Extracting Lignocelluloses from Various Spent Liquors via Adsorption

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Dedications

To my parents for their endless love, support and encouragement.

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ABSTRACT

The spent liquors of thermomechanical (TMP) and neutral sulfite semichemical (NSSC) pulping processes contain some lignocelluloses that are recently treated in the waste water of the processes, and thus wasted. In this dissertation, the adsorption concept was considered to separate lignocelluloses from the spent liquors (SL)s of TMP and NSSC processes. Various adsorbents such as activated carbon, fly ash, bentonite, kaolin, kaolinite, calcium carbonate, talc and aluminium silicate were used in order to adsorb lignocelluloses. The operating conditions of adsorption were optimized by adjusting pH, temperature and time of treatment. Moreover, various alternatives, such as pH adjustment, polymer addition and multi-stage adsorption processes were considered to improve the overall extraction of lignocelluloses from SLs. The properties of adsorbents, e.g. charge density and surface area, were related to the adsorption performance and the properties, e.g. turbidity and chemical oxygen demand (COD), of SLs after adsorption. The high removals in turbidity and COD showed that the suggested processes were not only effective in extracting lignocelluloses but also efficient in decreasing the load of wastewater treatment of the plant. Generally, the results showed that fly ash and precipitated calcium carbonate (PCC) were the best adsorbents for lignin removal, and the products could be used as fillers in composites.

Also, the lignin samples of pre-hydrolysis liquor (LPHL) and lignin isolated from SL of NSSC (LSL) were compared with two commercial lignosulfonastes (LS1 and LS2) and kraft lignin (KL). The results indicated that LSL and LS1 had the same hydrodynamic diameter (10.1 nm),

which was higher than that of KL, LPHL and LS2. The hydrodynamic diameter and charge density analyses confirmed that lignosulfonates (LSL, LS1 and LS2) were more appropriate to be used as a filler modifier, flocculants and dispersants. The results also indicated that KL and LPHL had better incineration efficiency than other samples with high heating value (HHV) of 27.02 and 19.2 MJ/kg, respectively. The results suggest that LPHL would be a suitable fuel source after KL.

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1 CHAPTER ONE: INTRODUCTION

1.1 OVERVIEW

Pulp and paper industries significantly contributes to the gross domestic products of Canada and the USA due to the enormous forest resources in these countries. However, the pulp and paper industry is currently struggling financially due to strong competition from countries with low labor costs. One scenario is to utilize the wasted materials of this industry more effectively in order to decrease the production costs, and subsequently to increase the economic benefits of the pulp and paper industry.

Spent liquor (SL) of neutral sulfite semichemical (NSSC) pulping contains approximately 60-70 g/l lignin, 2-25 g/l hemicelluloses (monomeric and oligomeric sugars), 12-29 g/l acetic acid and 0.5 g/l furfural and 50-70 g/l ash. The SL of NSSC process is currently treated in wastewater treatment of the plant. Similar to the NSSC process, the SL that is generated in the pretreatment stage of thermomechanical pulping (TMP) processes contains about 5-10 g/l lignin, 0.5-2.5 g/l hemicelluloses and 0.5-1.0 g/l ash. This SL also treated in wastewater plant of the mill.

On the other note, plenty of applications for lignin and hemicelluloses have been proposed recently in order to produce value-added products from these natural polymers. The application of lignin in the production of fillers and composites were the center of attention. However, to utilize lignocelluloses in these products, they should be first extracted from the spent liquors of pulping processes.

In this MSc study, adsorption concept was introduced as an alternative for the extraction of lignocelluloses from SL of NSSC and TMP processes. Moreover, the impact of this adsorption process on the properties of SL was comprehensively assessed. The final products of the studied processes can be used as fillers, additives or fuel.

In chapter one of this thesis (current chapter), an overall perspective of this thesis is discussed. Hypotheses and objectives are defined and the novelty of this work is described. Also, this chapter has a brief overlook on other chapters.

In chapter two, the overall aspect of lignocelluloses present in woody materials and pulping spent liquors were discussed. The methods of pulping were also reviewed and the alternatives for isolating lignocelluloses from various pulping liquors were discussed. Finally, different applications of fly ash were reviewed.

In chapter three, activated carbon was used as an adsorbent to extract lignocelluloses from SL (or pressate) of TMP processes. The adsorption process was optimized by investigating the ratio of adsorbent to SL, pH, temperature and time factors. The adsorption was then improved by adding another stage of adsorption. This chapter aimed to introduce the concept of single stage adsorption and two stage adsorption of lignocelluloses on activated carbon.

In chapter four, an industrial fly ash was considered as an adsorbent to isolate the lignocelluloses from SL (i.e. pressate) of TMP process. The effect of fly ash on the properties of SL after treatment was investigated. Then, the dosage of fly ash and treatment time were optimized. The process was subsequently modified through pH adjustment and adding another stage of adsorption. In another attempt, the impact of washing fly ash on its performance and the impact of pH adjustment on the adsorption process were studied.

