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Adsorption of lignocelluloses of pre-hydrolysis liquor on calcium carbonate to induce functional filler

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ABSTRACT

In this work, we aimed at adsorbing the oligo-sugars of prehydrolysis liquor on precipitated calcium carbonate (PCC) to produce modified PCC. The results showed that the adsorptions of oligo-sugars, lignin and furfural were greater on porous PCC (PCC2) than on nano-sized PCC (PCC1) due to the larger surface area of PCC2. The adsorption reached its maximum in 5 h on PCC1, but it gradually increased on PCC2 due to the diffusion of oligo-sugars and lignin into the pores of PCC2. Also, the experimental isotherm and kinetic results were well fitted into Langmuir and pseudo-second order models, respectively. The adsorption was greater at a lower temperature (i.e. 40 °C) and pH (i.e. 7). Alternatively, cationic poly acrylamide (CPAM) was added to the PHL/PCC system, which led to more promising results (than that to PHL/PCC system) with the maximum lignocelluloses adsorption of 0.36 g/g on PCC2, among which 0.22 g/g was oligo-sugars.

1. Introduction

Today, kraft technology is widely used for producing dissolving pulp. In this process, wood chips are treated with steam in a pre-hydrolysis stage, which removes a part of hemicelluloses and lignin of wood chips (Fatehi & Ni, 2011; Li, Saeed, Jahan, Ni, & van Heiningen, 2010; Saeed, Fatehi, & Ni, 2012; Saeed, Jahan, Li, Liu, & Ni, 2012). The produced pre-hydrolysis liquor (PHL) contains approximately 5–8% organic materials, but it is currently sent to the recovery boiler of kraft process for further treatment, which implies that the organic materials of PHL are currently underutilized (wasted) (Li et al., 2010; Liu, Fatehi, Jahan, & Ni, 2011; Saeed, Fatehi, et al., 2012; Saeed, Jahan, et al., 2012).

However, the organic materials of PHL can be utilized in the production of value-added chemicals provided that they are isolated from the PHL (Alvarado-Morales, Terra, Gernaey, Woodley, & Gani, 2009; Amidon et al., 2008; Carvalheiro, Durate, & Girio, 2008; Huang, Ramaswamy, Al-Dajani, & Tschirner, 2010; Liu, Fatehi, Jahan, et al., 2011). In the literature, adsorption concept was applied for removing organic materials from various spent liquors (Chaichanawong, Yamamoto, & Ohmori, 2010; Radovic, Moreno-Castilla, & Rivera-Utrilla, 2010; Schwarts & Lawoko, 2010; Weil et al., 2002). We previously demonstrated that activated carbon was an efficient adsorbent for the organic materials of PHL (Liu, Fatehi, & Ni, 2011a; Liu, Fatehi, & Ni, 2011b), and proposed various processes for isolating oligo-sugars and lignin of PHL in order to produce ethanol, papermaking additives and phenolic compounds (Liu, Fatehi, Jahan, et al., 2011; Liu et al., 2011b; Liu, Fatehi, & Ni, 2011c; Shen, Fatehi, Soleymani, & Ni, 2011).

Precipitated calcium carbonate (PCC) has extensively been used as filler in papermaking (Shen, Song, Qiaon, & Liu, 2009; Shen, Song, Qian, & Yang, 2010). As the retention of PCC in paper matrices is poor, various polymers were introduced as retention aids for PCC/cellulose fiber systems (Li, Du, Wu, & Zhan, 2004; Nystrom, Backfolk, Rosenholm, & Nurmi, 2003; Nystrom, Hedstrom, Gustafsson, & Rosenholm, 2004; Nystrom & Rosenholm, 2005). It was comprehensively demonstrated that these polymers (retention aids) interact with PCC and modify its surface structure and chemistry (Li et al., 2004; Nystrom et al., 2003, 2004; Nystrom & Rosenholm, 2005). Similarly, we propose that the oligo-sugars of PHL could interact with PCC and adsorb on it. Therefore, PCC will be encapsulated by the oligo-sugars of PHL. As is well-known, PCC is inorganic filler with limited charged groups on its surface. As these oligo-sugars possess anionic groups (e.g. carbonyl and carboxylic group), they could develop hydrogen bonding with fibers. Therefore, the adsorption of oligo-sugars would improve the surface characteristics of PCC, which in turn would improve the interaction of PCC with pulp fibers (via improving the hydrogen bonding

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development). The first objective of this study was to investigate the adsorption characteristics of the oligo-sugars of PHL on PCC.

The interaction of cationic with anionic polymers has comprehensively been studied in various flocculation systems in the past (Li et al., 2004; Nystrom et al., 2003, 2004). Flocculation concept was also applied to isolate the organic materials of various hydrolysis liquors (Duarte, Ramarao, & Amidon, 2010; Saeed, Fatehi, & Ni, 2011; Saeed, Fatehi, et al., 2012; Saeed, Jahan, et al., 2012; Yasarla & Ramarao, 2012). We also reported that the application of a cationic polymer to the system of PHL and activated carbon was effective in isolating the organic materials of PHL (Liu, Fatehi, & Ni, 2012). The second objective of this work was to investigate the influence of cationic polyacrylamide (CPAM), which is commonly used as a retention aid in papermaking (Antunes et al., 2008; Shan, Fu, & Qin, 2012; Zhang & Liu, 2010), in improving the adsorption of oligo-sugars, lignin and furfural on PCC.

