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Reduction of Patulin in Apple Juice Products by UV Light of Different Wavelengths in the UVC Range

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ABSTRACT

This study evaluated three UVC wavelengths (222, 254, and 282 nm) to degrade patulin introduced into apple juice or apple cider. The average UV fluences of 19.6, 84.3, 55.0, and 36.6 mJ·cm^{-2} achieved through exposure to UV lamps at 222-, 254-, and 282-nm wavelengths and the combination of these wavelengths, respectively, resulted in 90% reduction of patulin in apple juice. Therefore, the order of efficiency of the three wavelength lamps was as follows: far UVC (222 nm) > far UVC plus (282 nm) > UVC (254 nm). In terms of color, treatment of apple juice with 222 nm resulted in an increase in the L* (lightness) value but decreases in a* (redness) and b* (yellowness) values, although the changes were insignificantly different from the values for nontreated controls based on a sensory evaluation. The ascorbic acid loss in juice treated at 222 nm to support 90% reduction of patulin was 36.5%, compared with ascorbic acid losses of 45.3 and 36.1% in samples treated at 254 and 282 nm, respectively. The current work demonstrated that the 222-nm wavelength possesses the highest efficiency for patulin reduction in apple juice when compared with the reductions by 254 and 282 nm, with no benefit gained from using a combination of wavelengths.

The presence of patulin mycotoxin [4-hydroxy-4H-furo(3,2-*c*)-pyran-2-(6H)-one] in apple juice continues to represent a significant food safety issue *(31)*. Patulin associated with apple juice is commonly linked to the use of fruit contaminated with *Aspergillus*, *Penicillium,* and/or *Byssochlamys* and then stored in warm and humid environments *(1, 18, 24, 34)*. The presence of patulin resulting from bad quality of fruits and insufficient control measures encountered associated with apple fruit or juice varies significantly, although the levels found are typically in the order of 1 mg·kg^{-1} and 500 μg·liter^{-1}, respectively *(3, 13, 15, 24, 26)*. Long-term exposure to patulin can result in nervousness, convulsion, lung congestion, edema, hyperemia, and immunotoxic, immunosuppressive, and teratogenic effects *(30)*. Because of the prevalence and toxicity of patulin, the U.S. Food and Drug Administration set a maximum level of 50 μg·liter^{-1} in single-strength apple juice, reconstituted single-strength apple juice, or the single-strength apple juice component of food *(40)*. The European Union limited the patulin concentration to 50 μg·kg^{-1} in fruit juice, spirit drinks, and cider derived from apples *(10)*. The European Union also set lower limitations in solid apple products (25 μg·kg^{-1}) and apple juice and solid apple products for infants and young children (10 μg·kg^{-1}) *(10)*.

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UV has been approved as a nonthermal method for pasteurization of fresh juice products by the U.S. Food and Drug Administration *(39)*. Health Canada *(16)* also approved the application of the CiderSure 3500 UV reactor as an intervention against *Escherichia coli* O157:H7, the pathogen that is the primary target for pasteurization treatment, in apple juice. Although UV treatment is primarily designed to reduce the risk derived from *E. coli* O157:H7, it is also possible to reduce mycotoxin levels through photolytic degradation *(2, 8, 28, 43, 44)*.

As the part of electromagnetic radiation in the range between 100 and 400 nm, UV light is divided into vacuum UV (100 to 200 nm), UVC (200 to 280 nm), UVB (280 to 315 nm), and UVA (315 to 400 nm). The available UV sources include mercury lamps, amalgam lamps, excimer lamps, pulsed lamps, microwave lamps, and UV-light-emitting diode lamps *(21)*. Low-pressure mercury lamps are widely applied in the disinfection of pathogens due to their emission wavelength at 253.7 nm that targets DNA *(22)*. However, patulin has a peak absorption wavelength at 276 nm *(7),* suggesting that alternative UV wavelengths could enhance the degradation process. The excimer lamps were considered as alternative UV lamps due to their specific feature of a narrow emission band that depends on the choice of rare gas and/or halogen (e.g., KrCl* has a wavelength of 222 nm and XeBr* has a wavelength of 282 nm) *(21, 33)*. In this study, novel UVC lamps, monochromatic sources with specific wavelengths (222 and 282 nm) in the germicidal range, were specially

designed for emitting single-wavelength light based on the excimer discharge. These UV sources were used to enhance the reduction of patulin based on the potential mechanisms of either providing photons with higher energy or matching the absorption peak of patulin at 276 nm.

UV-based methods have received significant attention as a low-cost, reliable, nonthermal pasteurization technique, although the approach does have disadvantages, such as reductions in nutrients like ascorbic acid *(17, 35)*. The generation of photoproducts that alter the sensory properties of juices, such as apple juice, can also potentially occur *(6, 17, 29, 35)*. Consequently, a balance needs to be made with respect to degrading patulin without having adverse effects on the product. The extent of byproduct formation depends on the UV wavelength applied, although this aspect has not been studied to any great extent.

The objective of the following study was to investigate the patulin degradation kinetics at different UV wavelengths and study the generation of photoproducts that would negatively affect the sensory qualities of apple juice.

MATERIALS AND METHODS

Materials. Patulin, L-ascorbic acid, acetic acid, sodium bicarbonate, formic acid, liquid chromatography (LC)–grade tetrahydrofuran, acetonitrile, and ethyl acetate were obtained from the Sigma Chemical Company (St. Louis, MO). Pasteurized apple cider (pH 3.45) and apple juice enriched with ascorbic acid (pH 3.17) were purchased from a local supermarket and used directly.

UV processing unit. A triple-wavelength box equipped with three monochromatic-wavelength UV lamps (far UVC [222 nm], UVC [254 nm], and far UVC plus [282 nm]) from HEI (Dover, NH) was used to treat samples (Fig. 1). Excimer lamps emitting at 282 or 222 nm, along with a low-pressure mercury lamp (254 nm), were used as UV sources and placed 5.5 cm (far UVC 222 and far UVC plus 282) or 6.5 cm (UVC) above the sample. The apple juice sample was placed in a dish with a depth of 0.5 cm and diameter of 8.4 cm.

