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Chitosan as a flocculant for pre-hydrolysis liquor of kraft-based dissolving pulp production process

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ABSTRACT

In this work, the flocculation concept was employed to recover the dissolved lignocellulosic materials of industrially produced pre-hydrolysis liquor (PHL) using two different molecular weights of chitosan. The analysis revealed the maximum turbidity of 1000 NTU or 1900 NTU via adding 2.2 mg/g low molecular weight (LMW) or 1.7 mg/g high molecular weight (HMW) chitosan to the PHL, respectively. Also, the maximum furfural removal of 55% or 50% was obtained by adding 0.7 mg/g or 0.5 mg/g LMW or HMW chitosan to the PHL, respectively. The maximum recovery of oligomeric sugars was 20% or 25% by adding 1.5 or 0.5 mg/g LMW or HMW chitosan, while that of lignin was 40% or 35% by applying 2.2 mg/g or 1.7 mg/g LMW or HMW chitosan to the PHL, respectively. The removal of monomeric sugars and acetic acid was rather limited. The particle size and nitrogen analyses were also hired to characterize the properties of the formed complexes.

1. Introduction

The application of integrated forest biorefinery concept has received a great attention in the pulp and paper industry (Amidon et al., 2008; Saeed et al., 2010; van Heiningen, 2006). Such an application could improve the revenue of the mill, reduce its environmental impact and increase employment opportunities (Amidon et al., 2008; van Heiningen, 2006). Following this concept, different components of lignocellulosic materials are systematically separated and converted to various value-added bio-products.

In the kraft-based dissolving pulp production process, the hemicelluloses and a part of lignin are separated in the pre-hydrolysis stage, while the remaining lignin is removed from the solid residue (cellulose) in the subsequent kraft pulping and bleaching steps (T. Liu, He, Hu, & Ni, 2011; Saeed et al., 2010). The pre-hydrolysis liquor (PHL) from the pre-hydrolysis stage is presently mixed with black liquor and burned in the recovery boiler of the mill. However, the dissolved lignocellulosic materials could be potentially used for various purposes: wet end additives of papermaking from the recovered hemicelluloses (Ren, Peng, & Sun, 2009), fuel source from the recovered lignin (Leschinsky, Zuckerstätter, Weber, Patt, & Sixta, 2008; Z. Liu, Fatehi, Jahan, & Ni, 2011; van Heiningen, 2006), and ethanol production via fermentation of recovered hemicelluloses (Alvarado-Morales, Terra, Gernaey, Woodley, & Gani, 2009; Carvalheiro, Durate, & Girio, 2008; Huang, Ramaswamy, Al-Dajani, & Tschirner, 2010). One method to recover and subsequently utilize the lignocellulosic materials of the PHL is to employ flocculation concepts through a cationic polymer treatment. This method has been widely applied in various waste water treatment systems (Ji, Qiu, Wai, Wong, & Li, 2010; T. Liu et al., 2011; Mihai & Dragan, 2009; Saether, Holme, Maurstad, Smidsrod, & Stokke, 2008). In this system, the electrostatic interaction developed between oppositely charged polymers promotes the flocculation (Muzzarelli, 1990; Szygula, Guibal, Palacin, Ruiz, & Sastre, 2009). If the molecular weight of two oppositely charged polymers is significantly different, a patch flocculation may be developed, in which the low molecular weight polymer neutralizes a part of the charges associated with the high MW polymer (Guibal and Roussy, 2007; Schatz, Domard, Viton, Pichot, & Delair, 2004; Strom, Barla, & Stenius, 1985). If the molecular weight of polymers is relatively high, the charged polymer may bridge the formed complexes and create larger complexes (Guibal and Roussy, 2007; Schatz et al., 2004; Strom et al., 1985). As the PHL contains various anionic lignocellulosic materials (Li, Saeed, Ni, & van Heiningen, 2010; Saeed et al., 2010), the addition of cationic polymers to the PHL would facilitate the flocculation due to the formation of complexes of cationic polymers/anionic lignocellulosic materials.