In chapter five, bentonite (clay) was used as an adsorbent for separating lignocelluloses from SL of NSSC pulping. Operating conditions such as temperature, dosage of bentonite and time of treatment were studied. Subsequently, the impact of flocculation/adsorption on the extraction of lignocelluloses from SL was studied. The produced flocs were analysed and suggested as filler for corrugated pulp or composites.

In chapter six, various fillers (calcium carbonate, kaolin, kaolinite, talc and aluminium silicate) were used as adsorbents of lignocelluloses from the SL of TMP and NSSC pulping processes. In the second part of this chapter, various industrial fly ash samples were used as adsorbents of lignocelluloses from the SL of NSSC process and the impact of fly ash on the properties of SL was assessed. Based on the results, an equation for predicting the adsorption of lignocelluloses on fly ash as a function of charge density and surface area of fly ash was developed.

In chapter seven, lignin of SL of NSSC and prehydrolysis liquor of a kraft-based pulping were isolated and compared with kraft lignin and two commercial lignosulfonates. The properties such as charge density, sulfonated and carboxylate groups, hydraulic diameter, calorific value, ash content, thermogravimetric behaviour and activation energy of incineration of all lignin samples were measured and compared. The aim of this chapter was to identify the appropriate applications for utilizing different industrially produced lignin as dispersant, composites, flocculants, fillers and fuel.

In chapter eight, the overall conclusions were stated and future work are suggested.

In the appendices, the flocculation of lignocellulose from SL of NSSC via using polethyleneimine (PEI) was studied and pH, temperature and the dose of PEI were optimized. In another attempt, dual flocculation concept with polydiallyldimethyl-ammonium chloride

(PDADMAC) and PEI was introduced. To follow copyrights, all licence numbers given to the author of this thesis, Farshad Oveissi, were provided.

All experiments (except the study in the appendices) were solely conducted by Farshad Oveissi. The study in appendices was conducted by Thomas Sitter and Farshad Oveissi. This thesis was provided under the guidelines of Dr. Pedram Fatehi, as the sole supervisor.

1.2 HYPOTHESES

It is hypothesized that adsorption and flocculation are effective processes for isolating lignocelluloses that are dissolved in the SL of NSSC and TMP pulping processes. It is assumed that fly ash functions as adsorbent of lignocelluloses, and affects the properties of SL after adsorption treatment. It is also hypothesized that the adsorption of lignocelluloses on fillers, such as clay, occurs and this process will produce modify fillers with superior properties to unmodified fillers. Lignin that is produced via different pulping processes has different characteristics, and thus will have different end use applications. It is also hypothesized that by characterizing the structural, surface and thermal properties of lignin, its appropriate end use application can be identified.

1.3 OBJECTIVES:

This thesis has the following objectives:

1) Adsorption analysis of lignocelluloses from the SL of TMP and NSSC processes on altered adsorbents/fillers
2) Development of an integrated adsorption/flocculation process for extracting lignocelluloses from SL of TMP and NSSC processes under optimized conditions.
3) Adsorption analysis of lignocelluloses on fly ash and its impact on SL properties.
4) Investigation of the properties of extracted lignin to introduce end-use application.

1.4 NOVELTY OF THIS STUDY

This is the first attempt to isolate lignin from SL (pressate) of TMP via adsorption. For the first time, lignin dissolved in different commercially produced pulping spent liquors was comprehensively analysed and compared for introducing end use applications. There is also no report on the adsorption of lignocelluloses from pulping spent liquors on clay (i.e. bentonite, kaolin and kaolinite). Also, the utilization of power boiler fly ash in adsorbing lignocelluloses from spent liquors of pulping industries was introduced for the first time in this work.

2 CHAPTER TWO: LITERATURE REVIEW

2.1 INTRODUCTION

Forest biorefining has been introduced as an alternative for revisiting traditional pulp and paper industry (Dansereau et al., 2014; Saeed et al., 2011; Van Heiningen, 2006). Forest biorefining concept aims not only to reduce the production cost of energy, but also to produce value-added products from lignocelluloses (Van Heiningen, 2006). One scenario of biorefining is to produce value-added products from lignin and hemicelluloses that are generated, but wasted, in pulping processes. During pulping processes various liquors such as black liquor, pressates and spent liquors are produced and their lignocelluloses will be incinerated in the recovery cycle of the pulping process or treated in waste water system of the process, thus the lignocelluloses are not recovered from the liquors. This study aims to review the properties of these liquors, and compare several approaches attempted to separate lignin and hemicelluloses from the liquors and subsequently produce value-added products from the isolated lignocelluloses.

