Recycling of Colored Office Paper. Part II: Post-bleaching with Formamidine Sulfinic Acid and Hydrogen Peroxide

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In this study, the optimization of formamidine sulfinic acid (FAS) and hydrogen peroxide (P) bleaching stages of pre-bleached blue, red, yellow, green, and mixed colored office papers was investigated. The FAS was performed as a strong color stripping reagent on blue and green colored samples. However, due to reduced amine compounds FAS was not found to be effective on the red colored samples. In contrast, effective results were obtained with hydrogen peroxide on the red and yellow colored samples. These results showed that the two reagents must be used together in a sequence. Therefore, in this study, FASP and PFAS bleaching sequences were also investigated and the optical properties (absorbance (*k*/*s*) spectra, CIE *L**a*b** color values, and ISO brightness) of these sequences were compared. The color differences (CIE Δ*E*) of FASP and PFAS bleaching sequences of the mixed colored samples were calculated as 18.2% and 16.1%, respectively. The FASP bleaching sequence was determined to be more effective than the PFAS sequence for the bleaching of all samples. As a result, this study showed that FAS, a strong reducing agent, and hydrogen peroxide, an effective oxidative decolorizer, can be used together to obtain white writing papers from waste direct dye colored office papers.

*Keywords: Formamidine sulfinic acid; Hydrogen peroxide; Post-bleaching; L*a*b* Color values; Colored office paper*

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INTRODUCTION

An increasing number of offices have recognized the importance of using colored paper to upgrade the effectiveness of their paper communication system (Anonymous 1989). This and the attractiveness of colored products have increased the demand for colored office paper. However, a problem has arisen in eliminating color from these kinds of waste papers during recycling. Coloring agents are regarded as a contaminant during recycling. Colored paper can be recycled to produce the same color or bleached to improve whiteness (McKinney 1995). The first option is not very feasible in terms of collection and classification of waste papers of the same color. Therefore, the mixing and bleaching of such colored papers seems to be a more efficient use of resources.

Direct dyes are the most frequently used dyes in the paper industry. Direct dyes are partially similar to acid dyes but they do not require separate bonding agents and are of a higher molecular weight. Many direct dyes used in papermaking can be decolorized with reductive bleaching agents.

The azo linkage is sensitive to reduction and often gives colorless products. However, many of the reduced amine compounds have a yellowish color that must be eliminated by oxidative bleaching agents (Minor 1992). Therefore, an effective color removal can be achieved through a sequence of reducing and oxidative bleaching stages. For this purpose, in the study, reductive formamidine sulfinic acid (FAS) and oxidative hydrogen peroxide (P) were studied as bleaching agents. The preference for FAS as a reducing agent was due to its more effective reduction ability than the comparable equivalent "sodium hydrosulfite," and because it is more resistant to air oxygen (Patt *et al.* 1996; Gehr 1997). It is well known that hydrosulphite causes corrosion of steel when it reacts with oxygen by forming thiosulfate (Davaney and Guess 1982; Garner 1982; Bond *et al.* 1991). The other alternative is sodium borohydride, a much better reducing agent (Lee *et al.* 1993). However, sodium borohydride is much more expensive than FAS and sodium hydrosulphite (Peşman *et al.* 2011).

The bleaching of recycled papers by FAS has been studied by many researchers, and they have concluded that FAS is a very powerful reductive bleaching agent (Kronis 1992; Dumont *et al.* 1994; Forsberg and Genco 1994; Patt *et al.* 1996; Kang *et al.* 2000; Perng *et al.* 2014). Deneault *et al.* (1995) reported that the reaction of FAS was extremely fast, and the brightness gain was the same between 15 min and 2 h reaction time (Deneault *et al.* 1995). Similarly Fujiyasu (1997) achieved 84.4% ISO brightness with the FASZP bleaching sequence in his work on newsprint waste (contains lignin). He also worked on the FASP and PFAS sequences and achieved 81.3% and 81.9% ISO brightness values, respectively (Fujiyasu 1997). Vincent *et al.* (1997) studied FAS bleaching of wood-free waste paper, and it was concluded that FAS was primarily responsible for bleaching of dye components within the pulp. However, most of these studies have been conducted on waste mixed office papers and/or old newspapers. These kinds of waste papers include small amounts of dyed substances. Post-bleaching of colored broke with chlorine dioxide, hypochlorite, and hydrogen peroxide were studied by Vadivel *et al.* (2011). They had decided that the decolourisation of yellow broke was not possible with single stage chlorine dioxide, hydrogen peroxide, hypochlorite, or sodium hydrosulphite.

In the previous publication in this series, pre-bleaching of colored office papers with FAS was studied (Peşman and Laloğlu 2018). As is known, pre-bleaching is an auxiliary application during re-pulping of waste paper fiber. In that study, approximately 35% color removal (ΔE) was achieved in 10 minutes at pulper before flotation, washing, and post bleaching stages (Peşman and Laloğlu 2018).

Unlike other studies, this study investigated the post-bleaching stages of red, blue, green, and yellow colored office papers and the mixture of these colored office papers. The ISO brightness, CIE $L^*a^*b^*$, and CIE ΔE color differences of the samples were determined. In addition, the effects of the bleaching agent were investigated in more detail with the absorbance coefficient of samples in the 220 nm to 900 nm wavelength range.

EXPERIMENTAL

Materials

In this study pre-bleached pulps were used as materials. Pre-bleaching conditions in the pulper (Adirondack Machine Corporation, Hudson Falls, NY, USA) are shown in Table 1. The optical properties of pre-bleached pulps (materials) are shown in Table 2 according to data of previous study (Pesman and Laloğlu 2018).