Chitosan, a natural polysaccharide, is commercially prepared by partial deacetylation of chitin, which is a product found in crustacean shells. (Fredheim & Christensen, 2003; Guibal & Roussy, 2007; Saether et al., 2008). The abundance and comparative cost-effectiveness of chitosan with other cationic polymers make chitosan attractive for industrial usages in various areas (Fatehi, Kititerakun, Ni, & Xiao, 2010). One main advantage of chitosan is

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its natural cationic charge, which facilitates its interaction with anionic charged polymers in various media (Fatehi, Kititerakun et al., 2010). In fact, the cationic charge of chitosan eliminates the need for its further modification/cationization, which is in opposition to the preparation methodology of cationic synthetic polymers used in waste water treatment and papermaking systems. The interaction of chitosan with various anionic polymers in water was investigated in the literature (Fredheim & Christensen, 2003; Guibal & Roussy, 2007; Saether et al., 2008; Szygula et al., 2009). The performance of chitosan on interacting with various components of a chemical pulp suspension (Li, Du, Xu, Zhan, & Kennedy, 2004) and with various dyes have been evaluated in the literature (Guibal & Roussy, 2007; Szygula et al., 2009). The objective of this study was to investigate the flocculation behavior and efficiency of chitosan on interacting with the lignocellulosic materials of the PHL and on removing them from the PHL.

In the literature, the efficiencies of acidification and liming on removing various components of the PHL have been comprehensively investigated (Horvath, Sjode, Alriksson, Jonsson, & Nilvebrant, 2005; Z. Liu et al., 2011; Martinez, Rodriguez, York, Preston, & Ingram, 2000; Sun, 2008). Our focus in this study was to further improve the removal efficiency of lignocellulosic materials of PHL via using chitosan. In this work, two chitosan samples with different molecular weights (MW) were applied to industrially produced PHL. The removal of various dissolved organics in the PHL was assessed at different dosages of chitosan. The properties of chitosan/PHL mixture and the formed complexes were assessed and related to the removal of organics. Depending on the compositions of the formed complexes, they may be used as fuel source, or wet end additive (retention aid) in papermaking, as described above. Thus, the flocculation process via using chitosan suits well with the biorefinery concept applied to the kraft-based dissolving pulp production process.

2. Experimental

2.1. Raw material

The pre-hydrolysis liquor (PHL) was collected from a dissolving pulp production mill, located in Eastern Canada, and used as received. Chitosan with 70–180 kDa (448869) and 200–300 kDa (448877) molecular weights, 79% deacetylated, were purchased from Aldrich Co., and dissolved in the solutions of 0.5 g/l prior to analysis. The standard solutions of potassium polyvinyl sulfate (PVSK) or polydiallyldimethylammonium chloride (PDADMAC) (0.5 mM) were purchased from Aldrich Co., and used for measuring the charge density of chitosan and the PHL (Fatehi, Kititerakun et al., 2010). NaOH (1 M) and H_2SO_4 (1 M) were obtained from Fisher scientific.

In the literature, acidification has been regarded as the first step of PHL utilization in biorefinery concept (T. Liu et al., 2011; Sun, 2008). In this research, the PHL (500 ml) has been acidified to a pH of 2 by adding sulfuric acid at room temperature and then kept for 2 h. The precipitated materials were then removed from the PHL via filtering (0.45 μm nylon filters) (Z. Liu et al., 2011). Then, the acidified PHL sample was treated by CaO to a pH of 6–7 for the chitosan treatment. The application of lime has also been respected as a method to reduce the lignocellulosic materials of the PHL in the past (Horvath et al., 2005; Martinez et al., 2000). Afterwards, the PHL was filtered and this pretreated PHL was applied for the flocculation analysis via the chitosan treatment.

2.2. Addition of chitosan to PHL

Various amounts of low or high MW chitosan were subsequently added to 20 ml of the pretreated PHL for removing of the lignocellulosic materials at room temperature, while stirring. Then, the zeta potential, particle size, and turbidity of the chitosan/PHL mixture were analyzed. Afterwards, the formed complexes were isolated by centrifuging at 3000 rpm for 5 min. The concentrations of lignocellulosic materials before and after chitosan addition were determined, and removal efficiencies were calculated. The chitosan content of the formed complexes was identified via the Nitrogen analysis.

