Effects of Enzyme Treatment on Surface Properties of $Mg(OH)_2$-based Peroxide Bleached Deinked Pulp

Na Yun,[a,b,]* and Beihai He [b,c]

Enzyme (laccase/mediator or lipase) treatment, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) surface analysis techniques were combined to explore the surface properties of $Mg(OH)_2$-based peroxide bleached DIP (deinked pulp). The XPS survey spectra and SEM images showed that some trace elements, such as calcium, silicon, and aluminum, were present on the sample surface, in addition to the main elements, carbon and oxygen. The surface of enzyme-treated pulp was covered by the precipitated lignin or extractives. However, when the enzyme-treated pulps were bleached, the amount of precipitated lignin or extractives was considerably reduced. Lipase-treated, bleached pulp had better physical properties and lower effective residual ink concentration (ERIC) values than laccase/mediator-treated bleached pulp, which further indicated that lipase not only removed surface lignin and extractives, but it also was able to remove more residual ink contaminants.

Keywords: Deinked pulp; Hydrogen peroxide bleaching; $Mg(OH)_2$; Surface properties

Contact information: a: School of Chemical Engineering and Technology, Guangdong Industry Polytechnic, Guangzhou 510300 China; b: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640 China; c: National Engineering Research Center of Papermaking & Pollution Control, South China University of Technology, Guangzhou 510640 China;
** Corresponding author: yunna@126.com*

INTRODUCTION

The proportion of recycled pulp in the papermaking industry has been constantly increasing. Currently, approximately 65% of the raw materials used by the pulp and paper industry in China originates from recycled paper (China Paper Association 2018). Deinked pulp (DIP) is recycled pulp that is cleansed of printing ink through flotation or washing, flotation being the more common method. The use of recycled pulp for high brightness paper grades has increased the demand for bleaching chemicals, mainly hydrogen peroxide bleach, which can produce paper products with equivalent brightness to that produced from virgin pulp.

The alkali source used in conventional hydrogen peroxide bleaching is sodium hydroxide (NaOH). Recently, there has been a strong interest from the pulp and paper industry in a partial or total substitution of NaOH by $Mg(OH)_2$ as the alkali source in peroxide bleaching. This is more appealing due to less anionic waste, lower chemical oxygen demand load (COD) in the effluent, and better opacity, as well as decreased oxalate-related scaling (He *et al.* 2006; Yun and He 2013).

The surface properties of pulp fiber play an important role during the pulp and paper production. The understanding and control of surface chemical interactions is key to improving process efficiency and developing new paper products. Although the study of surface chemistry has increased over the past two decades, there is still a lot left to understand, including $Mg(OH)_2$-based peroxide bleached pulp. Most studies have focused on the physical properties of the pulp (*e.g.*, brightness and strength properties, *etc.*) and bleaching effluent properties (*e.g.*, COD, BOD, *etc.*), and have paid less attention to the surface properties (Yu *et al.* 2006; Kong *et al*. 2009; Leduc *et al*. 2010; Savoye *et al*. 2011).

Using of enzymes, such as lipase, laccase, in deinking and bleaching process have been reported in the literature (Leduc *et al*. 2011). Some previous results indicate that fines are contaminated with residual ink, which limits paper brightness improvement (Leduc *et al*. 2010). The deinking effect of lipase was caused by a partial degradation of the binder of soybean oil-based inks, thereby releasing the ink particles from paper. Also, the oxidation of pulp lignin by laccase can facilitate the detachment of ink particles from the fiber during the enzymatic treatment. This will possibly promote the peroxide bleaching efficiency and improve the quality of deinked pulp.

In this study, the enzyme laccase/mediator or lipase treatment together with surface analytical methods, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM), were used to explore the surface characterization of these pulps and paper.

EXPERIMENTAL

Materials

The DIP was obtained from the Guangzhou Paper Mill (Guangdong Province, China). Laccase (Novozyme 51003) was bought from Novozymes (Beijing, China), and the mediator (HBT) was bought from J&K Scientific Ltd (Beijing, China). The laccase activity was 1446 U/mL. Lipase was bought from Guangzhou Feibo Scientific Ltd. (Guangzhou, China). Lipase activity was 30000U/g, BR. Other chemicals used in bleaching and analyses were of analytical grade and supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China). Magnesium hydroxide powder was used in this experiment, containing $Mg(OH)_2$ 98%, Fe 31.5 ppm, Mn 1.7 ppm, and Cu less than 1ppm; the median size (D_{50}) was 10.62 μm, and the size distribution (D_{10} to D_{90}) was from 5.60 μm to 24. Chemical dosing of the additive was calculated on an oven dry (o.d.) pulp mass basis.

Methods

Enzymatic treatment

The deinked pulp was treated with laccase/mediator (X1) and lipase (X2), respectively. The enzymatic treatment with laccase/mediator (X1) or lipase (X2) was conducted at 50 °C, for 3h at 5% consistency. The lipase, laccase, and mediator dose were 10 U/g, 10 U/g, and 1%, respectively.