Table 1. Pre-bleaching/Pulping Conditions

	Blue	Green	Red	Yellow	Mix
Office Paper Mixture Before (Pre-bleaching)	25% blue colored office paper + 75% white office paper	25% green colored office paper + 75% white office paper	25% red colored office paper + 75% white office paper	25% yellow colored office paper + 75% white office paper	6.25% red + 6.25% blue + 6.25% green + 6.25% yellow colored office paper + 75% white office paper
FAS	1.00%	1.00%	1.00%	1.00%	1.00%
NaOH	2%	2%	2%	2%	2%
Temperature	50 °C	50 °C	50 °C	50 °C	50 °C
Time	10 min	10 min	10 min	10 min	10 min
Consistency	8%	8%	8%	8%	8%

Table 2. Optical Properties of Pre-bleached Pulps (Peşman and Laloğlu 2018)

	Blue	Green	Red	Yellow	Mix
ISO Brightness (%)	85.49	76.94	72.00	78.77	68.01
CIE L*	88.21	87.05	92.20	96.88	87.30
CIE a*	-12.27	-16.53	3.00	-3.67	-12.67
CIE b*	-9.30	-3.81	8.61	11.49	4.20
∆E CIE 76	7.18	37.10	48.20	35.41	32.02
Whiteness Index (WI)	117.30	89.98	41.37	40.45	44.45

Methods

Post-bleaching- Optimization of single stage P and FAS bleaching stages

Post-bleaching of pre-bleached pulp samples was conducted at 80 °C for 60 min in polyethylene bags in a water bath. Single stage hydrogen peroxide and FAS bleaching conditions of this study are shown in Table 3.

Table 3. Single Stage P and FAS Bleaching Conditions

	P		FAS
Peroxide - Alkaline (NaOH) - Sodium Silicate Charges (%) **(1:0.75:0.75 ratio)**	0.25 : 0.1875 : 0.1875 0.50 : 0.3750 : 0.3750 0.75 : 0.5625 : 0.5625 1.00 : 0.7500 : 0.7500 1.50 : 1.1250 : 1.1250 2.00 : 1.5000 : 1.5000 3.00 : 2.2500 : 2.2500	**FAS - Alkaline (NaOH) Charges (%)** **(1:0.50 ratio)**	0.25 : 0.125 0.50 : 0.250 0.75 : 0.375 1.00 : 0.500 1.50 : 0.750 2.00 : 1.000 3.00 : 1.500 4.00 : 2.000
Magnesium Sulphate (%)	0.5	**Magnesium Sulphate (%)**	-
EDTA (%)	0.2	**EDTA (%)**	-
Temp. (°C)	80	**Temp. (°C)**	80
Time (min)	60	**Time (min)**	60
Consistency (%)	10	**Consistency (%)**	10
EDTA : Ethylenediaminetetraacetic acid			

FASP and PFAS bleaching sequences

In this study, it was also investigated whether the P bleaching stage should be applied before or after the FAS bleaching stage. The bleaching conditions of P and the FAS stage of FASP and PFAS sequences are shown in Table 4.

Table 4. Bleaching Conditions of P and FAS Stages of FASP and PFAS Bleaching Sequences

	FAS Stage		P Stage	
FASP	Formamidine sulphinic acid (%)	1.00	Hydrogen peroxide (%)	2.00
	Alkaline (NaOH (%)	0.50	Alkaline (NaOH (%)	1.50
	Sodium silicate (%)	---	Sodium silicate (%)	1.50
	Magnesium sulphate (%)	---	Magnesium sulphate (%)	0.5
	EDTA (%)	---	EDTA (%)	0.2
	Temperature (°C)	80	Temperature (°C)	80
	Consistency (%)	10	Consistency (%)	10
	Time (min)	60	Time (min)	60
	P Stage		**FAS Stage**	
PFAS	Hydrogen peroxide (%)	2.00	Formamidine sulphinic acid (%)	1.00
	Alkaline (NaOH (%)	1.50	Alkaline (NaOH (%)	0.50
	Sodium silicate (%)	1.50	Sodium silicate (%)	---
	Magnesium sulphate (%)	0.5	Magnesium sulphate (%)	---
	EDTA (%)	0.2	EDTA (%)	---
	Temperature (°C)	80	Temperature (°C)	80
	Consistency (%)	10	Consistency (%)	10
	Time (min)	60	Time (min)	60

Optical properties of handsheets

For each pulp sample, 60 g/m^2 handsheets were formed, pressed, and dried according to the TAPPI T205 sp-12 (2012) standard on a Rapid Köthen handsheet machine (Estanit, Mülheim, Germany). Handsheets were conditioned at 20 °C and 50% humidity for one week before optical tests.

The brightness values of handsheets were measured according to the TAPPI T452 om-08 (2008) standard under a 457 nm wavelength. Measurements were done using a UV filter to avoid the disturbance of some fluorescence effects of residual materials. Color measurements of the test paper were achieved according to the TAPPI T527-om 13 (2013) standard. The CIE whiteness values of handsheets were determined in accordance with TAPPI T562 pm-10 (2010). The brightness, color values, and whiteness of handsheets were measured with a Konica-Minolta Cm-2600d spectrophotometer (Konica Minolta, Osaka, Japan). The ratios of scattering coefficient to absorbance coefficient (k/s) were calculated according to Kubelka-Munk theory (Kubelka and Munk 1931) from the reflectance of handsheets. The reflectance spectra of handsheets were recorded on a Shimadzu 3600 ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (Shimadzu, Tokyo, Japan) equipped with an ISR-3100 (Shimadzu, Tokyo, Japan) ($BaSO_4$-coated integrated sphere).