2.3. Charge density, zeta potential, particle size and turbidity analyses

The charge density of the PHL sample and chitosan solutions were measured by using a particle charge detector (Mütek PCD 03, Germany) with the standard PVSK or PDADMAC solutions. The charge densities of low and high MW chitosan were 3.09 meq/g and 3.05 meq/g, respectively. The quasi-elastic light scattering (QELS) analysis was conducted for measuring the size of complexes formed in the chitosan/PHL mixture. Chitosan and PHL solutions (20 ml) were first filtered by using syringe filters, sterile 0.2 μm pore size, to remove the impurities of the solutions. Then, various dosages of chitosan were added to the PHL at room temperature, and the hydrodynamic sizes and zeta potential of the solutions were quantified before and after mixing. The data was obtained at 25 °C with a ZetaPlus Brookhaven (Holtsville, NY, USA) with the software of 90 plus/BI-MASS. The scattering angle and operating wavelength were 90° and 658 nm, respectively. Analysis was conducted automatically to yield the mean diffusion coefficient. Then, from the Stokes–Einstein equation, the apparent hydrodynamic sizes of the formed complex were assessed. This method has been widely applied for determining the size of complexes in solutions (Buchhammer, Mende, & Oelmann, 2003; Fatehi, Kititerakun et al., 2010). The zeta potential was calculated by measuring the electrophoretic mobility, using the Smoluchwski's approximation by a ZetaPlus Zeta potential analyzer (Brookhevan, Holtsville, NY, USA) (Onesippe and Lagerge, 2008). The turbidity of the PHL samples before and after the cationic polymer treatments was conducted by using a turbidimeter, 2100AN, HACH co., CO, USA at room temperature.

2.4. Sugar analysis

The concentration of sugars in the PHL was determined by using an ion chromatography unit equipped with CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) (T. Liu et al., 2011; Saeed et al., 2010). To convert oligosaccharide of PHLs to monosaccharide, an additional acid hydrolysis was carried out on the PHL under the conditions of 4% sulfuric acid at 121 °C in an oil bath (Neslab Instruments, Inc., Portsmouth, NH, USA) (Saeed et al., 2010). The PAD settings were E1 = 0.1 V, E2 = 0.6 V and E3 = −0.8 V. Deionized water was used as the eluant with a flow rate of 1 mL/min. NaOH with the concentrations of 0.2 M and 0.5 M were used as the regeneration agent and supporting electrolyte with a flow rate of 1 mL/min. The sugar analysis prior to this additional acid hydrolysis reveals the content of monomeric sugars, while that after the additional acid hydrolysis reflects the total monomeric sugars existing in the PHL. The subtraction of total sugars from monomeric sugars reflects the amount of oligomeric sugars in the PHL.

2.5. Lignin, furfural and acetic acid analyses

The lignin content of the PHL was measured based on the UV/Vis spectrometric method at a wavelength of 205 nm (TAPPI UM 250). A Varian 300 ^{1}H NMR spectrometer was employed for determining the concentrations of furfural and acetic acid of the PHL (Z. Liu et al.,

Table 1
Properties of PHL.

Mono-sugars (wt.%)	Oligo-sugars (wt.%)	Lignin (wt.%)	Furfural (wt.%)	Acetic acid (wt.%)	Dry solid (wt.%)	Ash content (wt.%)	Charge density (mequiv./g)	Conductivity (mOhm)
0.93	0.69	0.93	0.20	1.03	8.22	4.34	−0.065	12.2

2011; Saeed et al., 2010). Calibration curves were established for both furfural and acetic acid. The solvent suppression method was used with D_2O to water ratio of 1:4.

2.6. Ash and solid content

The dry matter and ash contents of the PHL samples were measured according to TAPPI T211 and T412, respectively.

2.7. Nitrogen analysis

Since the chitosan contains Nitrogen, the Nitrogen analysis of the complexes can directly identify the chitosan content of the complexes. This is because there is no additional source of Nitrogen in the PHL, and hence in the formed complexes. The nitrogen analysis was conducted using a Nitrogen/Sulfur analyzer, 9000 series, Antek, TX, USA at the temperature of 1075 °C. A calibration curve was prepared by plotting the predefined concentrations of chitosan against the intensities of the Nitrogen peak. The concentrations of chitosan in the complexes were determined based on the calibration curve. A similar method was applied in the literature to identify the content of cationic surfactants in solutions (Fatehi, Outhouse, Xiao, & Ni, 2010).

3. Results and discussion

3.1. PHL properties

The chemical compositions and other properties of the pretreated PHL are listed in Table 1. The total dry solid of the PHL was 8.22 wt.%, among which the monomeric and oligomeric sugar contents were 0.93 wt.% and 0.69 wt.%, respectively. The lignin and acetic acid contents were 0.93 wt.% and 1.03 wt.%, respectively, while the furfural content was relatively low (0.2 wt.%). In our previous work, the formation of acetic acid and furfural and the proportion of various components of industrially produced PHL were described (Li et al., 2010; Saeed et al., 2010). The ash content of the PHL was 4.34%. The rather high conductivity (12.2 mOhm) of the PHL is due to the presence of salts (such as sodium salts) in the PHL from the black liquor/white liquor displacement of the process (Shi et al., 2011). Additionally, the acidification and liming during the pretreatment steps of the PHL increased some inorganic salt (ash) to the PHL. The anionic charge density of the PHL (−0.065 mequiv./g based on dry wt. of PHL) is due to the carboxylic groups associated with the dissolved lignocellulosic materials in the PHL (Li et al., 2010; Tunc, Lawoko, & van Heiningen, 2010). Therefore, it can be implied that the PHL is a mixture of various organic components in a polyelectrolyte solutions.

