Recycling of Colored Office Paper. Part I: Pre-bleaching with Formamidine Sulfinic Acid at Pulper

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The possible use of formamidine sulfinic acid (FAS) for pre-bleaching of colored office paper in the stage of pulping was investigated. In addition, the effects of FAS pre-bleaching on different colors were examined. Colored office papers were mixed with white office paper at a 1:4 ratio. FAS was added as 0.25%, 0.50%, 0.75%, 1.00%, and 2.00% into the pulper. Reduction ability of colors with FAS were determined as yellow, red, green, and blue according to *L**, *a**, *b**, Δ*E*, and reflectance spectrum at 220 nm to 900 nm wavelength. In other words, it was determined that FAS succeeded on the yellow, red, and green colored waste paper, but it failed on the blue colored waste paper at 10 minute pre-bleaching conditions. On the other hand, in mixed colored waste paper, which can better represent industrial applications, the color difference (Δ*E*) were calculated as 32.0 with 1% FAS pre-bleaching. This result is successful for pre-bleaching, which is an auxiliary process during re-pulping of waste paper.

*Keywords: Formamidine sulfinic acid; Pre-bleaching; L*a*b* Color values; Colored office paper; Pulper*

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INTRODUCTION

The workflow of paper recycling can be summarized as classification, cleaning, pulping, washing and/or flotation, thickening, and bleaching. The pulping and deinking processes are the most important stages of conventional paper recycling workflow. When there are dye colored fibers in the paper recycling process, pre- and post-bleaching stages gain importance. Much color is removed in the deinking step, especially if colored inks or pigments are only physically entrapped in the fiber matrix. However, many dyes adsorb onto fibers and are resistant to deinking and mild oxidative treatment, such as hydrogen peroxide (Minor 1992). Hydrogen peroxide has little color stripping capacity when utilized as a recycled pulp bleaching agent (Van Lierop and Liebergott 1994; Patt *et al.* 1996; Magnin *et al.* 2000). In this case, strong reducing or oxidizing reactants are required.

Traditionally, sodium hydrosulphite is an efficient and cheap color stripping agent due to its reducing effect of dye (Dumont *et al.* 1994; Fluet and Shepperd 1997; Carré *et al.* 2000). It reduces aldehyde and keto groups. However, the usage conditions and handling of sodium hydrosulphite are not suitable for a pulper (pre-bleaching). Hydrosulfphite causes corrosion of steel when reacting with oxygen by forming thiosulfate (Davaney and Guess 1982; Garner 1982; Bond *et al.* 1991). Furthermore, bleaching with dithionite is typically carried out at an acidic pH of 4.5 to 6.5 at 60 °C to 80 °C in a tower. However, the pulping of waste paper occurs at 45 °C to 50 °C in alkaline medium. Due to the handling and usage conditions, formamidine sulfinic acid (FAS) is the most suitable color stripping reagent for the pulping process during recycling. FAS can be activated under alkaline conditions and is less sensitive than hydrosulphite to air oxidation or decomposition by transition metal ions (Patt *et al.* 1996). Similarly, FAS is a stronger reducing reagent than hydrosulphite. Gehr (1994) studied the bleaching of wood without additives, and wood containing secondary fibers with hydrogen peroxide, sodium dithionite, and FAS. FAS reduces dyes more effectively than sodium dithionite (Gehr 1997). Daneault *et al.* (1995) reported that FAS was very fast and strong bleaching agent for softwood TMP. The reaction was extremely fast, and the brightness gain was the same between 15 min and 2 h reaction time (Daneault *et al.* 1995). Pesman *et al.* (2011) studied sodium dithionite, sodium borohydride, fomamidine sulfinic acid, hydrogen peroxide, and sodium percarbonate bleaching, and colour stability of waste old news and magazine paper pulp. The FAS was determined more effective than sodium hydrosulphite for the bleaching of old newspaper pulp (Pesman *et al.* 2011). 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. Imamoğlu *et al.* (2013) studied the removal of main colors of oil-based inks from uncoated and coated office papers. According to the results of this study, hydrogen peroxide was more successful than FAS during pulping (Imamoğlu *et al.* 2013). This was attributed to the presence of ink pigments, despite the fact that there were no dyeing 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 chlorine dioxide, hydrogen peroxide, hypochlorite, or sodium hydrosulphite. However, they also had decided that other broke such as green, blue, and pink, can be blended and bleached by a single stage of chlorine dioxide (Vadivel *et al.* 2011).