RESULTS AND DISCUSSION

Single stage FAS and peroxide bleaching

Figure 1 shows the ISO brightness of handsheets. The FAS bleaching stage had a limited effect on the ISO brightness value of the blue, green, and red colored samples (approximately 2% increase with 1% FAS). However, 0.5% to 0.75% FAS usage increased the ISO brightness of the yellow and mixed colored sample as approximately 8%. In contrast, the use of peroxide increased the ISO brightness of all samples after 0.75% charge. This may have been due to the fact that hydrogen peroxide was a more effective reagent in eliminating the residual yellowish color formed after the pre-bleaching stage. The ISO brightness of mixed colored pulp increased from 68.1% to 80.3% with 2% hydrogen peroxide usage, as shown in Fig. 1.

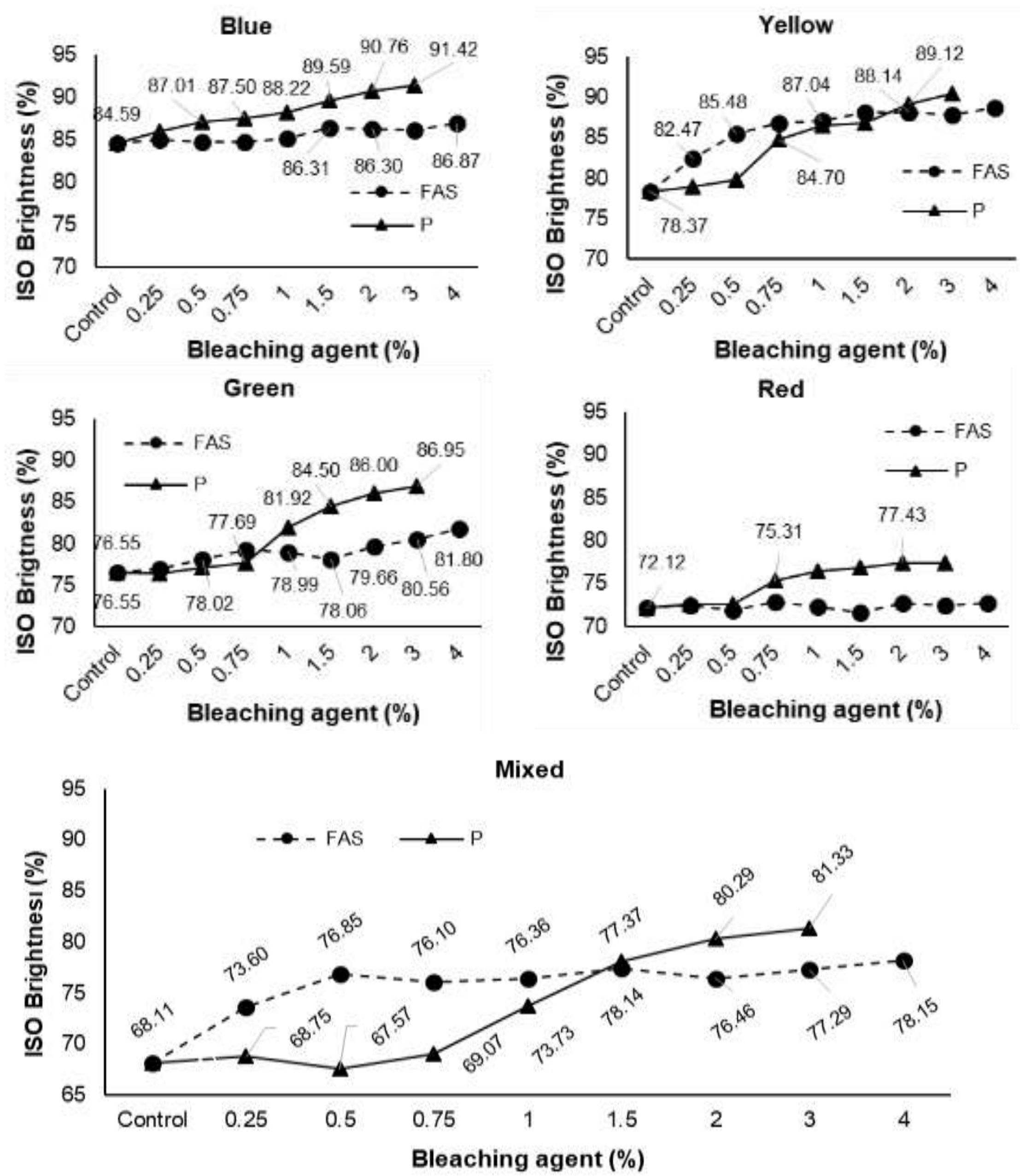

Fig. 1. The effect of FAS and peroxide ratios on ISO brightness of samples

As known, ISO brightness is only associated with blue light at 457 nm. In other words, this parameter does not give enough information about color stripping efficiency.

For this reason, the absorbance (*k*/*s*) spectrum in the UV-VIS region, CIE *L**a*b** color values, and Δ*E* color difference of samples were observed.

