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Improving the adsorption of lignocelluloses of prehydrolysis liquor on precipitated calcium carbonate

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ABSTRACT

In this work, the adsorption of lignocelluloses of pre-hydrolysis liquor (PHL) on precipitated calcium carbonate (PCC) was studied in the presence of poly diallyldimethylammonium chloride (PDADMAC) or cationic polyacrylamide (CPAM). The results revealed that adding PCC to PHL and subsequently adding cationic polymers to PHL/PCC systems was more effective than adding cationic polymers to PHL and then adding PCC to the cationic polymer/PHL systems. At the same dosage applied, PDADMAC resulted in a higher adsorption of lignocelluloses on PCC than CPAM did due to its higher charge density. The adsorption of lignocelluloses on PCC reached its maximum in 3 h, and a high temperature reduced the adsorption level as the adsorption was an exothermic process. The maximum adsorptions of 530 mg/g oligo-sugars, 203 mg/g lignin and 58 mg/g furfural on PCC were achieved via adding 0.8 mg/g PDADMAC2 (i.e. higher MW PDADMAC) to PCC/PHL system.

1. Introduction

In the present technology practiced in industry, pre-hydrolysis liquor (PHL) of kraft-based dissolving pulp production process is mixed with the black liquor of the process and is burned in a recovery boiler (Li, Saeed, Jahan, Ni, & van Heiningen, 2010; Saeed, Jahan, Li, Liu, & Ni, 2012). However, industrially produced PHL contains 3–8% lignocelluloses that can be used in the production of value-added chemicals. The production of value-added materials from the lignocelluloses of PHL will increase the revenues of this pulping process and assist in converting this process to a biorefinery complex (Liu, Fatehi, Jahan, & Ni, 2011; Saeed et al., 2012).

To possess an economically attractive biorefinery process, the lignocelluloses should be initially isolated from PHL due to the dilute nature of PHL. Alternative processes were introduced for separating the lignocelluloses of pulping spent liquors in the past (Liu, Fatehi, Jahan, et al., 2011; Liu, Fatehi, & Ni, 2011a, 2011b; Wallberg, Jonsson, & Wimmerstedt, 2003). Flocculation was employed as an effective process for removing the lignocelluloses of PHL in the literature (Burke, Anderson, Gilcrease, & Menkhaus, 2011; Saeed, Fatehi, & Ni, 2011; Shi, Fatehi, Xiao, & Ni, 2011; Yasarla & Ramarao, 2012). It was reported that chitosan, poly diallyldimethylammonium chloride (PDADMAC) (Burke et al., 2011; Saeed et al., 2011) and cationic poly acrylamide (CPAM) (Burke et al., 2011; Yasarla & Ramarao, 2012; Zhu, Li, Lu, Wang, & Yao, 2009) interacted with the lignocelluloses of industrially- or laboratory-produced PHL and generated complexes that were separated from PHL via filtration. An adsorption concept has also been employed for isolating the lignocelluloses of various spent liquors in the past (Berson, Young, Kamer, & Hanley, 2005; Radovic, Moreno-Castilla, & Rivera-Utrilla, 2000; Sainio, Turku, & Heinonen, 2011). The adsorptions of phenolic compounds and furfural on activated carbon (AC) were studied in the past (Fierro, Torne-Fernandez, Montane, & Celzard, 2008; Sahu, Srivastava, Mall, & Lataye, 2008; Singh, Srivastava, & Mall, 2009; Srivastava, Swamy, Mall, Prasad, & Mishra, 2006), and our analyses confirmed the adsorption of lignocelluloses of PHL on AC and clay (Liu, Fatehi, & Ni, 2012; Shen, Fatehi, Soleymani, & Ni, 2011).

In our previous work on this topic, the adsorption of lignocelluloses of PHL on precipitated calcium carbonate (PCC) was also studied (Fatehi, Hamdan, & Ni, 2012). PCC is widely used as filler in papermaking (Shen, Song, Qiaon, & Liu, 2009; Shen, Song, Qian, & Yang, 2010; Yoon & Deng, 2006), but it has limited affinity to interact with cellulose fibers due to its poor surface characteristics. The adsorption of lignocelluloses of PHL on PCC surface may improve its surface characteristics and hence improve its performance in papermaking or composites.

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In this case, the higher the lignocelluloses adsorption, the better performance of PCC could be. Various polymers, including PDADMAC and CPAM, were introduced as retention aids in papermaking (Nystrom, Backfolk, Rosenholm, & Nurmi, 2003; Nystrom, Hedstrom, Gustafsson, & Rosenholm, 2004). As these polymers interact with the dissolved lignocelluloses of PHL (Saeed et al., 2011; Zhu et al., 2009), they may assist in adsorbing lignocelluloses on PCC. In one study, the addition of PDADMAC to laboratory-made PHL induced flocs, which were adsorbed on kaolin upon its addition to PDADMAC/PHL system (Durarte, Ramarao, & Amidon, 2010). The first objective of this work was to investigate the performance of PDADMAC and CPAM in improving the adsorption of lignocelluloses on PCC.

It is well known that the properties of polymers affect their interaction affinity with other dissolved polymers in solutions (Li, Du, Wu, & Zhan, 2004; Yoon & Deng, 2004). In this respect, large cationic polymers interact with other dissolved polymers and particles in solutions via patch and bridging mechanisms, while small polymers interact via a charge neutralization mechanism (Petzold, Geissler, Smolka, & Schwarz, 2004; Yoon & Deng, 2004; Yu, Wang, Ge, Yan, & Yang, 2006). The second objective of this work was to investigate the influence of molecular weight of CPAM and PDADMAC in improving the adsorption of lignocelluloses on PCC.