Although there are many studies with FAS bleaching of waste paper, there has been no comprehensive study about recycling of direct dye colored office paper. Colored waste papers require a different workflow and recycling process. In this study, the possibility of FAS utilization instead of hydrogen peroxide for pre-bleaching of colored office paper in re-pulping was investigated. In addition, the bleachability of different color types (blue, green, yellow, red, and a mixture of these colors) with FAS were investigated.

EXPERIMENTAL

Materials

Blue, yellow, green, and red direct dye colored office papers and white office papers were used as a waste paper source. The mixture of waste paper used in this study is shown in Table 1. Colored and white office papers were obtained from commercial suppliers.

Table 1. The Mixture of Waste Papers Used in this Study

Code	Blue	Green	Red	Yellow	Mixed
Blue Colored Office Paper (%)	25	-	-	-	6.25
Green Colored Office Paper (%)	-	25	-	-	6.25
Red Colored Office Paper (%)	-	-	25	-	6.25
Yellow Colored Office Paper (%)	-	-	-	25	6.25
White Office Paper (%)	75	75	75	75	75

Methods

Pulping (pre-bleaching)

Pulping (pre-bleaching) was conducted at 50 °C for 10 min in a laboratory pulper at 8% consistency (Adirondack Machine Corporation, Hudson Falls, USA). The system was heated and speed controlled by digital processing. The loading of the pulper was executed manually, and 100 g of oven-dried office papers (75 g of white office, 25 g of colored office paper) were used in each experiment. The FAS charge was changed to 0%, 0.25%, 0.50, 0.75, 1.00%, and 2.00%. As is known, stoichiometrically the optimum NaOH charge to FAS is 1:2 for reductive bleaching, but pre-bleaching is only an auxiliary process during re-pulping. For fiber swelling and other following processes, extra alkalinity is necessary in a pulper. Therefore, in this study the NaOH ratio was kept constant at 2%.

The control samples were prepared at 50 °C for 10 min in the pulper without chemical addition.

Optical and strength tests of handsheets

For each pulp sample, 60 g/m^2 of handsheets were formed, pressed, and dried according to TAPPI T205 sp-12 (2012) on the handsheet machine (Estanit, Rapid Köthen, Mülheim an der Ruhr, Germany). Handsheets were conditioned at 20 °C and 50% humidity for 7 days before the optical tests. The brightness values of handsheets were measured according to TAPPI T452 om-08 (2008) standards under a 457 nm wavelength. Measurements were completed using a UV filter to avoid the disturbance of residual materials having some fluorescence effects. Color measurements of test paper were achieved according to TAPPI T527-om 13 (2013), giving L^*, a^*, b^* values and color difference (ΔE^*). The International Commission on Illumination (CIE) whiteness values of the handsheets were determined in accordance with TAPPI T562 pm-10 (2010), giving CIE values. Brightness, color values, and whiteness of handsheets were measured with a spectrophotometer (Cm-2600d, Konica-Minolta, Osaka, Japan). The ratio of scattering coefficient to absorbance coefficient (k/s) were calculated according to Kubelka-Munk (1931) from reflectance of the handsheets. The reflectance spectra of handsheets were recorded on a spectrophotometer (3600 UV-VIS-NIR, Shimadzu, Tokyo, Japan) equipped with an $BaSO_4$ coated integrated sphere (ISR-3100, Tokyo, Japan).

