hydroxide used. Therefore 24.6 grams of the acetate salt will be produced per liter of oxidized PVA solution (82 g acetate/40 g NaOH* 12 g NaOH). Similarly per equation 9 above, 68 g of sodium formate is produced from the neutralization reaction with 40 g of sodium hydroxide. This means 20.4 g of sodium formate is produced per liter of oxidized PVA (68 g formate/40 g NaOH* 12 g NaOH).

If one assumes that a liter of 100 % oxidized PVA solution contains only acetic and formic acids in a 1:1 ratio then the estimated average amount of salt in that solution would be 22.5 g per liter ((20.4 + 24.6)/2) or 22.5 grams of salt per liter of oxidized PVA solution. Note that a litter of 5% PVA solution initially (neat PVA solution) contains 50 grams of PVA fabric.

EVAPORATION AND COMPATIBILITY STUDIES WITH OXIDIZED AND NEAT PVA SOLUTIONS

Nuclear process wastewater simulant

The average nuclear process wastewater simulant composition used in this study is summarized in Table 6 above. The simulant, with an average sodium ion concentration of 5.6 molar, was spiked with 2% oxidized PVA solution. This 2% value is considered a conservative representation of volume of oxidized PVA per a given nuclear process wastewater storage tank. This spiked solution was used in the characterization of cesium-137 and plutonium-239 removal efficiencies with CST and MST ion exchange materials. A diluted spiked solution of the nuclear wastewater simulant, 4.7 molar sodium ion, was used for the characterization of cesium-137 removal from the nuclear wastewater using TPB.

Evaporation/mixing properties of liquid waste processing simulant with oxidized PVA.

Two, three and four percent PVA solutions were prepared by serial dilution of neat five percent PVA solutions and 500-mL portions of each solution put into 1000-mL beakers on a hot plate for continuous evaporation. The temperature of the hot plate was gradually raised by 10 ^{o}C every 20 minutes. The temperature of each heated beaker and its

contents was monitored regularly. The behavior of each PVA solution (2,3, 4 and 5% PVA) was monitored by looking for the formation of films of transparent PVA material on the beaker walls and around the general evaporation surface.

The above evaporation experiments were repeated with completely mineralized PVA solutions from both oxidation with hydrogen peroxide and acidified potassium permanganate.

To evaluate for interactions between nuclear process wastewater simulant and oxidized PVA solutions equal volumes of oxidized PVA and nuclear process wastewater simulant were mixed in 50-mL sampling vials. Similar experiment was repeated with neat PVA solutions. The pH of oxidized PVA solution (H_2O_2-based oxidation) was adjusted with 1.0 molar solution of sodium hydroxide until the solution pH was about 13.5. The resulting solution was treated with ultrasonic waves until all the excess hydrogen peroxide had been decomposed. This oxidized PVA solution, without excess H_2O_2, was also mixed with nuclear process wastewater simulant on a one-to-one basis.

The evaporation beakers containing neat PVA solutions started showing evidence of formation of PVA films (skins) at about 70 °C. By the time the temperature of each solution had reached 85 °C the entire evaporation surface of each beaker had been covered with thin transparent sheet of PVA film. After about six hours on the hot plate (average temperature of 98 °C) each of the beakers had lost all its water content and only the PVA film residue was in each beaker.

With oxidized PVA solutions (H_2O_2-based oxidation), under the same evaporation conditions, there were no films formed, and after about six hours there were no residue materials left on the bottom of each beaker. Oxidized PVA solutions derived from oxidation with potassium permanganate had a tendency to produce small amounts of black manganese dioxide precipitates on the sides of the evaporation vessel.

The mixing of even trace amounts of neat PVA with nuclear process wastewater simulant resulted in the formation of white "fluffy cotton ball" precipitates or suspensions in solution. This led to the existence of two distinct phases. With about one percent of the neat PVA in the simulant solution a clearly white fluffy ball suspension was formed at room temperature.

The mixing of a better than 90% oxidized PVA solution with nuclear wastewater simulant, even on a one-to one basis, produced no obvious solid particles or precipitates. However, the initial colorless mixture turned orange, probably due to the oxidation of sulfur, which is present in trace amounts in the nuclear process wastewater simulant. Since excess hydrogen peroxide was present in oxidized PVA solution the mixing of oxidized PVA with nuclear wastewater simulant led to the evolution of gases. This was probably due to the decomposition of hydrogen peroxide in an alkaline environment. The mixing of oxidized PVA solution, in which excess hydrogen peroxide had been removed, with nuclear process wastewater simulant did not result in the evolution of gases and no precipitation of solid particles were observed. Therefore, before mixing of oxidized PVA

waste with other nuclear process wastewater excess H_2O_2 must be removed by adjusting the pH to alkaline conditions while sonicating.

Nuclear process wastewater simulant spiked with two or more percent completely oxidized PVA solution, when evaporated to dryness contained no PVA evaporation residue, scales or films of PVA. With drop in temperature (overnight) there were still no film or scaly evaporation products formed. Salt crystals from the simulant itself were formed during the heating and evaporation of the oxidized PVA and nuclear process wastewater simulant.

Efficiency of ion exchange–based radionuclide removal in the presence of oxidized PVA.

The sorption of radionuclides present in a nuclear process wastewater simulant as spiked ions (cesium onto CST, cesium onto TPB, and Plutonium and strontium-90 onto MST) was studied by batch technique.

The general method used for these studies is described below:

The batch distribution coefficient (K_d) is an equilibrium measure of the overall ability of a solid phase ion exchange material to remove ions of interest from solution. It represents the theoretical volume of solution that can be processed per a given mass of the ion exchanger under equilibrium conditions (Klavetter et al.). In these tests, a known quantity of the sorbent ($\approx$ 0.1 g) was placed in contact with 25 ml of the simulant in a 50-ml polyethylene bottle. All samples were prepared in duplicates. The polyethylene bottles were placed in an orbital shaker and the mixture agitated for a given period at room temperature. After this contact time, the used sorbent material was separated from

the solution by filtering through a 0.2 microns nylon filter. The decanted portion, without sorbent was submitted for metal concentration analysis. The K_d value was obtained by determining the concentration (or activity for radionuclides) of metal ions of interest before and after contact and calculating the amount of metal ions of interest on the sorbent by difference.

