Improving Fly Ash Whiteness and the Influence of Modified Fly Ash on the Physical Strength of Paper

Huiming Fan, Shuo Wang, Jianan Liu,* and Jun Long

In order to improve the whiteness of fly ash, the particles were coated by *in-situ* precipitation of calcium carbonate. After different mass ratios of calcium oxide to fly ash were mixed into water, a certain amount of carbon dioxide was bubbled into the mixture to form a precipitated calcium carbonate deposit on the surface of fly ash. With the help of scanning electron microscopy (SEM), the process and the coating mechanism of the unmodified and modified fly ash were studied. The results showed that when a 1:1 mass ratio of calcium oxide to fly ash was implemented, the whiteness of fly ash was increased from 30.3 (the original fly ash) to 74.0 (the modified fly ash). After appropriately controlling for the rate of carbon dioxide, the whiteness was improved to meet the standard for filler in the papermaking industry, and also great advantages in paper physical strength were demonstrated.

Keywords: Fly ash; Precipitated calcium carbonate; Coating; Whiteness; Physical strength

*Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640, Guangzhou, China; *Corresponding author: hmfan@scut.edu.cn*

INTRODUCTION

Fly ash has properties of good porosity, low density, large specific surface area, good light resistance performance, and high bond strength characteristics. The main ingredients of fly ash are similar to those of kaolin, which is a common filler used in papermaking. The particle size of fly ash is sufficient to meet the industry requirements for fillers. In addition, fly ash decreases the cost of papermaking significantly (Xu *et al*. 2010; Lindon and Sear 2001; Zhao *et al*. 2008). Therefore, it seems logical that fly ash should be gradually applied to the papermaking industry in large quantities. However, the effects of fly ash on the optical properties of paper need to be addressed.

Several studies have compared fly ash with kaolin clay. These studies found that the mechanical strength properties of paper filled with fly ash were superior to those of paper filled with kaolin clay, although the brightness decreased as the percentage of fly ash filler increased (Fahmy and Mobarak 2008; Sinha 2008). This trend concerning the brightness has limited the further application of fly ash in papermaking.

In a recent study, the whiteness of fly ash was enhanced by using nonferrous carbon-efficient separation technology. The calcium carbonate prepared by fly ash was found capable of improving the whiteness values to some extent, but the fly ash contained a small quantity of nonferrous metal ions that had a negative impact on the whiteness of the filled paper (Zhang *et al*. 2011). In another study, a novel fly ash based on calcium silicate, which is a byproduct of aluminum extraction from fly ash, was considered as a potential filler in paper (Zhang *et al*. 2013). The whiteness of fly ash would be able to be indirectly increased by this process. However, the technological process of aluminum extraction from fly ash is costly and has strict requirements. Moreover, the use of calcium silicate as a filler would reduce the lifespan of the paper machine by increasing wear. It had been reported that composite fly ash, which has a rough surface and high whiteness, had been successfully prepared using a procedure based on a chemical sedimentation principle in the $Ca(OH)_2$-H_2O-CO_2 system (Yang *et al*. 2006; Nanri *et al*. 2008). However, in the early stage of the cladding, much of the process had proved expensive. What is particularly worth mentioning was that their samples contained an unusually high iron content and a small amount of carbon, which did not match the profile of the common fly ash produced by a general thermal power plant.

In the present study, the whiteness of fly ash was improved significantly when precipitated calcium carbonate crystals were precipitated onto the fly ash surface, which enabled it to meet the standards for value-added applications of filler in papermaking.

EXPERIMENTAL

Materials

Fly ash was supplied by Guangzhou Paper Co., Ltd. (China). Bleached eucalyptus pulp, with a drainage degree of 32 °SR, was supplied by Henan Tianbang Co., Ltd. (China). Calcium oxide, carbon dioxide, precipitated calcium carbonate (PCC) and polyethylene glycol (PEG) were all provided by Tianjin Kemiou Chemical Reagent Co., Ltd. (China). The pH tester was purchased from Shanghai Sanxin Instrument Factory (China).

Methods

Preparing different sizes of fly ash

Different sizes of fly ash particles were obtained from a BSJ-200 oscillating sieving machine (Yongda Ltd., Xinxiang, Henan, China) using mesh sizes of 200, 250, 300, 325, 400, 500, and 800.