Other constituents of PHL, such as lignin and furfural may also adsorb on PCC. Therefore, a pretreatment step is required to reduce their concentrations prior to adsorbing oligo-sugars of PHL on PCC. In this respect, the PHL was pretreated with a surfactant so that its lignin content could be reduced (Shi, Fatehi, & Ni, 2012). Then, the adsorption characteristics of organic materials remained in the pretreated PHL was investigated on PCC under different process conditions. Finally, CPAM was added to the PHL/PCC system in an effort to increase the adsorption of oligo-sugars of pretreated PHL on PCC. The main focus of this work was to maximize the adsorption of oligo-sugars of PHL on PCC (i.e. maximum removal of oligo-sugars from PHL). The modified PCC can be used as functional filler in composites and papermaking, for example, for the production of liner boards (Kontrec, Kralj, Brecevic, & Falini, 2008; Lam, Hoang, Quang, & Kim, 2009; Shen et al., 2009, 2010; Yoon & Deng, 2006).

2. Materials and methods

2.1. Materials

The pre-hydrolysis liquor (PHL) was collected from a kraft-based dissolving pulp plant located in Eastern Canada. The raw materials of this plant are a mixture of maple (70 wt%), poplar (20 wt%) and birch (10 wt%).

Nano-sized (PCC1) and porous (PCC2) precipitated calcium carbonates were obtained from Omya Company and used as received. Cationic polyacrylamide (CPAM) with the trade mark of Percol® 181 with the average molecular weight of 2×10^6 and the degree of substitution of 20% was received from Ciba Specialty Chemicals (Lam et al., 2009; Zhang & Liu, 2010). Dodecyltrimethyl ammonium chloride (DTAC) was received from Aldrich Company, while calcium oxide (analytical grade) was received from Fisher Scientific.

2.2. PCC characterization

The BET (Brunauer–Emmett–Teller) surface area of PCCs was determined by nitrogen adsorption/desorption isotherms using a BELSORP-max instrument (BEL Inc.) (Liu et al., 2011b). Approximately 0.1 g (o.d.) of PCCs was pretreated at 120 °C and 10^{-7} Torr overnight for contamination removal. Afterwards, the measurement was carried out using nitrogen, as a probe, at 77 K overnight. The isotherm data was recorded in a relative pressure of P/P_0 in the range of 10^{-7} to 0.99999.

First, 0.15 g of PCC was added to 65 mL of distilled water and shaken for 24 h at room temperature (the pH of samples was adjusted by HCl or NaOH to pH 7 or 9.5). The zeta potential of PCCs was determined via measuring the electrophoretic mobility using Smoluchwski's approximation on a ZetaPlus Zeta potential analyzer (Brookhaven, Holtsville, NY, USA).

2.3. Preparation of PHLs

The influence of DTAC in removing the lignin of PHL was studied in our previous work (Shi et al., 2012). In this work, DTAC was added to PHL (500 mL) at the weight ratio of 0.03% (i.e. optimum ratio according to the procedure established by Shi et al., 2012) in a 1 L-Erlenmeyer flask at room temperature and the mixture was shaken at 120 rpm for 1 h. We previously reported that DTAC interacted with lignin of PHL and made large complexes (Shi et al., 2012). The DTAC-treated PHL was then filtered using Whatman cellulose nitrate membranes (0.45 μm pore size) to remove the formed complexes, and then the pH of the treated PHL was adjusted to 7 or 9.5 via adding CaO at room temperature. Afterwards, undissolved particles were removed from PHL via filtering using the same type of membrane. The compositions of original PHL and those after adjusting pH were determined and listed in Table 1.

2.4. Treatment of PHL with PCC

In the following experiments, the pH-adjusted PHL samples were treated with PCCs under various conditions in 250 mL-Erlenmeyer flasks with 1 g of PCC. All experiments were carried out five times and the results within a 95% confidence interval were reported in this work. After adding the materials in the flasks, they were sealed and kept in a New Brunswick water bath shaker at 120 rpm. In one set of experiments, the PHL samples (having pHs 7 and 9.5) were treated with PCCs at PHL/PCC weight ratio of 40 and 40 °C for 24 h in order to select the more effective pH for adsorption process. The adsorption kinetic studies were conducted with PHL/PCC weight ratio of 40, at 40 °C and pH 7 for various time intervals. The adsorption isotherm analyses were conducted via mixing PHL (at pH 7) with PCC at different weight ratios (i.e. 20, 40, 60, 100 and 120), but at 40 °C for 24 h. To study the effect of temperature, the PHL was mixed with PCCs at the weight ratio of 40 and 120 rpm for 24 h, but at various temperatures. After shaking, the samples were filtered using the aforementioned cellulose membranes, and the filtrates were collected for composition analysis.

2.5. CPAM addition to PHL/PCC

In this set of experiments, PHL (having pH 7) was treated with PCC2 at 40 °C, 120 rpm and pH 7 for 24 h; CPAM was added to the PHL/PCC system; and then mixing was continued for another 90 min under the same conditions. Afterwards, the PHL samples were filtered using the aforementioned membranes and the filtrates were selected form composition analysis.

2.6. Oligo-sugars analysis

The concentration of oligo-sugars in the PHL samples was determined using an ion chromatography unit equipped with a CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) (Saeed, Fatehi, et al., 2012; Saeed, Jahan, et al., 2012). To convert oligo-sugars of PHLs to mono-sugars, 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). The PAD settings were E1 = 0.1 V, E2 = 0.6 V and E3 = −0.8 V. Deionized water was used as the eluant at a 1 mL/min flow rate, 0.2 N NaOH was used as the regeneration agent at a 1 mL/min flow rate and 0.5 N NaOH was used as a supporting electrolyte at a 1 mL/min flow rate. The PHLs were first filtered using the 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 total sugars of PHL. Thus, oligo-sugars content was determined by subtracting the mono-sugars content from

Table 1
Compositions of PHL before and after treating with DTAC and CaO (conducted at 40 °C).

