Ozonation-Based Decolorization of Food Dyes for Recovery of Fruit Leather Wastes

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ABSTRACT: Commercial manufacture of fruit leathers (FL) usually results in a portion of the product that is out of specification. The disposition of this material poses special challenges in the food industry. Because the material remains edible and contains valuable ingredients (fruit pulp, sugars, acidulates, etc.), an ideal solution would be to recover this material for product rework. A key practical obstacle to such recovery is that compositing of differently colored wastes results in an unsalable gray product. Therefore, a safe and scalable method for decolorization of FL prior to product rework is needed. This research introduces a novel approach utilizing ozonation for color removal.

To explore the use of ozonation as a decolorization step, we first applied it to simple solutions of the commonly used food colorants 2-naphthalenesulfonic acid (Red 40), tartrazine (Yellow 5), and erioglaucine (Blue 1). Decolorization was measured by UV/vis spectrometry at visible wavelengths and with a Hunter colorimeter. Volatile and semivolatile byproducts from ozone-based colorant decomposition were identified and quantified with solid phase microextraction coupled with gas chromatography—mass spectrometry (SPME-GC-MS). Removal of Yellow 5, Red 40 and Blue 1 of about 65%, 80%, and 90%, respectively, was accomplished with 70 g of ozone applied per 1 kg of redissolved and resuspended FL. Carbonyl compounds were identified as major byproducts from ozone-induced decomposition of the food colorants. A conservative risk assessment based on quantification results and published toxicity information of potentially toxic byproducts, determined that ozone-based decolorization of FL before recycling is acceptable from a safety standpoint. A preliminary cost estimate based on recycling of 1000 tons of FL annually suggests a potential of $275,000 annual profit from this practice at one production facility alone.

KEYWORDS: *fruit leather recycling, food colorants, ozone-based decolorization, colorant decomposition, carbonyl compounds*

■ INTRODUCTION

Fruit leathers (FL) are snack candies containing fruit pulp, sugars, and food-grade colorants. These are quite popular with children and produced at rates of tons per hour in the US. As with any product, the commercial production of FL results in some material that is not to specification. Disposal of this material is costly and wasteful, as it remains edible and contains valuable ingredients such as fruit pulp, sugars, and acidulates. Recovery of FL for product rework requires colorant removal in order to avoid an unappetizing brownish color resulting from compositing of different-colored lots of FL. In-plant separation of waste products according to color is not practical, because most of the waste is due to off-spec colors or to unavoidable mixing incurred when switching the production line from one color to another. We studied the effects of ozonation on three commonly used food colorants: Red 40, an acidic and azoic synthetic colorant; Yellow 5, an azoic synthetic colorant; and Blue 1, a synthetic colorant.[1]

Colorant removal is often achieved by oxidation processes,[2] such as ozonation, or advanced oxidation processes (AOPs) for decolorization using hydroxyl radicals, including photocatalytic oxidation, electrochemical treatment, or ozonation combined with ultraviolet (UV) radiation or ultrasonication. Nonoxidative decolorization methods include adsorption, biodegradation, coagulation, and ultrasonic irradiation.[2−4] Table 1 summarizes studies on different decolorization techniques. With a prospective application in food materials treatment, it is important that the implemented decolorization process is free of undesirable additive residues from decolorization reagents. In the processes of adsorption, electrochemical oxidation, biodegradation, and coagulation, addition of solid reagents is necessary. Activated carbon with a high adsorption capacity is the most widely used adsorbent,[5] while fly ash, waste red mud, biomass, and clay minerals are substituted as cheaper adsorbents.[6−8] Dead plant or microbial cells are additional choices as sorbent, which interact with the impurity through adsorption, deposition, and ion-exchange.[3,7] Electrochemical oxidation uses an electrolyte such as sodium chloride[10] and ferrous sulfate[11] for the purpose of conductivity with an applied direct current of low voltage to oxidize color. Unsatisfactory decolorizing efficiency using biodegradation and coagulation was reported in the treatment on azoic colorant and acidic colorants,[4] and Yellow 5 and Red 40

Table 1. Studies on Decolorization Techniques

technique	colorant	reagent	colorant occurrence	ref
adsorption	methylene blue	activated carbon	wastewater	5
	Blue 1, Red 40, and Yellow 5	activated carbon	food waste	6
	methylene blue	cedar sawdust and crushed brick	wastewater	7
biosorption	Gryfalan Black RL metal-complex dye	*Rhizopus arrhizus* and *Aspergillus niger*	wastewater	3
	Cu²⁺ ions	dried *R. microsporus* fungal biomass	wastewater	8
biodegradation	methyl orange	*Kocuria rosea*	wastewater	9
electrochemical oxidation	Reactive Yellow 3	graphite and NaCl	wastewater	10
	Acid Yellow 36	boron-doped diamond and ferrous sulfate	wastewater	11
photocatalytic decolorization	Direct Blue 87, Reactive Red 120, Basic Yellow 15, Acid Blue 40, and Direct Blue 160	UV/TiO₂	wastewater	12
	Acid Blue 80	UV−vis/TiO₂	wastewater	13
	Acid Blue 40	UV/TiO₂	wastewater	14
ultrasonic decolorization	Acid Blue 25	carbon tetrachloride	wastewater	15
ozonation	C.I. Reactive Blue 15	ozone	wastewater	16
	methylene blue−orange II	ozone	wastewater	17, 18
	Blue 1, Red 40, and Yellow 5	ozone	food waste	this study

are such colorants. Photocatalytic oxidation produces oxidative radicals, requiring a catalyst such as TiO_2 as an additional semiconductor phase.[12−14] All of the techniques listed above involve addition of reagents or additives that need to be removed or recovered, involving additional and often very complex processing. Ozonation is an effective process for oxidation of organic compounds. *Selective* oxidation is possible in the presence of other organic substances due to different oxidation rates and reductive properties of various compounds.[15−17] Ozone-based decolorization has been proven to be ideal for industrial food material processing because it is highly effective, free from solid waste, and free from additive residue from oxidative reagents or catalysts.[17,18]

