Fructose as a novel photosensitizer: Characterization of reactive oxygen species and an application in degradation of diuron and chlorpyrifos

Shaila Nayaka, Juan Muniz, Christopher M. Sales, Rohan V. Tikekar

*Corresponding author. Department of Nutrition and Food Science, 112 Skinner Building, College Park, MD 20742, USA. E-mail address: rtikekar@umd.edu (R.V. Tikekar).

**Highlights**
- Fructose underwent photolysis upon exposure to 254 nm UV light.
- Photolysis products include hydrogen peroxide, singlet oxygen and hydroxyl radicals.
- Fructose accelerated UV induced photocatalytic degradation of diuron and chlorpyrifos.
- Fructose is an attractive photosensitizer for decontamination of wastewater.

**Abstract**

The objective of this study was to identify reactive oxygen species (ROS) generated from the exposure of fructose solution to the 254 nm ultraviolet (UV) light and evaluate whether fructose can be used as a photosensitizer for accelerated photo-degradation of diuron and chlorpyrifos. We demonstrated that hydrogen peroxide, singlet oxygen ($^{1}O_2$) and acidic photolysis products were generated upon UV exposure of fructose. Consistent with these findings, UV induced degradation of chlorpyrifos and diuron was accelerated by the presence of 500 mM fructose. The average first order photo-degradation rate constants in the absence and presence of 500 mM fructose were 0.92 and 2.07 min$^{-1}$ respectively for diuron and 0.04 and 0.07 min$^{-1}$ for chlorpyrifos. The quantum yields ($\phi$) for direct photo-degradation of diuron and chlorpyrifos were 0.003 and 0.001 respectively. In the presence of 500 mM fructose, these values increased to 0.006 and 0.002 respectively. Thus, fructose may be an effective photosensitizer.

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1. Introduction

Fructose has shown significant reactivity upon exposure to 254 nm UV light. A previous study reported that UV (254 nm) exposure of fructose present in fruit juices results in the formation of furan (Bule et al., 2010). In previous studies, we demonstrated that fructose accelerates the degradation rates of patulin and...
ascorbic acid during UV treatment of apple juice (Tikekar et al., 2012, 2011). One study showed that pH of fructose solution decreased by 5.29% upon exposure to high intensity pulsed UV light. The lowering of pH was attributed to products formed due to photolysis of fructose when exposed to UV light at 254 nm. However, these products were not characterized (Orlowska et al., 2013). In another study, by identifying the stable degradation products from the photolysis of fructose, it was hypothesized that the open chain form of fructose (0.8% of total fructose in aqueous solution) undergoes photolysis when irradiated with 254 nm UV light resulting in generation of primary species such as hydroxalkyl, and hydroxalkyl acyl radicals. These species, upon interaction with oxygen were hypothesized to form secondary species such as, hydroxyl, peroxy, superoxide radicals and hydrogen peroxide (Triantaphylides et al., 1982). However, formation of only hydrogen peroxide was experimentally determined and the kinetics of its formation were not elucidated. In congruence with the above findings, we previously demonstrated that UV exposure of fructose generates miscellaneous reactive oxygen species (ROS), although we did not characterize the chemical nature of these species (Elsinghorst and Tikekar, 2014). Thus, although the reactivity of fructose in 254 nm UV light is known, scarce information is available on the formation of reactive oxidative intermediates such as free radicals upon exposure of fructose to UV light. The one study that investigated the photolysis of fructose upon exposure to UV light only hypothesized the formation of these reactive intermediates by identifying the degradation products. To address this need, the present study gives direct evidence for formation of some of these oxidative species and characterizes the kinetics of their formation using complimentary techniques. We also aimed to evaluate whether the ability of fructose to generate ROS upon exposure to UV light can be harnessed to accelerate photo-degradation of recalcitrant organic compounds. To that end, we investigated photo-degradation of an insecticide (chlorpyrifos) and an herbicide (diuron) using fructose. To the best of our knowledge, this is the first study that has reported the ability of fructose to act as a photosensitizer to accelerate the photo-degradation of xenobiotic compounds.

Chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl)phosphorothionate], an organophosphate insecticide and diuron [N’-(3,4-dichlorophenyl)-N,N-dimethylurea] a polyurea herbicide, are declared as emerging contaminants by the US-EPA (Richardson, 2007). Chlorpyrifos inhibits cholinesterase, an enzyme responsible for normal functioning of the nervous system both in insects and humans (Simon et al., 1998). The herbicide, diuron, exhibits its sensitivity to oxidation from diverse oxidative species including hydroxyl and peroxy radicals (Ou et al., 2002, 2001). Test solutions consisted of 1 mM fluorescein prepared in either distilled water or 100 mM phosphate buffer of pH 6.7. Fructose was added to each of these solutions at the concentrations of 10, 100 and 500 mM. Treatments were carried out by exposing 10 mL of each solution to UV light for up to 10 min. To ensure the uniformity of treatment within each sample, the solutions were stirred throughout the experiment. A 200 μL of the sample was obtained periodically and the fluorescence from fluorescein was measured using a Gemini XPS fluorescence micro-plate reader ( Molecular Devices, Sunnyvale, CA). The excitation and emission wavelengths were set at 485 nm and 510 nm respectively. Fluorescence data was fitted into the first order kinetics.

2.4. Detection of hydrogen peroxide

The concentration of hydrogen peroxide generated from UV exposure of fructose was measured using the ferrous oxidation-xylene orange (FOX) method. The principle of this method involves oxidation of ferrous ions by hydrogen peroxide to ferric ions. Ferric ions under acidic conditions form a complex with xylene orange which can be measured through spectrophotometry (Bou et al., 2008). The assay solution consisted of 2 mM xylene orange, 2.5 mM ferrous sulfate, 1 M sorbitol and 250 mM sulfuric acid. A 100 μL of this assay solution was immediately added to the 700 μL of test sample consisting of UV exposed 500 mM fructose prepared in distilled water or phosphate buffer. This mixture was incubated at room temperature for 30 min with continuous gentle shaking. After incubation, absorbance was measured at 560 nm with a UV–Vis Spectrophotometer ( Molecular Devices, Sunnyvale, CA).

2.5. Detection and quantification of singlet oxygen (1O2)

Singlet oxygen (1O2) produced during UV treatment of fructose solution was detected using Singlet oxygen sensor green (SOSG). SOSG can react with 1O2 to produce SOSG endoperoxides (SOSG-EP) that emit strong green fluorescence at 531 nm (Lin et al., 2013). A 5 mM SOSG stock solution was prepared in methanol. Test solution consisted of 500 mM fructose sample, prepared in phosphate buffer of pH 6.7 and mixed with 5 μM SOSG added from stock solution immediately before use. This solution was exposed to UV light at 254 nm. Fluorescence was measured at an interval of 1 min of UV exposure with excitation and emission wavelengths of 504 and 525 nm respectively. Furfuryl alcohol (FFA) degradation assay was
used for quantitative measurement of $^1$O$_2$ generated by UV exposure of fructose. A 40 μM FFA solution was prepared with a potassium phosphate buffer (pH 6.7). Test mixtures with fructose concentrations of 0 mM, 300 mM, 500 mM, and 1000 mM were prepared with the 40 μM FFA buffered solution. In addition, 125 mM of titanium was used as a positive control dissolved in same buffered solution. These mixtures were exposed to UV light with wavelength of 254 nm for 10 min. One-milliliter samples were taken at one-minute intervals in order to measure the concentration of FFA (Chinnici et al., 2003). FFA concentration was measured with a Shimadzu Prominence HPLC, using a C18 column of 5 μm thickness and dimensions of 45 mm length × 4.6 mm ID (Shimadzu, Columbia, MD), via UV−Vis at 215 nm. The isocratic mobile phase flow rate was 0.6 mL/min and was composed of 84% 0.10 N Phosphoric acid and 16% acetonitrile. The column oven and UV−Vis detector temperatures were set to 33 °C.