PHL	pH	Mono-sugars (g/l)	Oligo-sugars (g/l)	Furfural (g/l)	Acetic acid (g/l)	Lignin (g/l)	Ash (g/l)
Original	3.8	7.5 ± 0.5	24.1 ± 0.5	3.1 ± 0.1	14.1 ± 0.2	15.1 ± 0.3	12.1 ± 0.4
Pretreated	7	7.1 ± 0.4	22.1 ± 0.3	2.3 ± 0.1	12.1 ± 0.1	8.0 ± 0.2	14.7 ± 0.6
Pretreated	9.5	6.5 ± 0.5	18.5 ± 0.3	1.8 ± 0.2	11.4 ± 0.2	6.5 ± 0.4	16.1 ± 0.5

the total sugar content of PHL (Saeed, Fatehi, et al., 2012; Saeed, Jahan, et al., 2012).

2.7. Ash and lignin analyses

The ash contents of the PHL samples were measured according to TAPPI T412. The lignin content of PHLs was measured based on the UV–vis spectrometric method at a wavelength of 205 nm according to TAPPI UM 250.

2.8. Furfural and acetic acid analysis

A Varian 300 ^{1}H NMR spectrometer was employed for determining the concentrations of furfural and acetic acid based on previously established procedures (Saeed, Fatehi, et al., 2012; Saeed, Jahan, et al., 2012). Calibration curves were established for determining furfural concentrations using NMR.

2.9. Nitrogen analysis

Since DTAC contained nitrogen, the nitrogen analysis of PHL could directly be correlated to the concentration of DTAC in the PHL. This method was used to measure the concentration of various surfactants in water in our previous work (Fatehi, Outhouse, Xiao, & Ni, 2010). At first, 20 mL of PHL was collected after treating with DTAC 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, TX, USA at the temperature of 1075 °C. A calibration curve was prepared by plotting the predefined concentrations of DTAC against the intensities of the nitrogen peak. Our analysis showed that the nitrogen content of DTAC treated-PHL was below the detection limit.

3. Results and discussion

3.1. PCC properties

The surface area of PCC1 and PCC2 were 8 m^2/g and 63 m^2/g (the latter with the pore size of 68 nm) respectively. In the literature, the BET surface area of PCC was reported to be in the range of 3 and 75 m^2/g (Ferreira, Velho, Figueiredo, & Mendes, 2005; Lam et al., 2009; Wei, Mahuli, Agnihotri, & Fan, 1997). Zeta potential analyzer showed no detectable potential at pH 7 for both PCCs, but −8 mV and −12 mV at pH 9.5, respectively. In the literature, the zeta potential of PCC was reported to be −18 mV (pH was not specified) in one report (Ferreira et al., 2005) and −12 mV at pH 9.5 in another report (Wei et al., 1997). Our previous investigation showed −0.03 mequiv./g charge densities on the surface of PCC at neutral pH (Takahashi, Sheill, Fatehi, & Ni, 2012).

3.2. PHL properties

Table 1 shows the compositions of PHL before and after the DTAC treatment. As can be seen, the concentration of sugars (mono- and oligo-sugars) was 31.6 g/l, while that of acetic acid and lignin was 14 g/l and 15 g/l, respectively. The properties of PHL and the relationship between different components of PHL were comprehensively discussed in the past (Saeed, Jahan, et al., 2012). In our previous work, we reported that the molecular weight (*Mw*) and charge density of oligo-sugars were −0.15 mequiv./g and 5800 Da, and those of lignin were −0.34 mequiv./g and 2975 Da, respectively (Liu, Fatehi, Jahan, et al., 2011; Liu et al., 2011a).

Initially, the PHL was treated with DTAC and then its pH was increased from 4 to 7 via treating with CaO. The results in Table 1 shows that DTAC and CaO treatments reduced the sugar, furfural and acetic acid concentrations by less than 8%, 26% and 14%, while reduced that of lignin by 47% (Table 1). These results imply that the pretreatment of PHL was selective in removing lignin and furfural. It is well known that furfural is a hydrophobic molecule. Lignin and hemicelluloses of PHL have different structures: lignin usually contains phenolic group and thus is more hydrophobic than hemicelluloses that are macromolecules of pentose and hexose sugars (Liu et al., 2011a). Therefore, by adding DTAC to PHL, the phenolic group of lignin could interact with hydrophobic tail of DTAC via hydrophobic/hydrophobic interaction and make complexes (Shi et al., 2012). These formed hydrophobic complexes could be removed from PHL via filtering. The remaining macromolecules in PHL would thus be hemicelluloses and lignin-carbohydrate (hemicelluloses) compounds (LCC) that were relatively more hydrophilic and had limited interactions with DTAC (Saeed et al., 2011).

The results also showed that the mono-sugar content of PHL marginally changed, but the ash content of PHL slightly increased, which was due to the addition of CaO to the PHL for pH adjustment. After adding CaO for pH adjustment, the remaining lignocelluloses could be adsorbed on undissolved CaO and thus be removed from PHL (Shi et al., 2012). Therefore, the reduction of organic materials demonstrated above is attributed to the formation and removal of complexes from PHL as well as to the adsorption of complexes and organic materials of PHL on undissolved CaO (Shi et al., 2012).