2.2 LIGNOCELLULOSES AND THEIR APPLICATIONS

Lignocellulosic materials refer to plants (wood or no-wood based) that are made from cellulose, hemicellulose and lignin (Doherty et al., 2011). The configuration of these components in woody materials is depicted in Figure 2.1. As can be seen, cellulose is surrounded by a matrix of hemicellulose and lignin. Cellulose is fully utilized and used in pulp production. Hemicelluloses are heterogeneous polysaccharides, which are classified into two groups of glucomannans and xylans. Under alkaline conditions, xylans are dissolved in oligomeric form, but glucomannas are degraded rapidly (Van Heiningen, 2006). Lignin is a cross-linked polymer with phenylpropanoid monomer structure that adds rigidity to cell walls. Monomers in lignin connected to each other via carbon-carbon and carbon-oxygen bonds. Most of the bonds between monomer units are from the carbon-oxygen linkage between a p-hydroxymoiety and the β-end of the propenyl group (β−O−4) (Thakur et al., 2014). It should be highlighted that in this study lignocelluloses account for lignin and hemicelluloses obtained from wood-based pulping liquors.

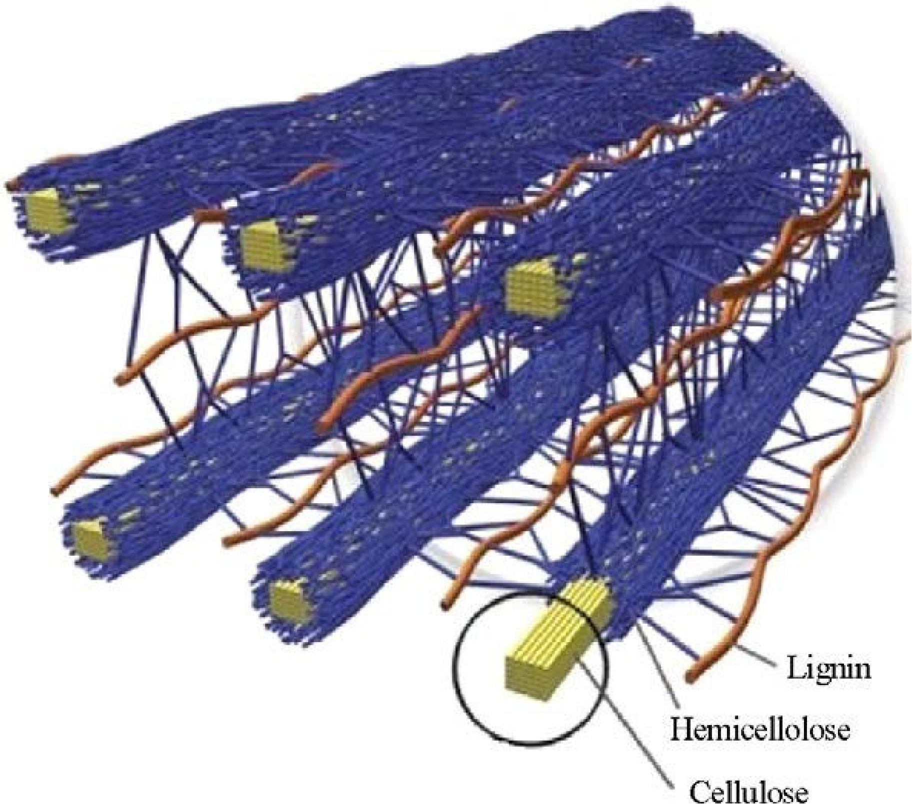

Figure 2.1. Matrix of cellulose strands surrounded by lignin and hemicellulose. Reprinted with permission from (Doherty et al., 2011). Copyright 2011 Elsevier.

2.2.1 Hemicelluloses applications

The hemicelluloses existing in pulping liquors (such as sulfite pulping spent liquor or pre-hydrolysis liquor) contain sugars that can be converted to ethanol. The production of ethanol from industrially produced spent liquor of sulfite pulping was investigated via fermentation by *S.cerevisiae* (Fatehi et al., 2011; Magdzinski, 2006). Ethanol was also produced by treating the spent liquor with other microorganisms such as *Escherichia coli* B (ATCC 11303 pLOI297) (Lawford & Rousseau, 1993) and *Pichia stipites* (Nigam, 2001). It was reported that, by utilizing the sulfite pulping spent liquor, an Eastern Canadian biorefinery (Tembec) unit produced 18 million litre ethanol via fermentation in 2006 (Magdzinski, 2006).

Generally, any lignocellulosic residual that contains 5- or 6- carbon mono sugars has the potentiality to be converted into acetic acid and furfural (Dashtban et al., 2012). In the literature, it was stated that furfural and levulinic acid can be produced from 5- and 6-carbon mono sugars in catalytic reactions (Hayes et al., 2006). The by-product of levulinic acid production is formic acid (Hayes et al., 2006). By further converting the levulinic acid, levulinate can be produced, which can be considered as fuel (Lange et al., 2010), or converted to succinic acid by oxidation.