Determination of UV fluence. To compare the rates of photodegradation of patulin through UV illumination with various wavelengths, applied and average UV fluences were determined in this study. Applied UV fluence is the energy generated by incident UV irradiance on the surface of a sample in a certain exposure time. Average UV fluence reflects the average energy in the whole liquid sample. The calculation of UV fluences was based on the geometric structure of the UV reactor (Fig. 2).

At any infinitely small volume in the liquid sample with a coordinate (x,y,z) which receives the UV irradiation from the point on the lamp with a given distance (l) to the center of the lamp, the UV fluence rate can be expressed as in equation 1 below. It is deduced from the equation proposed by Jacob and Dranoff *(19)* with consideration of the reflection factor. (See Table 1 for nomenclature used in this article.)

$$dE(x,y,z,l) = \frac{P \cdot dl}{4\pi d^2 L}(1-\mathrm{Re})10^{-\alpha d'} \quad (1)$$

where P is the output power of the UV lamp; L is the length of the UV lamp; α is the absorption coefficient of the liquid sample; d is the distance between the infinitely small segment of the UV source and any infinitely small volume (x,y,z), which can be calculated by

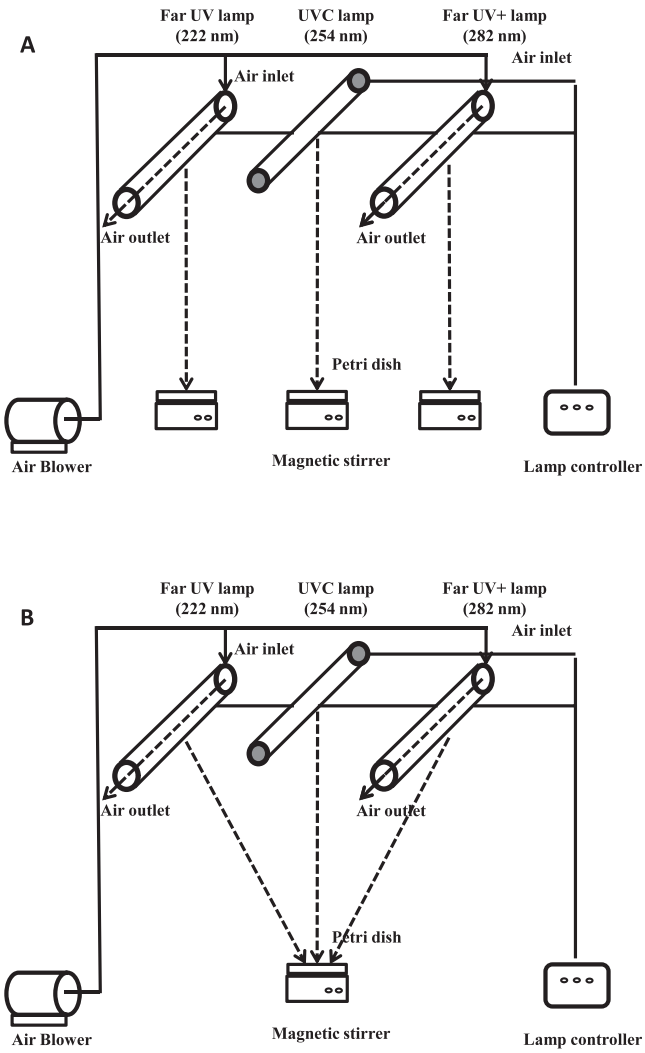

FIGURE 1. *Schematics of a triple-wavelength box UV reactor. (A) Exposure under a single UV lamp. (B) Exposure under three UV lamps.*

equation 2a for the lamp vertically above the sample or by equation 2b for the lamp diagonally above the sample; d' is the part of d in the liquid sample that can be calculated by equation 3; and Re is the reflectance, which can be calculated by equation 4. The refraction of UV light in the liquid sample was neglected to make the model simple. These equations are as follows:

$$d = \sqrt{(H+z)^2 + (l-x)^2 + y^2} \quad (2a)$$

$$d = \sqrt{(H+z)^2 + (l-x)^2 + (D-y)^2} \quad (2b)$$

$$d' = \frac{zd}{H+z} \quad (3)$$

where H is the distance between the UV lamp and the surface of the liquid sample and D is the vertical distance between the UV lamp and the plane across the center of the petri dish and is perpendicular to the sample surface, and

$$\mathrm{Re} = \frac{1}{2}\left[\left(\frac{n_2 \cdot \cos\varphi_1 - n_1 \cdot \cos\varphi_2}{n_1 \cdot \cos\varphi_2 + n_2 \cdot \cos\varphi_1}\right)^2 + \left(\frac{n_1 \cdot \cos\varphi_1 - n_2 \cdot \cos\varphi_2}{n_1 \cdot \cos\varphi_1 + n_2 \cdot \cos\varphi_2}\right)^2\right] \quad (4)$$

where φ_1 and φ_2 are incident and refracted angles at the interface between two media with refraction indices of n_1 and n_2.