3.2. Characteristics of chitosan/PHL mixture

The zeta potential of the PHL is shown as a function of chitosan dosage, in Fig. 1. In this figure, the chitosan dosage was reported in accordance with the charge ratio of chitosan to lignocellulosic materials in the PHL. The charge ratio of 1.7 or 2 for the HMW or LMW chitosan in Fig. 1 corresponds to the mass ratio of 0.5 mg/g or 0.7 mg/g on the PHL in other figures, respectively. As can be seen, the zeta potential of the PHL was −10 mV prior to adding chitosan. Regardless of the chitosan MW, the zeta potential increased, and when the charge ratio was 1.7 or 2 for the HMW or LMW chitosan, respectively, the solution was neutralized. By further chitosan addition, the solution was rendered cationic. The further increase in the charge ratio did not substantially increase the zeta potential of the PHL (Fig. 1). In the literature, the zeta potential of the filtrate of a fiber suspension was varied in a similar range via the addition of polyethyleneimine (Strom, Barla, & Stenius, 1979). The deviation from the charge stoichiometry has been reported for the polyelectrolyte solutions in the literature (Fredheim & Christensen, 2003; Strom, Barla, & Stenius, 1982). In a salt-free solution, a neutral charge point is reached if the cationic and anionic charges in the solution are the same, i.e., the charge balance is stoichiometrically developed. However, in a salt-containing system, some of the charges associated with polymers are screened, which affects the electrostatic interaction process. In other words, the ionic strength of the solution has a strong impact on the interaction of the charged polymer in solutions (Kekkonen, Lattu, & Stenius, 2002; Saether et al., 2008). Additionally, chitosan and some of the dissolved lignocellulosic materials in the PHL, e.g., oligomeric sugars and lignin, have relatively long chains. Thus, the charges associated with the backbone of these chains may not access the opposite charges associated with the neighboring polymers in the PHL solution due to the accessibility limitations. As described earlier, the PHL is a polyelectrolyte solution with rather high inorganic salt (ash). As a result, the zeta potential of the PHL was not at zero at the chitosan to PHL charge ratio of 1, and a higher cationic charge ratio (1.7, or 2) was necessary to achieve the neutral charge point (Fig. 1). In one study, the neutralization of the polyelectrolyte solution of xylan and polyethelyneimine was shifted from 0.18 weight ratio to 0.5, when the NaCl concentration was increased from 0.001 M to 0.01 M (Strom et al., 1985).

By adding chitosan to the PHL, chitosan interacts with the anionic lignocellulosic materials of the PHL, and complexes are formed. In our previous work, we reported that the MW of the lignocellulosic materials in the PHL is less than 10kDa (T. Liu et al., 2011). Most likely, the patch flocculation is the mechanism that prevails in the present system, and the concept is well documented in the literature (Guibal & Roussy, 2007; Mihai & Dragan, 2009; Schatz et al., 2004). Chitosan may also bridge the formed complexes, which facilitates their precipitations (Guibal & Roussy, 2007). Fig. 2 shows the

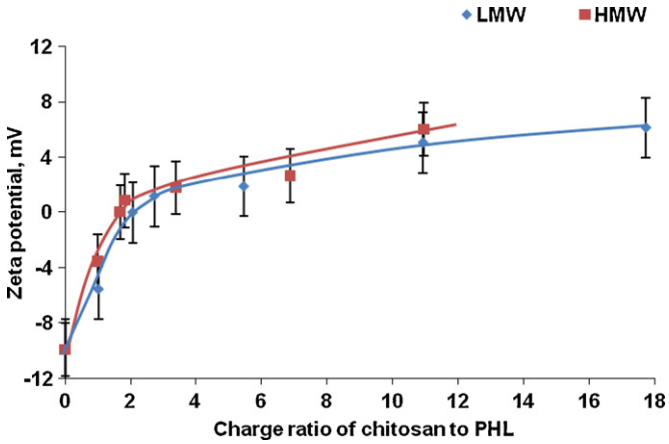

Fig. 1. Zeta potential of PHL as a function of chitosan dosage.