This work is a continuation of our previous study on producing hemicelluloses-modified PCC, which is a value-added product and can potentially be used in papermaking or composites. In this work, the adsorption of lignocelluloses of PHL was investigated on PCC in the presence of CPAM and PDADMAC, i.e. two commercially used retention aids and flocculants in various industries (Burke et al., 2011; Yasarla & Ramarao, 2012; Zhu et al., 2009). The effects of temperature and ordering sequence on treating PHL with cationic polymers and PCC were initially investigated in order to optimize the adsorption process. Subsequently, the adsorption isotherms and kinetics of lignocelluloses of PHL on PCC were evaluated. A turbidity analysis was also employed as a means to indicate the interaction of cationic polymers with lignocelluloses of PHL.

2. Materials and methods

2.1. Materials

The pre-hydrolysis liquor (PHL) was received from a kraft-based dissolving pulp production plant located in eastern Canada, which uses a mixture of maple (70 wt.%), poplar (20 wt.%) and birch (10 wt.%) as raw materials.

Porous precipitated calcium carbonates (PCC) was obtained from Omya Company and used as received. Cationic polyacrylamide (CPAM) with two different grades were received from Ciba specialty chemicals: Percol® 181 (CPAM1) having an average molecular weight of 2×10^6 Da and the degree of substitution of 20% and Percol® 292 (CPAM2) having an average molecular weight of 5×10^6 Da and the degree of substitution of 25%, respectively (Nystrom et al., 2004; Yu et al., 2006). Polydiallyldimethylammonium chloride (PDADMAC) with two molecular weights of 100–200 kDa (PDADMAC1) and 400–500 kDa (PDADMAC2) were purchased from Aldrich Company. Dodecyltrimethyl ammonium chloride (DTAC) was received from Aldrich Company, while calcium oxide (an analytical grade) was received from Fisher Scientific. Initially, 1% solutions of each cationic polymer was prepared by diluting the polymers in deionized distilled water, and these solutions were used throughout this research. The standard solutions of potassium polyvinyl sulfate (PVSK) or PDADMAC (0.5 mM) solutions were purchased from Aldrich Co., and used for measuring the charge densities of cationic polymers and PHL by using a particle charge detector (Mütek PCD 03, Germany) based on earlier established methods (Fatehi, Kititerakun, Ni, & Xiao, 2010; Saeed et al., 2011).

2.2. Preparation of PHLs

In our previous work, the impact of DTAC in removing lignin of PHL was studied (Fatehi et al., 2012; Shi, Fatehi, Xiao, & Ni, 2012), and the procedure was described as follows: DTAC was added to PHL (500 ml) at the weight ratio of 0.03% (i.e. optimum ratio) in a 1 L-Erlenmeyer flask at room temperature and 120 rpm (shaken for 1 h) in order to reduce the lignin content of PHL prior to adsorption experiments. Afterwards, the pH of the DTAC-treated PHL was adjusted to 7 via adding CaO at room temperature. Subsequently, the suspension was filtered and supernatant (i.e. pre-treated PHL) was used in this research.

2.3. Turbidity analysis

At first, the pretreated PHL, CPAM and PDADMAC solutions were filtered using a 0.45 μm Nylon syringe filter and preheated to 40 °C prior to turbidity analysis. Afterwards, various dosages (up to 1.4 mg/g) of CPAMs or PDADMACs were added to 50 g of PHL at 40 °C and shaken at 120 rpm for 30 min. Then, the samples were transferred to preheated vials at the same temperature, and the turbidity of these samples was immediately analyzed using a HACH 2100AN turbidity meter (CO, USA) and the average of five testing results was reported. In another set of experiments, CPAM2, PDADMAC2 solutions and PHL were preheated to 60 °C and 70 °C; and CPAM2 or PDADMAC2 were added to 50 g of PHL (dosage of 0.8 mg/g). Afterwards, the aforementioned procedures were followed for determining the turbidity of the samples.

2.4. Treatment of PHL with PCC

According to our previous work, oligo-sugars, lignin and furfural of pretreated PHL considerably adsorbed on PCC, but acetic acid and mono-sugars had marginal adsorption (Fatehi et al., 2012). In the current study, 50 g of pretreated PHL was treated with 1 g of PCC under various conditions in 250 mL-Erlenmeyer flasks. After adding materials to the flasks, they were sealed and kept in a New Brunswick water bath shaker at 120 rpm. In our previous work, 90 min of treatment time was sufficient to obtain a significant amount of lignocelluloses adsorption on PCC (Fatehi et al., 2012). In the work presented herein, the sequence of adding cationic polymers and PCC to PHL were differed in order to determine the sequence with a higher adsorption level: (1) 0.2 mg/g of CPAM2 or PDADMAC2 was initially added to the pretreated PHL and shaken for 90 min at 40 °C, and subsequently PCC (1/50 weight ratio of PCC/PHL) was added to cationic polymer/PHL systems and the shaking was continued for 24 h; (2) PCC was initially added to PHL (1/50 weight ratio of PCC/PHL) and shaken for 90 min at 40 °C, and then 0.2 mg/g of CPAM2 or PDADMAC2 was added to the PCC/PHL systems and shaking was extended for 24 h under the same experimental conditions. In another set of experiments, the pretreated PHL was treated with PCC (i.e. the more efficient ordering sequence) for 90 min at 40 °C, various dosages (up to 0.8 mg/g) of CPAM1, CPAM2, PDADMAC1 or PDADMAC2 were added to the PHL/PCC systems and then the samples were shaken for another 24 h. In another set of experiments, the PHL was treated with PCC (PCC/PHL wt. ratio 1/50) under the aforementioned conditions. Subsequently, CPAM2 or PDADMAC2 was added (0.2 mg/g based on PHL) to the PHL/PCC systems and the systems were shaken for various time intervals (up to 24 h). In other set of experiments, CPAM2 or PDADMAC2 was added (0.2 mg/g) to the PCC/PHL system (1/50 wt. ratio) and the samples were shaken, but at different temperatures (40, 60 and 70 °C) for 24 h. All experiments were carried out five times and the average values were reported in this work. After shaking, the samples were filtered using Whatman cellulose nitrate membranes (0.45 μm pore size), and the filtrates were collected for composition analysis.