The enzymatic treatments were conducted in heat-sealed plastic bags immersed in a pre-heated thermostatically controlled water bath. Before the enzymatic liquor was added, the pulp slurry was pre-heated to 50 ºC. Then, the enzymatic liquor was put into the bag and mixed well. The plastic bag was then sealed and fully immersed in the controlled water bath for the desired retention time. The pulp was mixed every 15 min for the duration of the experiment. After the required retention time, the pulp slurry was washed thoroughly with distilled water for next the step, hydrogen peroxide bleaching.

Hydrogen peroxide bleaching

Hydrogen peroxide bleaching experiments were conducted in heat-sealed plastic bags at 10% consistency. Before the bleaching liquor was added, the pulp slurry was pre-heated to 80 ºC. To make the bleaching liquor for peroxide bleaching, the chemicals were mixed in a beaker in the following order: distilled water, sodium silicate, ethylene diamine tetraacetic acid (EDTA), and $Mg(OH)_2$. Then, hydrogen peroxide was added directly to the pulp after the other chemicals were added and mixed thoroughly. The plastic bag was then sealed and fully immersed in a pre-heated thermostatically controlled water bath for the desired retention time. The pulp was mixed every 15 min for the duration of the experiment. The experimental conditions for hydrogen peroxide bleaching are listed in Table 1. After the required retention time, the pulp slurry was washed thoroughly with distilled water for further analysis.

Table 1. Experimental Conditions for Peroxide Bleaching

H_2O_2 Dose (%)	EDTA Dose (%)	Na_2SiO_3 Dose (%)	$Mg(OH)_2$ Dose (%)	Temperature (°C)	Reaction Time (min)	Pulp Consistency (%)
3.00	0.50	2.00	1.45	80	120	10

Formation of handsheets

Pulps were transformed to handsheets following the TAPPI T205sp-02 standard (2002) in a sheet former (RK3AKWT, Frank-PTI, Laakirchen, Austria). Then these handsheets were put into a standard conditioning and testing atmosphere according to TAPPI T402 sp-03 standard (2003) for further analysis.

Optical analysis

The brightness was measured according to the TAPPI T452 om-02 standard (2002) using a brightness apparatus (Elrepho 070, L&W, Kista, Sweden).

ERIC measurement

The effective residual ink concentration (ERIC) was measured according to the TAPPI T567 om-04 standard (2004) using an ERIC apparatus (Technidyne Color Touch PC with ERIC 950, New Albany, USA).

Physical analysis

The tensile index was determined according to the TAPPI T494om-01 standard (2001), using a tensile tester (062, L&W, Kista, Sweden).

SEM analysis

The handsheet samples were coated with gold in a coating apparatus (108Auto, Cressington, UK), then analyzed *via* SEM (Hitachi S-3700N, Tokyo, Japan).

XPS measurement

The handsheet samples were analyzed in an x-ray photoelectron spectroscopy (Axis Ultra DLD, Kratos, UK) instrument equipped with a monochromatic Al Kα X-ray source. The spot size was 700μm×300μm. The pass energy was 160 eV and 40 eV for survey and high resolution, respectively.

RESULTS AND DISCUSSION

Effect of Enzymatic Treatment on Surface Properties of Bleached Pulp

Enzymes, such as laccase/mediator and lipase, could remove the surface lignin and or ink particles deposited on the surface of deinked pulp. The aim of this experiment was to analyze the surface properties of the untreated and enzyme-treated deinked pulp, as well as $Mg(OH)_2$-based hydrogen peroxide bleached pulp. The efficiency of the two enzymes was compared.

XPS measurement

X-ray photoelectron spectroscopy (XPS) was used to detect the chemical compositions and C1s bond types of fiber surfaces (Brinen 1993; Orblin and Fardim 2010; Orblin *et al*. 2011). Survey and high resolution C1s spectra were used to determine the O/C ratio and the relative area of the C1for the pulp samples, respectively (Dorris and Gray1978; Johansson *et al*. 1999; Fardim *et al*. 2006). The XPS C1s peak of the pulps was deconvoluted into four peaks. The binding energies were assigned for carbon as follows: bonded only to carbon or hydrogen (C-C, C-H) for C1, bonded to a single oxygen (C-O)for C2, bonded to a carbonyl or two non-carbonyl oxygens (C=O, O-C-O) for C3, and bonded to a carbonyl and a non-carbonyl oxygen (O=C-O) for C4.

The survey XPS spectra of laccase/mediator-treated (X1) and lipase-treated (X2) unbleached DIP and $Mg(OH)_2$-based bleached DIP (Figs.1 and 2) had C and O as the main surface elements, and also had trace elements, such as Si, Ca, and Al, which originated from mineral particles used as paper fillers, such as clay, silicates, and $CaCO_3$.