For radioactive samples or simulants spiked with radionuclides, K_d values were determined radiometrically by using the following equation:

$$K_d = ((A_i - A_f)/A_f)(V/m) \qquad (10)$$

Where A_i and A_f are the activities of the radionuclide in solution at the beginning and at the end of sorption respectively, V is the volume in ml of the solution used for equilibration and m is the weight of the adsorbent in grams.
The decontamination factor, D_f , is defined as initial concentration over final concentration.

The determination of changes in the batch distribution coefficient, k_d, and decontamination factor for the uptake of radionuclides in the presence of nuclear process wastewater simulant (5.6 M Na^+) spiked with 2% oxidized PVA was carried out in the following manner. A 25-mL of the selected liquid per mixing vial was spiked with 0.5 mL Cs-137 (tracer) and mixed for 5 minutes. After mixing for 1 minutes, 1.0 ml of the sample was sent for counting to get initial Cs-137 concentration. 1.0 g of CST was then added into each vial and the slurry mixed for 30 minutes and filtered through a 0.25

micron syringe filter. One milliliter of the filtrate was sent for gamma counting to obtain cesium-137 left in solution. Based on equation 10 above, the batch distribution coefficient, K_d, was determined. The K_d for nuclear process wastewater simulant (5.6 M Na^+) containing no oxidized PVA was also determined in a similar fashion.

In evaluating changes in the decontamination factor, D_f, using TPB, 25 ml of the nuclear process wastewater simulant (4.7 M Na^+) and nuclear process wastewater simulant (4.7 M Na^+) containing 2% by volume oxidized PVA solution, were spiked with 0.75 mg cold cesium and 1.0 mL of cesium-137 tracer. Initial cesium activity was in the range of 1.98 to 2.21E05 d/min-mL. 0.4 gm of sodium tetraphenyl borate (NaTPB) was added to each solution and stirred. At the end of 30 minutes, the cesium-137 activity from the filtrate for each sample was determined. Similarly, 25 mL of the solutions (nuclear process wastewater simulant (5.6 M Na^+) and nuclear process wastewater simulant containing 2% by volume oxidized PVA solution) were spiked with Sr-90. The samples were treated with flow-sheet-level monosodium titanate slurry and the solutions agitated overnight. Samples for analysis were syringe filtered before submission for analysis. The above procedure was repeated with plutonium-239 tracer. Based on equation 10, the decontamination factors for cesium-137, strontium-90 and plutonium-239 were calculated.

The results for the sorption of principal nuclear process wastewater radionuclides (Cs-137, Sr-90, Pu-239) are summarized in Table 7. There are no significant differences in the magnitudes of decontamination factors or batch distribution coefficients for the

uptake of radionuclides in the presence of oxidized PVA solution in the nuclear process wastewater simulants.

Although a measure of D_f and K_d values above indicate no effects on ion-exchange properties in the presence of oxidation products, the potential exists for the complexing of products of PVA oxidation and even hydrogen peroxide with radionuclies like plutonium and other trivalent actinides and lanthanides. The extent of complexing of each radionuclide with the oxidation products (acetates from oxidation with H_2O_2 and oxalate from oxidation with $KMnO_4$) depends on the concentration of the radionuclide and pH of the wastewater stream. At high pH conditions, depending on the oxidation states of plutonium species present in any waste stream, the potential for the formation of plutonium hydroxides increases. These hydroxides of plutonium would eventually precipitate.

Determination of changes in total organic carbon for oxidized and neat PVA..

The average total organic carbon for neat 5% PVA and 100% oxidized PVA solutions were, respectively 25,700 ± 200 mg/L and 18,900 ± 310 mg/L. This is about 26.5% less carbon in oxidized PVA. This difference in total organic carbon may be attributed to reactions leading directly to carbon dioxide gas formation.

DISCUSSION AND CONCLUSIONS

Both acidified and unacidified potassium permanganate solutions and solid permanganate crystals can be used for the complete mineralization of 5% PVA to simpler organic compounds. This oxidation of PVA with potassium permanganate is rapid, being

practically complete in a few minutes at room temperature. Acidified potassium permanganate is relatively more efficient in this oxidative mineralization of 5% PVA, because it has a higher oxidation potential (1.51 Volts) than neutral or alkaline permanganate solution (1.23 Volts). The resulting PVA waste solution from oxidation with unacidified potassium permanganate, with a pH greater than 10, may require no further pH adjustment before delivery to the nuclear process wastewater system. However, because of the potential for the formation of solids, mostly black manganese dioxide during pH adjustment in the nuclear process wastewater treatment facility, oxidation of PVA with aqueous 50 % hydrogen peroxide in the presence of UV light at 302 ηm with ultrasonic treatment is preferred.

PVA oxidation products are mainly acetic, formic and oxalic acids. These carboxylic acids, in the presence of a neutralizing base like sodium hydroxide, are converted to their corresponding salts. The pH of 100 percent-mineralized PVA solution based on hydrogen peroxide oxidation is less than 3. Hence, pH adjustment with preferably sodium hydroxide would be required to bring the pH value above 9.7. Excess hydrogen peroxide will also have to be destroyed by heating the oxidized PVA waste solution between 70-85 ^{o}C. This destruction of excess hydrogen peroxide can be successfully carried out during pH adjustment by sonicating the oxidized PVA waste matrix. Unlike the rapid kinetics observed at room temperature for 5% PVA oxidation with permanganate ion, the oxidation of PVA with hydrogen peroxide is a slower reaction at room temperature. In these PVA oxidation reactions one of the goals was to determine an adequate minimum volume of H_2O_2 that could be used to obtain a reasonable

conversion (better than 90%) of PVA to minimize the overall volume of liquids waste generated from PVA oxidation. However, because of the slower reaction rates observed in the oxidation of 5% PVA with hydrogen peroxide at room temperature, and the steady increase in reaction rates in the presence of UV and ultrasonic treatments, it was difficult to adequately address the question of minimum H_2O_2 required without further study.

However, based on information in Figures 9 and 10, for any chosen percent hydrogen peroxide used in the oxidation of 5% PVA, the corresponding reaction rate constant and time required for a better than 90% mineralization of PVA can be determined by extrapolation. The parameters obtained from these plots are only valid for oxidation at the corresponding UV wavelength at which the data were obtained with ultrasonic energy at 4.6 Watt/cm^2 and UV energy at 2,350 Watt/m^2.