2.6. Photochemical degradation of diuron

A stock solution of diuron (1000 mg/L) was prepared in acetonitrile. The treatment solution consisted of 25 mg/L of diuron in de-ionized water incorporated with 0–500 mM fructose. Experiments were performed by exposing 15 mL of this solution in a petri dish to UV light for up to 4 min. Diuron concentration was measured using reverse phase high pressure liquid chromatography (Bioanalytical systems, In.In, USA). The mobile phase consisted of 70% acetonitrile and 30% 100 μM sodium phosphate buffer at pH of 3.5. The flow was isocratic and the rate was maintained at 1 mL/min throughout the analysis. Separation was carried out by a C18 column of 5 μm thickness and dimensions of 45 mm length × 4.6 mm ID (Shimadzu Inc., MD, USA). Diuron was detected by SPD-20A Prominence UV/Vis detector at 254 nm. The retention time for diuron with the above HPLC settings was 1.2 min. Data was fitted into the first order kinetics equation and rate constants were calculated.

2.7. Photochemical degradation of chlorpyrifos

Stock solution of chlorpyrifos (1000 mg/L) was prepared in acetonitrile and stored at 4 °C. Working solution of chlorpyrifos was prepared by diluting the stock solution with de-ionized water to a concentration of 2 mg/L. To this, 0–500 mM of fructose was added. Experiments were performed by exposing 15 mL of this final solution in a petri dish to UV light for up to 20 min. Samples were taken periodically and chlorpyrifos concentration was measured using the following method previously developed in our laboratory. Chlorpyrifos was extracted from the treatment solution by liquid−liquid extraction using iso-octane as the extracting solvent in a 1:1 ratio. Aqueous and organic phases were mixed gently for 15 min. The samples were then centrifuged at 5712 rcf for 5 min. Chlorpyrifos concentration in the iso-octane phase was measured using a gas chromatograph (5890 Series II GC, Hewlett−Packard) with a DB-5MS column (30 m length, 0.25 mm internal diameter, 0.25 μm film) (Agilent technologies, Delaware, USA). The carrier phase consisted of helium (1 mL/min) with hydrogen (12.1 mL/min) and air (10.3 mL/min). Injection temperature was 225 °C, the initial column temperature was set at 150 °C for 2 min, then increased to 200 °C at a rate of 15 °C/minute. A pulsed flame photometric detector set at 250 °C was used for detection. Retention time for chlorpyrifos was 12.28 min.

2.8. Data analysis

Statistical analysis was performed using software STATA 11 (StataCorp, Inc., TX). Two-tailed t-test was used to determine statistical significance between the samples.

3. Results and discussion

3.1. Generation of ROS from UV exposure of fructose

Fig. 1a shows the absorbance spectrum of 10% fructose solution. The absorbance of fructose solution was low at 254 nm (~0.08) and showed a peak at 278 nm that corresponds to the forbidden n to π* transition of electrons (Triantaphylides et al., 1982). Fig. 2a shows the loss of fluorescence of fluorescein in solutions containing various amounts of fructose prepared in distilled water and
fluorescence properties, the same experiment was repeated in 100 mM phosphate buffer as well (Fig. 2b). Similar to the treatment in distilled water, fluorescence decreased significantly when fluorescein solution prepared in 100 mM phosphate buffer was exposed to UV light in the presence of fructose. The reaction followed first order kinetics ($r^2 > 0.85$) and the average rate constants for 10, 100 and 500 mM fructose were $0.04 \pm 0.01, 0.19 \pm 0.05, 0.54 \pm 0.31$ min$^{-1}$ respectively. A statistical comparison of the two systems revealed that the rate constants were significantly lower in solutions prepared in 100 mM phosphate buffer versus those prepared in distilled water ($p < 0.05$). The results of this experiment suggest that ROS generated from UV exposure of fructose and some of the photolysis products of fructose were acidic in nature. The quantum yield for degradation of fructose by UV light was calculated based on the amount of UV energy incident ($\phi_{\text{incident}}$) as well as the amount of UV energy absorbed ($\phi_{\text{abs}}$) by the fructose solution. The calculations are given in the supplementary information section. These values were $6.9 \times 10^{-3}$ and 0.27 respectively. A large difference between the two values was a result of a very low absorbance of fructose at 254 nm. This is expected, since only a small amount of fructose that is present in the open chain configuration (0.8% of total sugar) is expected to absorb the 254 nm UV light (Triantaphylides et al., 1982). Based on a relatively large value of $\phi_{\text{abs}}$, it is evident that the fraction of photons that are absorbed are efficiently utilized to degrade fructose molecules (potentially the ones that are present in the open chain configuration) and produce ROS.