Ozone-based decolorization has been studied combined with other techniques such as ultrasonic irradiation,[19] UV catalysis,[20] or membrane filtration.[21] Oxidative radicals can be generated from ultrasonic irradiation of oxygen and water,[22] and this technique can be applied together with ozonation.[19] The use of ozone-based oxidative treatment started from the early 1900s and has been widely used in the food industry.[23] Ozone-based oxidation was proven to be selective and effective enough for colorant degradation.[18] Combination with other AOP techniques is expected to result in a higher oxidative potential[20,24,25] and lower selectivity in a complex system.[25] Considering the facility installation costs, treatment effectiveness, and selectivity, ozonation treatment alone was expected to serve as an optimum solution to the color removal in this study.

The study was performed on laboratory scale using ozonation for color removal from pure food colorant solutions and from solutions/suspensions of FL waste. Much of the research was focused on identifying ozonolysis reaction byproducts using the most sensitive methods for identification, that is, solid phase microextraction coupled with gas chromatography−mass spectrometry (SPME-GC-MS).

■ LITERATURE REVIEW

Ozone is commonly used in wastewater[26] and water treatment.[27] Ozonation was chosen as the most appropriate technique for colorant removal in this study because AOPs

are too reactive and not selective in oxidizing colorants. However, a major concern is byproduct generation from ozonolysis decomposition of the colorants. Common fluorophores of colorants include azo bonds and benzene rings, and these are the fluorescent groups of Yellow 5, Red 40, and Blue 1. Different breakdown mechanisms of these fluorescent groups have been observed in various decolorization processes (Table 2). The

Table 2. Studies on Colorant Degradation Products

colorant	reagent	degradation	ref
morin	ambient oxygen, light	ring intact	30
alizarin, alizarin crimson, pararosaniline base, basic fuchsin, acridone, quinacridone red, indigo, thioindigo violet, curcumin	ambient nitric acid	ring intact	31
curcumin	ambient ozone	ring intact	32
Blue 1	light	ring intact	33
Sunset Yellow FCF	light	ring intact	34,38
Chromotrope FB-E122	light	ring intact	34
Blue 1	potassium persulfate	ring intact	35
methyl orange	*Kocuria rosea*	ring intact	9
Acid Blue 40	UV/TiO₂	ring open	12
Reactive Black B	Co²⁺/peroxymonosulfate	ring open	36
C.I. Reactive Yellow 3	electrochemical oxidation	ring open	10
Acid Orange 6	ozone	mineralization	25
Acid Orange 6	Co²⁺/peroxymonosulfate	mineralization	37
Blue 1, Red 40, and Yellow 5	ozone	mineralization	this study

azo bonds are most subject to cleavage. The ring structures can be intact, opened, or mineralized. Some colorants were found to degrade in the natural environment without breaking the benzene rings.[28−32] Morin is a textile dye with a flavonoid backbone, which was found to break down under the oxidation of ambient oxygen with catalysis of visible light.[28] Grosjean et al.[29] reported the fading
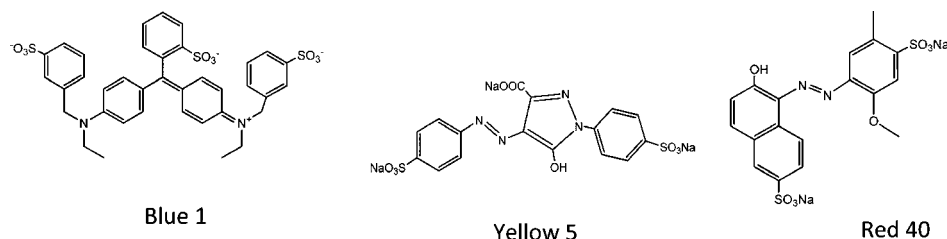
Figure 1. Chemical structures of the food colorants used in this study.

of some organic artists' colorants by atmospheric nitric acid and breakdown of curcumin by ambient ozone. Photodegradation of food colorants in beverage (Blue 1,[33] azo dye Sunset Yellow FCF,[30,34] and Chromotrope FB-E122[30]) was reported by Gosetti et al. In some decolorization treatments, potassium persulfate was found to degrade Blue 1 without opening the benzene ring,[31] and enzymatic selective cleavage of the azo bond of the azo dye methyl orange was observed with *Kocuria rosea*.[31] Ring-opening degradations were observed with advanced oxidation processes (AOPs): UV/TiO$_2$ oxidation of anthraquinone dye Acid Blue 40;[12] Co^{2+}/ peroxymonosulfate oxidation of azo dye Reactive Black B;[28] and electrochemical oxidation of azo dye C.I. Reactive Yellow 3.[10] A 50.7 mg L^{-1} h^{-1} ozone dose was found to mineralize azo dye Acid Orange 6 to nitrate and gaseous nitrogen compounds, while the colorant degraded ineffectively under the UV/TiO$_2$ treatment.[20] Mineralization of Acid Orange 6 was also realized in a Co^{2+}/peroxymonosulfate system.[35] Some of the degradation products from mineralization are small molecules and do not contain benzene rings. Mineralization is expected to generate compounds with low toxicity. A lower unsaturation degree is expected to be another indication of lower toxicity. Mineralization of colorants with ozone-based oxidation is possible according to previous studies.[20]

Ozone-based treatment was selected as the most likely decolorization procedure in FL recycling. This is the first study on ozone-based food colorant degradation for edible reuse. The FL sample is expected to be a complex matrix, with sugar, syrup, oil, etc. as major ingredients. Solid-phase microextraction (SPME) was chosen as an ideal sample preparation method with selectivity against the high-molecular weight compounds in the ingredients.[9] Byproducts from the treatment were captured with SPME and identified and quantified with gas chromatography coupled with mass spectrometry (GC-MS).