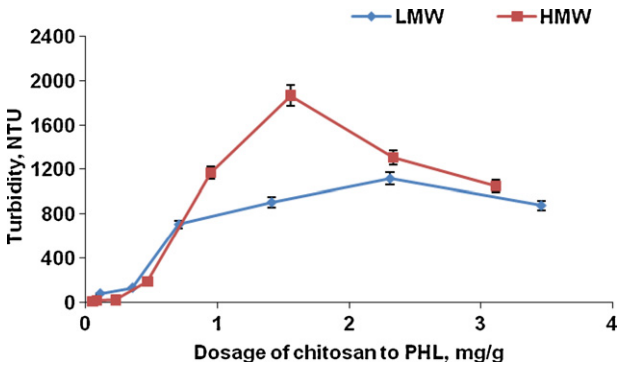

Fig. 2. Turbidity of the PHL as a function of chitosan dosage to the PHL.

turbidity of the PHL as a function of chitosan dosages. It is evident that the turbidity increased as the dosage of chitosan increased till reaching the maximum at 1000 NTU by adding 2.2 mg/g LMW chitosan or 1900 NTU by adding 1.7 mg/g HMW chitosan. The decrease in the turbidity beyond the maximum points is due to the complex precipitation.

The size of complexes formed in the PHL as a function of the chitosan dosage is shown in Fig. 3. Evidently, the maximum size was about 500 nm, which was reached at 0.7 mg/g of LMW or 0.5 mg/g HMW chitosan dosage. The interaction of chitosan (MW of 365 kDa) and dextran (MW of 10 kDa) at charge ratio of 1 resulted in the formation of complexes with the size of 600 nm in salt-free solution (Schatz et al., 2004). As described earlier, the patch flocculation and bridging mechanisms probably happen in the chitosan/PHL system (Guibal & Roussy, 2007). By increasing the MW of chitosan, the polymer bridging is more likely occurred (Guibal & Roussy, 2007), which is the reason for obtaining the maximum complex size at a lower chitosan dosage for the HMW chitosan than for the LMW one. The decrease in the complex size with further increase in the chitosan dosage is due to the precipitation via the chitosan bridging effect.

3.3. Removal of lignocellulosic materials from PHL

As described earlier, the flocculation and precipitation would result in the removal of lignocellulosic materials from the PHL. The removal of monomeric and oligomeric sugars of the PHL is shown in Fig. 4 as a function of chitosan dosage. It is evident that the maximum removal of 10% or 5% of monomeric sugars was obtained by adding 0.7 or 0.5 mg/g LMW or HMW chitosan to the PHL, respectively. Also, the maximum removal of 20% or 25% of oligomeric sugars was obtained by adding 1.5 or 0.5 mg/g LMW or HMW chitosan to the PHL, respectively. Therefore, it can be implied that

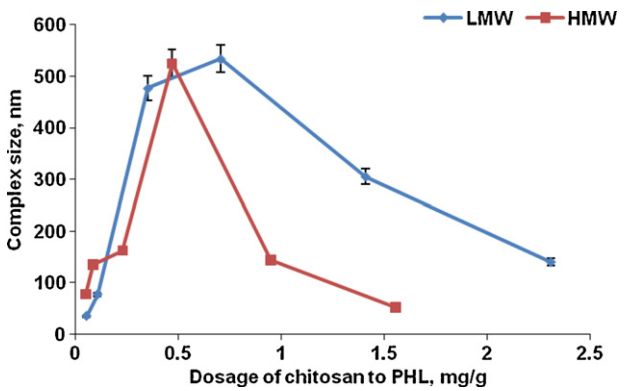

Fig. 3. Complexes size as a function of chitosan dosage to the PHL.