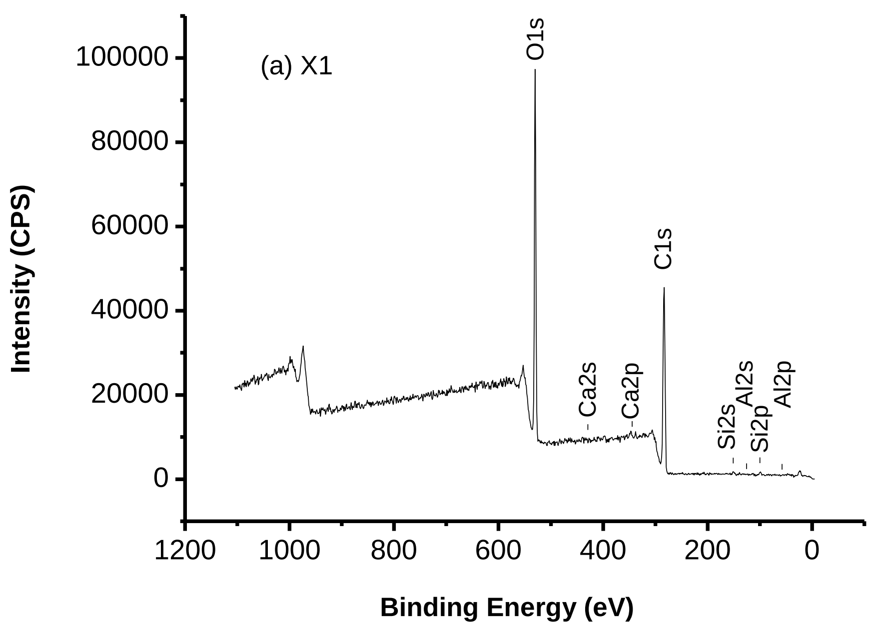

Fig.1a. Survey XPS spectra from the surface of laccase/mediator-treated unbleached pulp

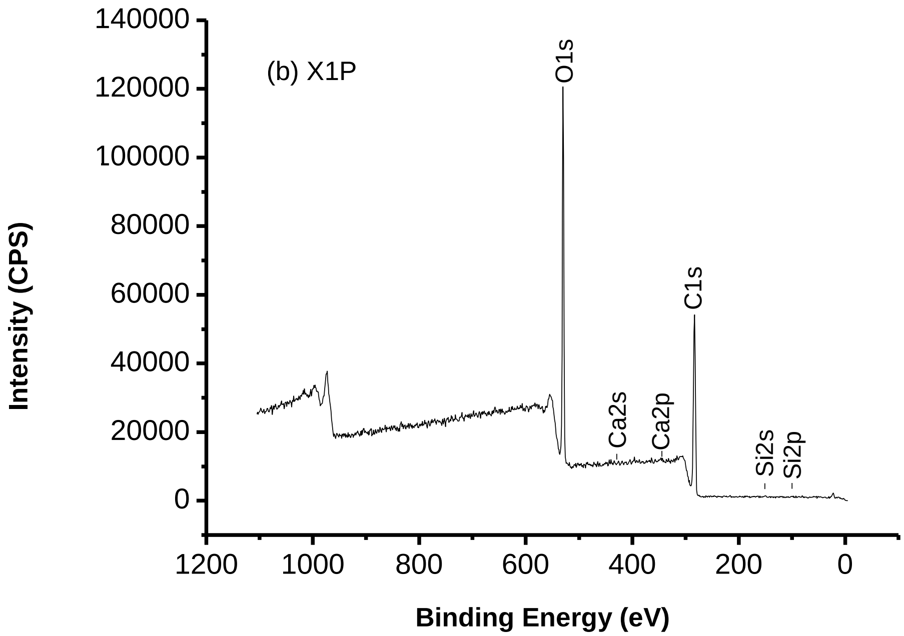

Fig.1b. Survey XPS spectra from the surface of laccase/mediator-treated bleached pulp