■ MATERIALS AND METHODS

Experimental Section. Ozonation was tested for the removal of color from solutions of food colorants (Blue 1, Yellow 5, and Red 40) and from solution or suspensions of waste FL. Figure 1 illustrates the chemical structure of food colorants used for coloring FL. The decolorization efficiency was tested with a UV/vis spectrometer and a Hunter colorimeter. Monitoring byproduct generation is important to evaluate the acceptability of the ozone-based treatment in this study. Further testing involved determining ozonolysis byproducts using SPME-GC-MS.

Ozone Treatment. The ozonation system was set up as shown in Figures 2 and 3. The 99.999% purity air in the air cylinder was the oxygen supply for the TOG C2B corona discharge ozone generator (Triogen, Craigton, Glasgow, UK). Air was introduced into the ozone generator at a constant flow rate. The flow rate was measured by a GFC 37 mass flow controller (Aalborg, Orangeburg, New York, USA). The oxygen in air was ruptured by corona discharge to radicals, which combine with an intact oxygen molecule to form ozone. A capillary grade hydrocarbon trap (Restek, Bellefonte, PA, USA) and an alumina adsorbent for moisture removal were connected in the air supply line to reduce impurities and nitric acid formation from nitrogen oxides
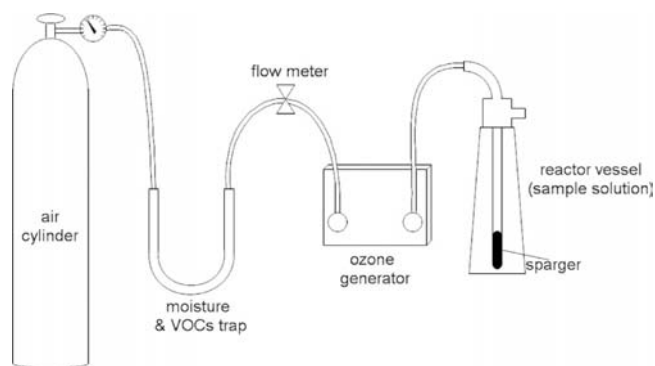

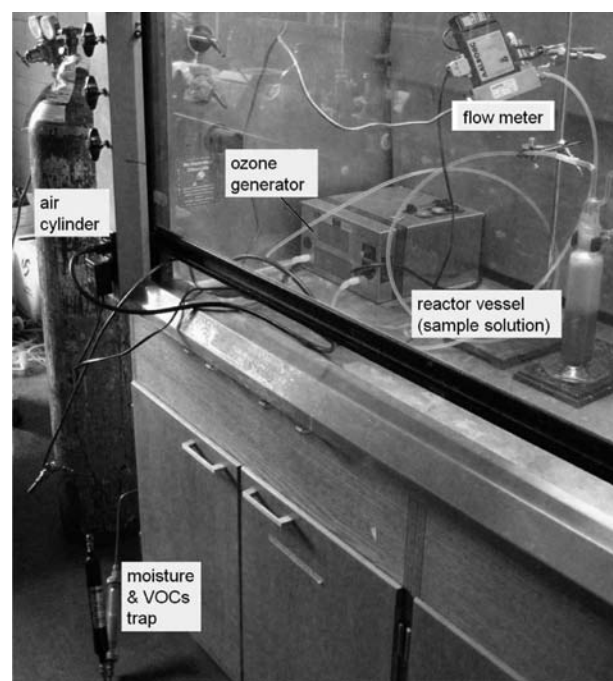**Figure 2.** Schematic diagram of the ozonation system.

Figure 3. Photo of the ozonation system used in this study.

formed in the corona discharge. Under a constant airflow rate, the ozone dose was constant. Specific ozone doses were reached during a specific ozonation period. In the ozonation process, parameters such as temperature and pH value in the system were found to influence the mass transfer of ozone and consequently decolorization efficiency.[36] Ozone mass transfer enhancement was also achieved through microbubble generation through fine porous diffusers.[37]

The ozone/air was introduced to a 200 mL sample solution in a reactor vessel through a glass tube with a sintered glass sparger and dosed at rates as shown in the results. A zero ozone dosage served as a control for comparison with the effect of various ozone dosages.

Ozone Dose Quantification with Iodometric Titration. A constant ozone dose was supplied by the corona discharge ozone

Table 3. Selected Scanning Ions in the SIM Mode for on-Fiber Derivatization SPME Analysis
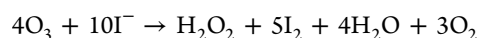
carbonyl (PFBHA derivative)	significant ions[a]	carbonyl (PFBHA derivative)	significant ions[a]
ethanal	181 **209** 239	octanal	181 **239** 323
propanal	181 195 **223** 236	acetone	181 223 **253**
butanal	181 **239** 267	2-heptanone	181 **253**
pentanal	181 **239** 281	2-furaldehyde	181 248 **291**
hexanal	114 181 **239** 295	benzaldehyde	181 271 **301**

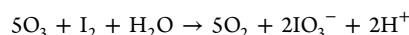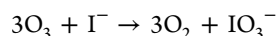[a]Quantification ions are in bold.

generator, with desiccated air feed as the oxygen supply. Ozone/air gas was introduced at a constant flow rate through a glass tube from top to the bottom with a sintered glass sparger and passed through 200 mL of 2% potassium iodide solution in a vessel.