Alternatively, the DTAC-treated PHL was subsequently treated with CaO to pH 9.5, and the results were also included in Table 1. Evidently, this treatment reduced the mono-sugars, oligo-sugars, furfural, acetic acid and lignin contents of PHL by 13%, 23%, 41%, 19% and 57%, respectively. These results imply that, by increasing the pH of DTAC-treated PHL (i.e. adding more CaO to PHL), the organic materials were more greatly removed from the PHL, which is probably due to the adsorption of more dissolved organic materials on undissolved CaO as explained earlier (Shi et al., 2012). It should be noted that the nitrogen analysis showed no detectable nitrogen in PHL after the pH adjustment treatment, implying that all of the added DTAC to PHL was removed from the PHL via complex formation, and thus its influence on the downstream processes should have been minimal.

3.3. Effect of pH of PHL on adsorption

The adsorption of organic materials of PHL (having different pHs) on PCCs was listed in Table 2. As can be seen, the organic materials adsorbed on PCCs more at pH 7 than pH 9.5, regardless of the PCC type. This behavior may be due to fact that organic materials were more soluble in PHL at a higher pH (i.e. 9.5) due to the presence of more hydroxyl ion (at pH 9.5) that could develop hydrogen bonding (i.e. interaction) with oligo-sugars and lignin in PHL. As the adsorption of organic materials on PCCs was greater at pH 7, the adsorption analysis was carried out at pH 7.

Table 2
Adsorption of organic materials on PCC at pH 7 and 9.5 (conducted at PHL/PCC weight ratio of 40, 40 °C and 120 rpm for 24 h).

PCC type	pH	Mono-sugars (mg/g)	Oligo-sugars (mg/g)	Furfural (mg/g)	Acetic acid (mg/g)	Lignin (mg/g)
PCC1	7	12 ± 3	55 ± 4	19 ± 2	12 ± 2	31 ± 2
PCC2	7	17 ± 4	120 ± 8	29 ± 1	14 ± 1	54 ± 3
PCC1	9.5	7 ± 2	44 ± 3	12 ± 1	10 ± 1	25 ± 2
PCC2	9.5	13 ± 3	95 ± 7	18 ± 2	13 ± 1	33 ± 1

3.4. Adsorption isotherms

As explained earlier, the adsorption of oligo-sugars (and probably mono-sugars) would have a positive effect on the surface properties of PCC. However, PHL contains other constituents, e.g. furfural, lignin and acetic acid. Our results showed that acetic acid and mono-sugars insignificantly adsorbed on PCC and thus insignificantly affected the surface property of PCC. This is because acetic acid and mono-sugars are small hydrophilic molecules with high solubility in aqueous solutions. Therefore, their tendency toward isolation from solutions (i.e. adsorption on PCC) was low.

Fig. 1 shows the adsorption isotherms of oligo-sugars, lignin and furfural of PHL on PCCs. It is evident that oligo-sugar, lignin and furfural adsorption was 200, 80 and 50 mg/g on PCC2 and 80, 40 and 30 mg/g on PCC1, via mixing PHL with PCC at the weight ratio of 120, respectively. The higher adsorption of oligo-sugars (than lignin and furfural) was due to their higher concentrations in the pH-adjusted PHL (Table 1). It is also evident in Fig. 1 that the oligo-sugars, lignin and furfural reached higher adsorption levels on PCC2 than PCC1, which is attributed to the larger surface area of PCC2, as described earlier.

Generally, hydrogen bonding, electrostatic charge interaction and hydrophobic/hydrophobic interaction are the main driving forces for the adsorption of various polymers on different surfaces in aqueous suspensions. As illustrated in Sections 3.1 and 3.2, all PCC, oligo-sugars and lignin of PHL had anionic charge densities. Therefore, no electrostatic charge interaction could have been developed among them during mixing of PHL and PCC. However, hydrogen bonding might have been developed between the anionic charges of PCC surface and that of lignin and oligo-sugars. As the surface of PCC is hydrophobic, the adsorption of oligo-sugars, lignin and furfural of PHL on PCC would also be developed through hydrophobic/hydrophobic interaction (van der waals interaction). In this case, the higher the hydrophobicity of organic materials, the higher would be their adsorption on PCC. As furfural is a hydrophobic material, it can easily adsorb on PCC (Chinn & King, 1999). The phenolic group of lignin (i.e. hydrophobic tail) assists the hydrophobic interaction of lignin and PCC (Chinn & King, 1999; Sulaymon & Ahmed, 2008). It is well known that the larger the polymers, the more insoluble they would be in aqueous solutions (Chinn & King, 1999; Sulaymon & Ahmed, 2008). Thus, they would have a higher tendency than small molecules (e.g. mono-sugars) to be separated from solutions (i.e. be adsorbed on PCC). On the other hand, not all of the adsorbed polymers on the PCC surface would remain attached to the PCC surface during the PHL/PCC treatment process, i.e. a part of adsorbed polymers would desorb from the PCC surface. In this case, the larger the polymers, the lower the affinity of polymers to desorb (i.e. the lower the desorption rate), and thus the higher the overall adsorption of polymers on PCC surface would be (De Witt & van de Ven, 1992; Dijt, Cohen Stuart, & Fleer, 1994; Hu, Gao, Wu, Auweter, & Iden, 2002; Mészáros, Varga, & Gilányi, 2004; Rakhnyanskaya et al., 2010; Ueda, Ishihara, & Nakabayashi, 1995). Therefore, the lower solubility and desorption rate were probably the reasons for the high adsorption of oligo-sugars on PCC.