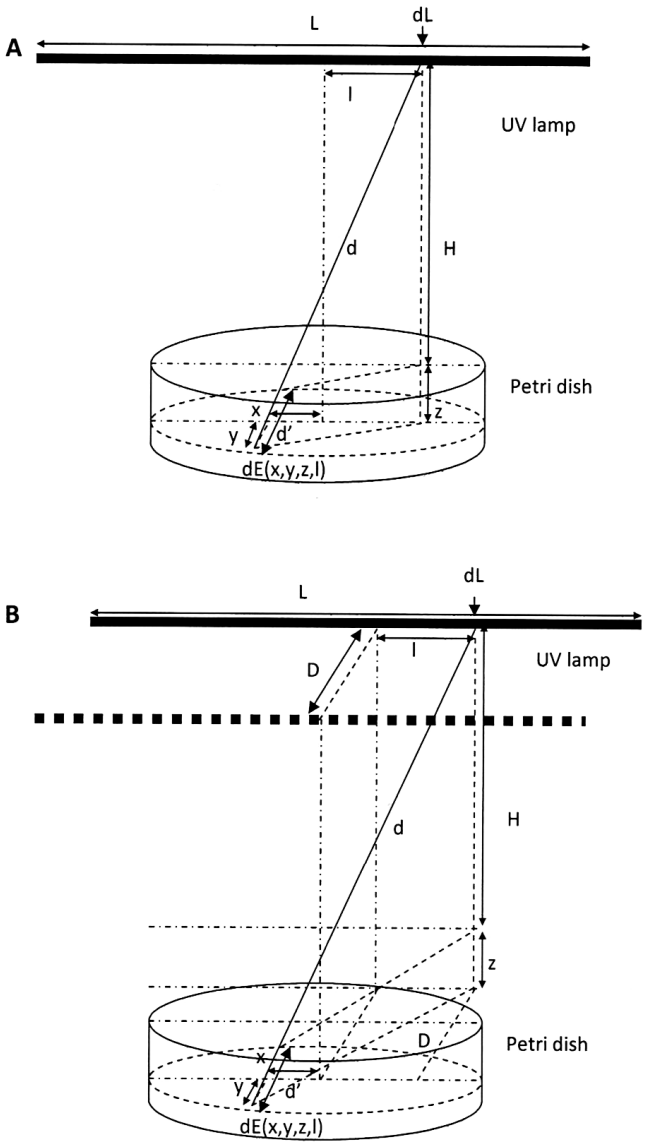

FIGURE 2. *Diagrammatic sketch of mathematic model of the determination of UV fluence rate. (A) Exposure under single UV lamp. (B) Exposure under three UV lamps (shows the lamp diagonally above the sample).*

Thus, the average UV fluence rate can be calculated by equation 5:

$$E_{\text{avg}} = \frac{\int_x \int_y \int_z \int_l dE(x,y,z,l) \cdot dx \cdot dy \cdot dz}{\int_x \int_y \int_z dx \cdot dy \cdot dz} \tag{5}$$

The average UV fluence can be calculated by equation 6:

$$H_{\text{avg}} = E_{\text{avg}} \cdot t \tag{6}$$

As equation 5 cannot be integrated analytically, equation 1 can be rewritten in a ''finite'' form, as follows:

$$E(x,y,z,l) = \frac{P}{4\pi d^2 n} \cdot (1 - \text{Re}) \cdot 10^{-\alpha d'} \tag{7}$$

In equation 7, n is the number of lamp segments with equal space. The total lamp output power P can be calculated based on the fluence rate at the center point of the sample surface measured by a radiometer (equations 8 and 9):

$$dE_0(l) = \frac{P \cdot dl}{4\pi(l^2 + H^2)L} \tag{8}$$

Equation 8 can be integrated into equation 9, as follows:

$$E_0 = \frac{P}{4\pi HL}\left(\arctan\frac{L_1}{H} + \arctan\frac{L_2}{H}\right) \tag{9}$$

where L_1 and L_2 are the parts of the lamp length from each edge to the point that projects to the center of the petri dish, and E_0 is the fluence rate at the center of the petri dish, which can be measured by a radiometer.

When the output power P is obtained, the fluence rate of any point in the sample with a coordinate of (x,y,z) which received UV irradiation from all parts of the lamp can be calculated (equation 7). The applied and average UV fluence rates can be calculated from a series of point fluence rates with equal increments along the axes of x (0.2 cm), y (0.2 cm), and z (0.005 cm).

Modeling of patulin reduction kinetics. An average-fluence-based first-order reduction model for inactivation of microorganisms was mentioned by Severin et al. *(32)* and Ye et al. *(42)*. Assatarakul et al. *(2)* and Zhu et al. *(44)* reported the application of the model to the photodegradation of patulin in apple cider and juice. The kinetics model is mathematically expressed as equation 10a. k_f is the average-fluence-based first-order reaction rate constant, with a unit of $\text{mW}^{-1}\cdot\text{cm}^2\cdot\text{s}^{-1}$. It was obtained from linear regression between $\ln(N/N_0)$ and the average UV fluence $(E_{\text{avg}}\cdot t)$. Alternately, an applied-fluence-based first-order reduction model was introduced through replacing the average UV fluence with the applied UV fluence (equation 10b). k_{f0} is the applied-fluence-based first-order reaction rate constant, with a unit of $\text{mW}^{-1}\cdot\text{cm}^2\cdot\text{s}^{-1}$. In this study, two fluence-based first-order reduction models were adopted. k_f was proposed to predict patulin reduction when the applied UV fluence rate, sample thickness, mixing condition, and media were known, and k_{f0} was used to compare the efficiencies of UV lamps with the same UV reactor, sample thickness mixing conditions, and media.

$$\ln\frac{N}{N_0} = -k_f E_{\text{avg}} t \tag{10a}$$

$$\ln\frac{N}{N_0} = -k_{f0} E_{\text{app}} t \tag{10b}$$

T_{90} is the exposure time required to reduce 90% of patulin in apple juice by the UV irradiation. It can be obtained from equation 11:

$$T_{90} = \frac{\ln(0.1)}{-k_f E_{\text{avg}}} \tag{11}$$

The average UV fluence required for 90% reduction of patulin (H_{90}) can be calculated from equation 12:

$$H_{90} = E_{\text{avg}} T_{90} \tag{12}$$

To compare the efficiencies of UV lamps with different wavelengths, the lamp efficiency index (LEI) was defined as the ratio of the applied-fluence-based first-order reaction rate constant (k_{f0}) to the value for a traditional UV lamp with a 254-nm wavelength, as follows:

$$\text{LEI} = \frac{k_{f0}}{k_{f0(254\text{nm})}} \tag{13}$$

UV radiation. In the patulin reduction study, the separate samples spiked with 1.0 $\text{mg}\cdot\text{liter}^{-1}$ of patulin were exposed for a series of sampling points. The UV fluence rates and exposure times are given in Table 2. In the quality study, the apple juice samples were exposed for the times (T_{90}) which resulted in UV fluence equivalent to that which resulted in patulin reduction (Table 3). The temperatures in samples before and after UV exposure were