Ozone oxidizes iodide to iodine and some iodate as follows:
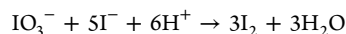
Main iodide oxidation reaction:

$$4O_3 + 10I^- \rightarrow H_2O_2 + 5I_2 + 4H_2O + 3O_2$$

Side reactions:

$$3O_3 + I^- \rightarrow 3O_2 + IO_3^-$$

$$5O_3 + I_2 + H_2O \rightarrow 5O_2 + 2IO_3^- + 2H^+$$

Post-treatment solution was transferred to a 500 mL conical beaker, and 10 mL of 2 M sulfuric acid solution was added and mixed into the solution.[37]

Sulfuric acid is added to the ozonated KI solution to reduce the iodate:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The solution was set aside at room temperature in dark storage for 3 h to release iodine from iodate as byproduct. After 3 h of low-pH reaction, free iodine reached a peak. Solution was then titrated with 0.05 M sodium thiosulfate solution. Because the yellow color almost disappeared, 2 mL of 1% starch indicator was added, turning the solution blue for a clearer end point. Titration was continued until the blue color disappeared.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Total reaction:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^-$$
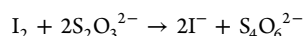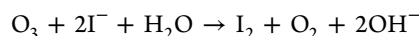
Ozone dose was calculated according to the summarized reactions as follows:

$$D_{ozone} = AN\frac{24}{T} \tag{1}$$

where D_{ozone} = ozone dose in mg/min, A = the amount of $Na_2S_2O_3$ in mL, N = the concentration of $Na_2S_2O_3$ in mol/L, T = ozonation time in min, and 24 = ozone molecular mass (48) divided by the number of electrons transferred (2).

Color Removal Measurements. Objective color measurement was carried out with a SpectraMax Plus 384 UV/vis spectrometer (Molecular Devices, Sunnyvale, CA, USA) and Hunter colorimeter (HunterLab, Reston, Virginia, USA). The UV/vis spectrometer measures absorbance of light in a sample at a specified wavelength. Colorant content in solution can be determined by measuring its absorbance at the wavelength with maximum absorbability. The instrument was calibrated with purified water in a sample cuvette before measurement. Colorant aqueous solution was directly transferred to a cuvette for measurement. The FL solution was centrifuged and filtered to get rid of impurities before being transferred to a cuvette. Absorbance of each sample at its maximum absorbability wavelength was recorded as A_{max}.

The Hunter colorimeter was used to measure the color of the FL solution without cleaning the sample. The color is expressed in the Hunter 3-D L,a,b space, where L is on the lightness axis (0 is black and 100 is white), a is on the red−green axis (positive is red and negative is green), and b is on the blue−yellow axis (positive is yellow and negative is blue).[39] The instrument was first calibrated with black and white reference tiles (L = 91.8; a = −0.8; b = 0.1). A plastic sample dish was filled with sample solution to the top to reach an identical depth in each measurement. The dish was covered with a plastic sample dish cover before measurement. The three-color coordinates were recorded, and total color difference, ΔE, was calculated based on eq 2:

$$\Delta E = [\{L_0 - L\}^2 + (a_0 - a)^2 + (b_0 - b)^2]^{1/2} \tag{2}$$

where L_0, a_0, and b_0 represent the readings from untreated fruit leather solution, and L, a and b represent those from sample treated with specific ozone dose.

Byproduct Analysis. Byproduct identification was performed by GC-MS analysis using three approaches: (1) direct immersion (DI) SPME with a 50/30 μm DVB/CAR/PDMS fiber, (2) headspace SPME, or (3) headspace on-fiber derivatization SPME with a 65 μm PDMS/DVB fiber.

The first and second approaches were used to screen for volatile and semivolatile byproducts. The third approach was particularly useful and selective toward carbonyls. All SPME fibers and holders were purchased from Supelco (Bellefonte, PA, USA). The GC-MS system was Agilent 6890N GC system coupled with Agilent 5975C VL MSD. Colorant aqueous solution was used as the model system for identification of byproducts from colorant decomposition. The DI-SPME was performed by immersing a 50/30 μm DVB/CAR/PDMS fiber into a 30 mL treated/untreated colorant solution in a 40 mL vial for 30 min at room temperature with 800 rpm stirring. The fruit leather solution samples were also analyzed by headspace (HS)-SPME, and the trend of aliphatic acid content against ozone dose was monitored. Most ozonation byproducts are as volatile or more volatile than the parent compound, making an adsorptive system for sampling of such byproducts a practical approach. A 50/30 μm DVB/CAR/PDMS fiber was exposed to the headspace of 10 mL sample in a 40 mL vial for 60 min at room temperature, with 800 rpm stirring.

A DI sample extracted by the 50/30 μm DVB/CAR/PDMS fiber was separated by a 60 m polar BP-21 column in GC-MS. Injector was at 250 °C.

For on-fiber derivatization SPME, derivatization reagent was first doped onto a 65 μm PDMS/DVB fiber, which was then used for extraction. The doping procedure and on-fiber derivatization were both performed in a thermal water bath at 60 °C. SPME fiber was introduced to the headspace of 1 mL × 17 mg/mL PFBHA (pentafluorobenzylhydroxylamine) aqueous solution in a 4 mL PTFE-capped vial. Doping of the SPME fiber was performed for 15 min immediately after introducing PFBHA to water and stirring the solution at 600 rpm, Headspace sampling was performed with doped SPME fiber exposed to the headspace of 1 mL of sample solution in a 4 mL vial for 5 s. Analyses of blanks were performed using the same doping procedure and pure water. Analyses of volatile composition of FL solution before and after the ozonation process were performed using the same procedure as described above.