RESULTS AND DISCUSSION

Figure 1 shows the ISO brightness and whiteness of handsheets. Blue colored office papers gave a higher brightness and whiteness than all other colored office papers. This is consistent with the fact that the reflection of blue color at the wavelength of 457 nm at which brightness and whiteness are measured is very high. There were no remarkable effects of the FAS charge on the brightness and whiteness of blue colored office paper during pre-bleaching. However, brightness and whiteness of other colored office papers increased with FAS addition. The critical dosage of FAS was determined as 0.75%, due to the remarkable increase that started at this ratio.

The brightness of yellow colored office papers increased from 34.8% to 68.7 and 78.8% with 0.75% and 1% FAS usage respectively. The brightness of red colored office papers increased 53.9 units from 23.4% to 77.3% with 2% FAS usage. The brightness of green colored office paper increased from 35.74% to 53.9% and 77% with 0.75% and 1% FAS usage respectively. The brightness of mixed colored office paper increased from

30.4% to 68.1% with 1% FAS usage. Similar trends were observed for whiteness index of each sample as well. The whiteness of mixed colored office paper increased from -63 to 2.1, 44.5 and 70.5 with 0.75%, 1% and 2% FAS charge, respectively. The whiteness of green colored office paper increased from -106.8 to 90 with 1% FAS usage. This result may be due to the conversion of the pulp color to blue by the reduction of green color with FAS.

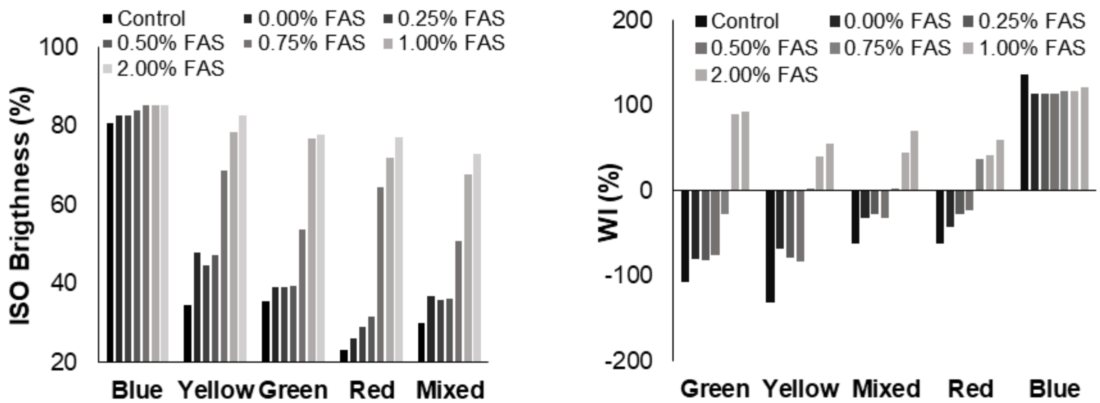

Fig. 1. The effects of FAS charge and color type on brightness and whiteness of handsheets

Because ISO brightness and whiteness index are only associated with a blue light at 457 nm, these parameters do not give enough information about the color stripping efficiency. For this reason, reflectance and absorbance spectrum in the UV-VIS region, CIE *L*a*b** color values, and Δ*E* color difference of samples were observed. Table 2 shows CIE *L*a*b** values, and Table 3 shows Δ*E* color difference and color chart of samples.

CIE *L** values indicate the luminance of samples. The CIE *L** value of each sample increased with increasing FAS charge except for the blue colored office paper. The CIE *a** value represents the red color at positive and the green color at negative coordinate. The CIE *b** value represent the yellow color at positive and the blue color at negative coordinate.

The CIE *b** values of yellow colored office papers were decreased from 45.74 to 8.09 with 2% FAS usage. Thus, the yellow color in pulp was reduced with FAS addition. Also, CIE *a** values decreased from -9.75 to -2.66. These color reductions are shown in Fig. 2. The reflectance of yellow colored office paper pulp at 500 nm to 600 nm range increased with 1% and 2% FAS addition. The 500 nm to 600 nm wavelength range indicates the yellow and green color. The most prominent absorbance peak of yellow colored office paper at 400 nm decreased with 1% FAS usage. In addition, the peak at 230 nm decreased with 1% FAS usage too. The decrease in the peak at 230 nm may be due to degradation of the structure of the phenolic compounds contained in the dyestuff (Pretsch *et al.* 2009).