2.5. PHL properties

The concentration of oligo-sugars in the PHL samples was determined using an ion chromatography unit equipped with a CarboPac^{TM} PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) (Liu, Fatehi, Jahan, et al., 2011; Liu, Fatehi, Ni, 2011a, 2011b). To convert oligosaccharides of PHLs to monosaccharides, an additional acid hydrolysis of PHLs was carried out with 4% sulfuric acid at 121 °C in an oil bath (Neslab Instruments, Inc., Portsmouth, NH, USA) (Liu, Fatehi, Jahan, et al., 2011; Liu, Fatehi, Ni, 2011a, 2011b). The PHLs were first filtered using the above-mentioned cellulose membrane, and then diluted with water prior to analysis. The sugar analysis of PHL samples prior to this additional hydrolysis accounts for mono-sugars of PHL, while that after this hydrolysis accounts for the total sugars of PHL. Thus, oligo-sugar content was determined by subtracting the mono-sugar content from the total sugar content of PHL (Liu, Fatehi, Jahan, et al., 2011; Liu, Fatehi, Ni, 2011a, 2011b).

The lignin content of PHLs was measured based on the UV/Vis spectophotometric method at the wavelength of 205 nm according to TAPPI UM 250. A Varian 300 ^{1}H NMR analyzer was employed for determining the concentration of furfural based on previously established procedures (Liu, Fatehi, Jahan, et al., 2011; Liu, Fatehi, Ni, 2011a, 2011b). Calibration curves were established for determining furfural concentrations using NMR.

2.6. Nitrogen analysis

Since DTAC, PDADMAC and CPAM contained nitrogen in their chemical structures, the nitrogen analysis of PHL could directly be correlated to the concentration of these components before or after treating PHL. This method was previously used for measuring the concentration of various surfactants in water (Fatehi, Outhouse, Xiao, & Ni, 2010). At first, 20 ml of PHL samples was collected and then dried in an oven at 70 °C for 24 h. The Nitrogen analysis of the dried samples was conducted using a Nitrogen/Sulfur analyzer, 9000 series, Antek, Texas, USA at the temperature of 1075 °C. A calibration curve was prepared by plotting the predefined concentrations of CPAM, PDADMAC and DTAC against the intensities of the nitrogen peak. Our analysis showed that the nitrogen contents of DTAC treated-PHL and the PHL filtrates after the cationic polymers/PCC/PHL analyses were below detection limits.

3. Results and discussion

3.1. Properties of cationic polymers

The charge density and MW of CPAMs and PDADMACs used in this study are listed in Table 1. Evidently, the charge densities of CPAMs were similar, but CPAM2 had a remarkably higher MW than CPAM1. In the same vein, PDADMACs had similar charge densities, but PDADMAC2 had a higher MW. A comparison between CPAMs and PDADMACs also showed that CPAM had generally a much higher MW, but a lower charge density, than PDADMAC.

Table 1
Charge density and MW of cationic polymers used in this study.

Polymer	Charge density (mequiv/g)	MW (kDa)
CPAM1	1.1	2000
CPAM2	1.7	5000
PDADMAC1	6.1	100–200
PDADMAC2	6.4	400–500

3.2. PHL properties

As demonstrated in the experimental section, PHL was initially pretreated with DTAC and CaO in order to reduce its lignin content. This process has been demonstrated in our previous work and thus not been discussed here (Fatehi et al., 2012; Shi et al., 2012). The pretreated PHL contained 7.1 g/l mono-sugars, 22.1 g/l oligo-sugars, 2.3 g/l furfural, 12.1 g/l acetic acid and 8 g/l lignin. The pH of PHL was 7, which was within the pH range of CPAM and PDADMAC effectiveness as flocculants in various media (Antunes et al., 2008; Chi, Li, Liu, & Zhan, 2007; Li et al., 2004; Nystrom et al., 2003, 2004; Nystrom & Rosenholm, 2005). As illustrated in the experimental section, the adsorption of mono-sugars and acetic acid on PCC was marginal (Fatehi et al., 2012) and thus was excluded from this study.

3.3. Cationic polymer in PHL

The influence of cationic polymer addition to pretreated PHL on the turbidity of PHL was shown in Fig. 1. It is observable that, by increasing the dosage of CPAM to 1.4 mg/g in PHL, the turbidity of PHL was gradually increased to 1340 NTU (for CPAM1) or 1550 NTU (for CPAM2). However, adding 0.8 mg/g PDADMAC1 or PDADMAC2 to PHL resulted in a maximum turbidity of 1200 or 1000 NTU, respectively. In the literature, similar trends were observed via adding CPAM and PDADMAC to laboratory-made PHL, and the turbidity change of PHL via adding CPAM was ascribed to the complex formation via patch and bridging mechanisms (Petzold et al., 2004; Shang, Liu, Zheng, & Wang, 2009; Yasarla & Ramarao, 2012), while that via adding PDADMAC was attributed to the charge neutralization mechanism (Petzold et al., 2004). It may also be inferred from the turbidity analysis that the complexes were probably larger via adding CPAM2 than CPAM1 and via adding PDADMAC2 than PDADMAC1, which was due to the higher MWs (larger sizes) of CPAM2 and PDADMAC2 (Table 1). In the literature, the addition of 5 ppm CPAM or 5.7 ppm PDADMAC to laboratory-made PHL induced complexes with the sizes of 2000 nm or 600 nm, respectively (Yasarla & Ramarao, 2012). In another study, CPAM produced larger complexes than PDADMAC did with clay and kaolin particles in water (Li et al., 2004; Yu et al., 2006).