Carbonyl compounds were found as major byproducts from ozone-based colorant decomposition and were selected as target compounds based on the published toxicity data. The major and high toxicity byproducts including ethanal, hexanal, 2-furaldehyde and benzaldehyde, in the real samples were quantified with on-fiber derivatization SPME analysis as described above. The rest of the byproducts are of low concentration and are slightly toxic or practically nontoxic with LD_{50}-rat-oral above 500 mg/kg, according to the Hodge and Sterner Scale.

Samples extracted by the 65 μm PDMS/DVB fiber were separated and analyzed by the same 60 m polar BP-21 column in GC-MS. The

Table 4. Optimization of Iodometric Titration for Ozone Quantification

				RSD (%)		
air supply (mL/min)	calibration curve[a]	release iodine for 3 h	R^2	average	intraday	interday
500	$D_{ozone} = 3.898T$	no	0.490	7.88	12.8 ($n = 4$)	b
500	$D_{ozone} = 4.522T$	yes	0.988	2.94	4.74 ($n = 6$)	4.50 ($n = 9$)
800	$D_{ozone} = 6.644T$	yes	0.999	0.37	0.52 ($n = 3$)	b

[a]The calibration curves were all forced to the intercept = 0. The frequency setting was at 1. In the equation, D_{ozone} is in mg/L of air flow and T is in min. [b]The value was not calculated.

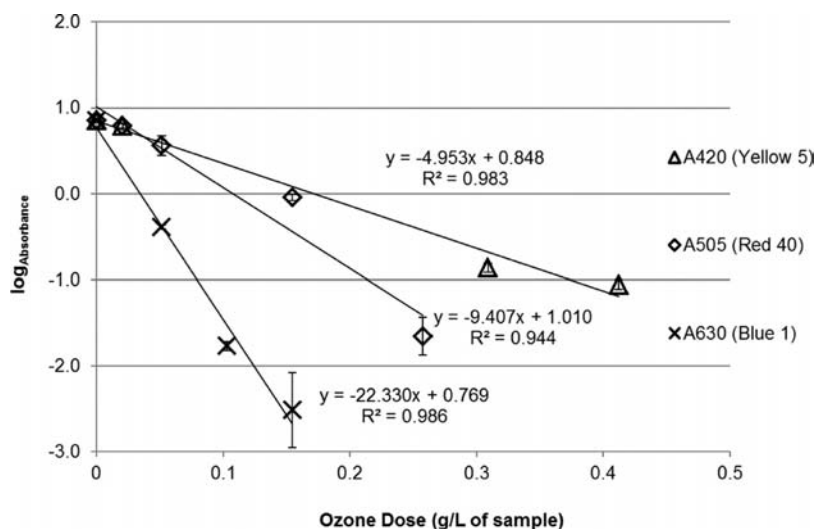**Figure 4.** Color removal progress with increased ozone dosage for food colorant solutions (200 mL food colorant solution; 11.3 mg L^{-1} min^{-1} ozone dosage rate).

injection port temperature was 250 °C. The oven temperature was raised from initially 120 to 180 °C at a 4.5 °C/min ramp, and then ramped to 220 °C at 15 °C/min, holding for 3 min. Helium was the carrier gas, and the flow rate was 1.7 mL/min. The scanning range of the MS detector was m/z = 33 to 352. Temperatures of the MS source and MS quadrupole were 230 and 150 °C respectively. A 70 eV voltage was used to for molecular decomposition. A selective ion monitoring (SIM) mode was run simultaneously with the total scanning mode for quantification. Table 3 shows the selected scanning ions in the SIM mode for on-derivatization SPME analysis.

RESULTS

Ozone Generator Calibration. A considerable enhancement of linearity and precision of the iodometric titration for ozone quantification was observed with a 3 h iodine release procedure (Table 4). The 3 h iodine release procedure was included in the following ozone quantification procedures. With a 500 mL/min air supply, setting at 1 (the lowest corona discharge frequency) was found to provide the same ozone generation efficiency as higher frequency settings. The knob was set at 1 in the following measurement and treatment procedures. Ozone generator calibration curves were generated with air supply at 500 and 800 mL/min (Table 4).

Colorant Solution as Model Sample. *Color Removal Efficiency.* A decolorization curve was obtained by plotting log A against ozone dose. A pseudo-first-order colorant decomposition reaction was observed for each colorant (Figure 4), which agrees with results from previous studies on ozone-based decolorization.[9,18] Among the three colorants studied, Blue 1 was found to be most rapidly decomposed, followed by Red 40, then Yellow 5.

Byproduct Analysis. According to previous studies, the N=N and C−N bonds are subject to oxidation and tend to break down.[17,30,33,34] Natural light or ambient nitric acid and ambient ozone were found to be oxidative enough to degrade colorants into smaller molecules.[29,30,33,34,40] However, carbonyl compounds were not found as colorant degradation products in previous studies. Generation of chemicals with low molecular weight in this study might be caused by the high oxidative potential of ozone at high concentration when introduced into the sample solution.

Carbonyl compounds were identified as major byproducts (Table 5). No nitrogen containing product was detected, which could be the result of mineralization of these colorants. The same observation was reported in ozone treatment of Acid Orange 6.[20] The high oxidation potential of ozone is expected to induce open-ring and mineralization reactions. The detection of carbonyl compounds as major products suggests ring-opening reaction mechanisms. Regarding carbonyl compound analysis, a considerable enhancement of selectivity and sensitivity of SPME was achieved by on-fiber derivatization in this study (Figure 5). The SPME-based method was selected in the following study to quantify carbonyl compounds as major and potentially toxic byproducts.