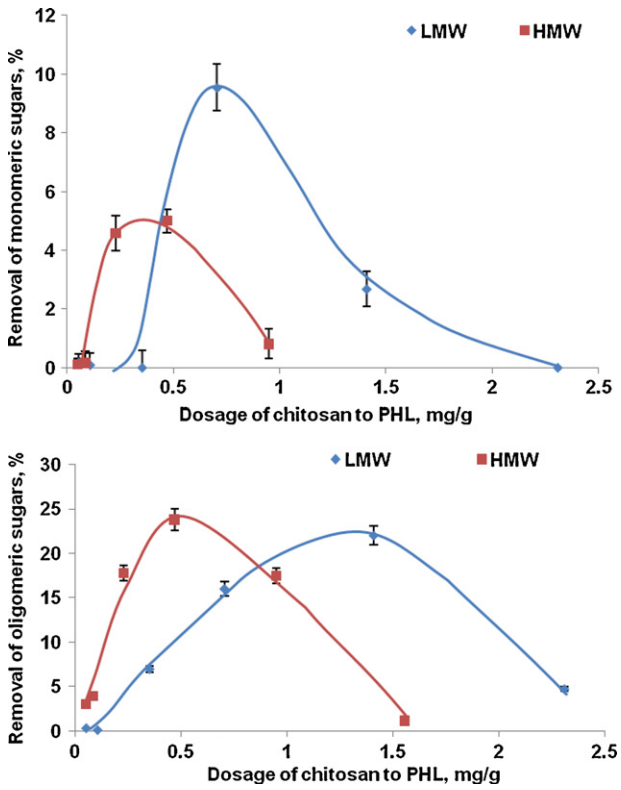

Fig. 4. Removal of monomeric (top) and oligomeric (bottom) sugars from the PHL as a function of chitosan dosage.

the removal was more significant for oligomeric sugars than for the monomeric sugars. In the literature, the formation of complexes made of pine xylan and acrylamide–acrylamine copolymers (1:1 wt. ratio) resulted in a maximum of 40 wt.% xylan removal in a solution containing 0.1 M NaCl (Strom et al., 1985).

The removals of furfural and acetic acid are shown in Fig. 5 as a function of chitosan dosage, respectively. It is noted that the maximum removal of 55% or 50% furfural was obtained by adding 0.7 mg/g LMW or 0.5 mg/g HMW chitosan, respectively. Such a high furfural removal is ascribed to the relatively low concentration of furfural in the PHL (Table 1).

Also, the the maximum removal of 10% or 13% acetic acid was obtained by adding 0.7 mg/g LMW or 0.5 mg/g HMW chitosan, respectively (Fig. 5). The removal of furfural may be due to the patch flocculation mechanisms and/or hydrogen bonding of furfural and chitosan (Guibal & Roussy, 2007), while that of acetic acid may be due to the trapment of acetic acid in the complexes and/or development of hydorgen bonding with chitosan or with the formed complexes.

The removal of lignin as a result of the chitosan addition is shown in Fig. 6. Evidently, the maximum removal of 40% or 35% was obtained by adding 2.2 mg/g or 1.7 mg/g LMW or HMW chitosan to the PHL, respectively. In the literature, 60% of lignosulfonates was removed by adding lignosulfonate to the chitosan in a polyelectrolyte solution (0.1 M NaCl) at pH 4.5 with the weight ratio of 3 (Fredheim & Christensen, 2003).

3.4. Effect of chitosan dosage on removal of lignocellulosic materials

The maximum precipitation occurs when the system containing opposite charges reaches the neutral point. Over- or under-charging results in complexes with a net charge; this would restabilize and compact the complexes in the solution and hamper

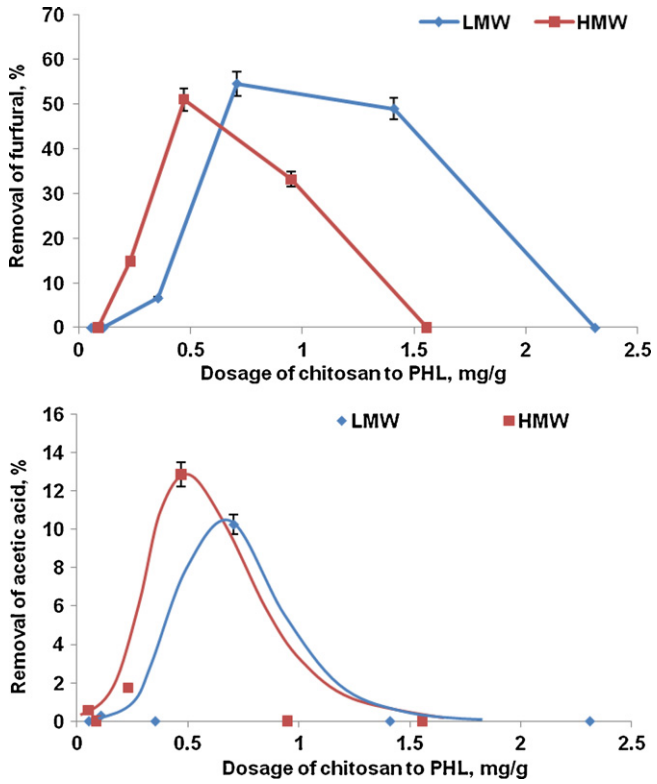

Fig. 5. Removal of furfural (top) and acetic acid (bottom) from the PHL as a function of chitosan dosage.

their precipitations (Guibal & Roussy, 2007; Szygula et al., 2009), which is in agreement with the trends in Figs. 4–6.