Similar trends were observed on red colored office paper fiber. Increased FAS charge decreased the CIE *a** values from 42.54 to 3.76 and CIE *b** values from 18.42 to 5.13. Significant reflectance increase was observed at 550 nm to 700 nm range with 1% FAS usage. The use of 1% FAS also decreased the absorbance peak at 500, 293, and 220 nm significantly. These results showed that FAS pre-bleaching is effective on red and yellow colored office paper.

The CIE *a** values of green colored office papers decreased at negative axis with increasing the FAS charge from -21.42 to -15.76. Therefore, the green color was mildly reduced by the addition of FAS. In addition, the CIE *b** values of green colored office papers decreased from 32.73 to -4.39 with 2% FAS addition. The yellow color was stripped with FAS charge, and then the blue color appeared in pulp with 1% FAS charge. These color transformations can be seen in Fig. 2. The reflectance peak of green colored office paper at 550 nm shifted to 498 nm with 1% FAS addition. Similarly, the absorbance peak of green colored office paper at 420 nm decreased with FAS pre-bleaching.

Table 2. CIE *L*a*b** Values of Samples

		Control	0.00 % FAS	0.25% FAS	0.50% FAS	0.75% FAS	1.00% FAS	2.00% FAS
Blue	*L**	83.26	87.10	87.38	88.00	88.41	88.21	87.29
	*a**	-13.71	-8.79	-10.90	-11.55	-12.06	-12.27	-13.76
	*b**	-14.29	-9.16	-8.97	-8.63	-9.10	-9.30	-11.10
Green	*L**	82.92	83.29	83.32	84.15	88.45	87.05	87.12
	*a**	-21.42	-20.36	-20.06	-20.40	-18.57	-16.53	-15.76
	*b**	32.73	27.18	28.85	27.82	19.37	-3.81	-4.39
Red	*L**	66.59	68.09	70.05	71.79	88.35	92.20	93.38
	*a**	42.54	41.19	39.30	36.90	6.04	3.00	3.76
	*b**	18.82	16.36	14.64	13.16	7.34	8.61	5.13
Yellow	*L**	90.26	91.55	91.04	93.65	96.14	96.88	96.93
	*a**	-9.75	-9.22	-9.61	-9.02	-5.54	-3.67	-2.66
	*b**	45.74	30.95	33.41	35.83	18.43	11.49	8.09
Mix	*L**	71.97	75.26	75.10	74.04	81.95	87.30	87.52
	*a**	10.61	12.35	12.37	13.44	-3.01	-12.67	-12.68
	*b**	19.96	13.81	13.32	16.18	11.42	4.20	-0.27

The FAS pre-bleaching did not predict the expected effect on the blue-colored office paper as shown in Table 3 and Fig. 2.

Mixed colored office paper data offers closer results to the industrial application. This is because paper mills usually recycle these papers together. In this study, a brown colored pulp was obtained by mixing equal amounts of red, yellow, green, and blue colored office paper in the pulper without chemical addition.

The CIE *a** values of mixed colored office paper pulp decreased from 10.61 to -3.01, and the CIE *b** values decreased from 19.96 to 11.42 with 0.75% FAS usage. Moreover, the brown color of the pulp was transformed to a khaki color with 0.75% FAS reduction. When the charge of FAS increased to 2%, CIE *a** and CIE *b** values decreased to -12.68 and -0.27, respectively. Namely, the color of pulp was transformed to blueish green. This situation can be observed in Fig. 3 too. Reflectance of samples increased at 500 nm after 0.75% charge of FAS. Similarly, absorbance peaks at 400 nm (indicating yellow color) and 490nm (indicating red color) decreased with the increased FAS charge. There was little change in the absorbance peaks at 618 nm and 676 nm wavelength.