The experimental adsorption data plotted in Fig. 1 was employed to determine the adsorption isotherm of oligo-sugars, lignin and furfural on PCC1 and PCC2. Two adsorption models, i.e. Freundlich and Langmuir isotherm models were adapted. Freundlich isotherm assumes that the adsorption of adsorbate occurs on a heterogeneous surface of adsorbents through a multilayer adsorption mechanism, and that the adsorption amount increases with the increment in the concentration according to Eq. (1):

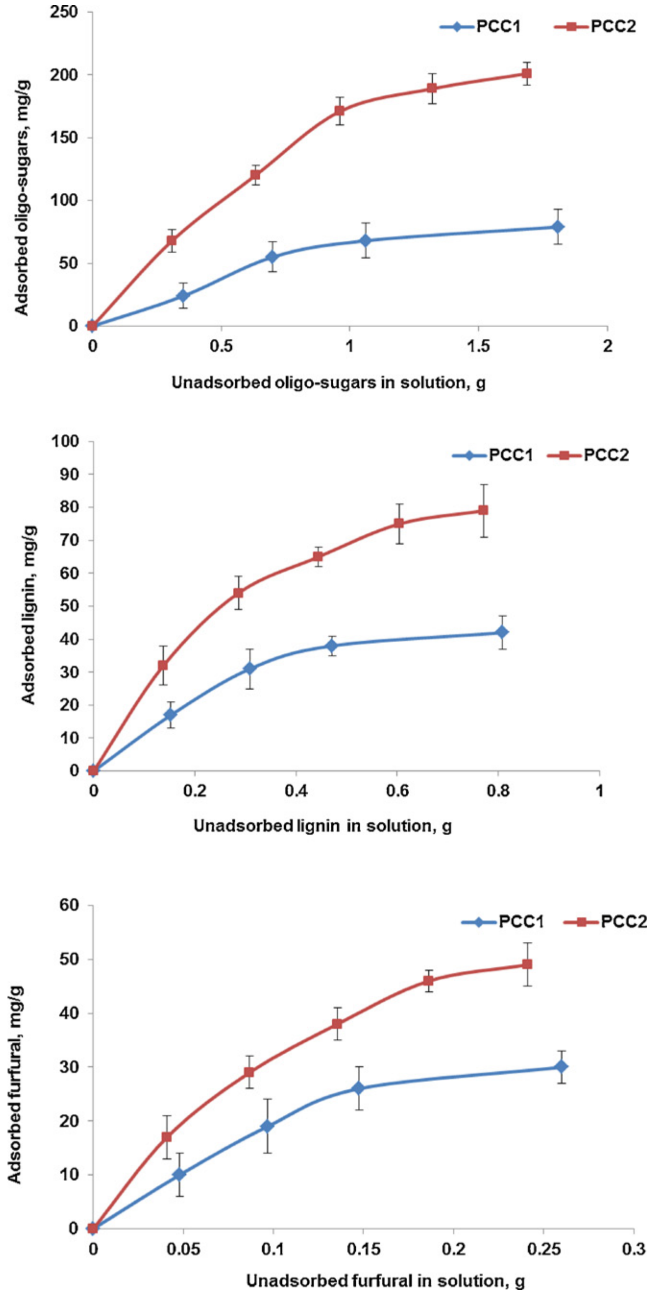

Fig. 1. Adsorption isotherms of lignocelluloses on PCCs (conducted at 40 °C, pH 7, 120 rpm for 24 h).

$$q_e = k_f \cdot C_e^{1/n} \tag{1}$$

where q_e is the adsorbed amount on PCCs at equilibrium (mg/g), C_e is the concentration of adsorbate in solutions at equilibrium (mg/l) and k_f is the Freundlich constant (Fierro, Torne-Fernandez, Montane, & Celzard, 2008; Srivastava, Swamy, Mall, Prasad, & Mishra, 2006).

The Langmuir adsorption isotherm model is based on the assumptions that there is a saturated monolayer of adsorbate molecules on the adsorbent surface, no interaction between the adsorbed molecules develops on the adsorbent surface and that all the adsorption sites on the adsorbent have the same sorption activation energy according to Eq. (2) (Fierro et al., 2008):

$$\frac{C_e}{q_e} = \frac{1}{Q_o\beta} + \frac{C_e}{Q_o} \qquad (2)$$

where Q_0 is the maximum possible adsorption amount (mg/g), and β is the Langmuir constant (l/mg). The results of the isotherm analysis were listed in Table 3. Generally, Langmuir models predicted the adsorption isotherm behavior of oligo-sugars, lignin and furfural more accurately than Freundlich did. This analysis implies that oligo-sugars, lignin and furfural probably developed a monolayer adsorption on the PCC surface and that the interaction between the adsorbed molecules on PCC was marginal. In the literature, the adsorption of phenols on activated carbon was well fitted into the Langmuir adsorption model (Fierro et al., 2008). However, the rather lower R^2 for the modeling of oligo-sugars adsorption cannot be explained and requires further investigation.

3.5. Adsorption kinetics

Fig. 2 shows the adsorption of oligo-sugars, lignin and furfural on PCCs as a function of time. Evidently, the oligo-sugars and lignin reached their saturation levels (i.e. 55 mg/g and 31 mg/g, respectively) on PCC1 in 5 h. In a previous study, the adsorption of organic materials of PHL on activated carbon reached their saturation level in 2 h (Liu et al., 2011b). However, the adsorption of oligo-sugars and lignin gradually increased to 120 mg/g and 54 mg/g on PCC2, respectively, which is due to the diffusion of these components into the pores of PCC2 (Liu et al., 2011b). The diffusion of lignin and oligo-sugars of PHL into the pores of activated carbon was observed in our previous study (Liu et al., 2011b). Additionally, furfural reached its saturation adsorption (19 mg/g on PCC1 and 29 mg/g on PCC2) in 5 h. This behavior is ascribed to the fact that furfural is a small molecule and it can easily diffuse into the pores of PCC2 in a relatively short period of time.