As depicted in Figs. 4–6, the overall removals of lignocellulosic materials were less than 50%. The reason for the low removals is partly due to the presence of inorganic salt in the PHL (Table 1), as described earlier. It was reported that the interaction of polyethyleneimine with xylan was reduced by increasing the salt concentration, which resulted in a lower formation of insoluble complexes (Strom et al., 1982). In one study, the interaction of xylan and polyethelenimine in a pulp suspension was studied at pH 5 and 22 °C (Strom et al., 1982). It was observed that, by adding 0.05 wt.% polyethelenimine to a fiber suspension containing 1 wt.% xylan and 0.001 M NaCl, 80% of xylan was removed. However, by adding the same amount of polyethelenimine to a fiber suspension containing 0.3% xylan and 0.1 M NaCl, 20% of the xylan was removed (Strom et al., 1982).

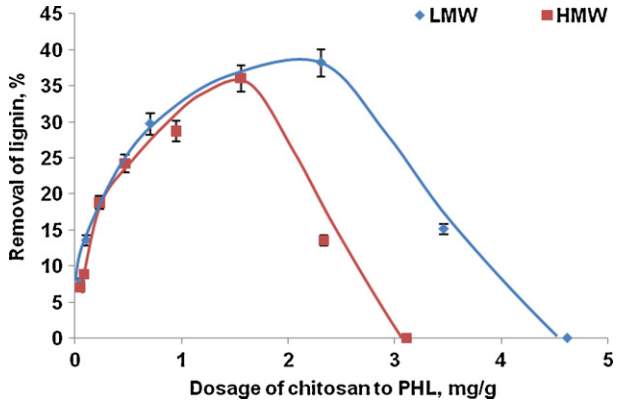

Fig. 6. Removal of lignin from the PHL as a function of chitosan dosage.

3.5. Effect of properties of lignocellulosic materials

As seen in Figs. 4–6, the maximum removal of furfural, acetic acid and monomeric sugars occurred by adding 0.7 mg/g LMW chitosan. However, a relatively higher dosage of LMW chitosan was required to obtain the maximum removal of oligomeric sugars and lignin. In contrast, the maximum removals of furfural, acetic acid, monomeric and oligomeric sugars were obtained by adding 0.5 mg/g HMW chitosan to the PHL, respectively, and a relatively higher dosage was required for obtaining the maximum removal of lignin.

It was reported that the charge and molecular weight of polymers affect their interaction and hence their precipitation (removal) (Fredheim & Christensen, 2003). By increasing the anionic charge of polymers, a higher dosage of cationic polymer is required for the neutralization and thus the removal of lignocellulosic materials from the solution. It is well known that lignin has a higher anionic charge than hemicelluloses do, which is originated from the carboxylic group. Therefore, a higher dosage of cationic polymer, e.g., chitosan, is necessary for the removal of lignin compared with that of other dissolved materials (Figs. 2–5 versus Fig. 6).

In a solution, if oppositely charged polymers have compatible sizes, their interaction, and thus precipitation, would increase. As described earlier, we reported that the molecular weight of dissolved hemicelluloses and lignin are less than 10 kDa in prehydrolysis liquor (Z. Liu et al., 2011). Therefore, the LMW chitosan should presumably be more effective than HMW chitosan on removing lignocellulosic materials. On the other hand, it was reported that lignin and xylan could form soluble complexes while interacting with cationic polymers in solutions (Strom et al., 1985; Strom & Stenium, 1981). To remove such complexes, the soluble complexes should be bridged to create relatively large particles. It is well known that the higher the MW of polymers, the higher their bridging affinity. Consequently, there is a compromise between the MW compatibility of oppositely charged materials and bridging performance of chitosan for the formed soluble complexes. It appears that the bridging affinity played a more significant role than the MW compatibility of chitosan/lignocellulosic materials on forming complexes. This is supported by the fact that a lower amount of the HMW chitosan than that of the LMW chitosan was required for removing the lignocellulosic materials (see Figs. 2–6). However, further investigation is necessary to prove this hypothesis.

As seen in Figs. 3–6, the largest complexes were formed when the maximum monomeric sugars, acetic acid and furfural removals were achieved. When the dosage of chitosan was increased to more than 1 mg/g in PHL, the size of complexes was reduced. There are two possibilities associated with this phenomenon: (1) by increasing the dosage to higher than 1 mg/g, lignin complexes were formed and precipitated (Fig. 6), which were excluded in the size measurement (Fig. 3); (2) by increasing the dosage of chitosan to the PHL, the complexes were more compact with a smaller size. Since the size of the largest complexes was similar via applying both MWs chitosan, it is probable that the 500–520 nm size was the maximum for the lignocellulosic complexes that are stable in the PHL solution under the conditions studied.