3.4. Cationic polymer/PHL/PCC system

PHL contains various lignocelluloses that possess carboxylic and carbonyl groups in their structures, which contribute to the anionic charge density of PHL (i.e. −0.065 mequiv/g) (Fatehi et al., 2012; Saeed et al., 2011). By adding CPAM or PDADMAC to PHL, the cationic groups associated with these polymers would interact with the anionic groups of lignocelluloses and form complexes, as confirmed by turbidity analysis (Fig. 1). These complexes could then be deposited on PCC surface if PCC were added to the system of PHL and cationic polymers. Simultaneously, cationic polymers that did not interact with lignocelluloses in PHL (i.e. free cationic polymers in PHL) could adsorb on PCC surface (Fatehi, Qian, Kititerakun, Rirksomboon, & Xiao, 2009; Van de Ven, 1994). This adsorption would introduce cationic charges to the surface of PCC, which in turn would create additional driving force for the adsorption of lignocelluloses on PCC via a charge interaction. In this case, a layer-by-layer adsorption of lignocelluloses and cationic polymers might randomly develop on the PCC surface (Petzold, Buchhammer, & Lunkwitz, 1996). Therefore, the deposition of complexes of lignocelluloses and cationic polymers as well as the layer-by-layer adsorption of lignocelluloses and cationic polymers on PCC surface

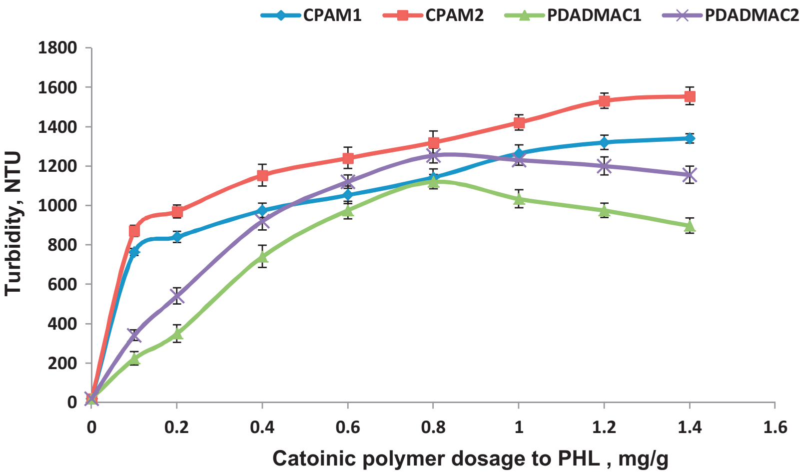

Fig. 1. Turbidity of pretreated PHL as a function of cationic polymer dosage to PHL.

were the main reasons for the adsorption of lignocelluloses on PCC surface in cationic polymer/PHL/PCC systems.

3.5. Polymer/PCC treatment order

In one set of experiments, the adding sequence of PCC and cationic polymers to PHL was changed in order to identify the more influential sequence for adsorbing lignocelluloses on PCC. Table 2 lists the adsorption of lignocelluloses on PCC for two different adding sequences of PCC/cationic polymers and cationic polymers/PCC to PHL. As is noticeable, treating PHL with PCC and subsequently adding cationic polymers to PCC/PHL systems (samples 2 and 4) resulted in higher adsorptions of oligo-sugars, lignin and furfural on PCC than treating PHL with cationic polymers and then adding PCC to cationic polymer/PCC systems (samples 1 and 3). Thus, the continuation of the current work was carried out via treating PCC with PHL prior to adding cationic polymers to PCC/PHL systems.

As explained earlier, a layer-by-layer assembly and complex deposition occurred in cationic polymers/PHL/PCC systems. In the case of samples 1 and 3, the PHL was initially treated with cationic polymers and complexes were formed prior to adding PCC to the system. When the PCC was added to the PHL/cationic polymer systems, the formed complexes were deposited on the PCC surface. The free cationic polymers in a cationic polymers/PHL system could also contribute to the layer-by-layer adsorption assembly. Although more or larger complexes could be formed in sample 1 and 3 than in samples 2 and 4 (as greater free lignocelluloses and cationic polymers were present in the systems of samples 1 and 3), the adsorption of these complexes on PCC would be constrained by their sizes. This is because the larger the complexes (or more complexes), the larger surface area they would need for adsorption (Petzold et al., 2004). In the case of samples 1 and 3, as the flocculation process was conducted prior to adsorption, the majority of cationic polymers had already interacted with lignocelluloses for a complex formation, and hence more complex deposition would occur than the layer-by-layer assembly. In the case of samples 2 and 4, a layer of lignocelluloses would initially be deposited on PCC surface, as PCC was treated with PHL prior to adding cationic polymers to the system (Fatehi et al., 2012). Therefore, a lower amount of lignocelluloses would be remained in the PHL and thus fewer or smaller complexes would be formed via adding cationic polymers to the PHL/PCC systems (sample 2 and 4). Additionally, the complex formation and layer-by-layer assembly would occur simultaneously via adding cationic polymers to PHL/PCC systems (samples 2 and 4). Therefore, treating PCC with PHL and subsequently adding cationic polymers to the PHL/PCC system would result in a greater layer-by-layer and complex depositions on the PCC surface.