The oxidation of 5% PVA in the presence of UV light at 302 ηm coupled with continuous ultrasonic treatment provided the best PVA oxidation results. AT this wavelength, based on changes of reaction rate constant and UV illumination time versus volume percent hydrogen peroxide plots, an adequate minimum H_2O_2 volume of 8.25 % has been determined to be sufficient for obtaining a better than 90 % mineralization of 5 % PVA.

Based on neutralization reactions between acidic solutions from PVA oxidation products and sodium hydroxide the amount of organo-sodium salts, which could be produced from pH adjustments of oxidized PVA solution (sodium acetate and sodium formate) have

been estimated. The estimated amount of combined sodium salts produced from pH adjustment reactions is 22.5 g per liter of mineralized 5% PVA processed.

The magnitude of the batch distribution coefficient and decontamination factors was found to be equal for nuclear process wastewater simulant solutions with and without 2% oxidized PVA. Therefore, efficiencies for cesium-137, strontium-90, and plutonium removal from the nuclear wastewater, using ion exchange sorbents (CST and MST) and precipitating agents (TPB), are not affected by the presence of oxidized PVA. The chelating or induced precipitation of the radionuclides in the presence of the carboxylic moieties from the oxidation of PVA, under alkaline conditions, is also unlikely.

However, plutonium in its lower oxidation states (Pu^{+3} and Pu^{+4}) and under low pH conditions for example, readily forms weak acetate ($Pu(C_2H_3O_2)^{2+}$) and oxalate ($Pu(C_2O_4)_2^{+}$) complexes and possibly formate complexes ($Pu(HCO_2)^{2+}$), too (Cleveland 1979). Other higher oxidation states of plutonium complex less effectively. On the other hand, any weak organic complexes, such as those formed between organic moieties and plutonium ion may be destroyed under radiolytic conditions such as those that exist in a nuclear process wastewater treatment facility. It is also worth noting that at high pH conditions, depending on the oxidation states of plutonium species present in any waste stream, the potential for the formation of plutonium hydroxides increases. These hydroxides of plutonium would eventually precipitate.

Plutonium is capable of complexing with hydrogen peroxide in acidic conditions (pH <3) to form a plutonium peroxy-complex [HO-Pu-OO-Pu-OOH]$^{4+}$]. However, H_2O_2 is destroyed by strong base; the addition of sodium hydroxide before discharge to nuclear process wastewater tanks would destroy excess H_2O_2 and any Pu-H_2O_2 complexes.

Because of the possibility for precipitating plutonium complexes from either the organic, peroxy and hydroxide complexes the design of a PVA oxidation reactor must take criticality concerns into consideration.

There are several other approaches to the oxidative degradation of PVA in the presence of hydrogen peroxide. Surface modification of transition metal oxide catalysts such as TiO_2 or doping of lanthanides (Augugliaro et al. 1990, Maurer, and Tanaka et al. 1989) and the application of photo-Fenton reaction (generation of hydroxyl radicals via photo-induced electron transfer from water to excited Fe^{3+}) (Bauer et al. 1997, Kiwi et al. 1994, Wei et al 1990 and Walling 1975), to name a few, are also available. However, these other organic degradation enhancement techniques may not be compatible with the nuclear process wastewater treatment facilities. For example, these techniques require the introduction of solid catalyst materials into the waste stream. Above all, these catalyst-based enhancement techniques seem to perform well only with solutions containing lower ppb (ug/L) to low ppm (mg/L) levels of organic compounds. In addition, solid catalysts in ppb levels may introduce unwanted side reactions under high alkaline conditions in the nuclear process wastewater facility.

Since the pH of the final PVA waste solution will be adjusted to alkaline conditions the potential for the formation of explosive organo-nitrates in the nuclear process wastewater storage tanks would be eliminated.

Waste solutions containing better than 90% mineralized PVA, when mixed with nuclear process wastewater, are not expected to adversely affect the rheological (pumpability, PVA film formation, coagulation and precipitation of solid PVA) and evaporation (film formation) properties of the nuclear process wastewater.

The viscosity of a completely mineralized 5% PVA solution is about 1.0 centiPoise as opposed to 32 centiPoise for neat unadulterated 5% PVA solution (Maurer). The density of oxidized PVA is 0.99 g/cc and that of neat 5% PVA solution is 1.05 g/cc. The pH of a freshly prepared 5% PVA solution is approximately 7, although with time, the pH drops to less than 7.

No radiolysis or hydrogen generation experiments were carried out with oxidized PVA solutions in the nuclear process wastewater simulants to evaluate the long or short-term effects of radiation on the stability of oxidized PVA products (Acetate and formate anions from PVA oxidation with H_2O_2 and oxalates anion from permanganate oxidation). However, based on aqueous radiolytic chemistry the introduction of oxidized PVA solution into a nuclear process wastewater system will not increase the production of flammable gases during storage and processing. Radiolysis of acetate, formate and oxalate anions will produce oxides of carbon, H_2O_2 and hydrogen as stable radiolytic

products. Since the oxidation of PVA will be carried out in an open oxygen-rich environment, methane formation is highly unlikely. The primary reducing species in the radiolytic decomposition of water and the anions from PVA oxidation (formate, acetate and oxalate) are aqueous electrons and hydroxyl radicals. In an oxygen-rich environment, aqueous electron will more often react to produce oxygen –based radicals instead of hydrogen radicals that are precursors for hydrogen production.

Assuming no nitrate and nitrite inhibitor effects on hydrogen production due to α and β/γ radiolysis, the g-value (number of hydrogen molecules per 100 eV absorbed) for hydrogen generation from radiolysis of water is equal in magnitude (0.45 forβ/γ radiolysis) to the g-values for hydrogen generation from the radiolysis of formate and oxalate anions in oxygenated solutions (Draganic et al. 1971 and Draganic and Gal 1971). In comparison, the average carbon dioxide and hydrogen peroxide g-values from radiolysis of oxalate ion (g-[CO_2] and g-[H_2O_2]) are, respectively, 5.5 and 3.9 (Draganic et al. 1971). Hence, the main stable products of radiolytic decomposition of these PVA oxidation products are mostly carbon dioxide and hydrogen peroxide. The hydrogen g-value from the radiolysis of the acetate anion in an alkaline condition is not well documented in literature, but based on the number of hydrogen atoms per mole of the acetate anion in comparison with water, the g-value could only be 0.68 at most. Even in a worst case scenario, if one assumes purely α-radiolytic activities the hydrogen generation value from the decomposition of acetate anion could not exceed 1.3 hydrogen molecules per 100 electron volts absorbed by the acetate anion (22). Therefore, the hydrogen generating g-value from each PVA oxidation product is within the range of

values for water due to both β/γ and α radiolysis [0.45 for β/γ radiolysis and 1.5 for α radiolysis.