Modified fly ash preparation

Calcium oxide (10%) was added to 50.4 mL of ultrapure water in a 250-mL tri-neck round-bottom flask and allowed to disperse. The flask was heated in a water bath to 80 °C and stirred at 400 rpm for 1 h. Fly ash (10%) and 63.4 mL of ultrapure water were added to the mixture and stirred at 400 rpm for 10min and then added PEG(0.1%) to the tri-neck round-bottom flask for another 20 min. Finally, when the temperature of the water bath had dropped below to 25 degrees, carbon dioxide was bubbled into the water. When the pH of the solution was 7, the experiment was considered complete.

Scanning electron microscopy (SEM) observations of filler

Dried samples of fly ash and modified fly ash were mounted on aluminum stubs with tape and sputter-coated with a gold alloy. Samples were observed using an EVO 18 Special Edition scanning electron microscope (Carl Zeiss, Germany) operating at an accelerating voltage of 10.0 kV.

Modified fly ash preparation and determination of its properties (whiteness)

The fly ash coated with precipitated calcium carbonate was dried at 105 °C for 2 h with a heat oven (JC202, Congyuan Chemistry Instruments Ltd., Guangzhou, China). After it had cooled down to room temperature and had been left to stand, the ISO 11475 whiteness of the fly ash was measured using an optical tester (MTCRO-TB-IC, USA).

Paper preparation and determination of paper properties

The bleached eucalyptus pulp was diluted to 0.3% in tap water, and various concentrations (%) of modified fly ash (based on slurry) were added during the process of handsheet formulation. The mixture was dispersed by a GBJ-A fiber standard dissociator (Zhongyuan Chemistry Instruments Ltd., Guangzhou, China), and 0.05% cationic polyacrylamide (CPAM) (based on dry pulp) was added as a retention aid. The handsheets were formed using a Rapid-Köthen Sheet former (RK3-KWTjul, PTI Ltd., Austria) at a basic weight of approximately 72 g/m^2.

Ash content measurement

The papers filled with modified fly ash were incinerated at 575 °C for 6 h with a SX muffler oven. The ash content was calculated using the following equation (Eq. 1),

$$R\% = \frac{a}{b} \times 100 \tag{1}$$

where *R* is the ash content, *a* is the weight of ash, and *b* is the weight of dried paper.

Characterization of paper

Handsheets were placed in an ISO constant temperature and humidity chamber for 24 h (23 ± 1 °C, 50 ± 2% RH). The tensile and burst strength of the papers were measured using an L&W CE062 tensile testing apparatus and an L&W CE180 burst testing apparatus, respectively.

RESULTS AND DISCUSSION

Relationship between Fly Ash Particle Size and Mesh Screen

Table 1 shows the relationship between fly ash particle size and the mesh screens.

Table 1. Particle Size Distribution of Fly Ash

Number	Mesh screen	Size (μm)	Retention rate (%)	Average (μm)
A	200	74.1	1.2	74.1
B	250	61.1	20.9	67.6
C	300	54.0	9.3	57.6
D	325	43.1	41.6	48.6
E	400	35.2	23.0	39.2
F	500	29.9	1.4	32.6
G	800	18.6	2.6	24.3

Note: The average particle size of fly ash was approximately 40 um.

As Table 1 shows, the particle sizes of the fly ash were mainly concentrated between about 35 μm and 61 μm. The largest particle size was 43.1 μm, followed by the particle size of 35.2 μm. Fly ash of particle sizes greater than 50 μm was judged not to be suitable for use as filler (Puurtinen 2004; Fan *et al*. 2014), and fly ash particles with a size of 29.9 μm were too rare. In order to ensure the consistency of particle size (inconsistent particle size would easily wear upon a paper machine) and increase the utilization rate of fly ash, fly ash with particle sizes of 35.2 μm and 43.1 μm were selected to be used as the filler in the experiment.

SEM Observations of Modified Fly Ash

An SEM image of unmodified fly ash is shown in Fig. 1a, while an SEM image of fly ash clad by precipitated calcium carbonate is shown in Fig. 1b. Figure 1a shows that the surface of the unmodified fly ash was porous, rough, and irregular. From the second SEM image, precipitated calcium carbonate coated the fly ash so tightly that the inner core of the fly ash could hardly be seen.