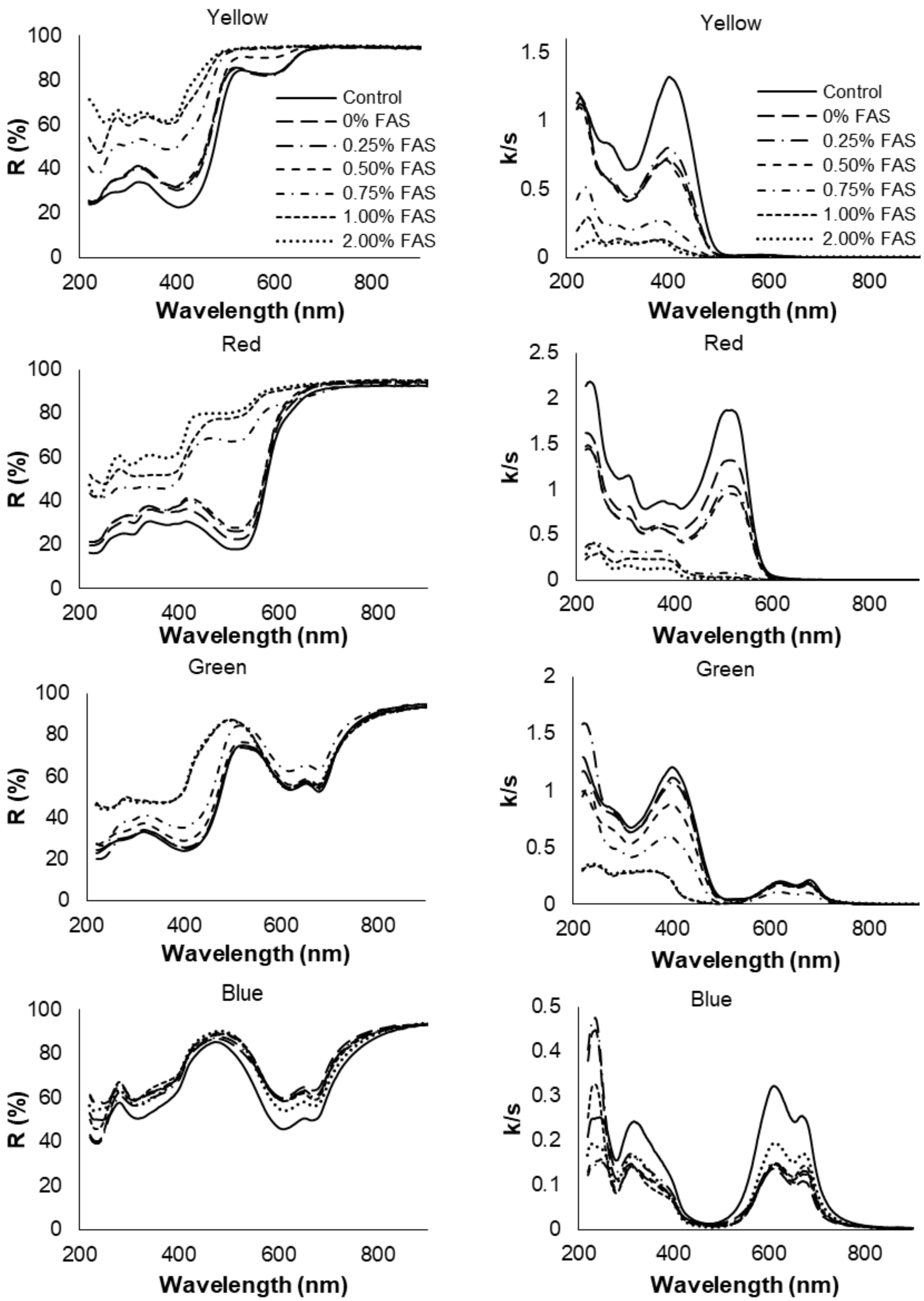

Fig. 2. Reflectance and absorbance spectrums of pre-bleached yellow, red, green, and blue colored office paper pulps