3.6. Impact of CPAM on adsorption

To have an economically viable process, a maximum of 0.8 mg/g of cationic polymers was added to the PCC/PHL system throughout this research. Fig. 2 shows the adsorption of oligo-sugars, lignin and furfural on PCC as a function of CPAM dosage in PCC/PHL system. Evidently, the adsorption of oligo-sugars, lignin and furfural on PCC was 120, 54 and 29 mg/g in the absence of CPAM. The adsorption behavior of PHL constituents on PCC in the absence of cationic polymers was described in our previous work (Fatehi et al., 2012). In the PCC/PHL system, a part of lignocelluloses could be adsorbed on the surface of PCC via developing van der waals interaction. The results showed that the adsorption of oligo-sugars, lignin and furfural increased up to 225, 98 and 47 mg/g on PCC via adding up to 0.8 mg/g CPAM1 and up to 255, 112 and 59 mg/g on PCC via adding up to 0.8 mg/g CPAM2 to PHL, respectively. As explained in sections 3.3 to 3.5, by adding CPAM to the PHL/PCC systems, a layer-by-layer assembly of CPAM and lignocelluloses as well as the deposition of lignoclelluloses/CPAM complexes would occur. In this case, the more CPAM in the PCC/PHL system (a higher dosage of CPAM), the more extensive a layer-by-layer assembly and complexes

Table 2
The adsorption of lignocelluloses on PCC for two different adding sequences of cationic polymers/PCC and PCC/cationic polymers to PHL.

Sample ID	Treatment	Oligo-sugars (mg/g)	Lignin (mg/g)	Furfural (mg/g)
1	CPAM2/PCC	115 ± 8	27.7 ± 3.2	21 ± 2
2	PCC/CPAM2	113 ± 9	31.4 ± 4.8	25 ± 3
3	PDADMAC2/PCC	123 ± 7	51.4 ± 5.2	29 ± 1
4	PCC/PDADMAC2	157 ± 12	62.5 ± 4.3	34 ± 4

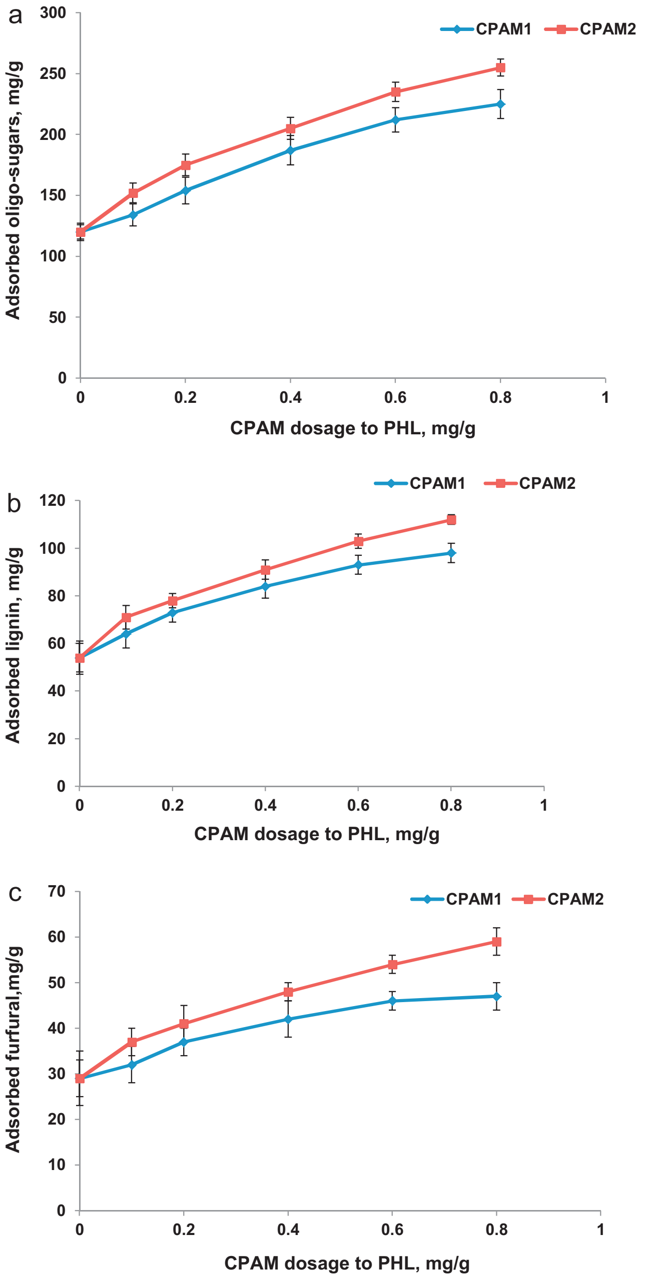

Fig. 2. Adsorption of lignocelluloses of pretreated PHL on PCC as a function of CPAM dosage to PHL in PCC/PHL system (initially PHL/PCC was mixed for 90 min, then CPAM was added to the system at 40 °C and shaken for 24 h).

deposition would occur, which would result in a higher overall adsorption of lignocelluloses on PCC.