Due to the low specificity of fluorescein, this probe did not provide an understanding of chemical identity of the ROS. Therefore, experiments were performed to identify specific ROS. Based on the available literature, we hypothesized that hydrogen peroxide and singlet oxygen were likely to generate from photolysis of fructose.

### 3.2. Generation of hydrogen peroxide in UV treated fructose solution

Fig. 3 shows the concentration of hydrogen peroxide generated by UV treatment of 500 mM fructose prepared in distilled water, or phosphate buffer of pH 4.5 and 6.7. Hydrogen peroxide was not detected in the control (distilled water, buffer solutions of pH 4.5 and 6.7) exposed to UV light. However, it was detected in UV exposed fructose solution prepared in distilled water and buffers. In exposed to UV light. In the absence of fructose, the relative fluorescence upon exposure to UV light remained close to 100% for up to 10 min. In the presence of fructose, the UV exposure of fluorescein resulted in a gradual decrease of fluorescence, indicating generation of ROS. The loss of fluorescence as a function of UV exposure followed first order kinetics ($r^2 > 0.9$) and the average rate constants of fluorescein degradation in the presence of 10, 100, and 500 mM fructose in distilled water were $0.07 \pm 0.0, 0.60 \pm 0.14,$ and $1.46 \pm 0.18$ min$^{-1}$ respectively. The rate of fluorescence quenching increased with concentration of fructose ($p < 0.05$). Interestingly, the pH of the 500 mM fructose solution decreased substantially, from $5.79 \pm 0.01$ to $3.53 \pm 0.25$ after 10 min of UV exposure. Similarly, 100 and 10 mM fructose solutions also showed a decrease in pH from $5.89 \pm 0.01$ to $3.84 \pm 0.034$ and $5.90 \pm 0.02$ to $5.64 \pm 0.087$ respectively. Thus, the pH change was concentration dependent with the highest decrease observed in 500 mM fructose solution. A decrease in pH indicates that UV exposure of fructose resulted in the generation of acidic species. These results are consistent with the study by Triantaphylides and others, who also showed formation of acidic species such as formic acid, glycolic acid, D-erythronic acid and D-arabinonic acid during photolysis of fructose (Triantaphylides et al., 1982).

The fluorescence of fluorescein in aqueous solutions is pH dependent and its quantum yield decreases substantially with a decrease in pH (Klonis and Sawyer, 1996). Thus, the observed loss of fluorescence was due to a combination of ROS generation and change in pH. In order to determine the effect of ROS alone on
all the samples, a rapid increase in concentration of hydrogen peroxide was observed in the first minute of exposure, followed by a more gradual increase in concentration for the next 4 min. After 5 min, the hydrogen peroxide concentrations stabilized and did not change significantly ($p < 0.05$). The average concentrations of hydrogen peroxide produced in 500 mM fructose solution in distilled water (initial pH 5.8) and buffers of pH 4.5 and 6.7 at the end of 7 min of UV exposure were $63.7 \pm 1.11$, $52.91 \pm 1.07$ and $67.08 \pm 1.08$ $\mu$M respectively. The stabilization of hydrogen peroxide concentration can be explained by the fact that hydrogen peroxide undergoes photolysis under UV light to produce two hydroxyl radicals per photon absorbed at 254 nm (Maillard et al., 1992). Thus, generation of hydrogen peroxide is accompanied by its photolysis, and the stable concentration observed after extended UV exposure was possibly the steady-state concentration reached after equilibration between the rate of formation and the rate of decomposition of hydrogen peroxide.

3.3. Generation of singlet oxygen in UV treated fructose solution

Singlet oxygen sensor green (SOSG) is a highly selective sensor for detecting singlet oxygen ($^1$O$_2$). It does not show any appreciable response to hydroxyl or superoxide radicals. In the presence of $^1$O$_2$, it shows green fluorescence due to formation of SOSG-endoperoxide (Lin et al., 2013). SOSG has been successfully used to detect singlet oxygen in diverse systems (Lin et al., 2013; Maisch et al., 2007).