The experimental kinetic results in Fig. 2 were hired to model the adsorption kinetics of oligo-sugars, lignin and furfural on PCC1 and PCC2. Pseudo-first order and pseudo-second order equations were employed in kinetic simulation, as they were comprehensively used in determining the adsorption kinetics of phenols and furfural on adsorbents in solutions (Fierro et al., 2008; Sahu, Srivastava, Mall, & Lataye, 2008; Srivastava et al., 2006).

The simplified form of pseudo-first order model is (Fierro et al., 2008):

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}(q_e) - \frac{kt}{2.303} \qquad (3)$$

where k is the kinetic constant (1/min), q_e and q_t (mg/g) represent the adsorption amounts at equilibrium and time (min), t, respectively. The simplified form of pseudo-second order equation is shown in Eq. (4) (Fierro et al., 2008):

$$\frac{t}{q_t} = \frac{1}{k' \cdot q_e^2} + \frac{1}{q_e} \cdot t \qquad (4)$$

where k' corresponds to kinetic constant (g/(mg min)). The results of this analysis were provided in Table 4. Evidently, the pseudo-second order model adequately predicted the adsorption kinetics of oligo-sugars, lignin and furfural on both PCC1 and PCC2. In the literature, the pseudo-second order model was the most suited one to predict the adsorption kinetic of phenols and furfural on activated carbon (Fierro et al., 2008; Sahu et al., 2008; Srivastava et al., 2006).

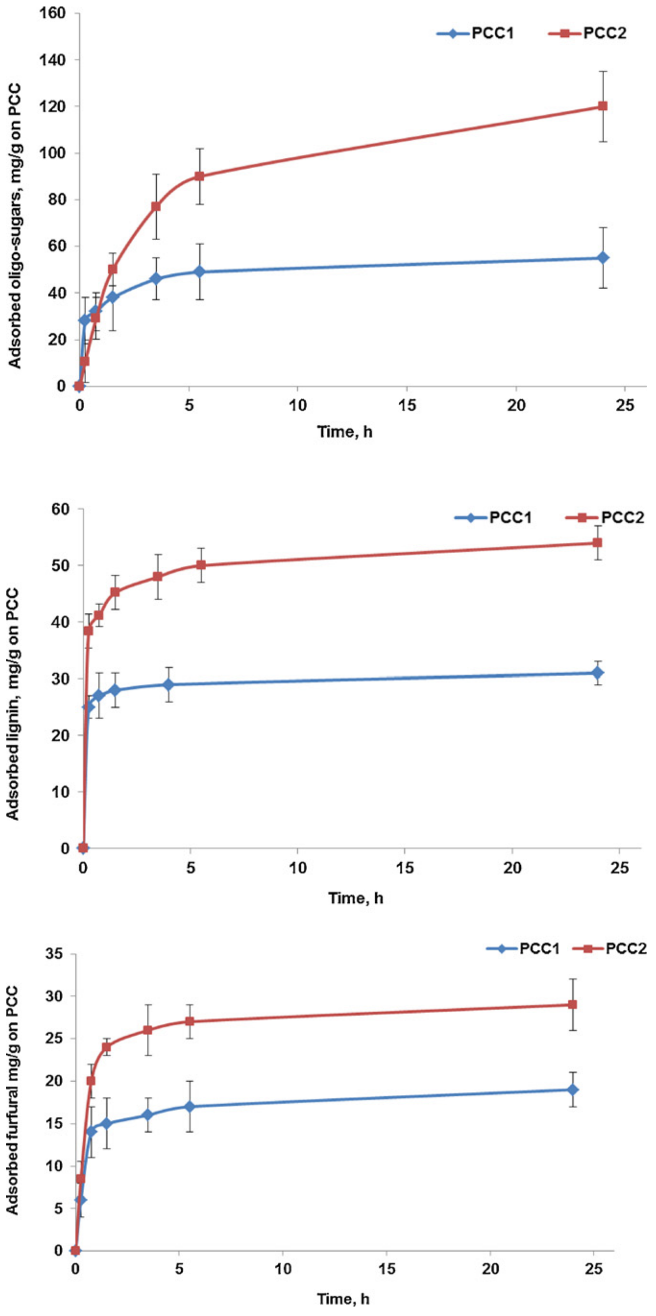

Fig. 2. Adsorption of lignocelluloses on PCCs as a function of time (conducted at 40 °C, pH 7 and120 rpm, PHL/PCC wt. ratio of 40).

3.6. Effect of temperature

Fig. 3 shows the adsorption of oligo-sugars, lignin and furfural on PCC2 versus the temperature of the adsorption process. Generally, by increasing the temperature, the adsorption decreased remarkably. A similar trend was obtained for PCC1, but not shown here. As the lignocelluloses will be confined on the surface of PCC (and/or inside its pores) via adsorption, their entropy level will reduce. Therefore, the occurrence of adsorption is possible if the enthalpy level of the organic

Table 3
Constant parameters derived from fitting the experimental data of Fig. 1 into isotherm models presented in Eqs. (1) and (2).