Thus, it can be concluded that the addition of oxidized PVA solutions into a nuclear process wastewater system does not increase the production of flammable compounds during storage and processing.

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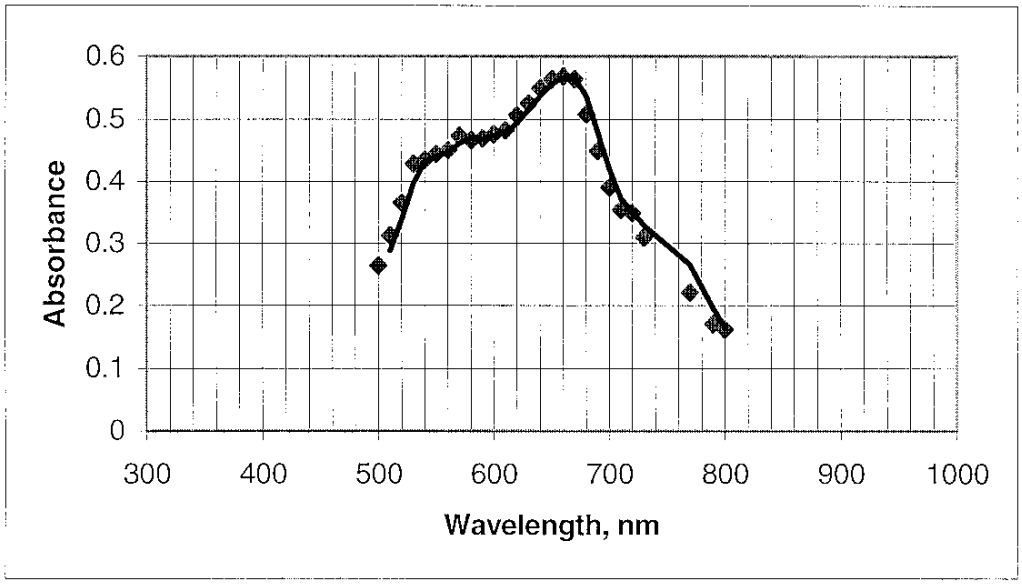

Figure 1. Absorption profile for PVA/Iodine?boric acid complex. λ-max. is 670 ηm.

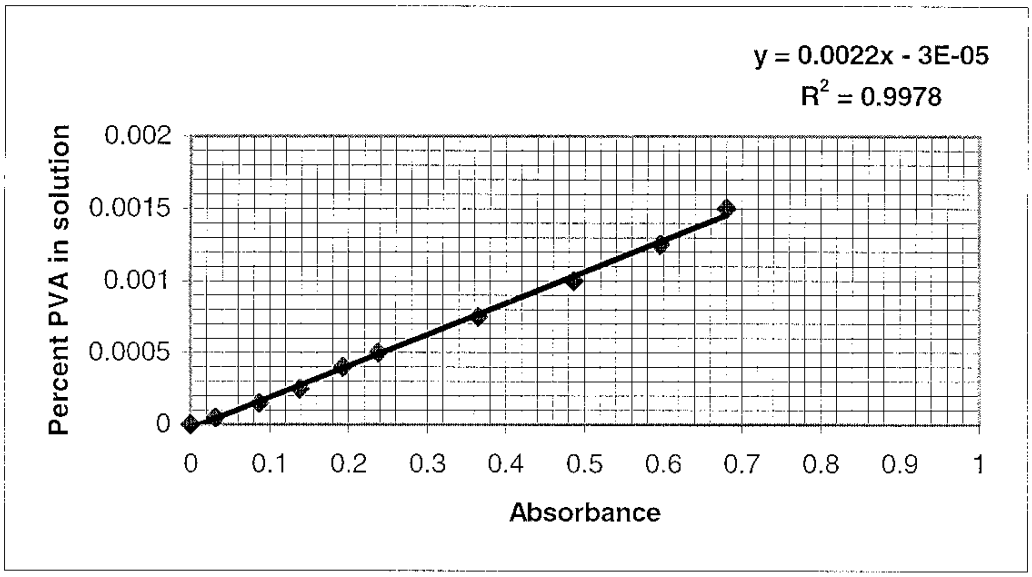

Figure 2. PVA calibration curve based on Iodine/boric acid/PVA complex absorbance at 670 ηm.

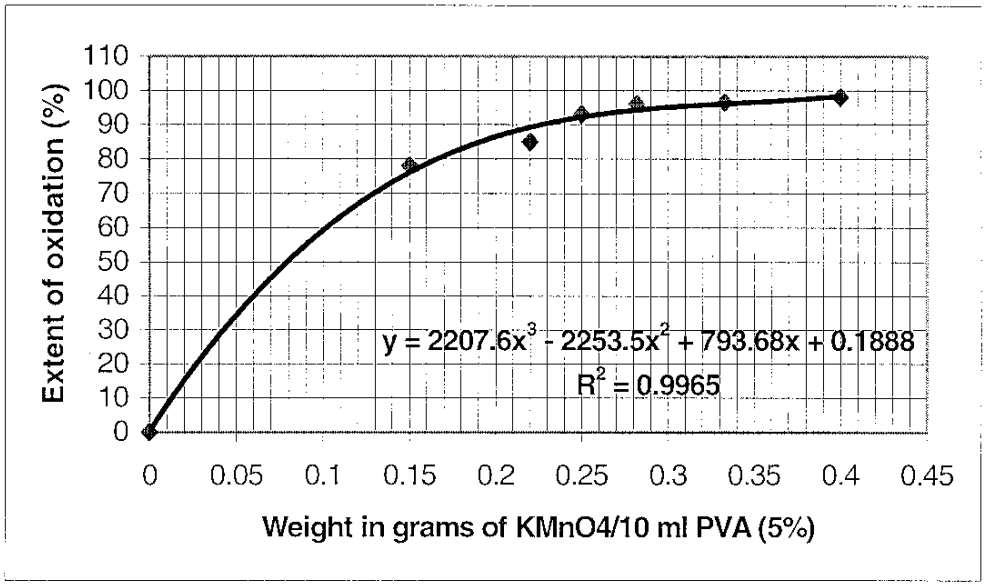

Figure 3. PVA oxidation with solid potassium permanganate crystals. About 24 grams of $KMnO_4$ crystals are required per liter of 5% PVA in order to obtain a better than 90% oxidation of PVA.