3.7. Impact of PDADMAC on adsorption

Fig. 3 shows the impact of PDADMAC on the adsorption of lignocelluloses of PHL on PCC. It is noted that the adsorption of oligo-sugars, lignin and furfural increased up to 418, 143 and 48 mg/g via adding up to 0.8 mg/g PDADMAC1 and up to 530, 203 and 58 mg/g via adding up to 0.8 mg/g PDADMAC2 to PCC, respectively. As explained earlier (Sections 3.3–3.5), the more cationic polymers in the PCC/PHL system (the higher dosage of PDADMAC), the more extensive layer-by-layer assembly and complex depositions would occur, which would improve the overall adsorption of lignocelluloses on PCC.

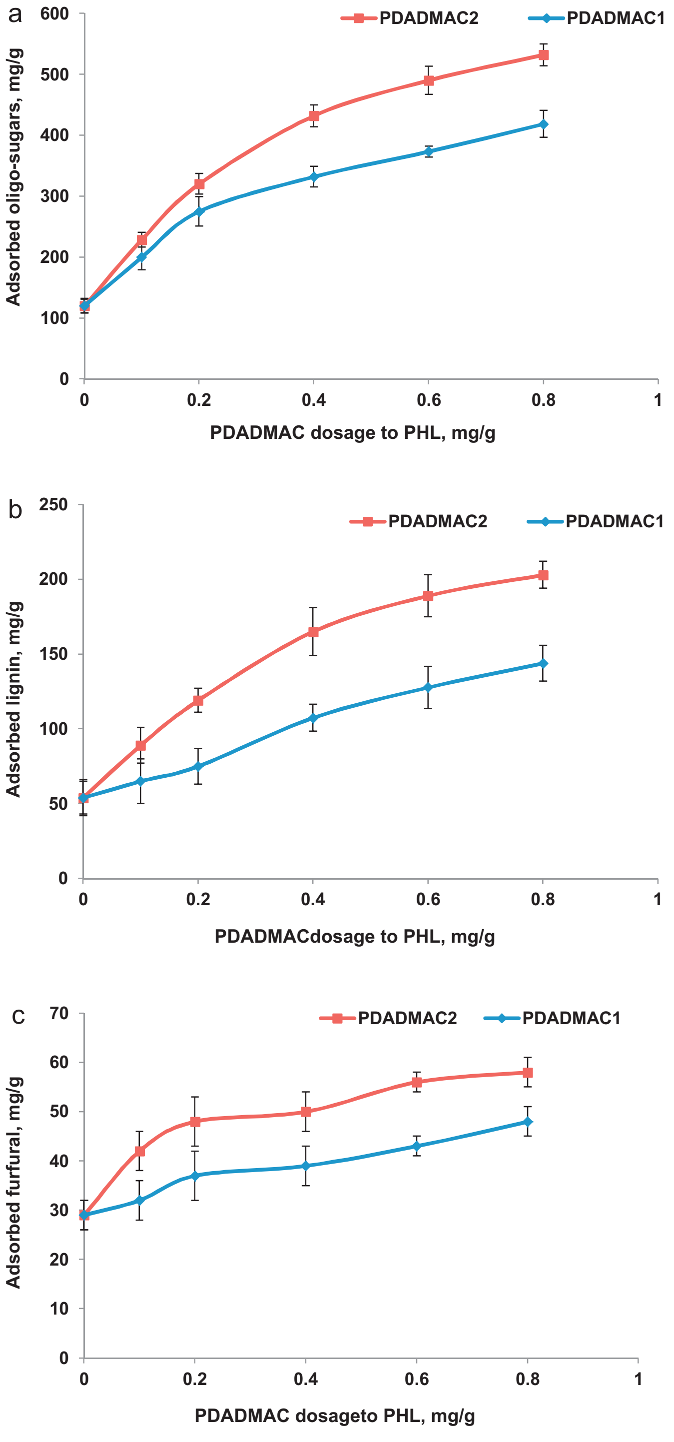

Fig. 3. Adsorption of lignocelluloses of pretreated PHL on PCC as a function of PDADMAC dosage to PHL in PCC/PHL system (initially PHL/PCC was mixed for 90 min, then PDADMAC was added to the system at 40 °C and shaken for 24 h).

3.8. Kinetics of adsorption

It was claimed that CPAM and PDADMAC had similar flocculation kinetics with lignocelluloses of PHL (Yasarla & Ramarao, 2012). Fig. 4 shows the adsorption of lignocelluloses on PCC in the presence of CPAM or PDADMAC as a function of time. As can be seen, the lignocelluloses reached their maximum adsorption in 3 h. In the literature, the subsequent additions of 47.3 ppm PDADMAC (with the MW of 50–100 kDa) and 5 wt.% kaolin to laboratory-made PHL resulted in a maximum lignocelluloses adsorption in 3 h at room