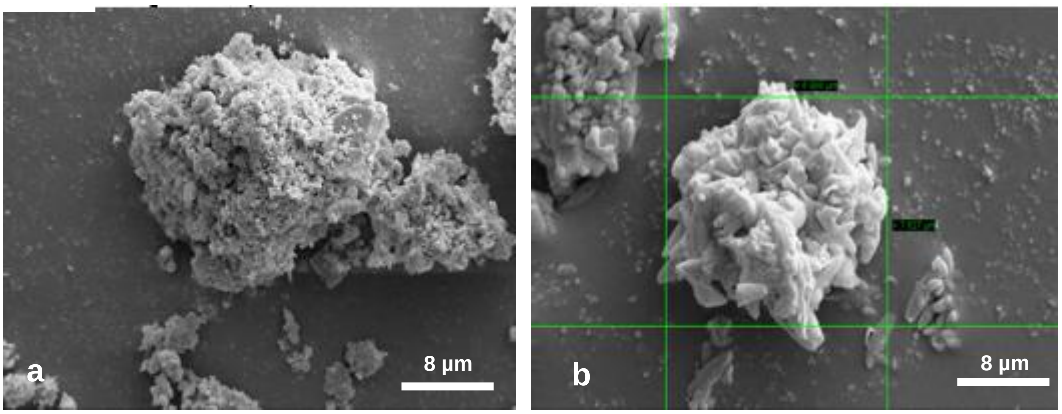

Fig. 1. SEM images of (a) unmodified fly ash and (b) fly ash modified by precipitated calcium carbonate

Whiteness of the Modified Fly ash

Calcium oxide and fly ash were mixed into the water in different mass ratios, and a certain amount of carbon dioxide was bubbled into the mixture to form the precipitated calcium carbonate deposited on the surface of the fly ash. The whiteness of the composite is shown in Fig. 2.

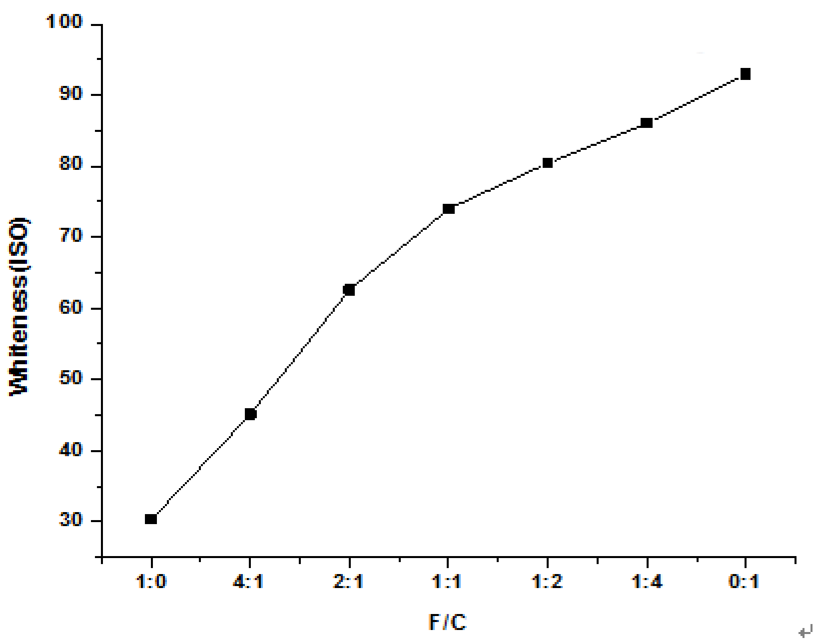

Fig. 2. The whiteness of different mass ratios of fly ash to calcium oxide (F denotes fly ash; C denotes calcium oxide)