The xyloses presented in hemicelluloses can be converted to xylitol through fermentation or hydrogenation (Mikkola et al., 1999; Rodrigues et al., 2008). Xylitol was used as sweeteners and adhesives. The production of xylitol from sulfite pulping spent liquor was extensively studied. To convert xylose to xylitol through fermentation, yeasts such as *Candida boidinii* (Vandeska et al., 1995), *Candida guiliermondii* (Rodrigues et al., 2006), *Candida tropicalis* (Kim & Oh, 2003), *Candida parapsilosis* (Oh et al., 1998) and *Debaryomyces hansenii* (Parajó et al., 1998) were used in the past. Xylitol dehydrogenase can reoxidize the produced xylitol to xylulose (Granström et al., 2007). Xylitol can also be produced by hydrogenating xylose under aqueous solution of alcohol (in the presence of Raney nickel catalyst) (Mikkola et al., 2000). Xylulose and arabinitol are the by-products of hydrogenation process (Mikkola et al., 2000). Xylanase is another chemical that can be produced through bioconversion of xylose in pulping liquors. One study on the stream obtained from the third evaporator of acid based sulfite pulping process showed that the maximum xylanse concentration of 200 U/ml was achieved after 10 h treating with *Aspergillus oryzae* NRRL 3485 or *Aspergillus phoenicis* ATCC 13157 (Chipeta et al., 2005). The optimum pH were 6.5 and 5 and the optimal temperatures were 65 and 50 °C for *Aspergillus oryzae* NRRL 3485 and *Aspergillus phoenicis*, respectively (Chipeta et al., 2005).

2.2.2 Lignin applications

Kraft lignin has a heating value of 27 MJ/kg, which worth $99 per oven dry metric ton (Van Heiningen, 2006). Possessing such a high heating value would make lignin as valuable fuel. Lignin can be used in production of value-added products such as carbon fiber, epoxy resins and adhesives (Kumar et al., 2009; Lora & Glasser, 2002). The carbon fiber made from lignin (steam-exploded lignin of birch wood) had the elongation of 1.63 ± 0.29 %, tensile strength of 660 ± 230 MPa and modulus of elasticity of 40.7 ± 6.3 GPa (Sudo & Shimizu, 1992). Lignin was suggested as an ideal polymer for developing composites due to its biodegradable nature, reinforcing capability and high abundance (Thakur et al., 2014). In the literature, methylated softwood ammonium lignosulfate and Eucalyptus lignin derived from bark were used to be substituted for phenol in phenol-formaldehyde composites (Khan et al., 2004). The integration of lignin into phenol-formaldehyde resins can be accomplished in different ways: 1) treating lignin with formaldyhide and then adding treated lignin to the phenol-formaldehyde resin (Forss & Fuhrmann, 1979); 2) adding lignin to a mixture of phenol and formaldehyde solutions (Khan et al., 2004) and 3) pretreating lignin with formaldehyde and/or phenol (OH et al., 1994).

Lignosulfonate that is produced in sulfite pulping process has a sulfonated group on its structure, which makes it an anionic hydrophilic material. It was claimed that lignosulfonate could also be utilized in phenol/formaldehyde resin insolation board as an adhesive (Budin et al., 1990). Additionally, lignosulfonate was suggested as dispersant, flocculant and adsorbant. In one study, the sulfonation of alkali lignin (i.e. lignin that is produced in alkaline pulping) was attempted and sulfonated alkali lignin was evaluated as a dispersing agent in cement (Ouyang et al., 2009). In another work, lignosulfonate was used as a flocculant for talc ($Mg_3Si_4O_{10}(OH)_3$) and other phyllosilicates in molybdenum concentrates (Hiscox et al., 1975). Lignin was also modified and used as an adsorbant of metal ions in various studies. In one study, the adsorption of heavy metal ions Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) from wastewater on lignin, isolated from black liquor, was investigated (Guo et al., 2008). The affinity of metal ions to be adsorbed on lignin was with the following order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II) (Guo et al., 2008). In another study, it was concluded that lignin, obtained from black liquor, had the potential to be considered as an effective and economical adsorbent for removing Cr(III) from wastewaters (Wu et al., 2008).

Recent studies on the adsorption of lignin and hemicelluloses from pre-hydrolysis liquor of kraft based dissolving pulp process on activated carbon, calcium carbonate and calcium oxide suggested that the products can be used as modified fillers in a variety of applications such as papermaking and composites (Fatehi et al., 2013a; Liu et al., 2011a; Shen et al., 2011a; Shen et al., 2011b).