Table 5. Correlation Between Wavelengths of Absorbed Radiation and Observed Color (Pretsch *et al.* 2009)

Wavelength (nm)	Absorbed Light/Corresponding Color	Observed Color (Transmitted)
400	Violet	Yellow-green
425	Indigo blue	Yellow
450	blue	Orange
490	Blue-green	Red
510	Green	Purple
530	Yellow-green	Violet
550	Yellow	Indigo blue
590	Orange	Blue
640	Red	Blue-green
730	Purple	Green

Table 6. CIE L*a*b* Values of FAS Bleached Samples

		Control	0.25% FAS	0.50% FAS	0.75% FAS	1.00% FAS	1.50% FAS	2.00% FAS	3.00% FAS	4.00% FAS
Blue	*L**	88.21	90.80	93.43	93.72	93.72	94.76	94.73	94.92	95.23
	*a**	-12.27	-7.39	-3.72	-3.31	-3.58	-2.14	-2.17	-1.04	-0.85
	*b**	-9.30	-3.57	0.00	0.35	0.08	0.98	0.83	1.40	1.40
	Δ*E*	**-**	**7.96**	**13.67**	**14.27**	**13.93**	**15.85**	**15.72**	**16.90**	**17.15**
Green	*L**	86.85	90.17	92.93	93.32	93.26	92.35	93.48	93.74	94.03
	*a**	-16.93	-10.16	-3.75	-2.28	-2.81	-2.14	-1.71	-1.20	-0.78
	*b**	-3.51	5.11	4.71	4.30	4.53	4.31	4.22	4.00	3.71
	Δ*E*	**-**	**11.56**	**16.81**	**17.95**	**17.60**	**17.31**	**18.45**	**18.87**	**19.22**
Red	*L**	91.20	91.71	92.08	92.14	92.25	92.16	92.42	92.47	92.53
	*a**	3.50	0.10	0.39	-0.07	-0.09	-0.10	-0.22	-0.13	-0.22
	*b**	7.61	7.80	7.98	7.82	7.92	8.05	7.97	8.30	8.34
	Δ*E*	**-**	**3.72**	**3.25**	**3.70**	**3.75**	**3.75**	**3.93**	**3.91**	**4.02**
Yellow	*L**	95.88	95.80	96.30	96.48	96.41	96.62	96.35	95.81	96.41
	*a**	-3.76	-2.10	-1.70	-1.43	-1.43	-1.35	-1.04	-0.79	-0.82
	*b**	11.69	6.39	4.96	4.35	3.94	3.58	3.10	2.66	2.62
	Δ*E*	**-**	**5.56**	**7.05**	**7.73**	**8.11**	**8.49**	**9.02**	**9.51**	**9.56**
Mixed	*L**	87.38	91.38	92.08	92.04	92.10	91.76	92.23	92.41	92.86
	*a**	-12.07	-5.35	-2.69	-2.35	-1.77	-1.31	-1.03	-0.65	-0.46
	*b**	5.50	5.08	4.88	4.44	4.26	3.97	4.02	3.81	3.21
	Δ*E*	**-**	**7.84**	**10.51**	**10.83**	**11.40**	**11.72**	**12.15**	**12.59**	**13.04**

The effects of FAS and hydrogen peroxide bleaching on the ratio of absorbance coefficient to light scattering coefficient (*k*/*s*) of blue, green, yellow, and red colored samples are shown in Fig. 2. Table 6 and 7 show the CIE *L*a*b** values and Δ*E* color differences of FAS and peroxide bleached pulp samples, respectively.

As is known, the chromophore is the heart of dyestuff and consists of extended sequences of conjugated double bonds, which means that the two bonds alternate with single bonds, thus forming a pi electron system. When visible light encounters this system the color seen is a result of the degree of absorbance of the light by the pi electron of the dyestuff (Mclow 2009). Table 5 shows the correlation between the wavelength of absorbed radiation and the observed color (Pretsch *et al*. 2009).

In this study, the peroxide bleaching stages had limited effect on the blue colored pulps, but FAS bleaching stages were very successful. The intensity of absorbance peaks of this pulp at 610 nm and 673 nm that indicate blue and blue-green, respectively, decreased from 0.148-0.142 to 0.02-0.03 with the addition of 1% FAS, as can be seen in Fig. 2. The absorbance coefficients of the same pulp at these peaks decreased to only 0.11 with 2% hydrogen peroxide addition (Fig. 2).

Table 7. CIE *L*a*b** Values of Hydrogen Peroxide Bleached Samples

		Control	**0.25% P**	**0.50% P**	**0.75% P**	**1.00% P**	**1.50% P**	**2.00% P**	**3.00% P**
Blue	*L**	88.21	88.09	88.83	88.98	89.24	89.74	90.24	90.95
	*a**	-12.27	-11.84	-11.44	-11.30	-10.81	-10.46	-10.23	-9.59
	*b**	-9.30	-9.29	-9.48	-9.55	-9.67	-9.74	-9.69	-9.04
	Δ*E*	**-**	**0.45**	**1.05**	**1.26**	**1.82**	**2.41**	**2.90**	**3.85**
Green	*L**	86.85	86.84	86.52	87.11	87.45	87.99	88.71	89.60
	*a**	-16.93	-16.43	-16.52	-15.55	-14.00	-13.41	-12.44	-11.73
	*b**	-3.51	-3.98	-4.21	-4.65	-7.48	-8.65	-8.58	-7.91
	Δ*E*	**-**	**0.76**	**0.81**	**1.88**	**5.02**	**6.39**	**7.12**	**7.48**
Red	*L**	91.20	91.60	91.55	91.99	92.07	92.36	92.49	92.34
	*a**	3.50	4.15	5.40	5.88	6.17	6.96	7.24	8.24
	*b**	7.61	6.30	5.08	4.11	3.90	3.53	3.53	3.42
	Δ*E*	**-**	**1.53**	**3.17**	**4.32**	**4.67**	**5.52**	**5.67**	**6.40**
Yellow	*L**	95.88	95.73	96.17	96.86	96.89	96.99	97.48	97.67
	*a**	-3.76	-3.44	-2.68	-2.04	-1.68	-1.50	-1.69	-1.59
	*b**	11.69	11.04	8.99	6.63	5.29	4.93	4.22	3.53
	Δ*E*	**-**	**0.75**	**2.92**	**5.43**	**6.80**	**7.15**	**7.92**	**8.63**
Mixed	*L**	87.38	86.60	86.07	86.17	87.23	88.17	88.53	89.14
	*a**	-12.07	-10.31	-9.75	-9.25	-7.32	-6.93	-6.27	-5.67
	*b**	5.20	1.64	1.60	0.80	-1.92	-4.02	-4.89	-4.72
	Δ*E*	**-**	**4.32**	**4.72**	**5.62**	**8.81**	**10.85**	**11.96**	**12.19**

This situation was also seen in the CIE *L*a*b** values of the FAS and peroxide bleached blue colored samples in Tables 6 and 7. The CIE *b** value of the blue colored pulp decreased from -9.30 to 0.08 with 1% FAS. Additionally, the CIE *a** value of the same pulp decreased from -12.27 to -3.58 with 1% FAS. However, with 2% hydrogen peroxide bleaching, the CIE *b** and CIE *a** values of the same pulps were measured as -9.04 and -9.59, respectively.