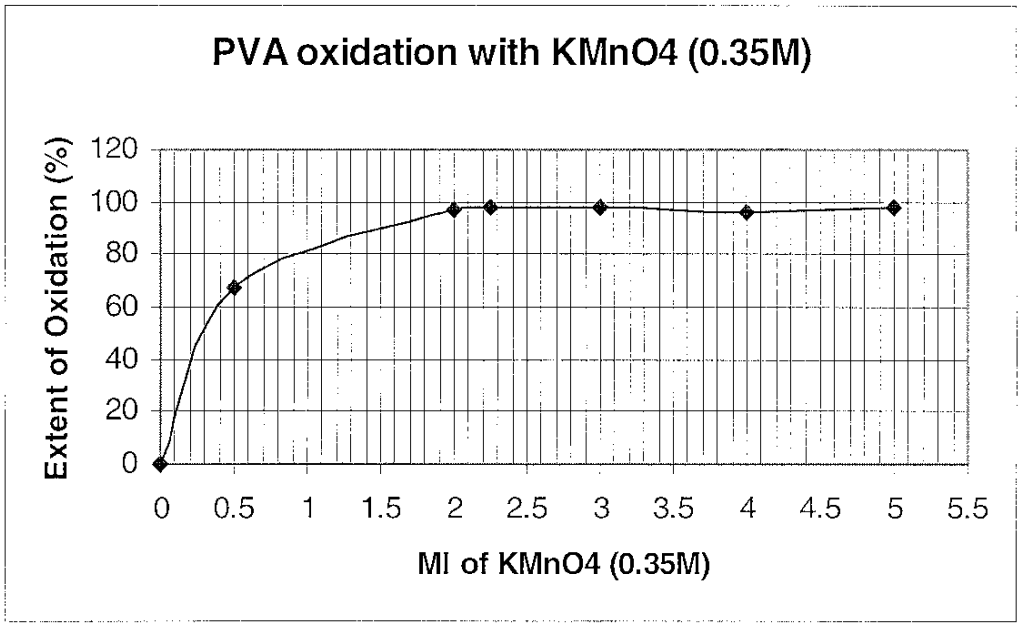

Figure 4. Oxidation of 5% PVA solution with 0.35 M solution of $KMnO_4$.

Approximately 2 mL of acidified $KMnO_4$ (0.35 M) per 10 mL of PVA (5%) is required to obtain a better than 97% oxidation of PVA (5%).

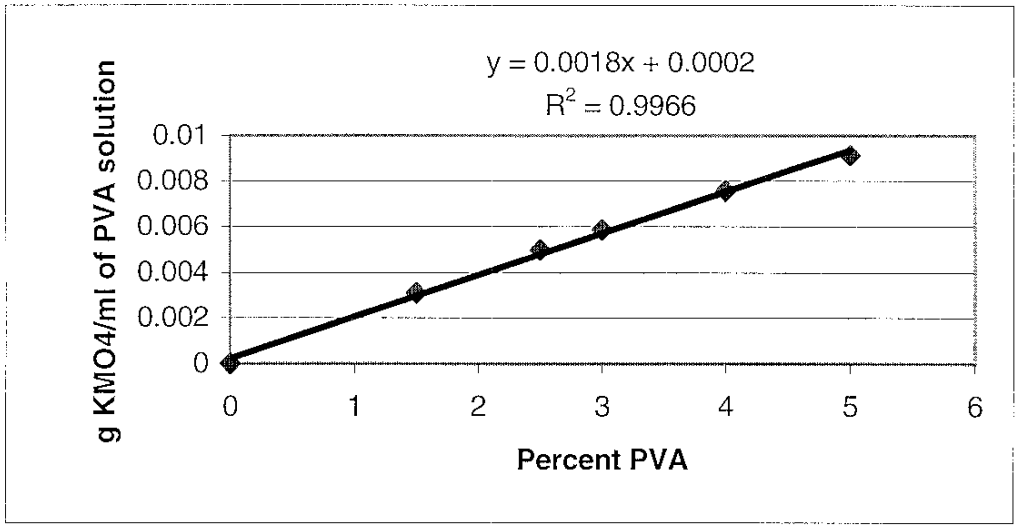

Figure 5. Plot of percent PVA versus gram of $KMnO_4$ per mL of acidified PVA.

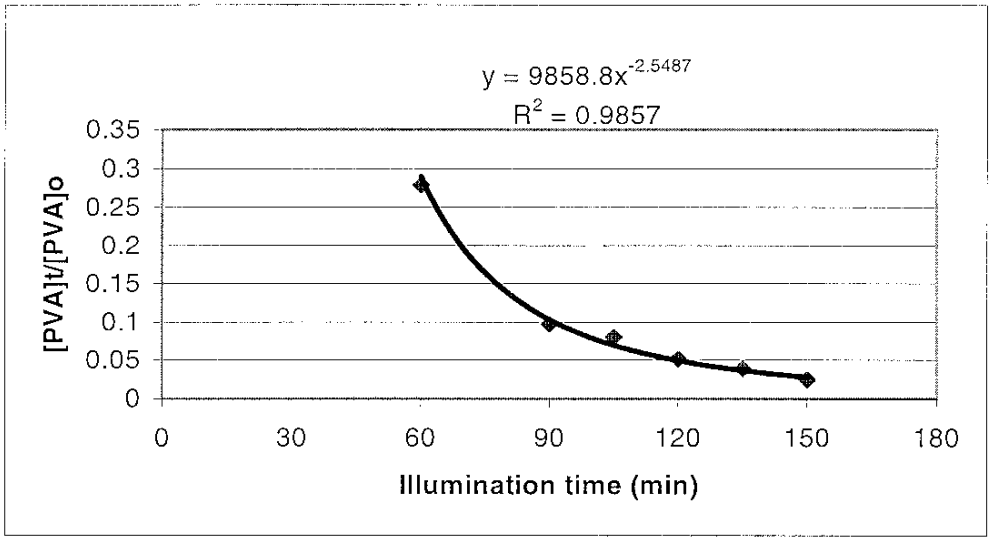

Figure 6. A typical decay curve for PVA oxidation with H_2O_2/UV at 366 ηm with ultrasonic treatment.