Waste Fruit Leather Solution/Suspension. Increasing ozone doses led to increased color removal, as expected. A pseudo-first-order colorant degradation reaction was also observed in ozone treatment of the mixed color FL (Figure 6). However, a significant decrease of degradation speed was observed in the real sample solution (Table 6). The suspended pulp ingredient from the FL products could be the obstacle in the contact between ozone and colorant. According to the L value obtained with the

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Table 5. Byproduct Chemicals Identified in Ozonated Colorant Aqueous Solutions[a]

compound	LD_{50} (rat, oral)[c] (mg/kg)	detected or not			
		blue	red	yellow	green
ethanal	661	yes	yes	yes	yes
propanal	1600	yes	yes	yes	yes
butanal	5890	yes	yes	yes	yes
pentanal	4581	yes	yes	yes	yes
hexanal	4890	yes	yes	yes	yes
heptanal	14000	yes	yes	yes	yes
octanal	5630	yes	yes	yes	yes
nonanal	5000	yes	yes	yes	yes
decanal	23000	yes	yes	yes	yes
acetone	5800	yes	yes	yes	yes
butanone	2737	yes	yes	yes	yes
2-pentanone	1600	yes	yes	yes	yes
2-heptanone	1670	yes	yes	yes	yes
6-methyl-2-heptanone	d	no	yes	yes	no
2-furaldehyde	65	yes	yes	yes	yes
benzaldehyde	1300	yes	yes	yes	yes
furan	300	yes	yes	yes	yes
acetic acid	3310	yes	yes	yes	yes
2-butenoic acid	400	no	no	yes	no
benzoic acid[b]	1700	yes	yes	yes	yes
2-ethyl-1-hexanol	3730	yes	yes	yes	yes
1-dodecanol	1800	yes	yes	yes	no
furfuryl alcohol[b]	177	yes	yes	yes	yes
phenol[b]	410	yes	yes	yes	yes
1-tetradecanol	5000	no	yes	yes	no
tetradecanol	5000	no	no	yes	no
ethoxy-1-dodecanol	d	no	no	yes	no
diethyl phthalate	8600	no	yes	yes	no

[a]Chemicals were identified in the chromatograms generated from DI-SPME-GC-MS and on-fiber derivatization SPME-GC-MS analysis. [b]The chemical was also identified in the untreated commercial food colorant aqueous solution. [c]The LD_{50} values were acquired from Material Safety Data Sheets. [d]Not available.

Hunter colorimeter, an increased lightness was observed against ozone dose increase (Figure 7), which resulted from removal of total colorant. Unlike results from the UV/vis measurement, the Hunter colorimeter readings did not indicate a specific degradation pattern of colorants. The random curves obtained from the Hunter colorimeter might be the result of mixed colorants and their difference in degradation kinetics.

Based on the on-fiber derivatization SPME-GC-MS analysis results, a carbonyl generation–dose of ozone profile was obtained (Figure 8). Generation of all carbonyls reached a peak value at the same ozone dosage. A decrease was observed following the highest generation, to which either vaporization or oxidation of carbonyl compounds or both could be contributing. The maximum generation is listed in Table 7. When the sample was submitted to HS-SPME-GC-MS analysis, oxidation being a contributing factor was supported by aldehyde generation at lower dosages (Figure 8) and aliphatic acid generation at higher dosages (Figure 9).

A primary risk assessment was performed regarding the carbonyl compounds as major byproducts in the recycled FL (Table 7). Assume that one would consume 10 g of FL every day and 1 kg of FL can be recycled from 1 L of decolorized 100% FL suspension. Take the highest generation (C_{max}) of each chemical as its concentration in recycled solution, then for recycled FL, the concentration (C_{fl}) equals $C_{max}/(1$ kg of FL/L of solution). A 70 kg adult weight consuming 10 g of FL each day would have an intake of $[10$ g $\times C_{fl}]/70$ kg body weight per day of byproduct chemical. The result is in Table 7. Chemical intake is far below the oral reference dose (RfD) value, an estimate of daily exposure that does not result in any appreciable risk to a human during a lifetime. The rest of the byproducts are of very low concentration. These chemicals are mostly practically nontoxic according to the Hodge and Sterner Scale.

■ DISCUSSION

A rough cost analysis was performed based on recycling of 1000 tons of FL per year, the quantity currently disposed of at the company where the samples originated.

Capital costs for this recycling system include an ozone generator, mixing tanks, ozone reactor, storage, conveyor, piping, and pumping. A 100% FL suspension requires 70 g of ozone/L for sufficient color removal. This equals 70 g of ozone/kg of FL or 70 kg/metric ton. Recycling of 1000 tons of FL per year would require 70 tons of ozone/year or a 10 kg/h ozone generator to have some spare capacity. The initial installation is expected to cost $500,000 or an amortized $75000 per year at 15% per year over 10 years of usage, although equipment life could be expected to be more than 10 years and this assumes a very steep interest rate.

The main operating costs are electricity, labor for equipment operation, and facility maintenance. Power cost varies, but a value of $0.09 per kWh is conservative and ozone generation requires 12 kWh/kg.[17] The power cost would then be 70 kg × $0.09/kWh × 12 kWh/kg, or about $76 per metric ton. The maintenance of such a system costs $4000−6000 per year.[17] Other costs, including labor, drying, and maintenance are expected to add $75 per ton, with a total operational expense of about $150/ton. The labor cost included here is based on only occasional operational adjustments.

The total estimated cost for ozonation and handling the recycled material is therefore $225 per ton of FL or $225,000 in a 1000 ton/year facility. The value of recycled FL is roughly $500/ton; thus, a 1000 ton recycle facility could potentially show a $275,000 profit or savings per year, not including the savings on waste FL disposal. The expected payback time on investment would therefore be less than 2 years.