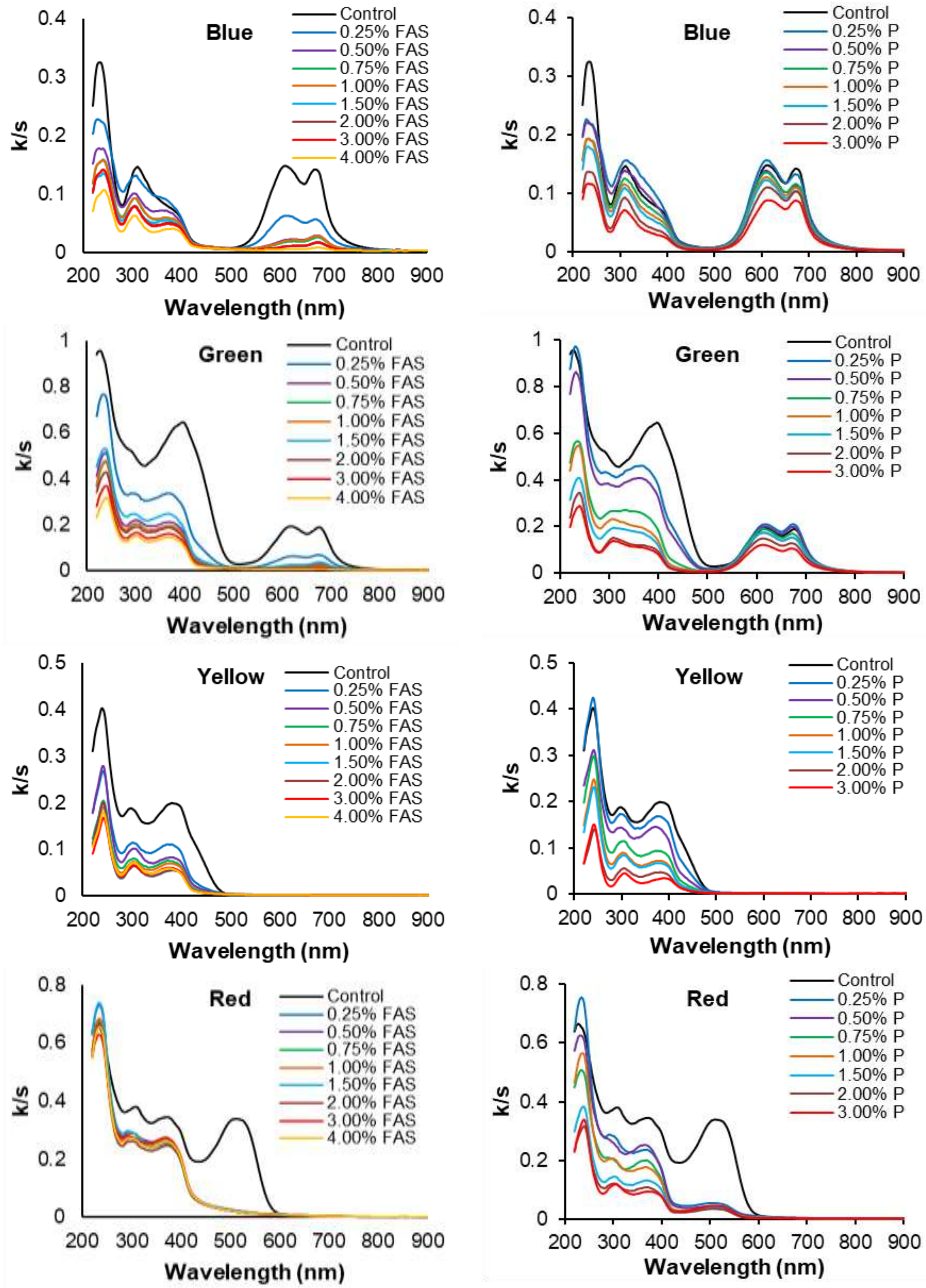

Fig. 2. Absorbance spectrums of FAS and P bleached yellow, red, green, and blue colored pulps

As expected, a similar situation was also observed with the green colored samples. The absorbance coefficient of this pulp at 618 nm (bluish green) and 676 nm (greenish blue) decreased from 0.194 to 0.015 and 0.19 to 0.024, respectively with 1% FAS usage (Fig. 2). However, the absorbance coefficients of this pulp were measured as 0.148 and 0.126, respectively, at the same wavelength with 2% hydrogen peroxide usage. Unlike blue colored pulp, green colored pulp also had a peak of yellow-green color at 397 nm wavelength. As seen in Fig. 2, hydrogen peroxide was more effective than FAS at reducing the absorbance of this peak. The CIE *b** value of green colored pulp was transformed from -3.51 to 4.53 with 1% FAS bleaching (Table 6). This meant that the blue color was reduced by FAS and as a result, the yellow color appeared in pulp. However, 2% hydrogen peroxide usage increased the CIE *b** value of green colored pulp to -8.58 at a negative axis (Table 7). In other words, the peak observed at 618 nm was shifted to 612 nm with 2% hydrogen peroxide usage. In other words, the color observed in this peak was shifted to a bluer color from the blue-green color. The CIE *a** value indicated a green color of the sample at a negative axis. As expected, the CIE *a** value of green colored pulp decreased from -16.93 to -2.81 with 1% FAS bleaching (Table 6). However, with 2% hydrogen peroxide, this value only decreased to -12.44 (Table 7).