Components	Freundlich						Langmuir					
	PCC1			PCC2			PCC1			PCC2		
	k_f	n	R^2	k_f	n	R^2	β	Q_0	R^2	β	Q_0	R^2
Oligo-sugars	58.9	1.37	0.89	156.5	1.51	0.96	0.61	158.7	0.90	0.77	370.3	0.96
Lignin	52.48	1.81	0.93	96.7	1.88	0.95	2.89	61.7	0.96	2.87	116.2	0.99
Furfural	82.37	1.50	0.90	123.3	1.63	0.94	5.4	52.9	0.93	6.42	81.9	0.99

Table 4
Constant parameters derived from fitting the experimental data of Fig. 2 into kinetic models presented in Eqs. (3) and (4).

Components	Pseudo-first order model				Pseudo-second order model			
	PCC1		PCC2		PCC1		PCC2	
	K	R^2	K	R^2	K'	R^2	K'	R^2
Oligo-sugars	0.056	0.75	0.244	0.98	0.029	0.99	0.00283	0.99
Lignin	0.074	0.94	0.25	0.96	0.150	0.99	0.0577	0.99
Furfural	0.053	0.54	0.388	0.84	0.094	0.99	0.0723	0.99

materials is lowered via adsorption, which implies that the adsorption process is exothermic (van de Ven, 1994; Vanerek & van de Ven, 2006). In other words, by decreasing the temperature of the process, more hydrophobic/hydrophobic interaction (van de waals attraction force) will be developed between the lignocelluloses and PCCs.

3.7. Impact of CPAM on adsorption

We previously demonstrated that a combination of flocculation and adsorption processes could be employed for obtaining an effective oligo-sugars adsorption on activated carbon (Liu et al., 2012). In this regard, a flocculant (e.g. CPAM) could interact with the dissolved oligo-sugars and lignin of PHL and form complexes that would eventually adsorb on PCC. In one study, kraft lignin was employed as a co-factor of CPAM to retain PCC on cellulose fibers (Sulaymon & Ahmed, 2008), which would directly imply the interaction developed among kraft lignin, CPAM and PCC. Fig. 4 shows the adsorption of oligo-sugars on PCCs as a function of CPAM dosage in PHL/PCC system. It is noted that the adsorption of oligo-sugars increased from 55 to 186 mg/g on PCC1 and from 120 to 225 mg/g on PCC2 via adding up to 8 mg/g CPAM to the system. Similarly, the adsorption of lignin increased from 31 to 63 mg/g on PCC1 and from 54 to 98 mg/g on PCC2, while that of furfural increased from 19 to 33 mg/g on PCC1 and from 29 to 47 mg/g on PCC2, respectively. These results imply that the adsorption of oligo-sugars on PCC was more greatly affected (than that of others) by CPAM addition. The interaction of oligo-sugars with CPAM resulted in forming complexes with cationic charges. Therefore, the complexes could have been adsorbed on PCC via an electrostatic charge interaction. As explained earlier, the large the polymers, the lower the desorption rate of adsorbed polymers from the PCC surface. It was illustrated that CPAM interacted with lignin and oligo-sugars, and created larger complexes. Therefore, the desorption rate of the already adsorbed complexes on PCC from the PCC surface would have been lower than that of individual oligo-sugars or lignin from PCC. Therefore, the charge interaction and lower desorption rate were probably the reasons for the higher adsorption of CPAM/oligo-sugars and/or CPAM/lignin complexes on PCC surface.

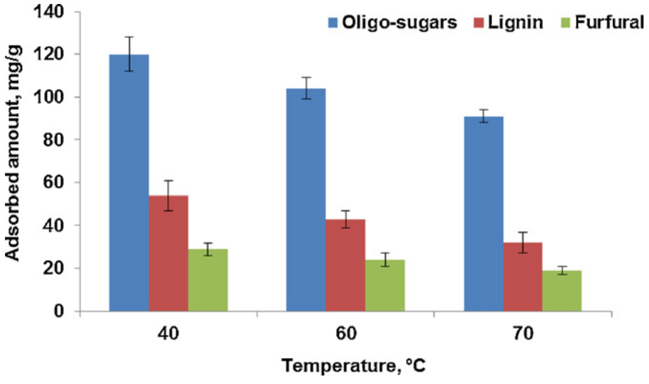

Fig. 3. Adsorption of lignocelluloses on PCC2 versus the temperature of adsorption (conducted at 120 rpm, pH 7, PHL/PCC2 wt. ratio of 40 for 24 h).

Furthermore, the results showed that the addition of CPAM improved the adsorption of oligo-sugars more greatly on PCC1 than on PCC2. It should be noted that the complexes formed via interacting polymers are more rigid than each individual polymer segment in solutions (i.e. PHL), and hence the diffusion of complexes into the pores of PCC is more restricted (Hovarth, Hovarth, Lindstrom, & Wagberg, 2008). Therefore, the formed complexes adsorbed more likely on the external surface of PCC rather than inside the pores, which entails that the outer surface of PCC plays an important role in adsorbing complexes. These results may indirectly suggest that the PCC1 had a larger external surface area than PCC2 did for the adsorption of complexes, but more analysis is necessary to prove this phenomenon.

3.8. Removal of organic materials and PCC modification

A comparison between the adsorbed organic materials on PCC and unadsorbed organic materials in PHL (Fig. 1) reveals that less than 15% of oligo-sugars and furfural and 10% of lignin were removed from the PHL via adsorbing on PCC2, and a lower removal was obtained for the PHL/PCC1 system. Such limited removals are due to the rather limited surface area of PCC for adsorption and a weak hydrophobic interaction developed between the organic materials and PCCs. However, with 8 mg/g addition of CPAM to PHL, the removals of oligo-sugars, furfural and lignin increased to 26%, 51% and 30% for PHL/PCC2 system and 22%, 36% and 19% for PHL/PCC1 system, respectively (Fig. 4 and Table 1). As illustrated earlier, the increase in the adsorption of lignocelluloses was due to formation and adsorption of complexes on PCCs.