TABLE 1. *Nomenclature*

Symbol	Definition	Unit
α	Absorption coefficient	cm^{-1}
α_{254}	Absorption coefficient at 254 nm	cm^{-1}
λ	Wavelength	m
φ_1	Incident angle	
φ_2	Refracted angle	
a*	Parameter in the CIELAB color scale positioned between green and red	
b*	Parameter in the CIELAB color scale positioned between blue and yellow	
c	Speed of light	$m \cdot s^{-1}$
d	Distance between an infinitely small segment of the UV source and an infinitely small volume in the sample	cm
d'	The part of d in the liquid sample that can be calculated as $d' = zd/(H + z)$	cm
D	Vertical distance between UV lamp and the plane that crosses the center of the petri dish and is perpendicular to the sample surface	cm
E_0	Fluence rate at center of petri dish	$mW \cdot cm^{-2}$
$E_{(x,y,z,l)}$	Fluence rate at point in sample which received light emitted from UV lamp at position l	$mW \cdot cm^{-2}$
E_{app}	Applied UV fluence rate	$mW \cdot cm^{-2}$
E_{avg}	Average UV fluence rate	$mW \cdot cm^{-2}$
E_p	Photon energy per mole	$kJ \cdot mol^{-1}$
ΔE^*	Total color difference in the CIELAB color scale	
h	Planck's constant	J·s
H	Distance between UV lamp and surface of sample	cm
H_{90}	Average UV fluence that results in 90% reduction of patulin	$mJ \cdot cm^{-2}$
H_{avg}	Average UV fluence	$mJ \cdot cm^{-2}$
k_f	Average-fluence-based first-order reaction rate constant	$mW^{-1} \cdot cm^2 \cdot s^{-1}$
k_{f0}	Applied-fluence-based first-order reaction rate constant	$mW^{-1} \cdot cm^2 \cdot s^{-1}$
L	Length of UV lamp	cm
L*	Lightness parameter in the CIELAB color scale	
n_1	Refraction index of air	
n_2	Refraction index of apple juice	
N	Patulin concentration	$mol \cdot liter^{-1}$
N_0	Initial patulin concentration (before UV irradiation)	$mol \cdot liter^{-1}$
N_A	Avogadro's number	
Re	Reflectance	
t	UV exposure time	s
T_{90}	UV exposure time that results in 90% reduction of patulin	s

monitored by measuring the liquid samples with an IKA ETS-D4 digital temperature probe (IKA Works, Inc., Wilmington, NC).

HPLC analysis for patulin and ascorbic acid concentration. Samples were extracted using solid-phase extraction as described by Eisele and Gibson *(9)*. Oasis HLB extraction cartridges (3 ml/60 mg; Waters, Milford, MA) were conditioned by passing 2 ml of water, 2 ml of methanol, and 2 ml of water at a flow rate of approximately 0.1 $ml \cdot s^{-1}$. The sample (1 ml) was applied to the column followed by 2 ml of a 1.0% (wt/vol) sodium bicarbonate solution and then 2 ml of 1.0% (vol/vol) acetic acid. The patulin was then eluted using 1.0 ml of ethyl acetate and evaporated to dryness under a stream of nitrogen. The residue was then dissolved in 0.5 ml of 0.1% (vol/vol) acetic acid prior to analysis. The standard patulin solutions of 10, 50, 100, 500, and 1,000 $\mu g \cdot liter^{-1}$ were prepared and extracted using the same method described above to form the linear working curve (10 to 1,000 $\mu g \cdot liter^{-1}$). Samples and standards were filtered by using syringe filters with a 0.45-μm pore size and were analyzed using a high-pressure LC (HPLC) system (1200 Series, Agilent

TABLE 2. *Experimental conditions of UV exposure*

Medium	UV lamp	Applied UV fluence rate ($mW \cdot cm^{-2}$)	Avg UV fluence rate ($mW \cdot cm^{-2}$)	Exposure times (s)
Apple cider	222 nm	4.63	0.10	0, 180, 360, 540, 720, 900
	254 nm	8.27	0.31	0, 180, 360, 540, 720, 900
	282 nm	7.85	0.31	0, 180, 360, 540, 720, 900
	Triple lamps	13.93	0.44	0, 60, 120, 180, 240, 300
Apple juice	222 nm	4.95	0.11	0, 60, 120, 180, 240, 300
	254 nm	8.18	0.30	0, 60, 120, 180, 240, 300
	282 nm	7.76	0.36	0, 60, 120, 180, 240, 300
	Triple lamps	13.94	0.41	0, 20, 40, 60, 80, 100

TABLE 3. *Patulin reduction by a triple-wavelength box UV reactor*[a]

Medium	UV lamp	Avg-fluence-based reaction rate constant ($mW^{-1}\cdot cm^2\cdot s^{-1}$)	T_{90} (s)	H_{90} ($mJ\cdot cm^{-2}$)
Apple cider	222 nm	1.30E−2 ± 4.55E−4 A	1,797 ± 62 A	177.9 ± 6.1 A
	254 nm	2.63E−3 ± 9.69E−5 B	2,812 ± 102 B	877.2 ± 31.8 B
	282 nm	3.09E−3 ± 2.45E−5 C	2,387 ± 19 C	744.8 ± 5.9 C
	Triple lamps	4.22E−3 ± 1.46E−4 D	1,231 ± 43 D	545.5 ± 19.2 D
Apple juice	222 nm	1.17E−1 ± 2.15E−3 A	175 ± 3 A	19.6 ± 0.4 A
	254 nm	2.73E−2 ± 6.01E−4 B	286 ± 6 B	84.2 ± 1.8 B
	282 nm	4.20E−2 ± 2.17E−3 C	151 ± 8 C	55.0 ± 2.8 C
	Triple lamps	6.30E−2 ± 2.68E−3 D	90 ± 4 D	36.6 ± 1.6 D

[a] Values are averages ± standard deviations ($n = 3$) for all analyses. Different letters (A, B, C, D) indicate that significant differences ($P < 0.05$) in mean values were observed.