Figure 2 shows that both bleaching reagents reduced the absorbance peaks of the yellow colored pulp at the 230 nm to 300 nm wavelength range. Both bleaching reagents also reduced the absorbance peak to 400 nm wavelength, which indicate yellow-green color. This situation is also observed in the CIE color values of samples. The CIE *b** value of yellow colored pulp decreased from 11.69 to 3.94, and the CIE *a** value decreased from -3.76 to -1.43 with 1% FAS (Table 6). The CIE *b** and CIE *a** values of the same pulp were measured as 4.22 and -1.69, respectively with 2% hydrogen peroxide (Table 7).

The absorbance peaks of the red colored sample at approximately 511 nm (purple) wavelength were readily abolished by FAS bleaching, but the absorbance peaks at 228 nm, 309 nm, and 374 nm were resistant to the FAS reduction (Fig. 2). It is believed that these absorbance peaks originate from reduced amine groups and other aromatic structures that form the dyestuff (Pretsch *et al.* 2009). Contrary to FAS bleaching, the absorbance intensity at 228 nm, 309 nm, and 374 nm decreased with 2% hydrogen peroxide usage. However, the hydrogen peroxide was not as effective as FAS at 511 nm wavelength. The CIE *L*a*b** values confirmed these results. The CIE *a** value of red colored pulp decreased from 3.50 to -0.09 and CIE *b** values of the same pulp increased from 7.61 to 7.92 with 1% FAS bleaching stage (Table 6). In contrast, 2% hydrogen peroxide increased the CIE *a** value of red colored pulp from 3.50 to 7.24 and decreased the CIE *b** value from 7.61 to 3.53 (Table 7).

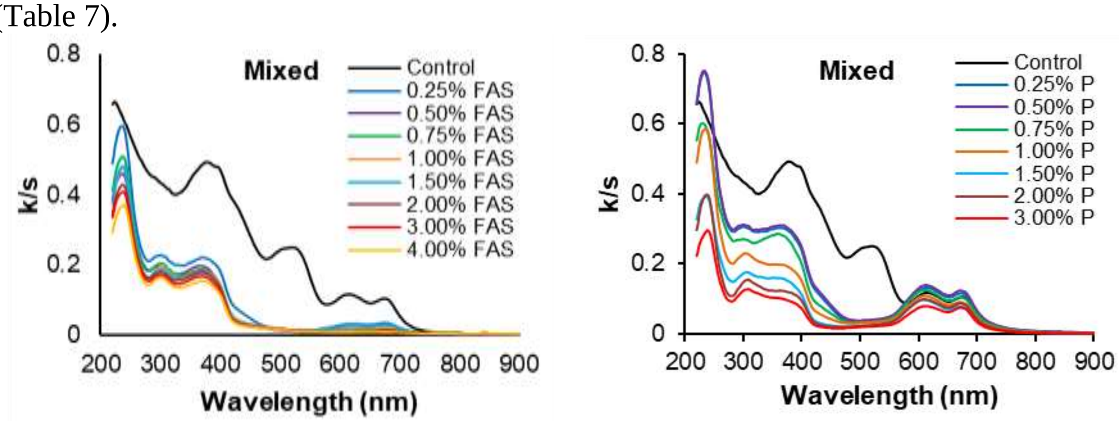

Fig. 3. Absorbance spectrums of FAS and P bleached yellow, red, green, and blue colored pulps

As can be seen in Fig. 3, both bleaching agents reduced the absorbance spectrum of mixed colored samples at different wavelength bands. The FAS bleaching stages were more effective than peroxide relative to absorbance peaks at 522 nm, 616 nm, and 675 nm wavelengths of mixed colored pulp, while the hydrogen peroxide bleaching stages were more effective than FAS at 224 nm and 377 nm wavelengths. When the color values were examined, the CIE *b** and CIE *a** values of mixed colored pulp decreased from 5.50 to 4.56 and from -12.67 to -1.77 respectively, with 1% FAS usage (Table 6). In contrast to FAS usage, the CIE *b** and CIE *a** values of mixed colored pulp decreased to -4.89 and to -6.27 respectively, with 2% hydrogen peroxide usage (Table 7).

It can be said that the rate of 0.75% to 1% was sufficient for single stage FAS bleaching of all samples. The optimum ratio in peroxide bleaching was approximately 2% according to Δ*E* values. The effect of FAS and hydrogen peroxide on colors according to ΔE values can be listed as follows:

Green > Blue > Mixed > Yellow > Red (According to 1% FAS)

Mixed > Yellow > Green > Red > Blue (According to 2% hydrogen peroxide)

Table 8. Color Chart of Single Stage FAS and P Bleached Samples

		Red		Yellow		Blue		Green		Mixed	
	%	P	FAS	P	FAS	P	FAS	P	FAS	P	FAS
Un-bleached	-										
Pre-bleached	0.00										
	0.25										
	0.50										
	0.75										
	1.00										
	1.50										
	2.00										
	3.00										
Post-bleached	4.00	x		x		x		x		x	

Table 8 shows the colors of the FAS and peroxide bleached pulps. As shown in Table 8, the hydrogen peroxide bleaching stages further clarified the redness of the red colored pulp, the blueness of the green colored pulp, and the blueness of the mixed colored pulp. This was because hydrogen peroxide (oxidative) bleaching was much more effective at removing the yellowish color resulting from reduced amine compounds (Minor 1992). In contrast, the FAS bleaching stages were more effective on the blue, green, mixed colored, and yellow colored pulp even if they were used at very low rates. However, after the FAS bleaching stages, a grayish yellow color was formed in all samples.