Table 6. Decolorization Efficiencies of Yellow 5, Red 40, and Blue 1

sample	colorant	equation[a]	R^2	average RSD (%)
aqueous solution	Yellow 5	$\log A = -4.953 D_{ozone} + 0.848$	0.983	3.47
	Red 40	$\log A = -9.407 D_{ozone} + 1.010$	0.944	22.7
	Blue 1	$\log A = -22.33 D_{ozone} + 0.769$	0.986	6.41
100% fruit leather solution	Yellow 5	$\log A = -0.006 D_{ozone} + 0.650$	0.912	6.39
	Red 40	$\log A = -0.010 D_{ozone} + 0.236$	0.951	13.6
	Blue 1	$\log A = -0.013 D_{ozone} + 0.170$	0.964	38.7

[a]In the equation, D_{ozone} is ozone dose in g/L of sample, and A is the light absorbance of the colorant at its maximum absorptivity wavelength.
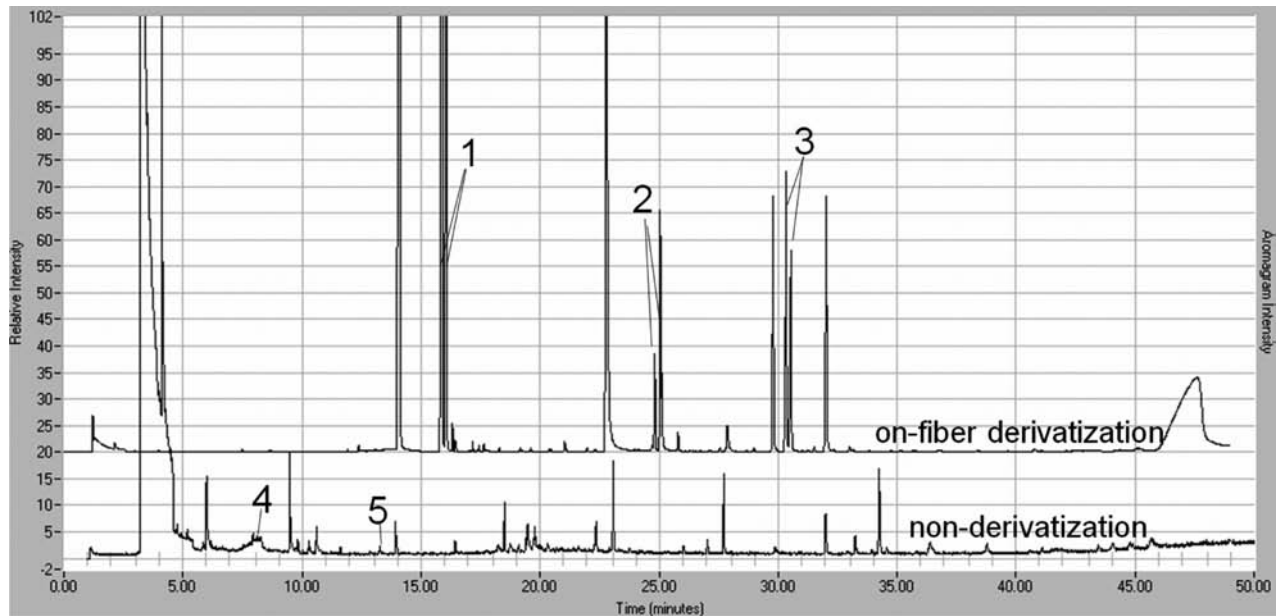
Figure 5. Comparison of on-fiber derivatization SPME and nonderivatization SPME: (1) *trans/cis*-ethanal-PFBHA oxime; (2) *trans/cis*-hexanal-PFBHA oxime; (3) *trans/cis*-octanal-PFBHA oxime; (4) hexanal; (5) octanal.
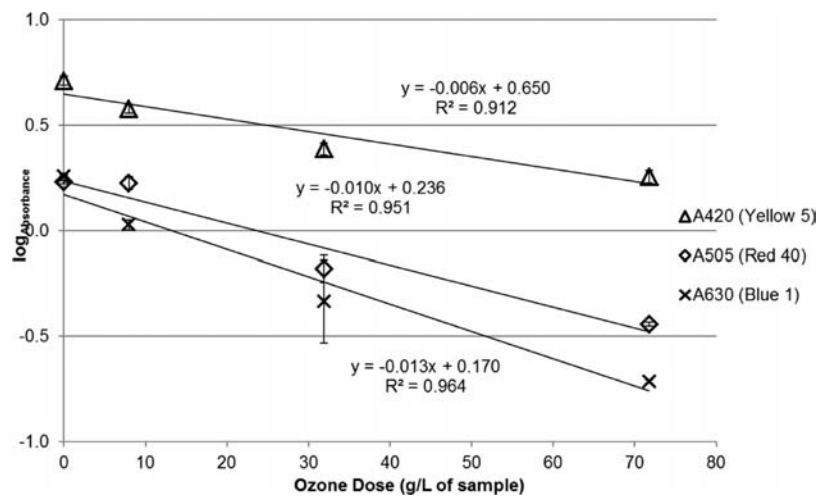
Figure 6. Color removal profiles for different colorants in fruit leather solutions (26.6 mg L^{-1} min^{-1} ozone dosage rate, 200 mL of 100% fruit leather solution, 800 mL/min air flow).
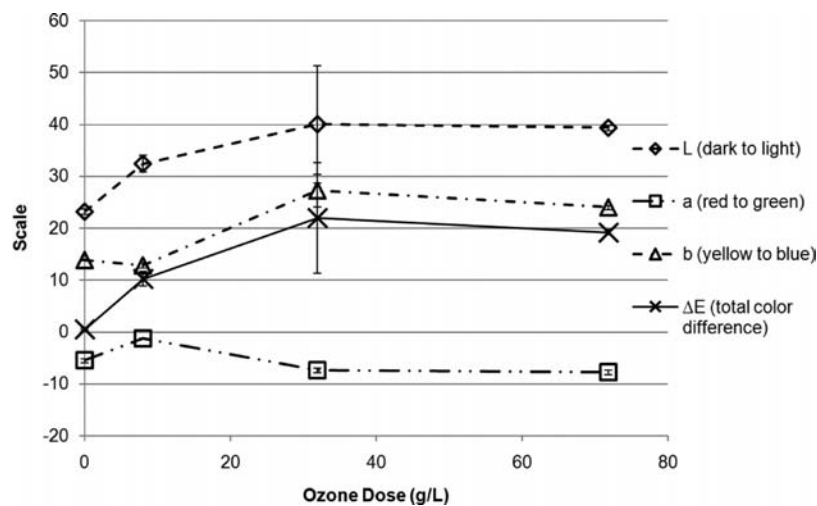
Figure 7. Hunter colorimeter measurement results.

