Bioresource Technology 196 (2015) 413–417

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Removal of hexenuronic acid by xylanase to reduce adsorbable organic halides formation in chlorine dioxide bleaching of bagasse pulp

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HIGHLIGHTS

- AOX could be reduced by 21.4–26.6% with xylanase treatment.
- Chlorine dioxide demand could be reduced by 12.5–22%.
- Lignin and hemicellulose (mainly HexA) were the main source for AOX formation.

ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form 27 July 2015
Accepted 28 July 2015
Available online 4 August 2015

Keywords:
Xylanase
AOX formation
Bagasse pulp
Chlorine dioxide bleaching
Surface chemistry

ABSTRACT

Xylanase-aided chlorine dioxide bleaching of bagasse pulp was investigated. The pulp was pretreated with xylanase and followed a chlorine dioxide bleaching stage. The ATR-FTIR and XPS were employed to determine the surface chemistry of the control pulp, xylanase treated and chlorine dioxide treated pulps. The hexenuronic acid (HexA) could obviously be reduced after xylanase pretreatment, and the adsorbable organic halides (AOX) were reduced after chlorine dioxide bleaching. Compared to the control pulp, AOX could be reduced by 21.4–26.6% with xylanase treatment. Chlorine dioxide demand could be reduced by 12.5–22% to achieve the same brightness. The ATR-FTIR and XPS results showed that lignin and hemicellulose (mainly HexA) were the main source for AOX formation. Xylanase pretreatment could remove HexA and expose more lignin, which decreased the chlorine dioxide demand and thus reduced formation of AOX.

1. Introduction

As the main chemical in elemental chlorine free (ECF) bleaching technology, chlorine dioxide has a good selectivity in delignification, but absorbable organic halogens (AOX) will still be produced during the bleaching. The AOX contains more than 300 different organochlorines (Leena et al., 1988; Mckague, 1988) and some of the compounds are toxic and they show the tendency of biological accumulation because of their lipophilic nature (Reeve, 1995).

Recently, xylanase aided pulp bleaching is widely applied to the production of bleached chemical pulp. Xylanase is a type of hemicellulase, and mainly hydrolyze the xylan that relocated and reprecipitated on the surface of the pulp microfibrils (Comlekcioglu et al., 2014). Xylanase aided bleaching also results from the cleavage of hemicellulose chains between lignin and carbohydrate complex, thereby removing loosened lignin, and therefore lowering bleaching chemical consumption (Saleem et al., 2012). Many research institutions put forward a series of opinions about xylanase aided bleaching with different raw materials. Saleem et al. found that the enzyme treated pulp can save 15% active chlorine demands in single bleaching stage and 18.7% in multiple with attainment of the same brightness of the control pulp (Saleem et al., 2009). Birijlall et al. evaluated the xylanase bleaching efficacy by bagasse pulp and observed a brightness of 47.4% ISO with 50 IU/g of xylanase, which was 2.1% ISO higher than the untreated pulps (Birijlall et al., 2011). These results indicate the potential of xylanase treatment of pulp for reduction in AOX formation from the pulp and paper industry.

Bagasse is one of the main non-wood raw materials for pulping and papermaking. The hemicellulose content of the bagasse fiber is over 30% (Ricardo de et al., 2011). The hexenuronic acid (HexA) is formed during the pulp cooking, where 4-*O*-methylglucuronic acid

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http://dx.doi.org/10.1016/j.biortech.2015.07.115
0960-8524/

of the hemicellulose side chain is turned into unsaturated HexA (4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid) (Cadena et al., 2011). Bjorklund et al. found that formation of AOX has a close relationship with HexA for Kraft hardwood pulp, and that AOX formation could be decreased by 20–25% when HexA was removed (Bjorklund et al., 2002, 2004). Nguyen et al. put the first evidence that the xylanase can have a direct bleaching effect on removing HexA (Nguyen et al., 2008). Our present study focused on xylanase aided chlorine dioxide bleaching of the bagasse pulp. The relationship of HexA and AOX was investigated and how xylanase helps in removing HexA was discussed. Changes of the fiber surface chemical composition was qualitatively and quantitatively measured by ATR-FTIR and XPS. Mechanisms of the xylanase aided pulp bleaching reduced AOX formation was therefore proposed, and this provides a theoretical basis for reducing AOX formation.

2. Methods

2.1. Chemicals and raw materials

All assay reagents were obtained from Sigma (USA). Activated carbon and ceramic wool were purchased from Analytik-Jena instrument company (Germany), other chemicals employed in this work were purchased from Chong Qing Kawahigashi Chemical Co. Ltd. China. The NKC-1 xylanase liquid production from *Bacillus subtilis* was obtained from College of Biological Science of Guangxi University. The main ingredient of the xylanase liquid was xylanase (99%), and the enzyme activity was 400 IU/mL. The unbleached pulp was taken from bagasse pulp mill of Guangxi China. The pulp Kappa number and brightness are 10.1% and 31.9% ISO, respectively.