Technology, Palo Alto, CA) equipped with a quaternary pump, an inline degasser, and a diode array detector set at 276 nm. A Phenomenex Luna 3-μm-particle-size C_{18} column (250 by 2.0 mm) with a C_{18} guard column (Torrance, CA) was used for the separation. Portions (50 μl each) of samples and standards were eluted isocratically using 0.8% (vol/vol) tetrahydrofuran in water at a flow rate of 0.2 $ml\cdot min^{-1}$ and with a run time of 25 min. The retention time of patulin was around 20 min. The 5-hydroxymethylfurfural, a compound that interferes with patulin detection, was eluted around 17.5 min, which ensured the baseline separation of these two compounds. The patulin detection limit in this system was approximately 10 $\mu g\cdot liter^{-1}$. Control samples were measured before UV treatment to confirm that they were patulin free. All samples and standards were analyzed in triplicate.

The concentrations of ascorbic acid were determined by HPLC. Apple juice samples were diluted 10 times with water. Standard ascorbic acid solutions of 5, 10, 20, 30, and 40 $mg\cdot liter^{-1}$ were prepared to form the linear working curve (5 to 40 $mg\cdot liter^{-1}$). Samples and standards were analyzed using an HPLC system (Agilent Technology 1200 Series) with a Phenomenex Luna 3-μm-particle-size C_{18} column (250 by 2.0 mm) (Torrance, CA) and a diode array detector set at 245 nm. The mobile phase was water–acetonitrile–formic acid (95%) (95:5:0.095 [vol/vol/vol], pH 1.8 adjusted by HCl), and the flow rate was 0.5 $ml\cdot min^{-1}$. The injection volume was 20 μl, and the retention time was around 4 min.

Optical properties, pH, and color of treated apple juice. A UV/visible spectrometer (Ultrospec 3100 Pro, Biochrom Ltd., Cambridge, England) was used to identify and quantify the absorbance of the samples. Each sample was tested in triplicate before and after UV treatment using demountable fused-quartz cuvettes (NSG Precision Cell, Inc., Farmingdale, NY). The apple cider and juice samples were tested in a series of cuvettes (0.01, 0.02, 0.05, 0.075, and 0.1 cm), and the absorbance coefficients were determined by the slope of the linear plot absorbance versus path length. pH was measured with a pH meter (Hack Company, Loveland, CO). The soluble solids contents were determined by using a Leica Mark II ABBE refractometer (Leica Microsystems, Inc., Buffalo, NY). Color was measured in the CIELAB scale with the Lab Scan XE spectrocolorimeter (HunterLab, Reston, VA). L* (lightness), a* (redness), and b* (yellowness) were measured, and the total color difference (ΔE^*) was calculated using equation 14:

$$\Delta E^* = \sqrt{(L^*_{control} - L^*)^2 + (a^*_{control} - a^*)^2 + (b^*_{control} - b^*)^2} \quad (14)$$

A ΔE^* value of around 2.3 corresponds to a just noticeable difference *(27),* and it was used to evaluate the change of color after UV treatment.

Sensory evaluation. A triangle test was performed to determine whether a significant color change occurs in apple juice after UV radiation. The 20 experienced panelists were employees and students in the Department of Food Science at the University of Guelph. Apple juice samples without patulin spiking were treated by UV radiation for the time (T_{90}) that resulted in UV fluence equivalent to that used for patulin reduction (Table 3). For each treatment, two control samples without UV radiation and one UV-treated sample were numbered randomly with 3-digit codes and placed in a random order. The panelists were asked to identify the odd one from each set of samples. The results were evaluated with the chi-square distribution, and statistically significant differences were determined by comparison between the calculated chi-square value (χ^2) and the reference value of 3.84 ($df = 1$, $\alpha = 0.05$) *(25)*. If the calculated value was lower than the reference one, the null hypothesis could not be rejected and we concluded there was no significant difference between the control and UV-treated samples.

Statistical analysis. All UV-processing conditions were performed in triplicate with a completely independent and randomized design. The statistical analyses of experimental data were carried out with SPSS version 20 (IBM, Armonk, NY). Statistically significant differences between control and UV treatments were evaluated through paired t test. The data of applied-fluence-based first-order reaction rate constants which were used to compare the efficiencies of UV lamps with different wavelengths, as well as the relative changes in pH, total soluble solids, absorption coefficients at 254 nm, color, and concentrations of ascorbic acid after UV treatments among different wavelengths, were evaluated through one-way analysis of variance with the post hoc Fisher's least significance difference significance test. All patulin reduction rate constants were calculated from regression plots based on the series data of patulin concentrations at the sampling points during UV exposure. The coefficients of determination (R^2) were calculated.

RESULTS

Reduction of patulin with UV exposure at three wavelengths. UV treatment of apple juice at all three wavelengths tested (222, 254, and 282 nm) resulted in a significant reduction ($P < 0.05$) in patulin compared with the amount in nontreated controls. The UV inactivation kinetics followed first-order inactivation kinetics, with the degradation rate being dependent on the applied wavelength (Figs. 3 to 5 and Table 3). Based on the first-order reaction model and equation 12, average UV fluences of 19.6, 84.3,