2.3 PULPING METHODS

2.3.1 Mechanical pulping

Mechanical pulping is the oldest method of pulping, which involves shredding wood chips between the rotating discs of a refiner. The product of this process is known as refiner mechanical pulp (RMP). Thermomechanical pulping (TMP) is a modified RMP method, which involves steaming the wood chips at 130 °C prior to refining. This process dissolved a part of lignin, extractives (and sometime hemicelluloses) in the spelt liquor. The spent liquor (pressate) of this pretreatment dissolves a portion of lignocelluloses, which is currently treated in wastewater of the mill. The dominant product of TMP pulping is high-tear pulp with high tear strength for newsprint and boards.

2.3.2 Chemical pulping

2.3.2.1 Sulfite process

In the sulfite pulping process, wood chips are treated with cooking liquors in a digester. The cooking liquor is prepared by incinerating sulfur (to produce SO_2 gas) followed by absorbing the generated SO_2 in an alkaline base solution such as NH_4OH, $Mg(OH)_2$ and Na_2CO_3 (Smook, 2002). The digester is initially filled with wood chips and capped. Then sufficient amount of cooking liquor is added to fill the vessel. The cooking process is usually conducted in the pH range of 1.5-5 and the temperature range of 140-160 °C (Smook, 2002). The residual liquor is known as spent sulfite liquor.

The sulfite pulping dissolves the majority of lignin (by the cleavage of the α-ether and β-ether linkages existing in native lignin) and a part of hemicelluloses of wood chips in the present liquor (Alen, 2000). This process can be described as four distinct stages from chemical reaction point of view: (1) the generation of relatively insoluble lignosulfonic acid from the reaction of lignin and sulfuric acid; (2) the formation of semi-soluble lignosulfonates with various cations (NH_4^+, Mg^{2+} or Na^+); (3) the fragmentation of lignosulfonates (Alen, 2000) and (4) the hydrolysis of hemicelluloses into soluble sugars (Smook, 2002). The lignosulfonates produced from sulfite pulping process is cross-linked with an average sulfur content of 5% and highly soluble in water (Hawley & Wise, 1926).

2.3.2.2 Kraft process

The most predominant pulping method is kraft (the German word for strength) (Smook, 2002). In kraft pulping, white liquor containing sodium sulfide and sodium hydroxide is used for cooking wood chips. After cooking and washing, pulp is separated from the residual pulping spent liquor (black liquor). Black liquor, which contains the reaction products of lignin solubilisation, is concentrated and burned in the recovery furnace to yield sodium carbonate and sodium sulfide. Subsequently, the smelt chemicals are dissolved to form a green liquor, which is reacted with quick lime (calcium oxide) in order to convert sodium carbonate into sodium hydroxide and regenerate the white liquor.

During kraft process, a part of β-1-4 linkage in the cellulose of wood chips is cleaved by the alkaline hydrolysis provided by sodium sulfide and sodium hydroxide. Also, the ether linkages in lignin are cleaved by base-induced hydrolysis (Baucher et al., 2003). The α-ethyl bonds are more vulnerable to cleavage than the β-aryl ether bonds, if there is a free phenolic hydroxide group present (all of the phenyl propene subunits present in lignin contain this group) (Baucher et al., 2003; Sakakibara et al., 1966). The kraft process produces lignin that marginally contains sulfur (less than 2 wt.%) (Doherty et al., 2011). The sulfur is present as aliphatic thiol groups in kraft lignin. Consequently, the produced lignin is hydrophobic due to the lack of sulfonated groups on its structure (Hu et al., 2011). However, the hemicelluloses dissolved in black liquor are degraded to organic acids under strong alkaline conditions.

2.3.2.3 Dissolving pulp

Dissolving pulps are chemical pulps that are used in manufacturing rayon fibers, cellulose acetate, cellophane, cellulose nitrate and carboxymethyl cellulose. Dissolving pulps can be produced by either a modified kraft or sulfite process (Zhu et al., 2011). It was reported that in 2011, 40 % of current dissolving pulp was manufactured through kraft-based pulping and the rest was produced via sulfite-based pulping (Zhu et al., 2011). In dissolving pulp processes, both lignin and hemicelluloses must be removed as they are considered unfavorable. Therefore, in kraft-based pulping, wood chips are hydrolyzed with steam prior to digesting. The liquor that is generated in this pretreatment stage is known as pre-hydrolysis liquor (PHL), which contains hemicelluloses and lignin. Currently, PHL is combined with black liquor and incinerated in the recovery cycle of the kraft process (Liu et al., 2011a; Saeed et al., 2011).

2.3.3 Hybrid pulping

Hybrid pulping combines chemical and mechanical pulping methods. The most widely used hybrid method is neutral sulfite semichemical (NSSC) pulping. In this process wood chips are cooked with sodium sulfite cooking liquor that is usually buffered with sodium carbonate to neutralize the organic acids released from the wood chips during cooking. During this process, a part of lignin was removed by sulfite ion. The spent liquor that is generated the digester dissolved lignocelluloses, which is currently treated in wastewater of the mill. The main product of NSSC pulping is corrugated board.