As Fig. 2 shows, the whiteness of modified fly ash was enhanced when the mass ratio of calcium oxide to fly ash was increased. The whiteness value of unmodified fly ash was 30.3 ISO, while that of the isolated precipitated calcium carbonate was 93.0 ISO. When the F/C was in the range of 1:0 to 2:1, the whiteness value increased the most rapidly. This was probably because the precipitated calcium carbonate had good coverage, high brightness, and fine particle size (Subramanian *et al*. 2007; Koivunen and Paulapuro 2010; Chen *et al*. 2011). Particles of smaller sizes were relatively more easily adsorbed onto the surfaces of the larger particles (Tang *et al*. 2003; Ibrahim *et al*. 2009). This indicated that the particle size of the precipitated calcium carbonate played an important role in cladding the fly ash. As can be seen in Fig. 2, when the mass ratio of fly ash and calcium oxide had reached 2:3, the whiteness value of the modified fly ash surpassed 80 ISO, which represents the common minimum requirement for fillers used in papermaking. From Fig. 3 (a) and (b), it can be found that the color of modified fly ash changed from dark to white compared with the unmodified one. As the whiteness of modified fly ash could reach more than 80 ISO which means it could meet the whiteness requirement of filler, it could be used directly in printing paper, let alone use in brown, grey, and other dark-colored papers and boards. What is worth noting is that the cost of fly ash and calcium oxide are extremely low, and using this mixture as filler in papermaking could greatly reduce costs.

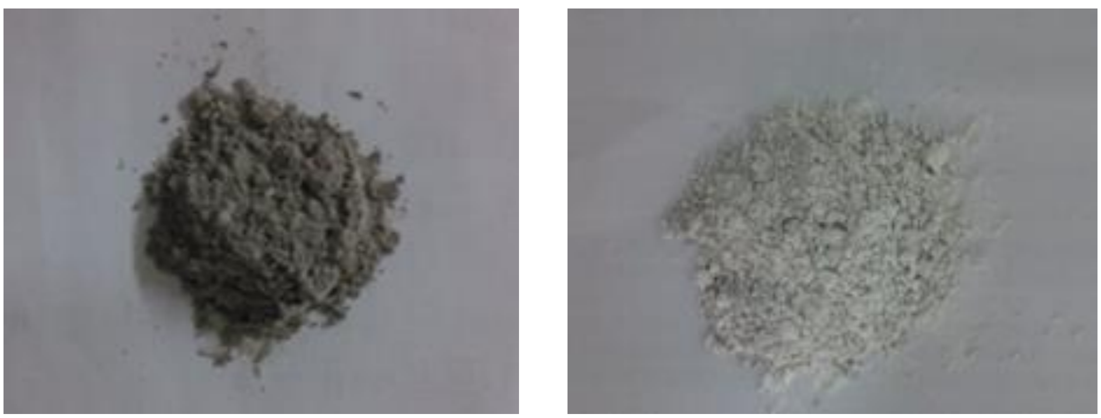

Fig. 3. Images of (a) unmodified fly ash and (b) modified fly ash

Effects of the Modified Fly Ash on Paper Strength Properties

The strength properties (tensile and burst indices) of the handsheets made using modified fly ash (when the mass ratio of fly ash to calcium oxide was 1:1), unmodified fly ash, and precipitated calcium carbonate (PCC) at concentrations between 15% and 45% are evaluated below.

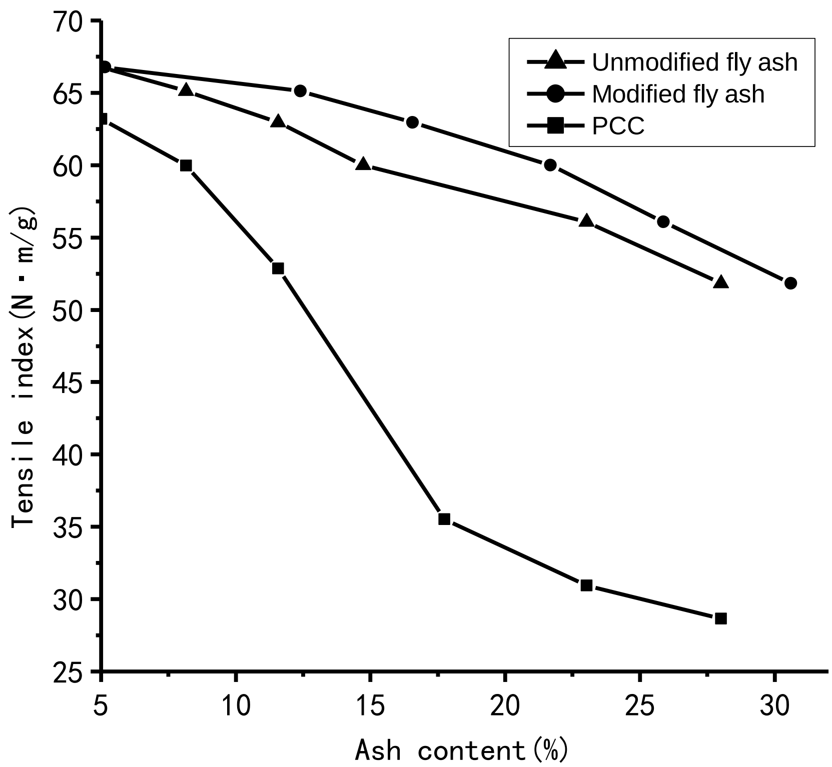

Fig. 4. Tensile index as a function of ash content in paper containing fly ash and PCC