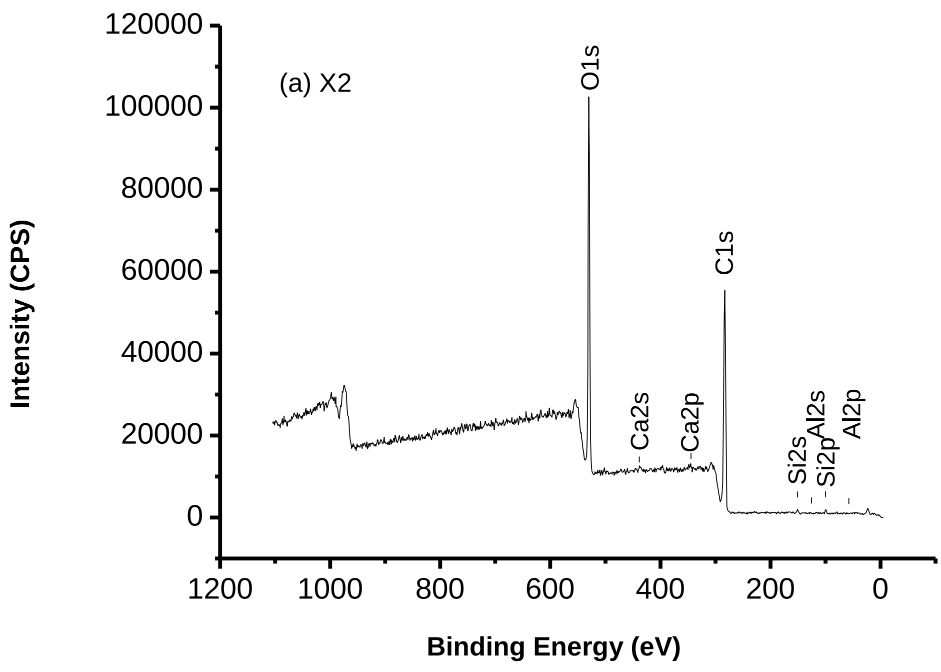

Fig. 2a. Survey XPS spectra from the surface of lipase-treated unbleached pulp

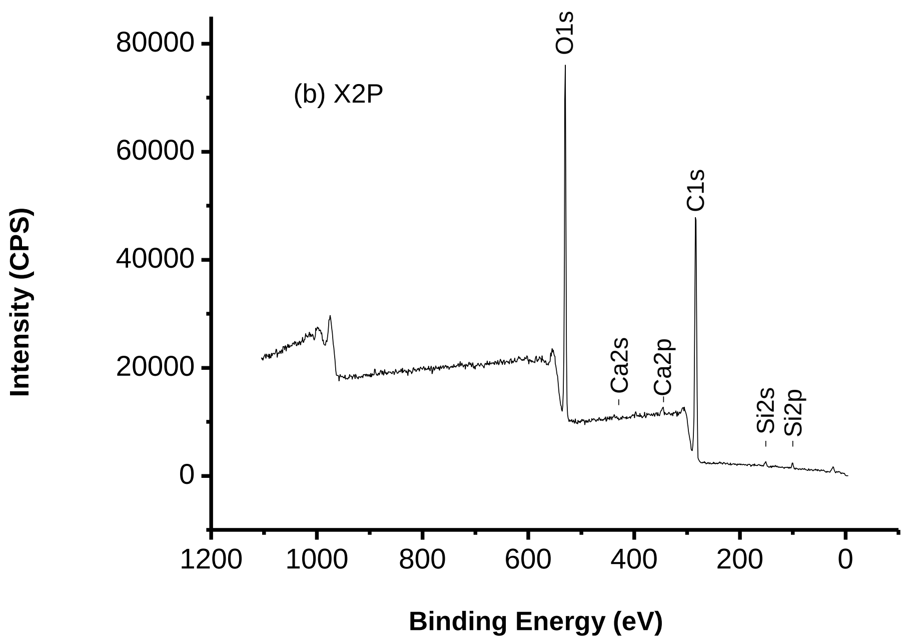

Fig. 2b. Survey XPS spectra from the surface of lipase-treated bleached pulp

The high-resolution XPS C1s spectra from the surface of laccase/mediator-treated (X1) or lipase-treated (X2) unbleached pulp and the following $Mg(OH)_2$-based hydrogen peroxide bleached pulps are shown in Figs. 3 and 4. The O/C ratio and the relative area of the C1 of laccase/mediator or lipase-treated unbleached pulp and the following $Mg(OH)_2$-based hydrogen peroxide bleached pulps are listed in Table 3. As shown in Figs. 3 and 4 as well as Table 3, the C1 area increased after the unbleached pulp was treated with the enzyme, which meant the surface of the treated pulp was covered with precipitated lignin and extractives. The enzyme-treated pulp was then bleached with $Mg(OH)_2$-based hydrogen peroxide bleaching. The C1 area decreased, which indicated that the precipitated lignin and extractives at the pulp surface were removed by hydrogen peroxide bleaching. Compare the laccase/mediator treatment with the lipase treatment, the relative area of C1 was lower after the lipase treatment, which meant the lipase treatment was more effective on removing lignin and extractives than the laccase/mediator treatment.