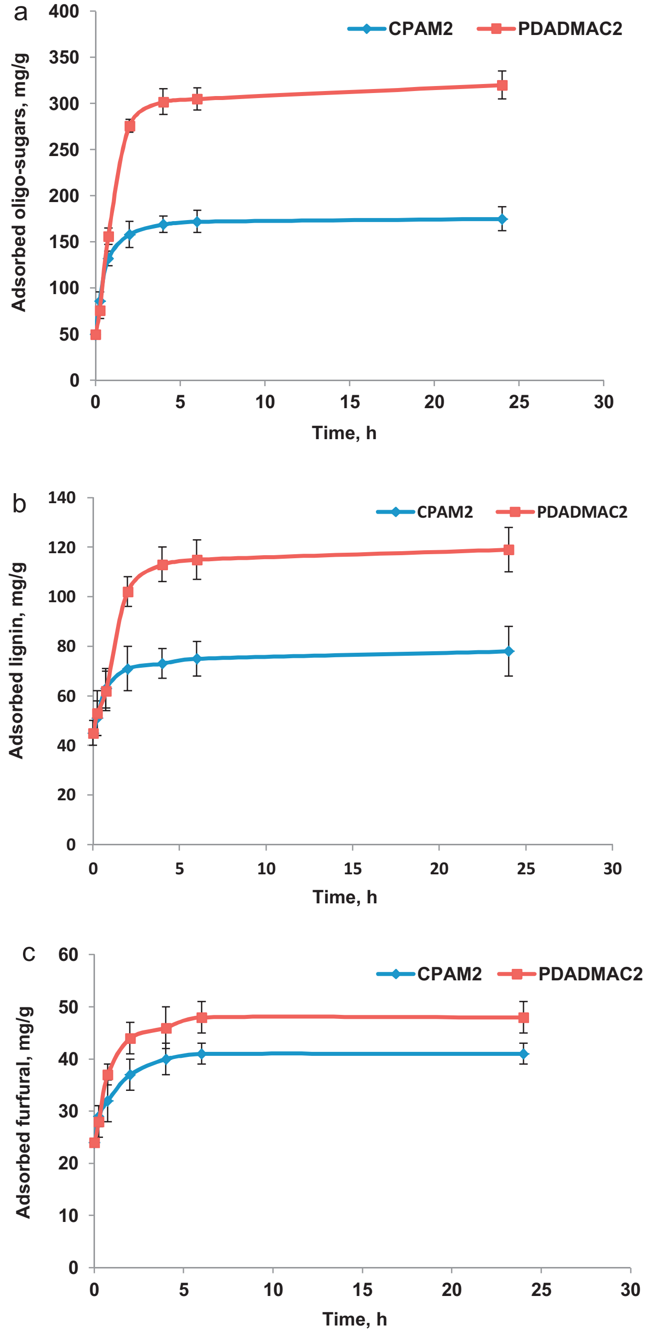

Fig. 4. Adsorption of lignocelluloses of PHL on PCC via adding 0.2 mg/g CPAM2 or PDADMAC2 as a function of time (initially PHL/PCC was mixed for 90 min, then 0.2 mg/g PDADMAC was added to the system at 40 °C and shaken for various time intervals).

temperature (Durarte et al., 2010). As the flocculation process of CPAM and PDADMAC with lignocelluloses of PHL is relatively fast (complexes form within seconds) (Yasarla & Ramarao, 2012), the slow increment in the overall adsorption is probably due to the rather slow adsorption of complexes on PCC surface (and diffusion into the PCC pores) and slow formation of layer-by-layer assembly of lignocelluloses and cationic polymers on PCC.

3.9. Impact of temperature

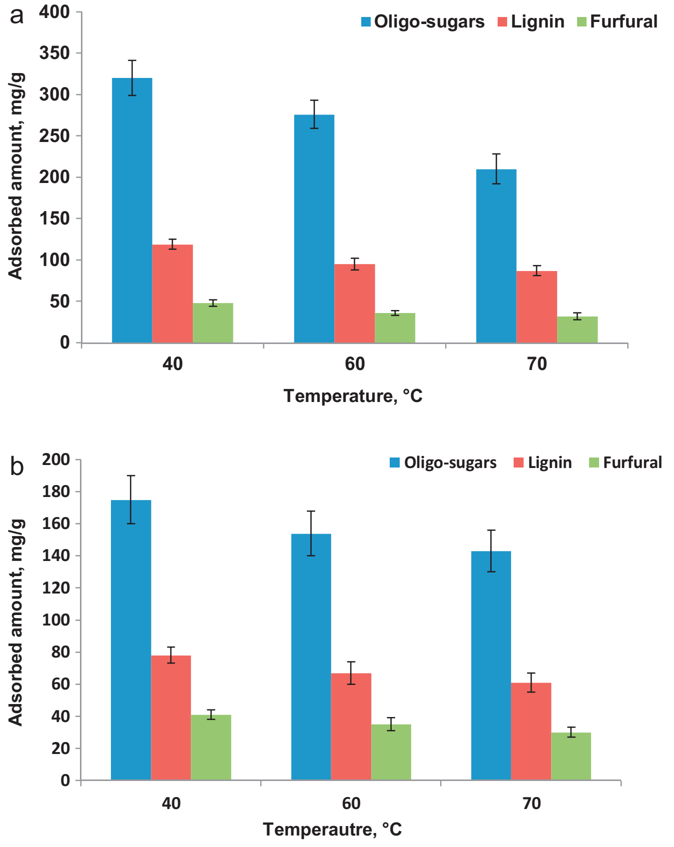

Fig. 5. Adsorption of lignocelluloses of PHL on PCC at different temperatures in the systems of (a) PCC/PHL/PDADMAC2 and (b) PCC/PHL/CPAM2 (initially PHL/PCC was mixed for 90 min at different temperatures, then 0.2 mg/g PDADMAC2 or CPAM2 was added to the system and shaken for 24 h).

Fig. 5 shows the effect of temperature on the adsorption of lignocelluloses on PCC in the systems of PCC/PHL/PDADMAC and PCC/PHL/CPAM. As can be seen, the increase in the temperature tended to decrease the adsorption of these components on PCC for both systems. As is well known, the adsorption of lignocelluloses on a surface, i.e. PCC surface, will reduce their entropy level. Based on the second law of thermodynamics, the adsorption would occur if the enthalpy levels of these components would also be reduced. In other words, the adsorption of polymers on surfaces is an exothermic process so is that of complexes (Petzold et al., 1996). Therefore, the lower temperature favors the adsorption of polymers in layer-by-layer assembly and the deposition of complexes on PCC surface.