Furthermore, the results in Figs. 1–4 could be used for optimizing the process conditions of PCC modification in order to obtain the maximum adsorption of oligo-sugars on the PCC modification process. It is also inferred from Fig. 4 that a maximum amount of lignocelluloses adsorbed was 0.28 g/g on PCC1, among which

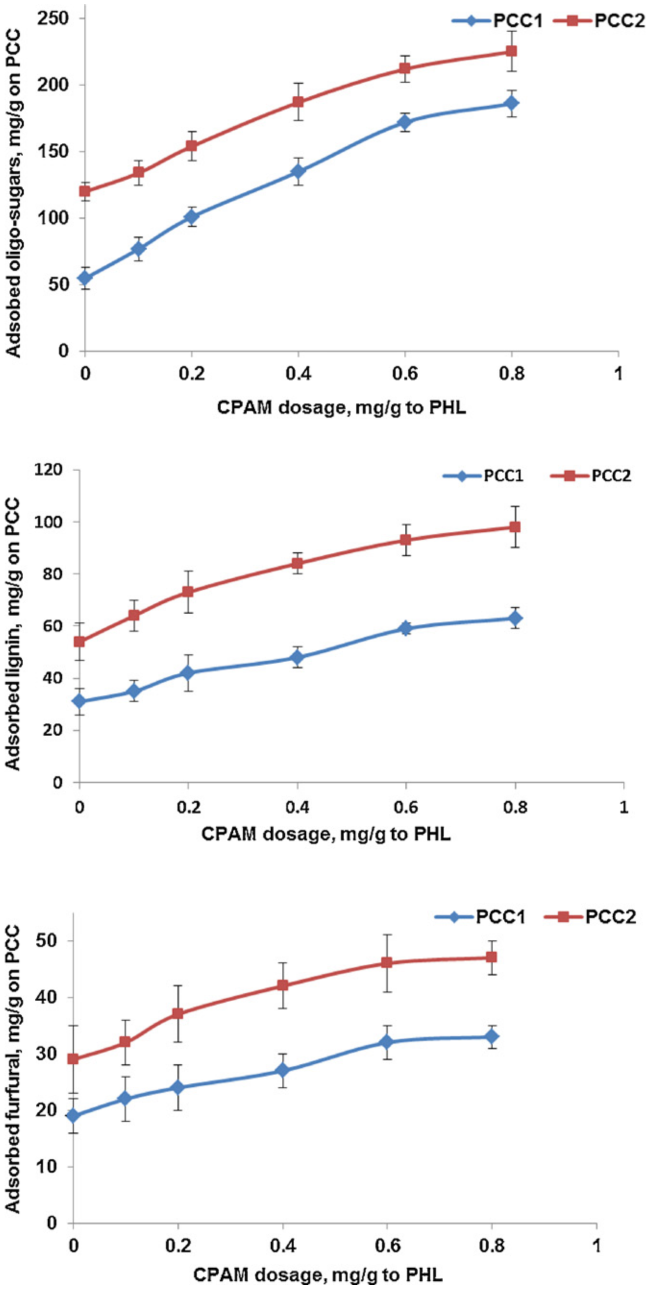

Fig. 4. Adsorption of lignocelluloses on PCCs as a function of CPAM dosage in PHL (PHL/PCC treatment conducted at the weight ratio of 40, 40 °C, 120 rpm, pH 7 for 24 h and then CPAM was added to the system and treated for another 90 min under the same conditions).

0.19 g/g was oligo-sugars. Similarly, a maximum amount of lignocelluloses adsorbed was 0.36 g/g on PCC2, among which 0.22 g/g was oligo-sugars. These results are promising considering the end-use application of modified PCC as functional filler in papermaking or composites. However, further investigation is necessary to assess the effect of adsorbed furfural on the surface characteristics and retention of modified PCC in papermaking.

4. Conclusions

The DTAC surfactant treatment of PHL, followed by the addition of lime (for pH adjustment to 7), decreased the oligo-sugar, furfural and acetic acid concentrations by 8%, 26% and 14%, while decreased the lignin concentration by 47%. Alternatively, the DTAC treatment and pH adjustment to pH 9.5 reduced the mono-sugars, oligo-sugars, furfural, acetic acid and lignin contents of PHL by 13%, 23%, 41%, 19% and 57%, respectively. However, the adsorption of lignocelluloses on PCCs was less significant at pH 9.5 than 7. The maximum adsorptions of 200 mg/g oligo-sugars, 80 mg/g lignin and 50 mg/g furfural on PCC2 and 80 mg/g oligo-sugars, 40 mg/g lignin and 30 mg/g furfural on PCC1 were obtained via mixing PHL and PCCs with the weight ratio of up to 120, respectively. The higher adsorption of lignocelluloses on PCC2 was due to its larger surface area, and the higher adsorption of oligo-sugars was due to their higher concentration in the pretreated PHL. The lower treatment temperature of 40 °C resulted in a higher adsorption on PCCs. The addition of up to 8 mg/g CPAM to PHL led to the maximum lignocelluloses adsorption of 0.36 g/g (among which 0.22 g/g was oligo-sugars) on PCC2, and that of 0.28 g/g lignocelluloses (among which 0.19 g/g was oligo-sugars) on PCC1. The experimental isotherm and kinetic results were well fitted into Langmuir and pseudo-second order models, respectively.

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