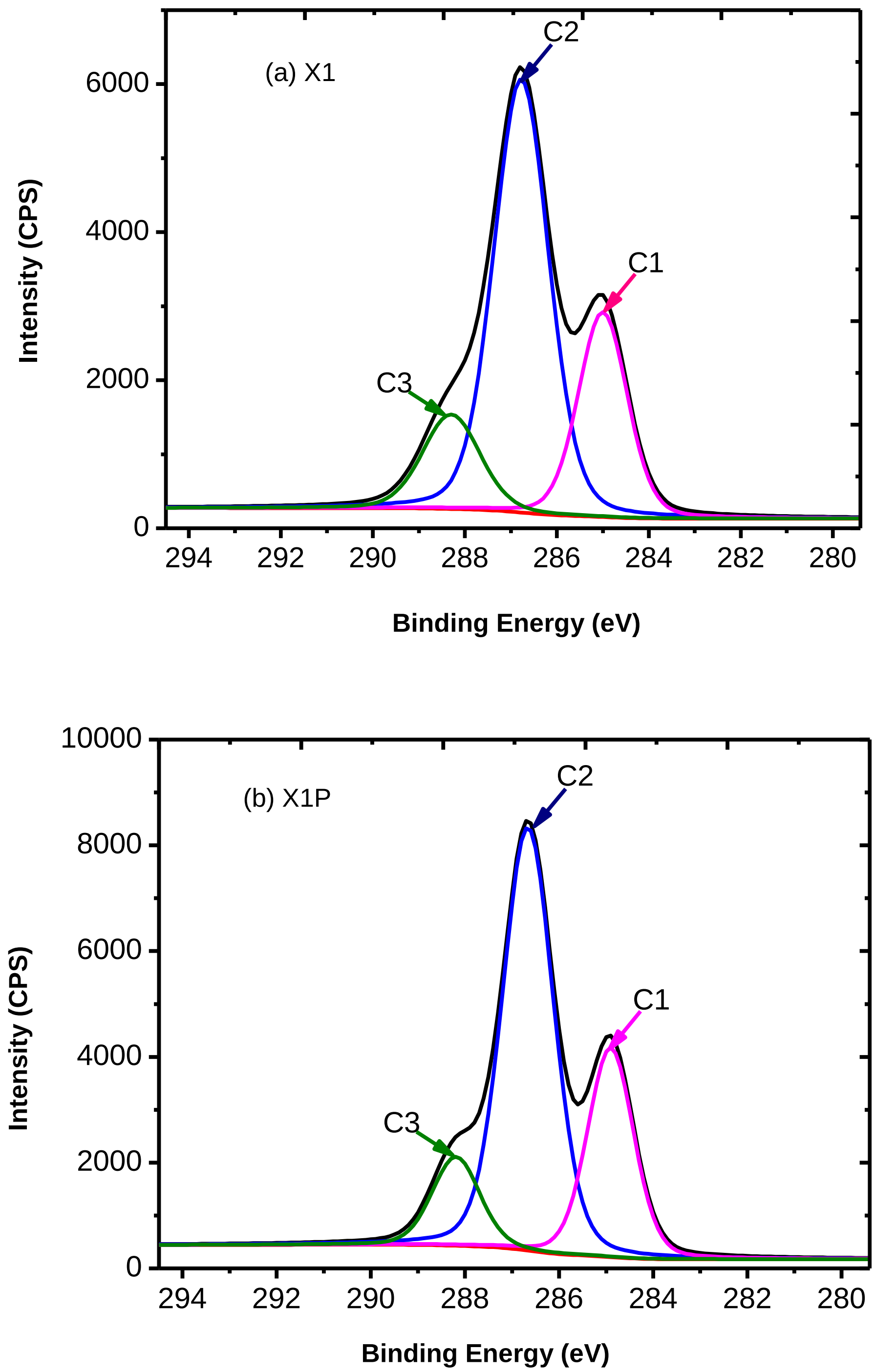

Fig. 3. High-resolution XPS C1s spectra from the surface of laccase/mediator-treated unbleached pulp (a) and bleached pulps (b)