According to all these results, FAS and hydrogen peroxide were complementary to each other and should be used together for bleaching colored samples.

FASP and PFAS bleaching sequences

In this study, it was also investigated whether the P bleaching stage should be applied before or after the FAS bleaching stage. Figure 4 shows the ISO brightness of the P, FAS, PFAS, and FASP bleaching sequences. The highest ISO brightness values were obtained with the FASP bleaching sequence for the blue, mixed, and green colored pulp. However, the highest ISO brightness values of yellow and red colored samples were obtained with the PFAS sequence but the differences did not even exceed 1%. Similarly, Deneault and Leduc (1995) studied the PFAS and FASP bleaching sequences of thermomechanical pulp (lignin-rich yellow pulp), and they found that the PFAS bleaching sequence achieved higher brightness values than the FASP sequence. The ISO brightness of mixed colored pulp was measured as 83% after PFAS bleaching. This value increased to 87.3% with the FASP bleaching sequence.

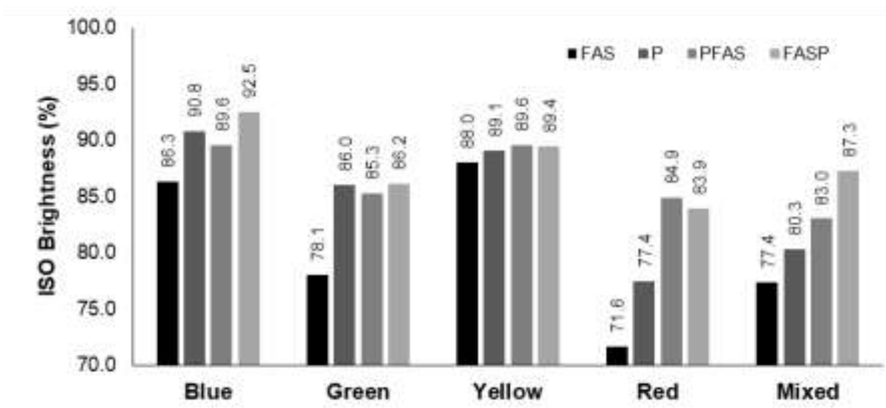

Fig. 4. The % ISO brightness of PFAS and FASP bleaching sequences

Table 9. CIE *L*a*b** Values of PFAS and FASP Bleaching Sequences

			FAS	P	PFAS	FASP
		Control	**1.00% FAS**	**2.00% P**	**2.00% P + 1.00% FAS**	**1.00% FAS + 2.00% P**
Blue	*L**	88.21	93.72	90.24	96.11	97.29
	*a**	-12.27	-3.58	-10.23	-0.28	1.10
	*b**	-9.30	0.08	-9.69	-8.26	-7.70
Green	*L**	86.85	93.26	88.71	94.57	95.91
	*a**	-16.93	-2.81	-12.44	-3.64	0.25
	*b**	-3.51	4.53	-8.58	-6.65	-4.30
Red	*L**	91.20	92.25	92.49	95.79	95.80
	*a**	3.50	-0.09	7.24	1.79	1.90
	*b**	7.61	7.92	3.53	-2.19	-1.83
Yellow	*L**	95.88	96.41	97.48	97.74	97.41
	*a**	-3.76	-1.43	-1.69	0.62	0.71
	*b**	11.69	3.94	4.22	-3.88	-4.07
Mixed	*L**	87.38	92.10	88.53	95.41	95.67
	*a**	-12.07	-1.77	-6.27	-0.53	-0.78
	*b**	5.20	4.26	-4.89	-3.34	-5.60

Figure 5 shows the effects of the PFAS and FASP bleaching sequences on the absorbance spectra of different colored samples. The FASP and PFAS bleaching sequences for the red and yellow colored samples were not very different from each other. However, it was clear that the FASP bleaching sequence was more effective than the PFAS on the blue and green colored samples. Similarly, FASP was also more effective on the mixed colored samples too.