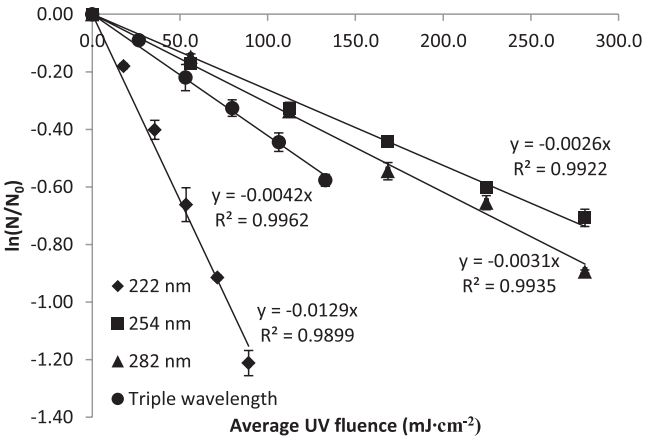

FIGURE 3. *Reduction of patulin in apple cider by UV exposure with individual 222-, 254-, and 282-nm wavelength UV lamps and the combination of the three UV lamps.*

55.0, and 36.6 mJ·cm^{-2} resulted in 90% reduction of patulin in apple juice through exposure to UV lamps with 222-, 254-, and 282-nm wavelengths and the combination of the three wavelengths, respectively. The average UV fluences that resulted in 90% reduction of patulin in apple cider were 177.9, 877.2, 744.8, and 545.5 mJ·cm^{-2}, respectively.

Efficiencies of far UVC (222 nm), UVC (254 nm), and far UVC plus (282 nm) lamps. The patulin reduction efficiencies of the UV lamps were determined by comparing the applied-fluence-based first-order reaction rate constants (k_{f0}). The lamp efficiency indices, defined by equation 13, were 2.80, 1.00, 2.00, and 1.87 for apple juice and 2.69, 1.00, 1.24, and 1.36 for apple cider exposed to far UVC (222 nm), UVC (254 nm), far UVC plus (282 nm), and the combination of the three lamps, respectively (Table 4).The order of efficiency of the three monochromatic-wavelength lamps was determined to be 222 nm > 282 nm > 254 nm.

Quality attribute study. A separate study evaluated the effects of UV treatment on quality factors, such as pH, total soluble solids, absorption coefficient at 254 nm, color,

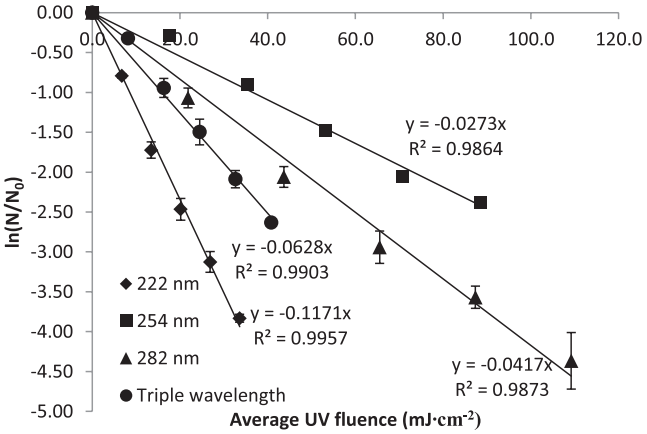

FIGURE 4. *Reduction of patulin in apple juice by UV exposure with individual 222-, 254-, and 282-nm wavelength UV lamps and the combination of the three UV lamps.*

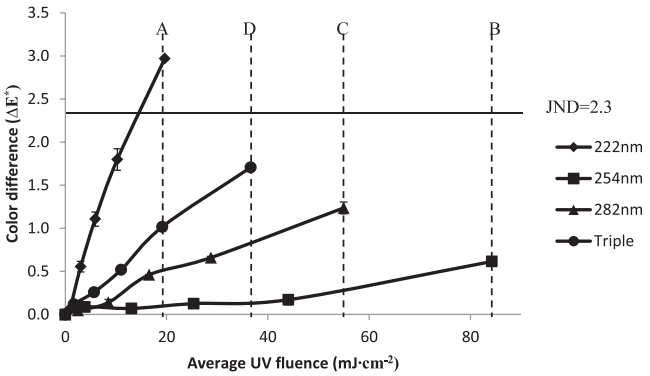

FIGURE 5. *Color changes in apple juice by UV exposure with individual 222-, 254-, and 282-nm wavelength UV lamps and the combination of the three UV lamps. (A, B, C, D) Applied UV fluences of 222-, 254-, and 282-nm lamps and the combination of the three lamps, respectively, corresponding to the time for 90% patulin reduction (T_{90}).*

and concentration of ascorbic acid. Apple juice samples were treated at the different UV wavelengths with UV fluences equivalent to those supporting a 90% reduction of patulin (Table 3). The data in Table 5 show that the treatments did not significantly affect ($P > 0.05$) the pH values and total soluble solids (°Brix) of the apple juice. The absorption coefficients at 254 nm were compared, and all four treatments showed significant decreases ($P < 0.05$) after UV exposure (Table 5). The greatest decrease of the absorption coefficient (23.85%) was observed for exposure under the 254-nm UV lamp, which indicated that components in the apple juice with peak absorption near 254 nm underwent photodegradation. There were significant decreases ($P < 0.05$) in the ascorbic acid concentration of apple juice at all UV wavelengths tested (Table 5). The highest loss in ascorbic acid was observed at 254 nm (45.3%).

The total color differences (ΔE^*) in the apple juice after exposure (T_{90}) under 222, 254, and 282 nm, and the combination of the three lamps, were 2.97, 0.61, 1.24, and 1.71, respectively (Fig. 5). Because a ΔE^* value of around 2.3 corresponds to a just noticeable difference *(27),* the color changes caused by 254 nm, 282 nm, and combined UV lamps were unnoticeable, whereas the color changes that resulted from 222 nm were slightly noticeable. However, the triangle sensory test showed no significant color changes between samples before and after UV irradiation.

Temperature monitoring during UV exposure. A maximum of 1.9°C of temperature increase was observed by measuring apple cider and apple juice samples with the various applied UV fluence rates and exposure times listed in Table 2. The fact that the change of temperature was within 2°C indicated that no heating effect resulted from UV sources in this study.