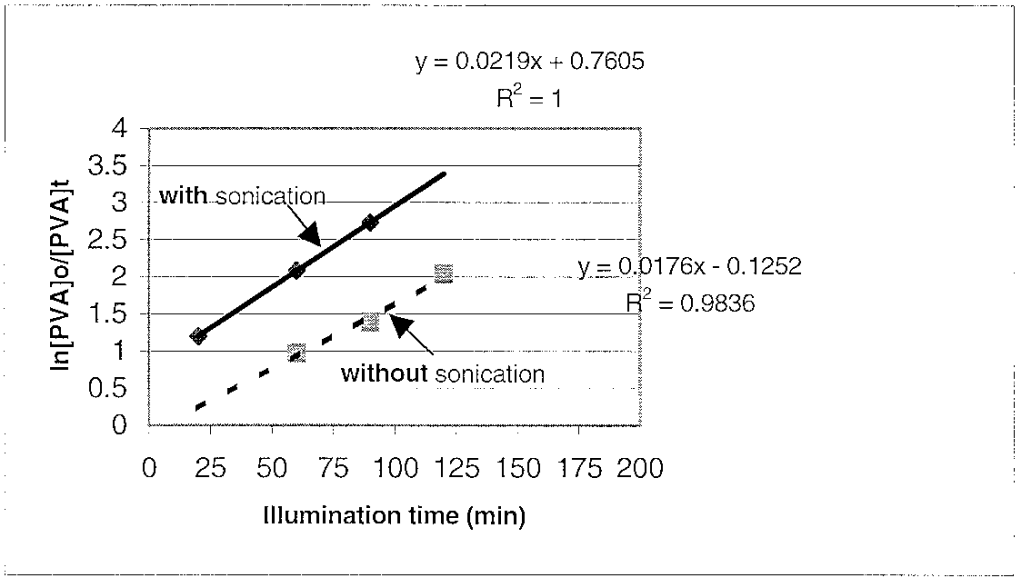

Figure 7. Plots per equation 6 for oxidation with and without ultrasonic treatment wit UV light at 366 ηm. Sonictaed samples have higher reaction rates constant values.

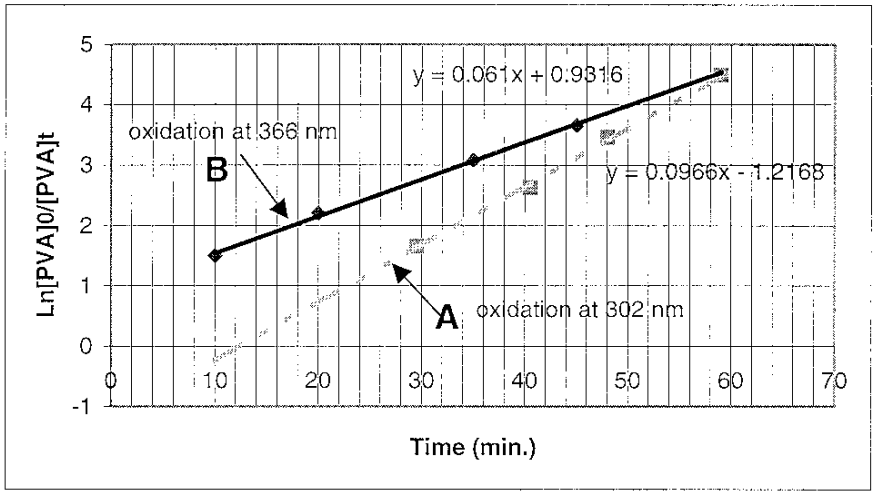

Figure 8. A typical PVA oxidation profile per equation 6 for oxidation at 302 and 366 ηm and with ultrasonic treatment. Overlays A and B are, respectively, oxidation profile plots for 302 and 366 ηm.

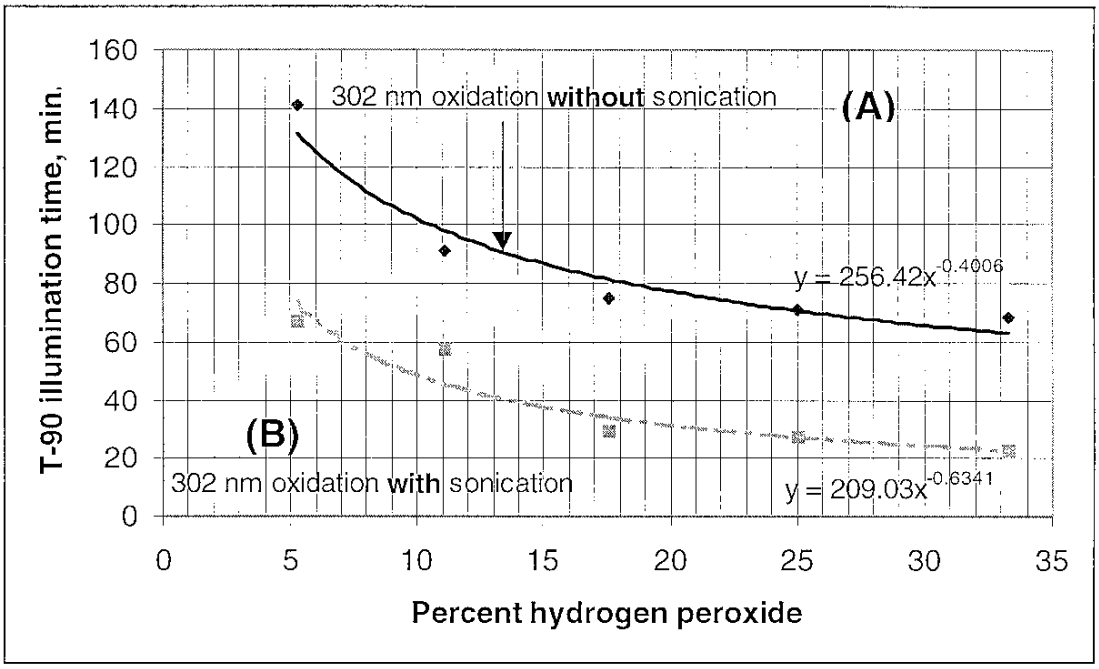

Figure 9. Variation of illumination time (T-90) with percent hydrogen peroxide at 302 ηm. Overlay plot (A) and (B) are, respectively, T-90 for oxidation at 302 ηm without ultrasonic treatment and 302 ηm with ultrasonic treatment on H_2O_2/PVA reaction mixtures.