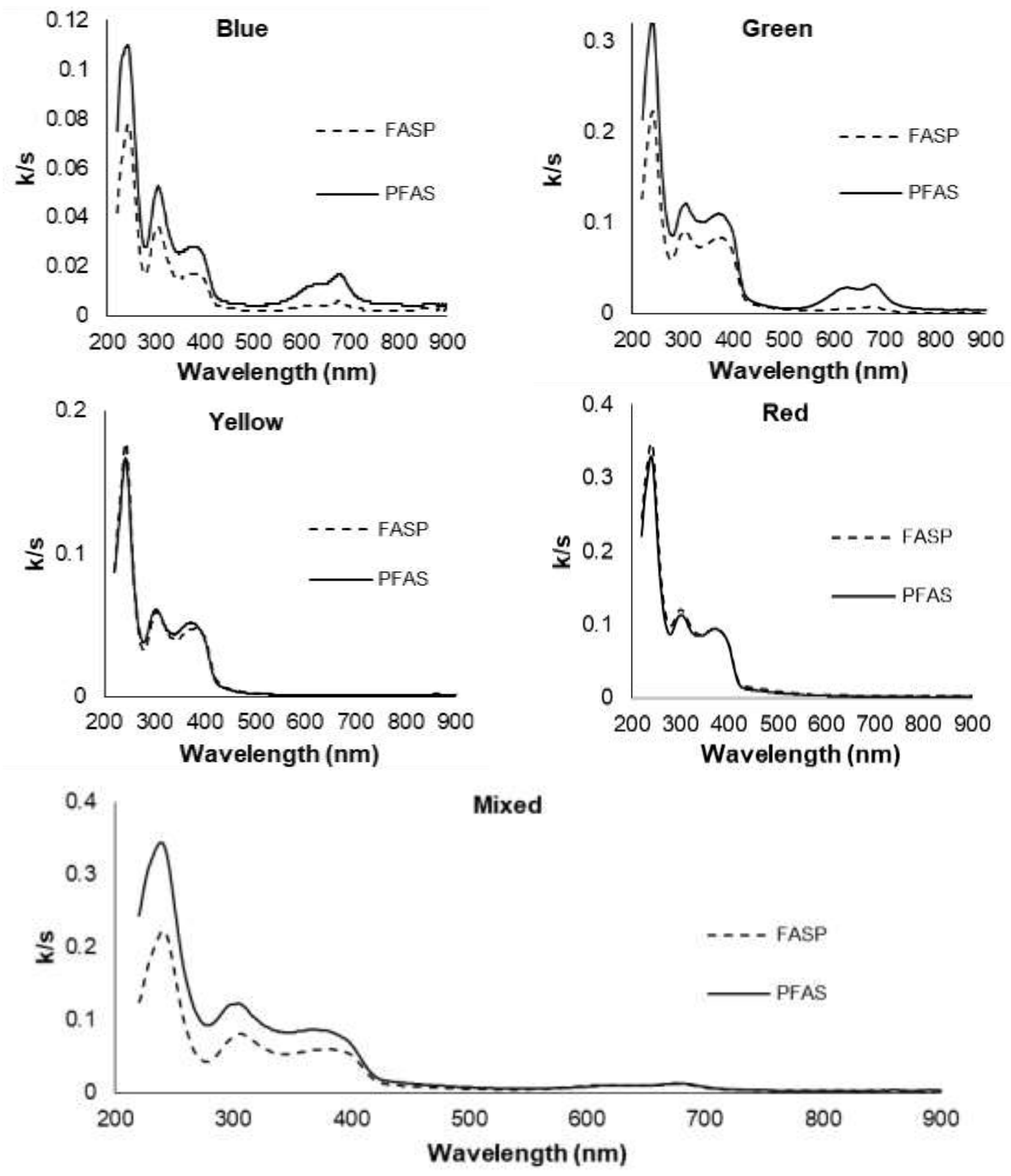

Fig. 5. The absorbance spectrum of FASP an PFAS bleached pulps

The CIE color values of the PFAS and FASP bleaching sequences are shown in Table 9. The CIE color values of samples also support the results obtained from the absorbance spectra. Table 10 shows the final colors and Δ*E* values of PFAS and FASP bleached pulps. The CIE Δ*E* value of the mixed colored pulp was 17.7 after the FASP bleaching sequence according to the pre-bleached pulp color and red was the most difficult color for bleaching. However, when the FAS and peroxide were used together, the colors of all samples were successfully removed and bright white pulps were obtained.

The most similar study to this present study was performed by Vadivel *et al.* (2011) on the bleaching of colored broke. In their work they used different bleaching agents in a single step, and they did not reach high brightness except for with chlorine dioxide. They also argued that yellow-colored broke could not be bleached with single stage chlorine dioxide, hydrosulphite, peroxide, or hypochlorite. However, in the present study, whiter pulp with 86% to 92% ISO brightness was obtained with pre-bleaching (FAS usage in pulper) and two-stage post-bleaching sequences (FASP).

Table 10. CIE ΔE Color Difference and Color Chart of Samples

		Red	ΔE	Yell.	ΔE	Blue	ΔE	Gre.	ΔE	Mixed	ΔE
Un-bleached	-		-		-		-		-		-
Pre-bleached	-		-		-		-		-		-
Post-bleached	P		5.7		7.9		2.9		7.1		12.0
	FAS		3.8		8.5		15.9		17.9		11.7
	PFAS		10.1		16.3		14.4		15.7		16.4
	FASP		10.6		16.5		16.2		19.4		17.7

ΔE values were calculated from L*a*b* values of pre-bleached pulps

CONCLUSIONS

In this study, the optimization of single stage FAS and hydrogen peroxide sequences and the efficiency of two stage FASP and PFAS bleaching sequences of pre-bleached colored office paper were investigated. Results of this study led the authors to the following conclusions:

1. The FAS was much more effective than hydrogen peroxide at color removal due to its reductive ability.
2. Single-stage FAS bleaching was more effective on the green, blue, and mixed colored pulps compared to the yellow and red colored pulps.
3. In the single-stage FAS bleaching, a grayish yellow color was formed due to the reduced amine compounds in all pulps.
4. Hydrogen peroxide was more effective at removing the yellowish color from pulp.
5. The optimum single stage FAS ratio was in the range of 0.75% to 1%.
6. The optimum single stage hydrogen peroxide (P) ratio was 2%.
7. By using two bleaching agents together, high brightness levels (in the range of 86% to 92%) were achieved with effective color removal.

8. The two-stage FASP bleaching sequence was more effective on the green, blue, and mixed colored pulps. However, PFAS was slightly more effective on the yellow and red colored pulps.

The study results showed that after the pre-bleaching process using 1% FAS during pulping from waste papers containing mixed colored pulps, colorless papers can be produced at an 87% brightness ratio through a two-stage FASP post-bleaching process.

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Article submitted: February 19, 2018; Peer review completed: April 29, 2018; Revised version received: May 6, 2018; Accepted: May 7, 2018; Published: May 9, 2018.
DOI: 10.15376/biores.13.3.4841-4855