Fig. 6 shows the turbidity of pretreated PHL via adding 0.8 mg/g CPAM2 or PDADMAC2 at different temperatures. Evidently, the turbidity of both PDADMAC2 and CPAM2 was decreased by increasing

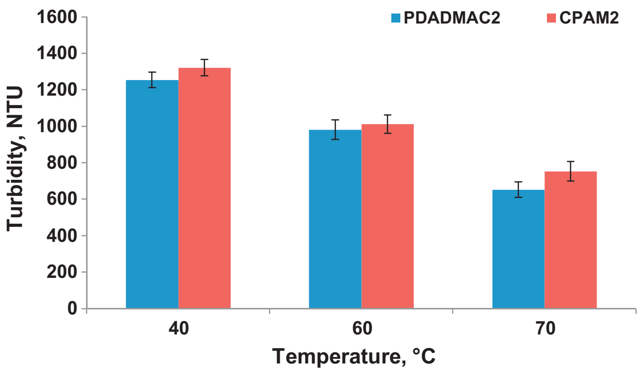

Fig. 6. Turbidity of pretreated PHL via adding 0.8 mg/g CPAM2 or PDADMAC2 to PHL at different temperatures.

temperature. Such a decrease may imply that the formation of complexes would adversely be affected at a higher temperature. Generally, polymers dissolve more easily at a high temperature. Similarly, the dissolution of complexes and polymers might be higher at a higher temperature implying that the polymers and formed complexes tend to stay in solution rather than to adsorb on the PCC surface at a higher temperature.

3.10. CPAM vs PDADMAC

In the literature, PDADMAC was more efficient than CPAM in retaining various fillers in cellulosic fiber matrices and in flocculating lignocelluloses of pre-hydrolysis (Burke et al., 2011; Yasarla & Ramarao, 2012; Zhu et al., 2009). Furthermore, it was comprehensively described that a high charge density and low MW polymers would interact with colloidal particles via charge neutralization, while a low charge density and high MW polymers would interact with colloidal particles via patch and bridging mechanisms (Fatehi et al., 2009; Yoon & Deng, 2004; Yu et al., 2006; Zhu et al., 2009). The results in Figs. 2 and 3 reveal that the higher the MW of CPAM or PDADMAC, the higher the adsorption of lignocelluloses on PCC would occur. This is because polymers with larger sizes tend to induce bridges between the surfaces and formed complexes/particles more effectively in solutions (i.e. PHL) (Yoon & Deng, 2004).

Moreover, the results in Figs. 2 and 3 depicted that the charge density played a more significant role than MW in adsorbing lignocelluloses on PCC (Barany & Szepesszentgyorgyi, 2004; Chi et al., 2007). At the same polymer dosage applied to PHL, more cationic charges was introduced via adding PDADMAC than CPAM to the PHL/PCC system, due to the higher charge density of PDADMAC. Consequently, more lignocelluloses would interact with PDADMAC in PHL/PCC system, and complexes with higher charge density would probably be formed (but the complex size may be smaller as seen in Fig. 1). Additionally, PDADMAC would adsorb more than CPAM on PCC due to its smaller size and higher charge density (Petzold et al., 1996). Therefore, the number of cationic sites on PCC would be greater upon adsorbing PDADMAC than CPAM, implying that more lignocelluloses could adsorb on PCC via the layer-by-layer assembly. Therefore, more complex formation and adsorption of lignocellulose via layer-by-layer assembly were probably the main reasons for the higher adsorption of lignocelluloses on PCC via applying PDADMAC than applying CPAM.

3.11. PCC modification

The nitrogen analysis revealed no detectable CPAM or PDADMAC in the supernatants of PHL/PCC/cationic polymer systems, thus all the added cationic polymers to the system were adsorbed on PCC. Therefore, the maximum amount of 0.04 g of cationic polymer was adsorbed on 1 g of PCC. The results also revealed that PDADMAC2 improved the adsorption of oligo-sugars, lignin and furfural the most (by 410, 149 and 29 mg/g, respectively) and that the maximum of 0.79 g organic (among which 0.53 g was oligo-sugar) was adsorbed on 1 g inorganic (PCC).

4. Conclusions

The results depicted that the addition of CPAM, and specially PDADMAC, was very effective in improving the adsorption of lignocelluloses, in particular that of oligo-sugars, on PCC in order to produce modified PCC. A higher adsorption of oligo-sugars than that of other constituents was obtained on PCC, regardless of the type of cationic polymer applied, which was due to the higher concentration of oligo-sugars in the pretreated PHL. The turbidity analysis confirmed that lignocelluloses interacted with cationic polymers in the pretreated PHL, and a lower turbidity was obtained at a higher temperature. Adding PCC to the pretreated PHL and subsequently adding cationic polymers to the system caused a higher lignocelluloses adsorption on PCC than adding cationic polymers to PHL and subsequently adding PCC to the system. Generally, PDADMACs resulted in a higher lignocelluloses adsorption than CPAMs due to the higher charge densities of PDADMACs. The adsorption of lignocelluloses reached plateau on PCC in 3 h, and a lower temperature caused a higher lignocelluloses adsorption on PCC, regardless of the type of cationic polymers in PHL/PCC systems. Also, PDADMAC2 was the most efficient cationic polymers, which improved the adsorption of oligo-sugars, lignin and furfural on PCC by 410, 149 and 29 mg/g, respectively.

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