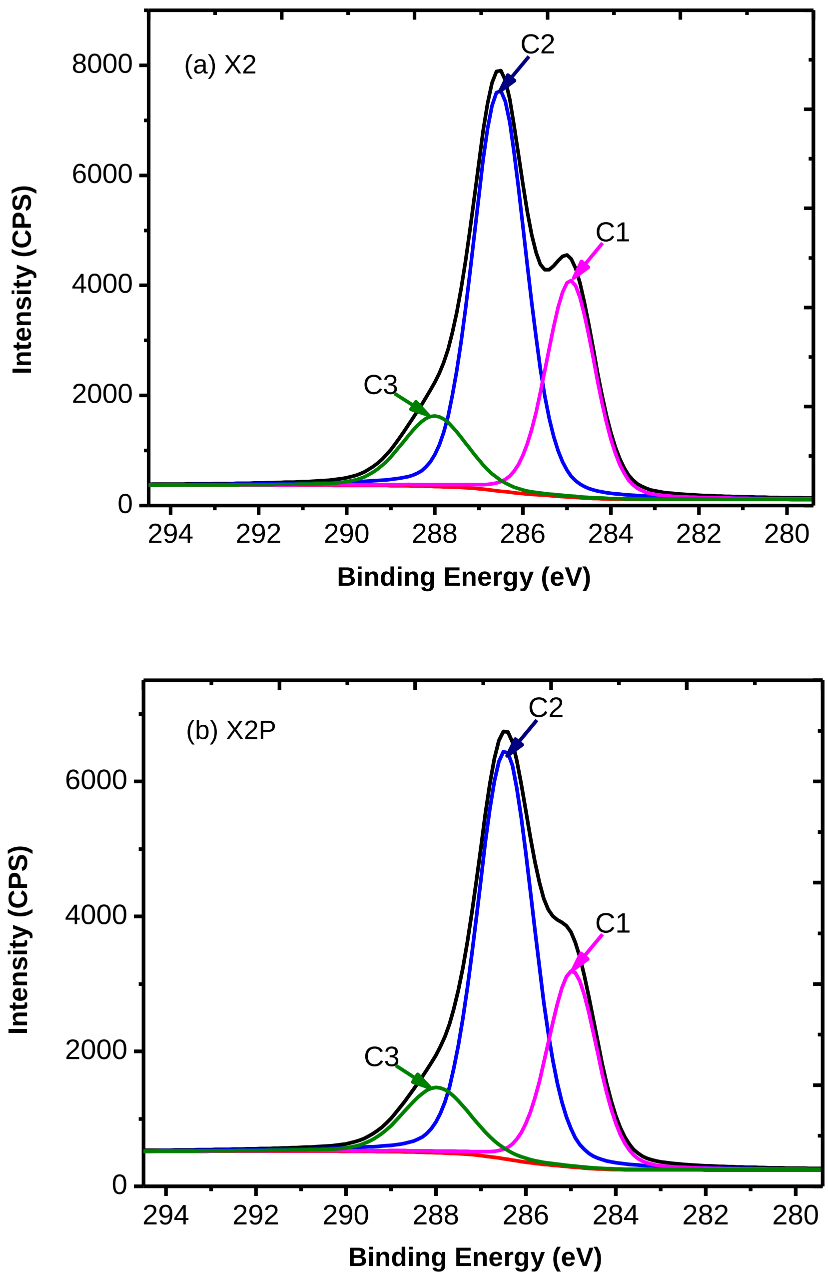

Fig. 4. High-resolution XPS C1s spectra from the surface of lipase-treated unbleached pulp (a) and bleached pulps (b)

Table 3. XPS Results of Enzyme-treated Unbleached Pulp and Bleached Pulps

Pulps	Unbleached	X1	X1P	X2	X2P
O/C Ratio	0.39	0.38	0.45	0.50	0.54
C_1 (%)	27.5	29.2	26.3	27.9	25.5

SEM analysis

Scanning electron microscopy (SEM) in this experiment was used to further analyze the effects of the enzyme treatment on unbleached pulp and the following bleached pulps. The SEM images (1000× magnification) of unbleached pulp, laccase/mediator, and lipase-treated pulps, and the following $Mg(OH)_2$-based hydrogen peroxide bleached pulps were shown in Figs. 5 through 7.

From Figs. 5 through 7, it can be seen that the fibers fibrillation was clear and these fibrils tangled with the coverings after the enzyme treatment and before bleaching.

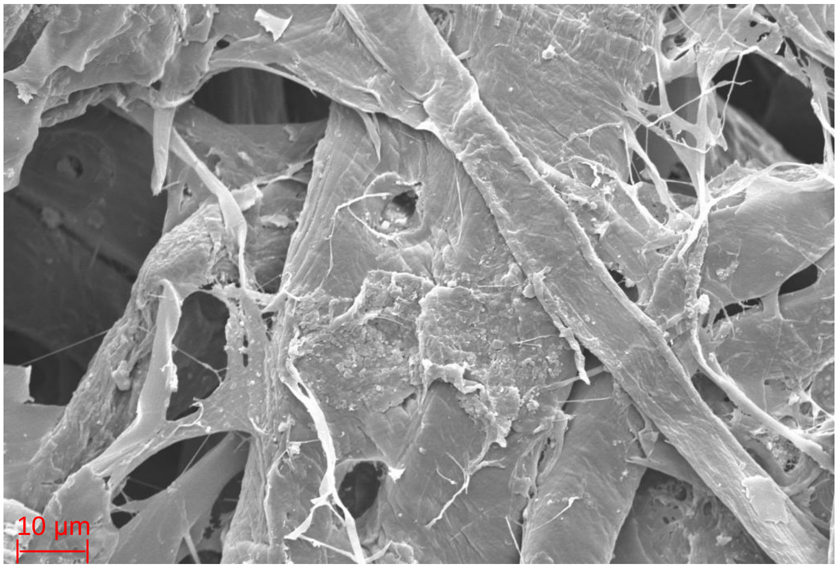

Fig. 5. SEM Image of the unbleached pulp at 1000x magnification

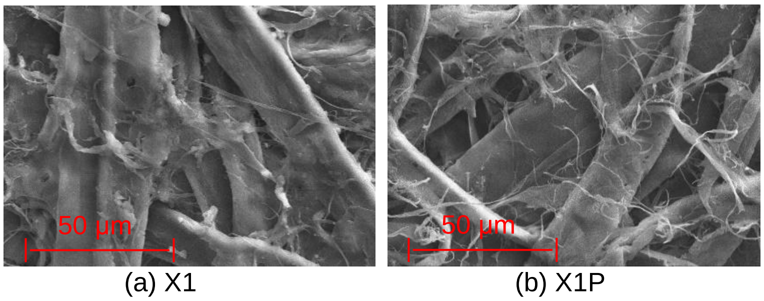

Fig. 6. SEM Images of the laccase/mediator-treated unbleached and bleached pulps at 1000x magnification