2.4 ALTERNATIVES FOR SEPARATING LIGNOCELLULOSES FROM PULPING SPENT LIQUORS

As was discussed in the previous section, pulping liquors contain lignin and hemicelluloses. These lignocelluloses could be used in the production of various value-added products. In this regard, several alternatives were suggested in literature.

2.4.1 Acidification

The aim of this method is to precipitate soluble lignin by acidifying spent liquors. In the literature, this process was mostly suggested for black liquor (Lisboa et al., 2005; Mussatto et al., 2007; Sun & Tomkinson, 2001; Yuan et al., 2009). It was reported that 81.43 % of soluble lignin was removed from black liquor by decreasing the pH from 12.5 to 2.15 (Mussatto et al., 2007). Acidification may degrade some oligomeric sugars from pulping liquors. It was previously observed that by acidifying black liquor, a major part of the 4-O-methylglucuronic units in xylan were degraded to hexenuronic (4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid) units (Lisboa et al., 2005). This process is considered as an effective pretreatment for further enzymatic hydrolysis (Alvira et al., 2010; Taherzadeh & Karimi, 2008). The main disadvantage of this process is the cost of treatment and the use of acid that is corrosive (Alvira et al., 2010).

2.4.2 LignoBoost and LignoForce technologies

Lignin has been traditionally separated from black liquors based on acidification concept. The acidification is usually followed by filtration and these filters have blocking issues. The high amount of impurities within the separated lignin is another problem of this method. Recently, two methods have been commercially developed to isolate lignin from black liquor; LignoBoost and LignoForce.

2.4.2.1 LignoBoost

In this process, black liquor is treated with carbon dioxide to reduce its pH to 10, which aids lignin to precipitate (Tomani, 2010). The LignoBoost process is slightly different from traditional acidification. In LignoBoost process, after acidification with carbon dioxide, the precipitates are dispersed and washed with acid before filtration. Compared to the traditional methods, LignoBoost has been found to reduce investment costs by circumventing the need for larger filters, decrease the operational costs by reducing the amount of sulfuric acid and is able to increase the yield and purity of produced kraft lignin.

2.4.2.2 LignoForce

LignoForce is the most recent technology to isolate lignin from black liquor (Kouisni et al., 2012). In this method, black liquor is concentrated, cooled and precipitated by adding a mixture of carbon dioxide and oxygen. Subsequently, the lignin is washed without forming cake, but filter pressed. This process results a high purity of kraft lignin, reduces consumption of carbon dioxide and removes the H_2S emissions. A pilot plant facility, built by FPInnovations and NORAM, at the Resolute Thunder Bay (Ontario, Canada) mill produces 12.5 kg/h of high quality lignin via LignoForce technology.

2.4.3 Evaporation

Evaporation has been used industrially to concentrate sulfite pulping's spent liquor (Benjamin et al., 1984; Kringstad & Lindström, 1984; Marques et al., 2009). It was reported that a mill in Portugal concentrated its spent sulfite liquor with 7 evaporators with an average residence time of 50-60 min (Marques et al., 2009). The temperatures of the first and the last effects of evaporation in the aforementioned mill were 142 and 74 °C, respectively (Marques et al., 2009). During the evaporation process, inorganic salts may precipitate and cause fouling problems (Fatehi et al., 2011). Also, evaporation would not be economical for most pulping liquors due to the high volume of these liquors per ton of pulp produced (Fatehi et al., 2011).

2.4.4 Solvent extraction

Liquid-liquid extraction was suggested as an alternative to separate lignocelluloses from spent liquor of sulfite pulping process (Lin, 1992). In this process, lignocelluloses absorb to an organic solvent such as polyethylenimine (Haars et al., 1981), tri-n-hexyl-amine (Eisenbraun, 1963) and long chain aliphatic amine (Kontturi & Sundholm, 1986) to develop adducts that are insoluble in the aqueous phase. After extraction, the solvent (amine) is totally removed to recover the lignocelluloses, which is a disadvantage (Ringena et al., 2005). Other issues of extraction with amine based solvents are foaming, formation of NaCl and handling emulsions (Ringena et al., 2005). In addition, the molar mass and the degree of sulfonation of lignosulfonates complicates the extraction process (Fatehi et al., 2011; Ringena et al., 2005). The high consumption of organic solvent makes this method expensive (Fatehi et al., 2011).