DISCUSSION

Occurrences of patulin contamination in apple cider and juice have been reported in several studies and surveillances *(13, 24, 26),* and most of the contamination levels were

TABLE 4. *Lamp efficiencies for patulin reduction*

Media	UV lamp	Applied-fluence-based reaction rate constant ($mW^{-1}\cdot cm^2\cdot s^{-1}$)[a]	LEI[b]
Apple cider	222 nm	2.77E−4 ± 9.72E−6 A	2.80
	254 nm	9.91E−5 ± 3.66E−6 B	1.00
	282 nm	1.24E−4 ± 9.73E−7 C	1.24
	Triple lamps	1.34E−4 ± 4.64E−6 D	1.36
Apple juice	222 nm	2.65E−3 ± 4.87E−5 A	2.69
	254 nm	9.86E−4 ± 2.17E−5 B	1.00
	282 nm	1.97E−3 ± 1.02E−4 C	2.00
	Triple lamps	1.84E−3 ± 7.86E−5 C	1.87

[a] Values are averages ± standard deviations ($n = 3$) for all analyses. Different letters (A, B, C, D) indicate that significant differences ($P < 0.05$) in mean values were observed.
[b] LEI, lamp efficiency index.

lower than 500 $\mu g\cdot liter^{-1}$. Thus, the UV fluence that results in a 90% reduction of patulin became an essential parameter for the design of potential commercial UV reactors to reduce the mycotoxin in apple cider and juice to the level of 50 $\mu g\cdot liter^{-1}$ that is acceptable according to national regulations *(10, 40)*. The average-fluence-based first-order reaction rate constants obtained by experimental results can be used to predict the UV fluence required to lead to a greater reduction of patulin (e.g., 99%). Assatarakul et al. *(2)* investigated the kinetics models of patulin degradation at 254 nm and provided first-order rate constants of 0.0294 $mW^{-1}\cdot cm^2\cdot s^{-1}$ in apple juice and 0.0053 $mW^{-1}\cdot cm^2\cdot s^{-1}$ in apple cider. The corresponding data determined in the current study (0.0273 $mW^{-1}\cdot cm^2\cdot s^{-1}$ in apple juice and 0.0026 $mW^{-1}\cdot cm^2\cdot s^{-1}$ in apple cider) agreed with the previous study; however, there were no data reported previously for the use of 222- and 282-nm UV lamps.

Because processing of liquid apple products with UV light is designed mainly for inactivation of pathogens, it is worth comparing the UV fluences resulting in 90% of patulin reduction to those necessary for reduction of microbial pathogens. Many studies identified a germicidal performance of UV reactors at 254 nm on *E. coli* O157:H7 and its surrogates *(12, 23, 41)*. Wright et al. *(41)* reported that a 5.4-log reduction of *E. coli* O157:H7 in apple cider was achieved by a UV fluence of 61 $mJ\cdot cm^{-2}$ using a thin-film UV disinfection unit. Forney et al. *(12)* also examined

TABLE 5. *Effects of the UV irradiation on pH, total soluble solids, absorption coefficient, color, and concentration of ascorbic acid*

Quality attribute	Sample type or difference[a]	Value (mean ± SD) obtained using[b]: Far UV lamp (222 nm)	UVC lamp (254 nm)	Far UV plus lamp (282 nm)	Triple lamps
pH	C	3.18 ± 0.01	3.19 ± 0.01	3.16 ± 0.01	3.17 ± 0.01
	T	3.19 ± 0.01	3.18 ± 0.01	3.18 ± 0.01	3.18 ± 0.01
	RC (%)	0.31 ± 0.32 AB	−0.10 ± 0.18 A	0.42 ± 0.18 B	0.32 ± 0.32 AB
Soluble solids (°Brix)	C	11.17 ± 0.06	11.13 ± 0.06	11.17 ± 0.06	11.10 ± 0.00
	T	11.13 ± 0.06	11.17 ± 0.06	11.13 ± 0.06	11.10 ± 0.10
	RC (%)	−0.30 ± 0.51 A	0.30 ± 1.03 A	−0.30 ± 0.51 A	0.00 ± 0.90 A
α_{254}	C	24.66 ± 0.02	24.79 ± 0.03	24.68 ± 0.03	24.77 ± 0.01
	T	20.62 ± 0.04	18.88 ± 0.07	19.98 ± 0.07	20.51 ± 0.07
	RC (%)	−16.36 ± 0.11* A	−23.85 ± 0.22* B	−19.04 ± 0.25* C	−17.22 ± 0.26* D
L*	C	49.30 ± 0.02	49.36 ± 0.07	49.23 ± 0.02	49.28 ± 0.06
	T	50.23 ± 0.07	49.71 ± 0.04	49.73 ± 0.05	49.83 ± 0.06
	RC (%)	1.88 ± 0.13* A	0.72 ± 0.12* B	1.01 ± 0.11* C	1.12 ± 0.05* C
a*	C	−1.67 ± 0.01	−1.67 ± 0.01	−1.64 ± 0.01	−1.63 ± 0.01
	T	−2.45 ± 0.01	−1.88 ± 0.01	−2.06 ± 0.01	−2.14 ± 0.01
	RC (%)	−46.42 ± 0.79* A	−12.57 ± 0.60* B	−26.07 ± 0.41* C	−31.56 ± 0.47* D
b*	C	25.00 ± 0.05	24.97 ± 0.03	25.00 ± 0.02	24.97 ± 0.03
	T	22.29 ± 0.03	24.52 ± 0.03	23.96 ± 0.06	23.44 ± 0.07
	RC (%)	−10.84 ± 0.20* A	−1.81 ± 0.23* B	−4.19 ± 0.19* C	−6.13 ± 0.15* D
Ascorbic acid ($mg\cdot liter^{-1}$)	C	277.57 ± 0.37	267.17 ± 5.07	271.54 ± 3.92	270.63 ± 1.43
	T	176.36 ± 4.67	146.04 ± 4.26	173.53 ± 5.11	172.62 ± 4.76
	RC (%)	36.46 ± 1.62* A	45.34 ± 0.56* B	36.07 ± 2.75* A	36.22 ± 1.47* A

[a] C, control sample without UV treatment; T, sample treated with UV light for T_{90}; RC, relative change.
[b] *, significant difference ($P < 0.05$) between control and UV-treated sample. Different letters (A, B, C, and D) indicate that significant differences ($P < 0.05$) in mean values were observed between the UV treatments.