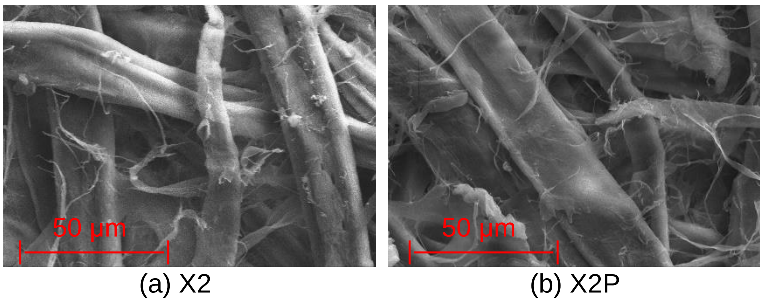

Fig. 7. SEM Images of the Lipase-treated unbleached and bleached pulps at 1000x magnification

However, after bleaching, the surface of the pulp was cleaner and more fibrils were present, which indicated that the precipitate lignin and extractives were removed during bleaching. Comparing Fig. 6 to Fig. 7, the surface of the pulps treated by the lipase treatment was cleaner and smoother than the laccase/mediator treatment, which meant that the lipase treatment removed more lignin and extractives at the surface of the deinked pulps.

Effect of Enzymatic Treatment on Physical Properties of Bleached Pulp

ERIC analysis

The ERIC measurement has become a paper industry standard for the measurement of residual ink in recycled pulp and paper using recycled pulp. The ERIC measurement is also a good tool for evaluating process changes and improvements.

As shown in Table 4, after laccase/mediator (X1) and lipase (X2) treatments, the ERIC values of both decreased slightly, and after the following bleaching, the ERIC values decreased by 55.7% to 68.1%, which meant the enzyme treatment and bleaching could decrease the residual ink. The ERIC values of the lipase-treated pulp were less than the laccase/mediator-treated pulp, which indicated that the lipase treatment was more effective on removing residual ink.

Table 4. ERIC Values of Laccase/mediator-treated (X1) and Lipase-treated (X2) Pulps

Pulps	Unbleached	X1	X2	X1P	X2P
ERIC Values	364.88	319.56	284.66	161.71	147.94

Brightness and tensile strength analysis

In this experiment, the unbleached deinked pulps were treated with laccase/ mediator (X1) and lipase (X2), then the treated pulps were bleached with $Mg(OH)_2$-based hydrogen peroxide. The brightness and tensile indices were measured and the effects of the laccase/mediator and lipase were compared (Table 5).

Table 5. Physical Properties of Laccase/mediator-treated and Lipase-treated Pulps

Pulps	Untreated	P	X1	X1P	X2	X2P
Brightness (%ISO)	47.0	55.1	44.7	57.2	45.8	59.0
Tensile Index (N·m/g)	15.8	20.6	19.6	21.9	20.0	23.5

As shown in Table 5, after the unbleached deinked pulps were treated with laccase/mediator (X1) and lipase (X2), the brightness of the pulp decreased while the tensile index increased. Then the treated pulps were bleached with $Mg(OH)_2$-based hydrogen peroxide, the brightness increased to 17.2%ISO after $Mg(OH)_2$-based hydrogen peroxide bleaching. The brightness increase of the enzyme treated bleached pulps was higher than that of the untreated bleached pulp, which indicated that the enzyme treatment could greatly improve the ability to bleach the pulp. With enzyme treatment, the tensile index also increased, from 38.6% to 48.7% after $Mg(OH)_2$-based hydrogen peroxide bleaching. Moreover, the lipase treatment was better than the laccase/mediator treatment after $Mg(OH)_2$-based peroxide bleaching, both the brightness and the tensile index of the lipase-treated pulp were higher than the laccase/mediator-treated pulp.

The data in Tables 4 and 5 showed that the physical properties of paper not only had a relationship with the lignin content and extractives on the pulp surface, but were also influenced by residual ink on its surface.

CONCLUSIONS

1. The survey XPS spectra and SEM images showed that, whether through enzyme treatment or bleaching, the main elements on the pulp surface were C and O, and some trace elements, such as Ca, Si, and Al, were also on the surface.
2. The high-resolution XPS spectra and SEM images showed that, C1 area increased after the enzyme treatment, which indicated that the surface of enzyme-treated pulp were covered by precipitated lignin and extractives. However, when the enzyme-treated pulps were bleached, C1 area decreased, which indicated that the precipitated lignin and extractives were removed by the following peroxide bleaching.
3. The brightness and the tensile index of the enzyme-treated pulps were higher than those of untreated pulp, which indicated that the enzyme treatment could improve the ability to bleach the pulp. The lipase treatment had better ERIC results than the laccase/mediator treatment, which indicated that lipase did not only remove more surface lignin and extractives, but also removed more residual ink contaminants.