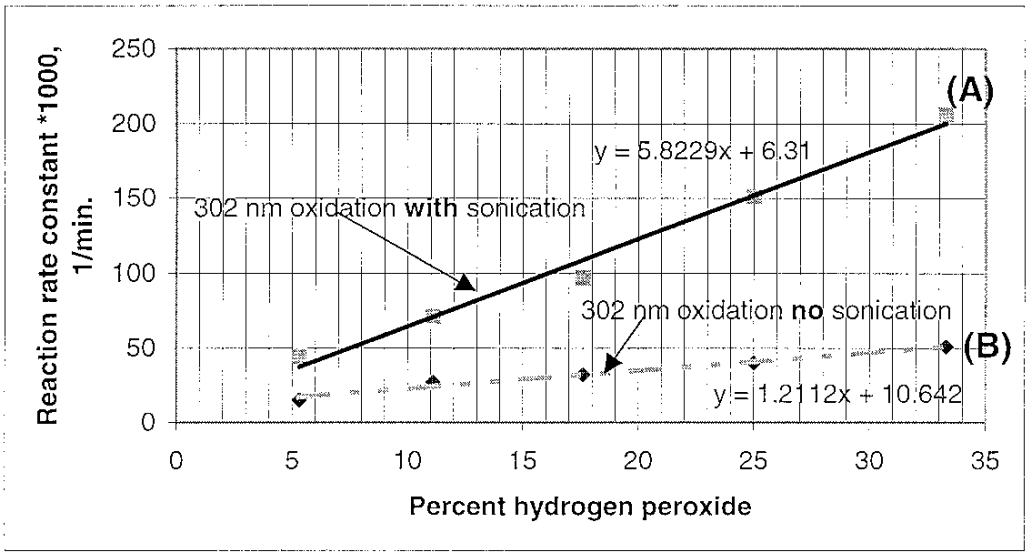

Figure 10. Changes in reaction rate constant with percent hydrogen peroxide used in oxidative mineralization of 5% polyvinyl alcohol solution at 302 ηm with (plot (A)) and without (plot (B)) ultrasonic treatment of H_2O_2/PVA reaction mixtures.

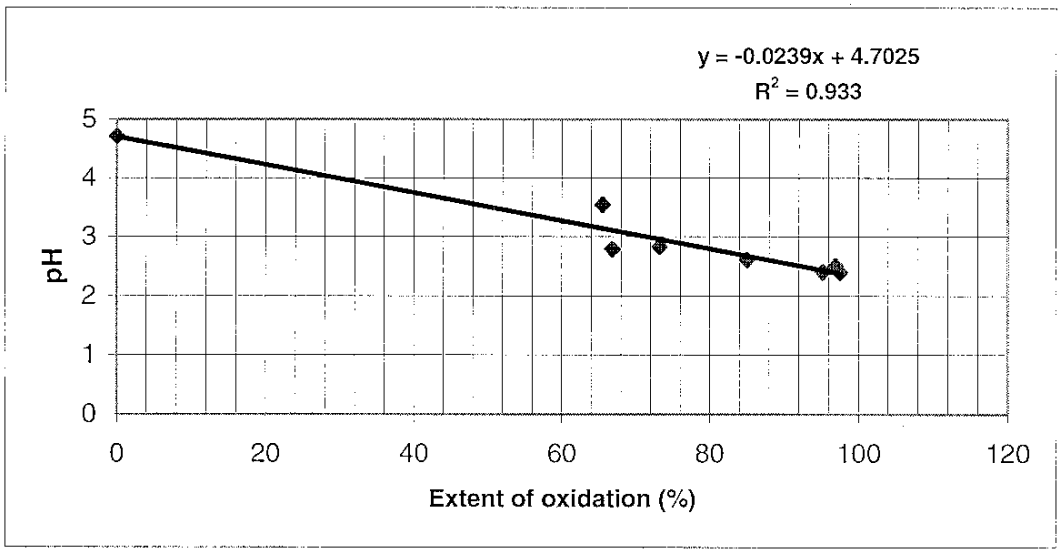

Figure 11. pH changes with extent of oxidation for PVA oxidation at 302 ηm with ultrasonic treatment.

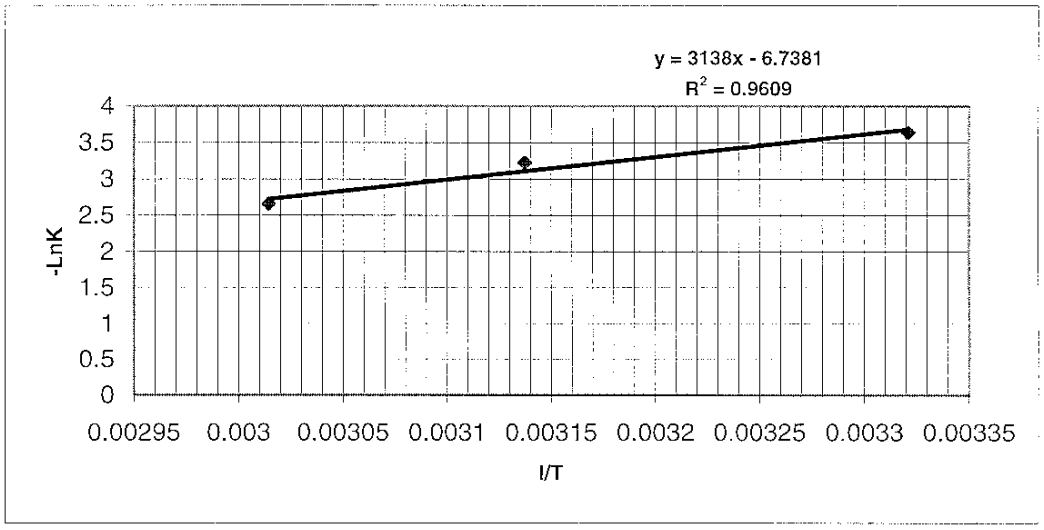

Figure 12. Activation energy plot for PVA oxidation with H_2O_2/UV at 302 ηm with ultrasonic treatment.