2.4.5 Membrane

The recovery of lignocelluloses from pulping liquors through membrane processes have been extensively studied over the past decades (Jonsson & Wallberg, 2009; Restolho et al., 2009; Wallberg & Jönsson, 2006). Table 2.1 lists some of the membrane processes that were applied on various pulping liquors. It should be stated that the transmembrane pressure (Δp) in Table 2.1, was defined as the pressure difference across the membrane (Jonsson & Wallberg, 2009):

$$\Delta p = \frac{p_{in} + p_{out}}{2}$$

−

p��$_p$

��$_p$��$_p$

��pppp

p��o��

pp

and the rejection ratio (a.k.a. retention) of lignin or hemicelluloses was calculated by (Albright, 2008):

$$RR = 1 - \frac{C_{permeate}}{C_{retentate}}$$

which $C_{permeate}$ and $C_{retentate}$ are the concentrations of a component (lignin or hemicelluloses) in the permeate and in the retentate, correspondingly. As can be seen, the rejections of lignin and hemicelluloses through polymeric membranes were higher than that of ceramic membranes.

Numerous studies were conducted on the isolation of lignocelluloses from spent liquor of sulfite pulping process via ultrafiltration (Bhattacharya et al., 2005; Collins et al., 1973; Kovasin & Norden, 1984; Weis et al., 2003; Weis et al., 2005). One study on separating hemicelluloses from spent liquor of neutral sulfite semi-chemical (NSSC) pulping process using cellulose acetate membrane showed that the concentration of hemicelluloses increased from 22-26 wt. % to 40-52 wt.% and the rejection of lignosulfonates was within the range of 80-96 wt. % (Collins et al., 1973). Another study on ultrafiltration of lignosulfonates (from spent liquors) using polysulphone, cellulose acetate, fluoropolymer showed that the rejections of lignosulfonate were almost constant and equal to 80-84 % at the molecular cut-offs of 20-100 kDa (Weis et al., 2005).Based on Table 2.1, it is evident the polymeric membranes (i.e. polysulfone, polyethersulfone, polyamide) were resulted in higher rejections of lignocelluloses than ceramic ones. Table 2.1 also illustrates that a high rejection of lignin is mostly occurred at higher transmembrane pressures (more than 10 bar) in ultrafiltration. The rejections of lignin and hemicelluloses were generally higher via reverse osmosis than ultrafiltration. However, the purity of lignin was higher through ultrafiltration than reverse osmosis, as the ultrafiltration was more selective to lignin than hemicelluloses.

Nanofiltration was also used for rejection of lignocelluloses, however, the main disadvantage of these membranes are blocking and high costs.

The main advantage of membrane process is that it can be conducted in almost any range of pHs and temperatures. (Jonsson & Wallberg, 2009; Nordin & Jonsson, 2009). However, to avoid liquor flashing and breaking the membrane, the pressures on retentate and permeate sides of the membrane must be higher than the saturation pressure of the pulping liquor (Wallberg & Jönsson, 2006). Consequently, membrane processes could not be economical for separation lignocelluloses in dilute form such as pressates and pre-hydrolysis liquor (PHL) of kraft pulping due to their high cost of operations (Zaied & Bellakhal, 2009).

Table 2.1. Membrane processes for isolation of lignin and hemicelluloses from different liquors

Method	**Type of liquor**	**Process condition**	**Retentate**	**Reference**
Ultrafiltration and Nanofiltration	Black liquor ($C_{L,0}^1 = 60$ g/l)	Ultrafiltration at Δp^2=120 kPa, 5 m/s, 90 °C, $VR^3 = 0.9$ with a 15 kDa ceramic membrane followed by nanofiltration at 60 °C with a polymeric membrane and the nominal cut-off of 1 kDa.	R_L^4= 80%	(Jönsson et al., 2008)
Ultrafiltration	Kraft (softwood) cooking liquor ($C_{L,0}$ = 69 g/l)	145 °C, Δp = 400 kPa, VR = 0.3, 100 L/m, 2 h with a 1 ceramic membrane and nominal cut-off of 5 kDa.	R_L= 20 % C_L = 110 g/l	(Wallberg & Jönsson, 2006)
Ultrafiltration and diafiltration	Spent sulphate black liquor ($C_{L,0}$ = 75 kg/m^3)	Δp = 1MPa, 0.450 m^3/m^{2}d, 0.5 m/s, 28 h, with a polyacrylonitrile membrane with the nominal cut-off of 20 kDa.	R_L= 85.2 %	(Tanistra & Bodzek, 1998)
Ultrafiltration	Kraft black liquor ($C_{L,0}$ = 62 kg/m^3)	Δp = 200 kPa, 90 °C, 0.160 L/m^{2}h, VR = 0.9, via a ceramic membrane with nominal weight cut-off of 15 kDa.	R_L= 35 %	(Holmqvist et al., 2005)
Nanofiltration	Softwood black liquor ($C_{L,0}$ = 78.6 g/l)	Δp = 0.5MPa, 70 °C, ceramic membrane with nominal weight cut-off of 1 kDa molecular weight cut-off coated with ZrO_2.	R_L= NR C_L= 25.2 g/l	(Keyoumu et al., 2004)

[1] $C_{0,L}$ and $C_{0,H}$ represent initial concentrations of lignin and hemicelluloses, respectively.