Formation of singlet oxygen in UV exposed fructose was depicted by an increase in solution fluorescence from SOSG-EP (Fig. 4a). The relative fluorescence increased in control (phosphate buffer) as well as treatment (500 mM fructose) solutions indicating that $^1$O$_2$ was generated in both the samples. Production of $^1$O$_2$ in UV-treated SOSG solutions in the absence of photosensitizers has been reported previously (Rágas et al., 2009; Lin et al., 2013). Nevertheless, based on the comparison of increase in relative fluorescence values, a significantly higher amount of $^1$O$_2$ was generated in the treatment sample compared to control ($p < 0.05$). In an experiment to validate that the increase in fluorescence was not due to an interaction between SOSG and hydrogen peroxide or hydroxyl radicals, SOSG was incubated with 50 mM H$_2$O$_2$ or a mixture of 5 $\mu$M ferrous sulfate and 50 $\mu$M H$_2$O$_2$ respectively and fluorescence was measured immediately. There was no significant difference ($p > 0.05$) in the fluorescence intensity of the three solutions (Fig. S1), indicating that the change in fluorescence was not due to the interaction of the dye with either hydrogen peroxide or hydroxyl radicals. However, interestingly, the relative fluorescence began to decrease in fructose solution after one minute of UV exposure and continued to decrease for the duration of the experiment. On the contrary, the fluorescence of control solution continued to increase in control samples through the duration of the experiment. We hypothesized that it may be due to reduction of SOSG-EP by fructose present in the cyclic form (99.2% of total fructose). Cyclic form of fructose is known to act as a reducing agent (Dong et al., 2014). Therefore, it is plausible that the reduction of SOSG-EP by cyclic fructose would lower the fluorescence intensity. To test this hypothesis, ascorbic acid (AA), a mild reducing agent was added to the buffer solution of pH 6.7 after 2 min of UV exposure at concentration of 50 mg/L. As shown in Fig. 4b the fluorescence of control solution continued to increase in the absence of AA. After its addition though, the fluorescence remained at the level observed after 2 min of exposure and did not increase upon further UV exposure. The fluorescence values of the two systems were significantly different after 5 min of UV exposure (two-tailed, $p < 0.05$). These results provide an indication that the presence of a reducing agent (such as cyclic fructose or AA) can inhibit SOSG-EP formation, such as that observed in experiments involving fructose. However, it does not fully explain the observed decrease in fluorescence intensity in presence of fructose, and further research is needed to address this unexpected behavior. It is also possible that the decrease in fluorescence intensity was due to photo-bleaching of the dye (Rágas et al., 2009). In our study, it is also interesting to observe that generation of $^1$O$_2$ followed a similar path as generation of hydrogen peroxide, in that both products showed a swift increase in concentration in the first minute of exposure. It may be that hydrogen peroxide and $^1$O$_2$ generation were correlated.

In addition to using SOSG, we used furfuryl alcohol (FFA) to quantify the steady-state concentration of $^1$O$_2$ generated from the varying concentrations of fructose (0, 100, 500, and 1000 mM) exposed to 254 nm UV light. Solutions containing 40 $\mu$M FFA and 0–1000 mM fructose were exposed at 254 nm in phosphate buffer and the steady-state $^1$O$_2$ concentration was calculated for each condition by dividing the observed FFA degradation rate by the reaction rate between FFA and $^1$O$_2$ ($8.3 \times 10^7$ M$^{-1}$ s$^{-1}$) (Latch et al., 2003). It was determined that the steady-state $^1$O$_2$ concentration ranged from 21 to 56 pM for the fructose concentrations tested (see Fig. S2). These concentrations of $^1$O$_2$ are within an order of magnitude of the range seen for the vitamin riboflavin at 20 $\mu$M and exposure to 365 nm light (Remucal and McNeill, 2011), albeit at significantly higher concentrations (0–20 $\mu$M of riboflavin vs. 0–1000 mM of fructose). It is important to reiterate that only the acyclic form of fructose is responsible for photosensitization, which...
is estimated to be present at 0.8% of the total concentration of fructose. Also using the FFA assay, exposure of 125 mM TiO2 to 254 nm light led to the production of a steady-state 1O2 concentration of 52 pM.