ACKNOWLEDGMENTS

This work was supported by State Key Laboratory of Pulp and Paper Engineering (201739) and Guangdong Industry Polytechnic Innovation Fund (KYRC2017-0037).

REFERENCES CITED

Brinen, J. S. (1993). "The observation and distribution of organic additives on paper surfaces using surface spectroscopic techniques," *Nordic Pulp & Paper Research Journal* 8(1), 123-129. DOI: 10.3183/npprj-1993-08-01-p123-129

China Paper Association (2018). "China paper industry 2017 annual report," (http://www.chinappi.org/reps/20180508160836956678.html), Accessed 8 May 2018.

Dorris, G. M., and Gray, D. G. (1978). "Surface analysis of paper and wood fibres by ESCA. II. Surface composition of mechanical pulps," *Cellulose Chemistry and Technology* 12(6), 721-734.

Fardim, P., Hulten, A. H., Boisvert, J., Johansson, L., Ernstsson, M., Campbell, J. M., Lejeune, A., Holmbom, B., Laine, J., and Gray, D. (2006). "Critical comparison of methods for surface coverage by extractives and lignin in pulps by X-ray photoelectron spectroscopy (XPS)," *Holzforschung* 60(2), 149-155. DOI: 10.1515/HF.2006.024

He, Z., Wekesa M., and Ni, Y. (2006). "A comparative study of Mg $(OH)_2$-based and NaOH-based peroxide bleaching of TMP: Anionic trash formation and its impact on filler retention," *Pulp & Paper Canada*107(3), 29-32.

Johansson, L., Campbell, J. M., Koljonen, K., and Stenius, P. (1999). "Evaluation of surface lignin on cellulose fibers with XPS," *Applied Surface Science*144-145(2), 92-95. DOI: 10.1016/s0169-4332(98)00920-9

Kong, F., Ni, Y., and He, Z. (2009). "A partial magnesium hydroxide substitution for sodium hydroxide in peroxide bleaching of an aspen CTMP," *Journal of Wood Chemistry and Technology* 29(2), 136-149. DOI:10.1080/02773810902822355

Leduc, C., Lanteigne-Roch, L., and Daneault, C. (2011). "Use of enzymes in deinked pulp bleaching," *Cellulose Chemistry and Technology* 45(9-10), 657-663.

Leduc, C., Martel, J., and Daneault, C. (2010). "Efficiency and effluent characteristics from $Mg(OH)_2$-based peroxide bleaching of high-yield pulps and deinked pulp," *Cellulose Chemistry and Technology* 44(7-8), 271-276.

Leduc, C., Pairotpitukkul, P., Chabot B. and Daneault, C. (2010). "Bleaching of deinked pulp – Efficiency and limitation," *Progress in Paper Recycling* 1(19), 11-17.

Orblin, E., and Fardim, P. (2010). "Surface chemistry of deinked pulps as analysed by XPS and ToF-SIMS," *Surface and Interface Analysis* 42(12-13), 1712-1722. DOI: 10.1002/sia.3500

Orblin, E., Eta, V., and Fardim, P. (2011). "Surface chemistry of vessel elements by FE-SEM, μ-XPS and ToF-SIMS," *Holzforschung* 65(5), 681-688. DOI: 10.1515/hf.2011.064

Savoye, L., Petit-Conil, M., and Meyer, V. (2011). "Mechanisms of TMP peroxide bleaching using Mg-based alkalis," *Holzforschung* 65(6), 797-803. DOI: 10.1515/hf.2011.109

TAPPI T205 (2002). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA.

TAPPI T402 (2003). "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products," TAPPI Press, Atlanta, GA.

TAPPI T452 (2002). "Brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)," TAPPI Press, Atlanta, GA.

TAPPI T494 (2001). "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)," TAPPI Press, Atlanta, GA.

TAPPI T567 (2004). "Determination of effective residual ink concentration byinfrared reflectance measurement," TAPPI Press, Atlanta, GA.

Yun, N., and He, B. (2013). "$Mg(OH)_2$-based hydrogen peroxide bleaching of deinked pulp,"*BioResources* 8(3), 4609-4618. DOI: 10.15376/biores.8.3.4609-4618

Yu, L., and Ni, Y. H. (2006). "Decreasing calcium oxalate scaling by partial substitution of Mg(OH)2 for NaOH in the peroxide bleaching of mechanical pulps," *Tappi Journal* 5(2), 9-12.

Article submitted: February 2, 2017; Peer review completed: April 15, 2017; Revised version received: February 13, 2019; Accepted: February 14, 2019; Published: February 20, 2019.
DOI: 10.15376/biores.14.2.2861-2872