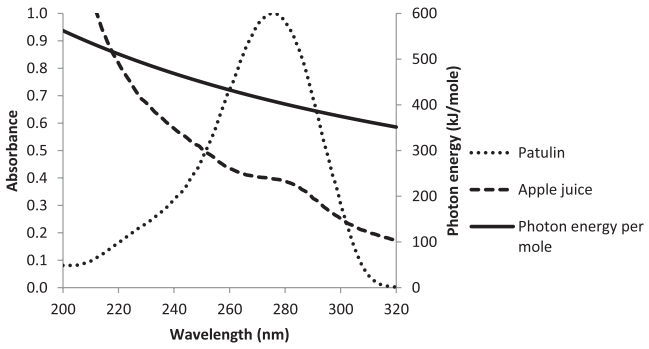

FIGURE 6. *Relationship between the photon energy and the absorbance spectrums of apple juice (0.2 cm of light path length) and 10 mg·liter^{-1} patulin (1 cm of light path length).*

the Taylor-Couette flow UV reactor, and a UV fluence of 21.7 mJ·cm^{-2} for 3- to 5-log reduction of *E. coli* 15597 in apple juice was determined. In addition, Koutchma and Parisi *(23)* determined decimal reduction UV fluences of 4.60 and 6.46 mJ·cm^{-2} on *E. coli* K-12 in apple juice and apple cider, respectively. The average UV fluence resulting in 90% patulin reduction in apple juice (84.2 mJ·cm^{-2}) from 254-nm UV light indicated that it was enough to reduce *E. coli* O157:H7 by 5 log, although the UV reactors and experimental settings were different. Therefore, future work will determine the UV fluences required for 5-log reduction of pathogens in apple juice using 222-, 254-, and 282-nm UV light and confirm whether the fluence resulting in 90% patulin reduction can simultaneously reduce pathogens by 5 log.

Although UV irradiation with a 254-nm wavelength is widely recognized as a successful nonthermal technique for pathogen inactivation, the study of UV lamps with other wavelengths to determine the specific characteristics of their propagated photons is still valuable. Under similar applied UV fluences, the efficiencies of patulin photodegradation through UV lamps at the specific wavelengths were influenced by the photon energy, absorption spectrum of patulin, and absorption spectrum of apple juice. Among them, the photon energy (E_p) is inversely proportional to the wavelength (equation 15):

$$E_p = \frac{hcN_A}{\gamma} \tag{15}$$

Most of the bond energies are coincident with the photon energies in the UV range *(4)*. In general, the photon with a lower wavelength has sufficient energy to break the bonds and consequently promotes a photochemical reaction of the component of interest. The spectrum of patulin absorption affects the reduction rate. Based on the Grotthuss-Draper law of photochemistry *(14),* the light must be absorbed by a chemical substance in order for a photochemical reaction to take place. The photons with the wavelength closer to its peak absorption at 276 nm can be easily absorbed by patulin and then photodegrade patulin efficiently. A higher absorption coefficient impedes the penetration of UV light and reduces the average UV fluence in the whole sample. The relationships among the three factors are shown in Figure 6. The experimental data assessed the overall effects of these three factors on patulin reduction among UV lamps with three wavelengths. The fact that the reduction rate caused by 222 nm was far greater than the reduction rates caused by 282 and 254 nm indicated that the order of priority for choosing a UV lamp with a specific wavelength was photon energy, spectrum of patulin absorption, and spectrum of apple juice absorption. Meanwhile, the potential quality changes of apple juice should be evaluated.

Liquid apple products are complex matrices containing sugars, organic acids, polyphenolic groups, and added ascorbic acid *(5),* although the natural concentration of ascorbic acid in apple juice is as low as 9.0 mg·liter^{-1} *(37)*. Normally, additional ascorbic acid is added to enhance the nutrient value of apple juice to a level of 385 mg·liter^{-1} *(38)*. The loss of ascorbic acid in all UV treatments was significant and could be viewed as a limitation of the nonthermal pasteurization method. Several studies have reported loss of ascorbic acid in fruit juices when exposed to UV light *(11, 20, 35, 36, 42)*. However, by using 222 nm, not only is a higher level of patulin degradation achieved but the ascorbic acid losses are numerically lower. Because of the UV instability of ascorbic acid, it would be beneficial to replenish the nutrient after UV radiation.

As with other UV treatments, there was a change in color following treatment due to the generation of photo byproducts. Typically, UV treatment results in an increase in L* and decrease of a* (from red to green) and b* (from yellow to blue) *(17)*. The same observation was made in the current study, although the color changes using 222, 254, and 282 nm did not result in any significant changes in the apple juice. Flavor evaluation is another important sensory test to discriminate the quality change of apple juice after UV treatment. The current study did not perform the test due to the nonfood-grade UV reactor and processing facility. This evaluation will be included in future work.

The patulin degradation products resulting from UV radiation are still unknown. Seeking the photoproducts of patulin and evaluating the toxicological effects of extracted byproducts of patulin and/or UV-treated apple cider and juice spiked with patulin should be done in future work.

In conclusion, the rate of patulin photodegradation is wavelength dependent. Among UV lamps with wavelengths of 222, 254, and 282 nm, the far UVC lamp (222 nm) was the most effective UV source due to the best performance of the photon energy and apple juice and patulin absorbance at this wavelength. Meanwhile, the advantages of no significant changes in pH, total soluble solids, and color in apple juice after UV exposure at 222 nm for a time sufficient to degrade 90% of patulin (T_{90}) demonstrate the potential for further development of this novel UV source for commercial applications.

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