UV exposure of fructose results in generation of ROS including hydrogen peroxide, hydroxyl radicals (likely to originate from photolysis of hydrogen peroxide) and 1O2. Since UV-assisted advanced oxidative processes typically employ hydrogen peroxide, hydroxyl radicals and singlet oxygen for degradation of chemicals including pesticides (Badawy et al., 2006; Coelho et al., 2011), it is plausible that fructose can act as a photosensitizer in accelerating the UV induced degradation of the selected contaminants, diuron and chlorpyrifos.

3.4. Photochemical degradation of diuron

Fig. 1b shows the absorbance spectrum of diuron (25 mg/L). Diuron absorbed significantly in the UV-C region with a peak absorbance at 248 nm and an absorbance value of 1.69 at 254 nm. Fig. 5a shows the UV induced degradation of diuron in the absence and presence of fructose (300 and 500 mM). UV alone induced degradation of diuron and the degradation followed first order kinetics ($r^2 > 0.99$). Presence of fructose accelerated the degradation of diuron. The average degradation rate constants for diuron in presence of 0, 300 and 500 mM fructose were 0.92 ± 0.03, 1.55 ± 0.49 and 2.07 ± 0.61 min⁻¹ respectively. Statistical analysis showed that the rate constant for degradation was significantly higher in presence of 500 mM fructose compared to control (one-tailed, p < 0.05), while it was not significantly different at 300 mM fructose (p > 0.05). The t50% (time required for 50% degradation of diuron) were calculated based on the reaction constants. The t50% in presence of 500 mM fructose was 0.334 min compared to 0.74 min in the absence of fructose, indicating doubling of degradation rate in presence of fructose. The quantum yield (ɸ) for direct photodegradation of diuron in the absence and presence of 500 mM fructose was 0.003 and 0.006 respectively. The photosensitization activity of fructose was compared with commonly used photosensitizers such as titanium dioxide (TiO2) and hydrogen peroxide (H2O2) (Fig. 5b). The degradation rate constants for diuron in the presence of 1.5 mM H2O2 and 125 mM TiO2 were 1.58 ± 0.4 and 1.47 ± 0.4 min⁻¹ respectively. These concentrations for TiO2 and H2O2 were selected based on preliminary studies (Supplementary Fig. S3 and S4). These values are comparable to the degradation rate constants obtained in presence of 500 mM fructose.

Photo-degradation of diuron by UV irradiation in the absence of photosensitizer results in the formation of N-4,5-dichloro-phenyl-isocyanate, N-dichloro-phenyl-isocyanate, benzene-isocyanate, N-(4-isopropyl-phenyl)-formamide, aniline and 2-methyl-propionic acid (Kiss and Virág, 2009). Photodegradation of diuron by hydroxyl radical arising from ferrous ions resulted in formation of 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea as the major product (Mazellier et al., 1997). Since UV exposed fructose was shown to generate similar oxidative species, we anticipate that diuron degradation by UV exposed fructose would follow similar pathways. However, more research is needed to determine if fructose produced other degradation products as well and to determine their toxicity.

3.5. Photochemical degradation of chlorpyrifos

Fig. 1c shows the absorbance spectrum of chlorpyrifos (2 mg/L). Chlorpyrifos did not absorb significantly in the UV-C region and a maximum absorbance of 0.06 was observed at 230 nm. The average extraction efficiency using the solvent extraction process was approximately 85%. Fig. 6a shows UV induced degradation of chlorpyrifos in the absence (control) and presence of various concentrations of fructose. Chlorpyrifos was inactivated by UV light alone. However, the UV induced degradation of chlorpyrifos was accelerated in presence of fructose. The degradation kinetics followed first order ($r^2 > 0.85$) and the average degradation rate constants for chlorpyrifos in the presence of 0, 300 and 500 mM of fructose were 0.04 ± 0.05 ± 0.01, and 0.07 ± 0 min⁻¹ respectively. Statistical analysis of the degradation rate constants showed that the presence of 500 mM fructose significantly increased the rate of degradation compared to UV exposure alone, (p < 0.05), while 300 mM fructose did not have a significant effect (p > 0.05). The t50% (time required for 50% degradation of chlorpyrifos) was calculated based on the reaction constants. The t50% in presence of 500 mM fructose was 10.04 min compared to 18.7 min in the absence of fructose. The quantum yield (ɸ) for direct photo-degradation of chlorpyrifos and in the absence and presence of 500 mM fructose was 0.001 and 0.002 respectively. Hence it can be predicted that the oxidative species produced by fructose under UV light at 254 nm are capable of degrading chlorpyrifos with the optimum concentration of fructose at 500 mM, reducing the pesticide to nearly 20% at the end of 20 min. Photosensitizer induced degradation experiments for chlorpyrifos were also performed using H2O2 and TiO2. Fig. 6b shows the relative concentration of chlorpyrifos remaining as a function of UV exposure time in the presence of 1.5 mM H2O2 and 125 mM TiO2. Chlorpyrifos inactivation followed first order kinetics. The average
TiO$_2$, we expect formation of similar by-products of photodegradation (Affam and Chaudhuri, 2013). Since the oxidative species generated in presence of UV light exposure in (a) aqueous solution containing no photosensitizer (control), 300 and 500 mM fructose, and (b) 1.5 mM hydrogen peroxide or 125 mM titanium dioxide. Each data point is an average of triplicate measurement ± standard deviation. The solid lines indicate the fit for the first order rate equation.