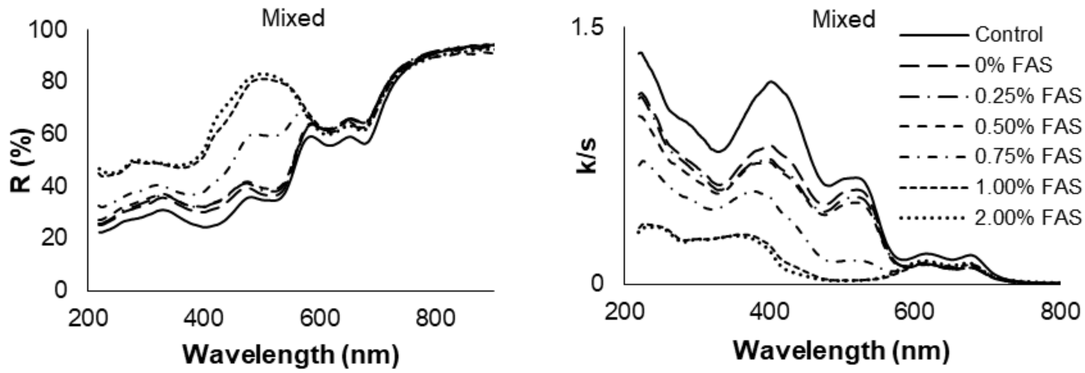

Fig. 3. Reflectance and absorbance spectrums of pre-bleached mix colored office paper pulp

Table 3 shows the Δ*E* color difference and color charts of FAS pre-bleached pulps. According to the Δ*E* values, when the color removal activities of samples are compared, the sequence was as follows: red colored office paper pulp > yellow colored office paper pulp > green colored office paper pulp > mixed colored office paper pulp > blue colored office paper pulp. FAS was determined as a successful reductive agent for red, yellow, green and mixed color. However, blue colors were determined to be more resistant to FAS reduction in the pulper.

Table 3. CIE ΔE Color Difference and Color Chart of Samples

	Red	ΔE	Yellow	ΔE	Blue	ΔE	Green	ΔE	Mixed	ΔE
Control		-		-		-		-		-
0.00% FAS		3.18		14.85		8.08		5.67		7.19
0.25% FAS		6.31		12.35		7.29		4.14		7.55
0.50% FAS		9.53		10.50		7.69		5.17		5.15
0.75% FAS		44.02		28.25		7.49		14.75		18.92
1.00% FAS		48.20		35.41		7.18		37.10		32.02
2.00% FAS		49.08		38.88		5.14		37.79		34.54

CONCLUSIONS

1. In this study, the possibility of FAS utilization instead of hydrogen peroxide for pre-bleaching of colored office paper in the stage of pulping was investigated.
2. Due to the fast reaction time and alkaline activation, formamidine sulfinic acid (FAS) was determined as the effective color stripping agent for pre-bleaching of colored fiber matrix in pulper.
3. Optimum FAS charge was determined within the range of 0.75% to 1%. There was no

significant effect observed on the color removal up to 0.75% FAS charge.

4. The red and yellow colored office paper fibers were bleached more easily than the green and blue colored office paper.
5. The blue color present in the dyed paper was determined to be more resistant to FAS reduction reaction.
6. The color of the green colored office paper fibers turned to a turquoise color with 1% FAS usage.
7. The mixture of blue, green, yellow, and red office paper gave brown colored fiber without FAS usage. The color of this sample was turned to pale bluish-green with 1% FAS bleaching of 10 min during pulping.
8. Pre-bleaching is an auxiliary application during re-pulping of waste paper fiber. From this point of view, approximately 35% color removal (ΔE) obtained at this stage before flotation, washing, and post bleaching is quite successful.

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Article submitted: February 19, 2018; Peer review completed: April 2, 2018; Revised version received and accepted: April 7, 2018; Published: April 18, 2018.
DOI: 10.15376/biores.13.2.3949-3957