2.2. Bleaching operation

2.2.1. Xylanase pretreatment

The bagasse pulp (20 g bone dry) was pretreated with xylanase and followed by a chlorine dioxide bleaching stage. The xylanase loading started from 0 to 25 IU/g, and pretreated for 2 h. Bagasse pulp and a certain amount of deionized water were placed in plastic bag. Then sodium hydroxide was added to adjust the initial pH to make sure it remained at 9.0. The pulp consistency was kept at 10% during the pretreatment, and diluted the xylanase to a given concentration. The xylanase was added to the pulp slurry once the reaction temperature reached 65 °C. The pulp was washed for three times after the xylanase pretreatment, and kept for the chlorine dioxide bleaching.

2.2.2. Chlorine dioxide bleaching

The xylanase pretreated pulps were completely washed and put in plastic bags, and the pulp consistency was kept at 10% during the bleaching process. Then sulfuric acid was added to adjust the initial pH to make sure it remained at 3.5–4. Chlorine dioxide was added to the pulp slurry once the reaction temperature reached 65 °C. The pulps were kneaded every 5 min and were washed after the bleaching reaction. The pulps were extracted by acetone for 4–6 h after xylanase and chlorine dioxide treatment and kept dry for ATR-FTIR and XPS analysis.

2.3. Analysis

2.3.1. AOX content analysis

The Multi X2500 AOX analyzer (Germany) was employed to determinate the AOX content of the bleaching effluent. For the basic method and process referred to our previous studies (Nie et al., 2013; Nie et al., 2014a,b).

2.3.2. ATR-FTIR spectra analysis

ATR-FTIR spectra (4000–450 cm^{-1}) were recorded by employing ZnSe crystal ATR (USA) and NEXUS 470 FTIR spectrometer (Canada). Spectra were obtained with 4 cm^{-1} resolution and 256 scans were carried out for sample spectra.

2.3.3. XPS analysis

XPS analysis of the fiber surface was performed on a Leybold Max200 XPS system. The hand sheets were dried after fully washed (basis weight: 80 g/m^2). After drying, samples were put into the Soxhlet and extracted for 4–6 h with acetone and distilled water. The samples were then placed on clean smooth metal slides, pressed lightly, and dried at room temperature. The smooth sides were used for XPS measurement. The X radiation source was obtained by electron bombardment of Al under 12 or 15 kV and at 15–25 mA. The XPS spectra were obtained with a vacuum of 1138×10^{-7} Pa, and a photoelectron take-off angle of 90°. The Oxygen and carbon atoms ratio (O/C) were calculated by a low-resolution X-ray photoelectron spectroscopy where the pass energy was 192 eV. The sensitivity factor of carbon and oxygen are 0.32 and 0.75, respectively (Li and Reeve, 2005).

3. Results and discussions

3.1. Impact of HexA on AOX formation

Xylanase usually plays an important role in the pretreatment stage of current ECF bleaching sequences. It has been proved to be an economic way for pulp plants to realize great benefits in the bleaching stage. After xylanase pretreatment, chlorine dioxide demand was reduced, which therefore decreases the AOX formation (Fillat et al., 2012; Sharma et al., 2014; Thakur et al., 2012). Influence of xylanase dosage on AOX and HexA for pretreatment of bagasse pulp is shown in Fig. 1. It indicated that both HexA of the pulp and AOX content of the effluent decreased with increase in enzyme dosage.

There is a significant relationship between the HexA (after xylanase pretreatment) and AOX (after chlorine dioxide bleaching), the AOX could be reduced by 37.6% when the HexA was decreased from 14.7 mmol/kg to 8.88 mmol/kg as shown in Fig. 2. This indicated that the HexA is partially responsible for the higher AOX formation in the pulp. These results are in agreement with the studies of Bjorklund et al. who have also found that the formation of AOX during bleaching has a close relationship with HexA content in

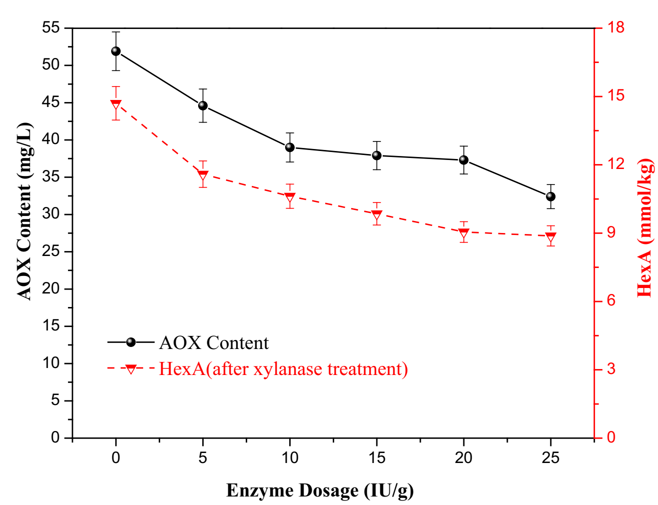

Fig. 1. Influence of xylanase dosage on AOX and HexA.