Fig. 6. (a) Relative concentration of chlorpyrifos remaining as a function of duration of UV light exposure in (a) aqueous solution containing no photosensitizer (control), 300 and 500 mM fructose, and (b) 1.5 mM hydrogen peroxide or 125 mM titanium dioxide. Each data point is an average of triplicate measurement ± standard deviation. The solid lines indicate the fit for the first order rate equation.

degradation rate constants for 1.47 mM H$_2$O$_2$ and 125 mM TiO$_2$ were 0.91 ± 0.05 and 0.98 ± 0.47 min$^{-1}$ respectively. Thus, the inactivation rate of chlorpyrifos in presence of H$_2$O$_2$ and TiO$_2$ was significantly higher than in the presence of 500 mM fructose. A previous study showed that UV/H$_2$O$_2$/TiO$_2$ treated chlorpyrifos solution resulted in the formation of carbonyls groups such as aldehyde and carboxylic acids, and isomerization of the pesticide (Affam and Chaudhuri, 2013). Since the oxidative species generated by UV exposed fructose are similar to those produced by UV/H$_2$O$_2$/TiO$_2$, we expect formation of similar by-products of photodegradation of chlorpyrifos. However more research is needed to investigate whether fructose produced other degradation compounds and their toxicity.

Based on the comparison between the rate constants, it is evident that chlorpyrifos was more recalcitrant than diuron regardless of the type of photosensitizer used. However, the effect was more pronounced with fructose, possibly due to the differences in the relative concentration of individual oxidizing species produced by each photosensitizer. The rate constants for photodegradation in the presence or absence of fructose degradation was significantly lower for chlorpyrifos compared to diuron. This can be explained at least partially by a significantly lower absorbance of chlorpyrifos at 254 nm compared to diuron (Fig. 1). Although diuron and chlorpyrifos are both known to be susceptible to oxidation by hydroxyl radicals, singlet oxygen occupies a more important role than hydroxyl radicals in the oxidation of chlorpyrifos (Remulac, 2014; Zeng and Arnold, 2013). The varying susceptibility of the two compounds to the different ROS generated by UV exposure of fructose can also explain the differences in their degradation rates. However, it is important to highlight that it is difficult to control the type of ROS generated by a given sensitizer. Thus, the selection of photosensitizer can be based upon the type of contaminant and its relative susceptibility to the diverse ROS.

4. Conclusion

Exposure to 254 nm UV light causes photolysis of fructose resulting in generation of oxidizing species such as hydrogen peroxide, hydroxyl radicals, singlet oxygen and miscellaneous acidic molecules. Due to generation of these oxidizing species, fructose can act as a photosensitizer and accelerate UV induced degradation of compounds. This was demonstrated by the accelerated photo-degradation of chlorpyrifos and diuron in the presence of fructose. Thus, the results of this study highlight a novel application of fructose as a photosensitizer. This may be particularly attractive to the food and beverage processing industry as the effluents emanating from them typically contain high amounts of fructose. The relatively lower cost of fructose, its biodegradability and significantly higher chemical safety can make fructose an attractive alternative to the conventional photosensitizers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.10.074.

References