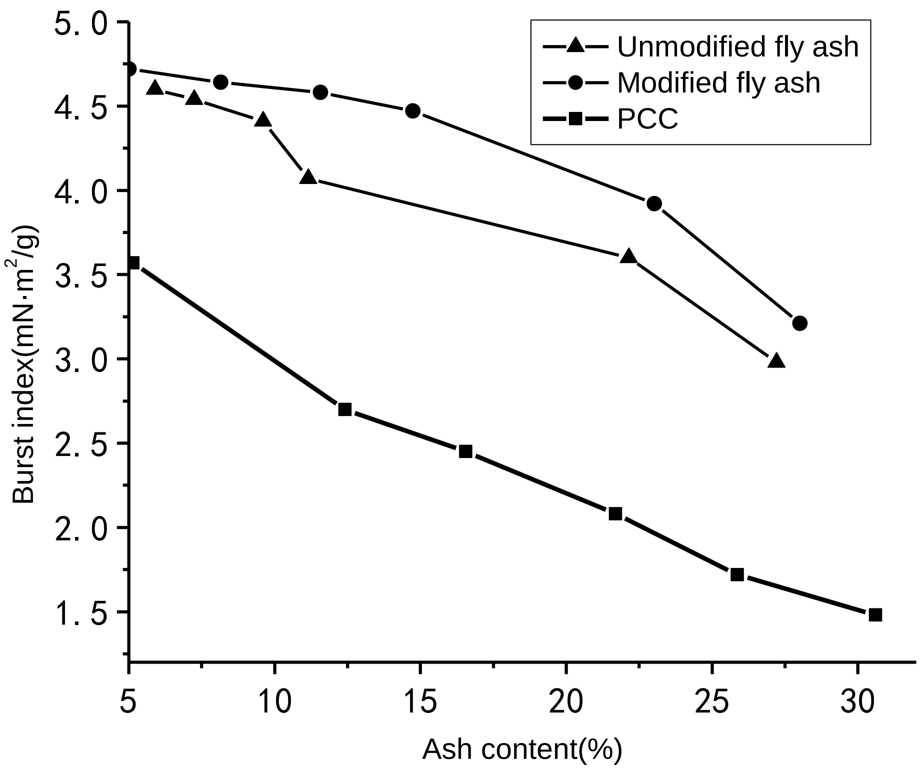

Fig. 5. Burst index as a function of ash content in paper containing fly ash and PCC

As can be seen in Figs.4 and 5, the tensile strength and burst strength of the tested papers were reduced when the ash content was increased. It was clear that the strength index (tensile index and burst index) of the paper filled with modified fly ash was higher than that of the paper filled with unmodified fly ash or with PCC. At the same ash content, the tensile index of paper filled with modified fly ash was at least 70% higher than that of PCC-filled paper, and the burst index of paper filled with modified fly ash was at least 60% higher than that of PCC-filled paper. From a different perspective, when the tensile index was about 50 N·m/g, the ash content of PCC-filled paper was only 11%, while the ash content of the paper filled with unmodified fly ash reached 27%, and the paper filled with modified fly ash reached 30%. At the same time, when the ash content was 5%, the burst index of the paper filled with modified fly ash was about 3.6 N·m^2/g, whereas, when the ash content was 25%, the burst index of paper filled with modified fly ash was about 3.6 mN·m^2/g. This indicated that modified fly ash might offer great advantages in terms of its paper strength properties.