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Figure 9. Variation of illumination time (T-90) with percent hydrogen peroxide at 302 ηm. Overlay plot (A) and (B) are, respectively, T-90 for oxidation at 302 ηm without ultrasonic treatment and 302 ηm with ultrasonic treatment on H_2O_2/PVA reaction mixtures.

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Figure 11. pH changes with extent of oxidation for PVA oxidation at 302 ηm with ultrasonic treatment.

Figure 12. Activation energy plot for PVA oxidation with H_2O_2/UV at 302 ηm with ultrasonic treatment.

Standard #	mL of intermediate stock per 100 mL	%PVA in standard	Average absorbance
0	0.0 (iodine and boric acid in water)	0	0.0
1	1.0	0.00005	0.032 ±0.006
2	3	0.00015	0.087 ± 0.010
3	5	0.00025	0.138 ±0.006
4	8	0.00040	0.193 ±0.010
5	10	0.00050	0.238 ±0.014
6	15	0.00075	0.365 ±0.008
7	20	0.00100	0.486 ±0.012
8	25	0.00125	0.596 ±0.010
9	30	0.00150	0.680 ±0.007

Table 1. Typical set of calibration standards with absorbance values at λ max.

Initial [PVA], %	$KMnO_{4\ (0.35M)}$ Volume required for >97 % oxidation of PVA, mL	Extent of oxidation obtained experimen-tally (%)	$KMnO_4$ per mL of PVA solution (g)
5	2.0	97.6	0.0092
4	1.6	97.8	0.0073
3	1.2	97.4	0.0059
2.5	1.0	96.8	0.0050
1.5	0.6	95.7	0.0031

Table 2. Summary of oxidation data for PVA oxidation with acidified $KMnO_4$
Extent of PVA oxidation is about 97%.

	Without Sonication				With sonication			
%H_2O_2	Rate*1000 ($min.^{-1}$)	2σ	T-90 (min.)	2σ	Rate*1000 (min^{-1})	2σ	T-90 (min.)	2σ
33.3					58	0.6	15	0.3
25								
20					33	1.1	30	0.7
17.6	11	1.7	233	4.4	21	0.5	60	1.2
12.5					18	2.2	120	0.9
11.1								
10								
5.3					3	0.2	300	1.6

Table 3. Summary of PVA oxidation data with H_2O_2 and UV at 366 ηm.

	Without Sonication				With sonication			
%H_2O_2	Rate*1000 ($min.^{-1}$)	2σ	T-90 (min.)	2σ	Rate*1000 (min^{-1})	2σ	T-90 (min.)	2σ
33.3	51	1	68	0.9	206	4	23	0.2
25	40	0.6	71	1.4	151	1.3	27	0.5
20								
17.6	32	0.6	75	1.1	97	2	29	0.3
12.5								
11.1	27	0.3	91	1.8	71	1.4	57	1.2
10								
5.3	15	0.4	141	2.8	44	0.9	67	0.9

Table 4. Summary for PVA oxidation data with H_2O_2 and UV at 302 ηm

I/T (Kelvin)	Degrees centigrade	Rate constant, K (1/min.)	-Ln K
0.003321	28	0.0263	3.63818
0.0031373	45.6	0.04	3.21887
0.0030143	58.6	0.0704	2.65356

Table 5. Summary of activation energy data for PVA oxidation at 302 ηm with ultrasonic treatment.

Target ion /precursor	Average molar concentration
Na^+ (from all sodium precursors)	5.6
Cs^+ / $CsNO_3$	0.00014
K^+ / KOH	0.015
OH^- / NaOH, KOH	1.191
NO_3^- / $NaNO_3$	2.140
NO_2^- /$NaNO_2$	0.52
AlO_2^- /$NaAlO_2$	0.31
CO_3^{-2} /Na_2CO_3	0.16
SO_4^{-2} /Na_2SO_4	0.15
Cl^- /NaCl	0.025
F^- /NaF	0.032
PO_4^{-3} /$Na_2PO_4.12H_2O$	0.01
$C_2O_4^{-2}$ /$Na_2C_2O_4$	0.008
SiO_3^{-2} /$Na_2SiO_3.9H_2O$	0.004
MoO_4^{-2} /Na_2MoO_4	0.0002

Table 6. Average inorganic composition for a typical nuclear process wastewater simulant.

Radionuclide /sorbent	K_d or D_f in 4.7 M Na^+ simulant	K_d or D_f in 2% PVA spiked simulant.	K_d or D_f in 5.6 M Na^+.Simulant,
Cs-137/CST	2366, K_d	2354 (5.6 M Na^+), K_d	1619, K_d
Cs-137/TPB	282 (D_f)	302 (D_f) (4.7 M Na^+)	249 (D_f)
Sr-90/MST	20 (D_f)	19 (5.6 M Na^+) (D_f)	Not applicable
Pu-MST	>30 (D_f)	23 (5.6 M Na^+) (D_f)	21 (D_f)

Table 7. Batch distribution coefficients and decontamination factors for removal of target radionuclides from nuclear process wastewater simulant.

Table 1. Typical set of calibration standards with absorbance values at λ max.

Table 2. Summary of oxidation data for PVA oxidation with acidified $KMnO_4$ Extent of PVA oxidation is about 97%.

Table 3. Summary of PVA oxidation data with H_2O_2 and UV at 366 ηm.

Table 4. Summary for PVA oxidation data with H_2O_2 and UV at 302 ηm

Table 5. Summary of activation energy data for PVA oxidation at 302 ηm with ultrasonic treatment.

Table 6. Average inorganic composition for a typical nuclear process wastewater simulant.

Table 7. Batch distribution coefficients and decontamination factors for removal of target radionuclides from nuclear process wastewater simulant.