The turbidity, complex size and removal analyses also reveal that the complexes with a large size of 500–520 nm were precipitated. The small ones with a size of 200 nm were stable in the PHL (Fig. 3), which were noticed in the turbidity analysis (Fig. 2). It is also implied that the maximum turbidity was coincided with the maximum lignin removal for the application of LMW or HMW chitosan (Figs. 2 and 6).

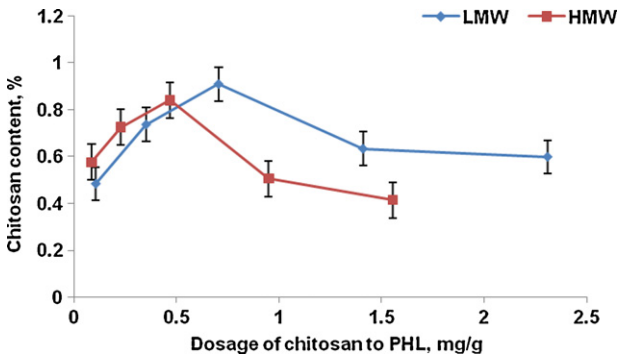

Fig. 7. Chitosan content of complexes formed after precipitation as a function of chitosan dosage to PHL.

3.6. Chitosan content of formed complexes

Chitosan is a part of the formed lignocellulosic complexes. The chitosan content of complexes precipitated, and subsequently separated, from the PHL is shown in Fig. 7 as a function of chitosan dosage to the PHL. Evidently, less than 1 wt.% of the precipitated mass of the isolated complexes was chitosan. Additionally, the chitosan content in the complexes reached the maximum at 0.5 mg/g HMW or 0.7 mg/g LMW chitosan addition, respectively. Considering the dosage of chitosan in the PHL and the chitosan content of complexes, it can be inferred that approximately 15% of the added chitosan is in the complexes, while the majority still remains in the PHL system. The remaining chitosan in the PHL interacts with the lignocellulosic materials, which is responsible for the high turbidity of the PHL (Fig. 2). The formation of soluble xylan/polyethyleneimine and lignosulfonates/polyethyleneimine complexes were reported in the literature (Strom et al., 1985; Strom & Stenium, 1981).

Additionally, it is inferred from the results in Figs. 4–7 that the maximum removal of monomeric sugars, acetic acid and furfural are in agreement with the maximum chitosan content in the precipitated complexes. The results in Table 1 and Figs. 2–6 showed that more lignin and oligomeric sugars were generally removed compared with other lignocellulosic materials. Thus, the portion of chitosan in the complexes was less when the weight of oligomeric sugars and lignin were increased in the complexes (chitosan dosage > 0.7 mg/g).

4. Conclusions

The concept of using chitosan, a cationic natural polymer, as an aid to recover dissolved lignocellulosic material from industrial pre-hydrolysis liquor was studied. The results showed that the zeta potential of the PHL did not reach zero at the charge neutralization point, and insignificantly varied by adding differnet amounts of chitosan. The turbidity analysis of chitosan/PHL mixture revealed the maximum turbidity of 1000 NTU or 1900 NTU by adding 2.2 mg/g LMW or 1.7 mg/g HMW chitosan, respectively. The maximum removal of 10% or 5% monomeric sugars, 55% or 50% furfural, and 10% or 13% of acetic acid were obtained by adding 0.7 mg/g or 0.5 mg/g LMW or HMW chitosan to the PHL, respectively. The maximum removal for oligomeric sugars was 20% or 25% by adding 1.5 or 0.5 mg/g LMW or HMW chitosan, while that for lignin was 40% or 35% by adding 2.2 mg/g or 1.7 mg/g LMW or HMW chitosan, respectively. Overall, the recovery degrees of dissolved organics from the PHL using LMW and HMW chitosan were similar, while more LMW than HMW chitosan was required to achieve the maximum recovery. The relatively high turbidity of the chitosan/PHL mixture and the marginal removal of the lignocelluosic materials at a relatively high dosage of chitosan (e.g., 2 mg/g) indicated that the formed complexes were stable in the PHL system under the conditions studied. The maximum size of complexes (500–520 nm) and chitosan content of precipitated complexes (1 wt.%) were obtained at 0.7 mg/g LMW or 0.5 mg/g HMW chitosan, respectively, which is consistent with the amounts of recovered monomeric sugars, furfural and acetic acid.

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