CONCLUSIONS

1. Using precipitated calcium carbonate as a coating for fly ash improved the whiteness value of fly ash to a certain extent.
2. The mass ratio of fly ash to calcium oxide played an important role in enhancing the optical properties of fly ash.
3. When the mass ratio of fly ash and calcium oxide reached 2:3, the whiteness value of modified fly ash surpassed 80 ISO, thus meeting the common minimum requirement for fillers used in papermaking.
4. Because the cost of fly ash and calcium oxide are extremely low, using this mixture as filler in papermaking would greatly reduce the production costs.
5. Modified fly ash demonstrated great advantages in terms of paper strength properties.

ACKNOWLEDGMENTS

The authors would like to acknowledge support from the Fundamental Research Funds (2013B010402010) for the Central Universities of China. The authors also wish to thank Ming Wang for his kind assistance in performing the relevant experimental work for this paper.

REFERENCES CITED

Chen, X., Qian, X., and An, X. (2011). "Using calcium carbonate whiskers as paper-making filler," *BioResources* 6(3), 2435-2447. DOI: 10.15376/biores.6.3.2435-2447

Fahmy, T. Y. A., and Mobarak, F. (2008). "Nanocomposites from natural cellulose fibers filled with kaolin in presence of sucrose," *Carbohydrate Polymers* 72(4), 751-755.

DOI: 10.1016/j.carbpol.2008.01.008

Fan, H.-M., Wang, S., and Liu, J.-A. (2014). "The influence of particle size of starch-sodium stearate complex modified-GCC filler on paper physical strength," *BioResources* 9(4), 5883-5892. DOI: 10.15376/biores.9.4.5883-5892

Ibrahim, M. A., Mobarak, F., El-Din, E. I. S., Ebaid, A. E. E., and Youssef, M. A. (2009). "Modified Egyptian talc as internal and surface treatments for papermaking," *TAPPI Journal* 8(4), 15-22.

Koivunen, K., and Paulapuro, H. (2010). "Papermaking potential of novel structured PCC fillers with enhanced refractive index," *TAPPI Journal* 10(1), 4-11.

Lindon, K., and Sear, A. (2001). "Properties and use of fly ash: A valuable industrial by-product," *United Kingdom Quality Ash Association* 12(1), 64-65.

Nanri, Y., Konno, H., and Goto, H. (2008). "A new process to produce high-quality PCC by the causticizing process in a kraft pulp mill," *TAPPI Journal* 10(5), 19-24.

Puurtinen, A. (2004). "Controlling filler distribution for improved fine paper properties," *Appita Journal* 57(3), 204-208.

Sinha, A. S. K. (2008). "Effects of pulverized coal fly-ash addition as a wet-end filler in papermaking," *TAPPI Journal* 7(9), 3-7.

Subramanian, R., Fordsmand, H., and Paulapuro, H. (2007). "Precipitated calcium carbonate (PCC)-cellulose composite fillers: Effect of PCC particle structure on the production and properties of uncoated fine paper," *BioResources* 2(1), 91-105. DOI:10.15376/biores.2.1.91-105

Tang, Z. Y., Chen, G., Zhang, H.W., and Tang, A.M. (2003). "The effect of the properties of fillers on retention and paper strength," *Paper Science ＆ Technology* 22(6), 51-53.

Xu, Y., Yuan, R.-F., and Dong, W.-W. (2010). "On comprehensive utilization of fly ash," *China Well and Rock Salt* 41(1), 29-32.

Yang, Y.-F., Gai, G.-S., and Cai, Z.-F. (2006). "Surface modification of purified fly ash and application in polymer," *Journal of Hazardous Materials* 133(1), 276-282. DOI:10.1016/j.jhazmat.2005.10.028

Zhang, M., Song, S., and Wang, J. (2013). "Using a novel fly ash based calcium silicate as a potential paper filler," *BioResources* 8(2), 2768-2779. DOI:10.15376/biores.8.2.2768-2779

Zhang, M., Wang, W., and Yuan, G.-X., (2011). "Calcium carbonate was prepared by fly ash and its application in papermaking," *Jing Su Papermaking* 1(4), 42-44. DOI:10.15376/biores.8.2.2768-2779

Zhao, Y. L., Kim, D., and White, D. (2008). "Developing a new paradigm for liner board fillers," *TAPPI Journal* 7(3), 3-7.

Article submitted: June 25, 2015; Peer review completed: August 24, 2015; Revised version received: August 25, 2015; Second revision received and tentatively accepted: August 30, 2015; Accepted: August 31, 2015; Published: September 18, 2015.
DOI: 10.15376/biores.10.4.7434-7441.