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Figure 8. Carbonyl generation-ozone dose profile (26.6 mg L^{-1} min^{-1} ozone dosage rate, 200 mL of 100% fruit leather solution).
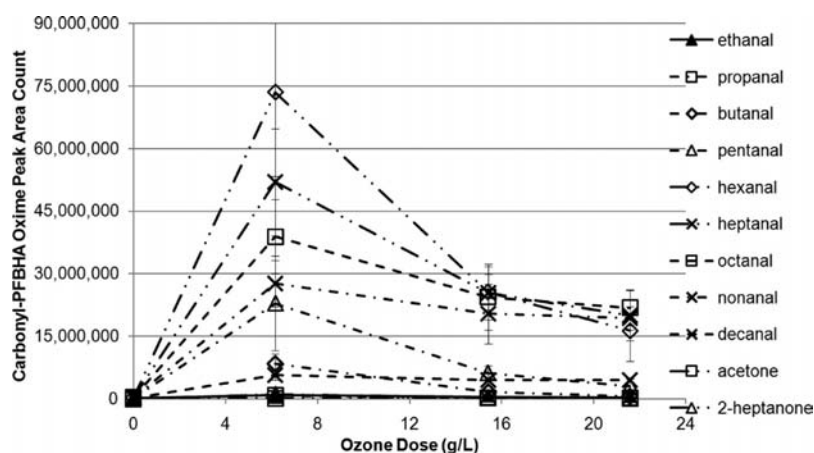
Table 7. Quantification Results of Major Potentially Toxic Carbonyl Compounds

compound	calibration curve	LOD (μg/L)	C_{max} (mg/L)	intake^{a} (mg/kg·day^{-1})	oral RfD (mg/kg·day^{-1})
ethanal	$y = (1.2 \times 10^3)x + 70324$	0.030	0.644 ± 0.188	$(9.2 \pm 2.7) \times 10^{-5}$	0.04[41]
hexanal	$y = (9.2 \times 10^2)x + 29024$	0.029	80.0 ± 22.0	0.011 ± 0.003	
2-furaldehyde^{b}	$y = (3.7 \times 10^4)x + 35313$	0.016	$<1.6 \times 10^{-5}$	$<2.29 \times 10^{-9}$	
benzaldehyde	$y = (4.1 \times 10^4)x + 38523$	0.016	$<1.6 \times 10^{-5}$	$<2.29 \times 10^{-9}$	0.1[42]

^{a}Conservative assumptions were made to estimate intake values. ^{b}5-Nitro-4-(3-(diethylamino)propyl)semicarbazone, 5-nitro-2-furaldehyde 4-(3-(diethylamino)propyl)semicarbazone, or 1-(5-nitro-2-furfurylidine)-3-N,N-diethylpropylaminourea hydrochloride.
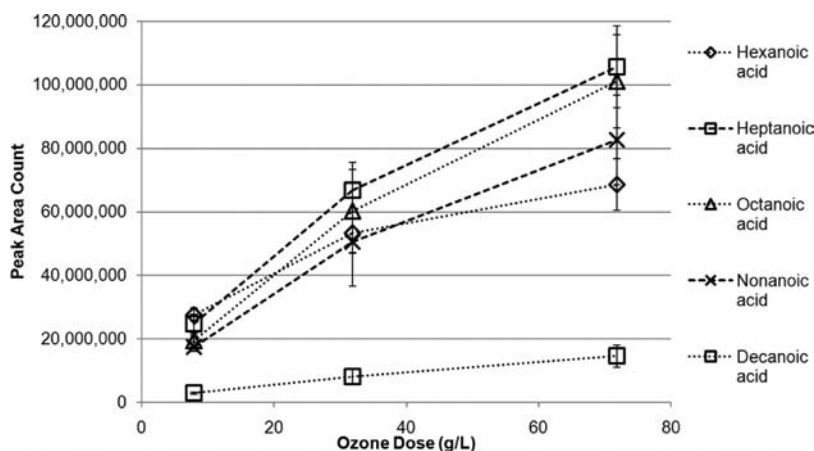

Figure 9. Aliphatic acid generation−ozone dose profile (26.6 mg L^{-1} min^{-1} ozone dosage rate, 200 mL of 100% fruit leather solution.

Conclusion. The ozone-based decolorization method was proven to be an effective method of removing colorants in FL products and to be low in additive residues. With selectivity based on the absorptivity of different colorants, UV/vis spectrometry was proven to be an appropriate technique in the measurement of mixed colorants. The measurement results demonstrated that colorant degradation was pseudo-first-order.

SPME-GC-MS identified a number of carbonyl compounds as major byproducts. The analytical results suggested mineralization and ring-opening reactions during colorant decomposition. The initial formation of aldehydes, which are then oxidized to carboxylic acids, is very typical of the progress of ozonation of aromatic and natural compounds.[15,16]

A conservative risk assessment based on quantification results and toxicity information of the chemicals confirmed the acceptability of ozone-based decolorization in FL recycling.

The cost of facility installation and operation was estimated against quantities recycled, and an annual profit or savings potential of $275,000 in a 1000 ton recycling facility is quite feasible.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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