[2] Transmembrane pressure (Δp)

[3] Volumetric reduction (the ratio between the volume of permeate withdrawn and the initial feed volume)

[4] R_L and R_H corresponds to rejections of lignin and hemicelluloses, respectively.

Continued on next page

Table 2.1 continued

Method	Type of liquor	Process condition	Retentate	Reference
Ultrafiltration	Filtrate from a disc filter of thermo-mechanical pulping ($C_{H,0}$ = 0.7 g/l, $C_{L,0}$ = 0.6 g/l)	Δp = 4 bar, 65-75 °C, VR = 0.45 with permanently hydrophilic polysulphone membrane and nominal weight cut-off of 5 kDa.	R_L= 40 % R_H= 90 % C_L = 2 g/l C_H = 12 g/l	(Persson & Jönsson, 2010)
Nanofiltration	Eucalyptus spent sulphite liquor ($C_{H,0}$ = 32 g/l, $C_{L,0}$ = 59 g/l)	Δp = 20 bar, 25 °C and polyethersulphone membrane weight cut-off of 1 kDa.	R_L= 98 % R_H= 77 %	(Restolho et al., 2009)
Reverse osmosis	Eucalyptus spent sulphite liquor ($C_{H,0}$ = 32 g/l, $C_{L,0}$ = 59 g/l)	Δp = 20 bar, 25 °C and Polyamide thin film composite weight cut-off of 10 kDa.	R_L= 97 % R_H= 95 %	(Restolho et al., 2009)
Ultrafiltration	Eucalyptus spent sulphite liquor ($C_{H,0}$ = 32 g/l, $C_{L,0}$ = 59 g/l)	Δp = 7 bar, 25 °C and polyethersulphone membrane with nominal weight cut-off of 10 kDa.	R_L= 68 % R_H= 3 %	(Restolho et al., 2009)

2.4.6 Adsorption

Adsorption has a wide application in many industries including the mining. In this phenomenon, adsorbent which is a porous solid with active sites adsorbs specific constituent (adsorbate) from solutions/suspensions. If adsorption occurs based on a physical attraction, it would be called as physisorption (Albright, 2008). Chemisorption is defined when adsorption is based on chemical bonding through electron transfer. The efficiency of adsorption mostly reported via percentage of adsorbate's removal from fluid. Adsorption isotherm can describe the mobility of adsorbate from fluid into the solid phase. In this regard, numerous isotherm models (i.e. Langmuir and Freundlich expressions) have been defined and widely used over the years (Foo & Hameed, 2010). Adsorption is generally fast, selective and economical depending on the type of adsorbents. Adsorption is also a feasible process to treat dilute concentration of constituents. Hence, the adsorption concept has been subjected in several studies on pulping liquors recently, and the results are listed in Table 2.2. As can be seen, one significant advantage of adsorption of lignocelluloses from pulping liquors is the mild process condition (maximum adsorption was mostly achieved in neutral pH and room temperature). The highest adsorption was achieved on activated carbons. Activated carbons have been selected as an adsorbent in various industries due to their relatively large specific surface area, porous medium, relatively high charge density and low price (Fatehi et al., 2013b; Lin et al., 2008; Liu et al., 2011a). It was reported that the price of activated carbon is in the range of $US 1,650-9,900 per ton depending on its origin (Zhi et al., 2014). Also, activated carbon could be easily recovered for reuse (Gutsch & Sixta, 2012; Palomar et al., 2012). Table 2.2 also shows that the modification of activated carbon with cationic polymers (i.e. polydiallyldimethyl-ammonium chloride (PDADMAC) and chitosan) and sulfuric acid could increase the adsorption of lignocelluloses. These modifications had been applied to increase the cationic charges associated with the surface of activated carbons. It was claimed that lignocelluloses had anionic charge densities, which might be due to their carboxylated, sulfonated or carbonyl groups (Saeed et al., 2011). Therefore, introducing oxygen to the sorbent or taking electrons from activated carbon would enhance the efficiency of adsorption.

Fly ash is generated in power generating boilers by burning wood residual, bark and coals, and they were considered as an adsorbent recently (Andersson et al., 2012). The utilization of fly ash for the adsorption of several organic compounds (i.e. phenols) from wastewater effluents and air was expressively discussed (Ahmaruzzaman, 2010). Also, lignin has been removed from aqueous solutions via using fly ash (Andersson et al., 2012; Li et al., 2012).

Recently, clay (i.e. bentonite) was also considered for the removals of phenols and toxic metals from aqueous solutions (Fernández-Pérez et al., 2005; Lee & Tiwari, 2012; Richards & Bouazza, 2007). One study revealed that 8 mg/g of phenol (initial concentration of 60 mg/l) adsorbed on modified bentonite at 25 °C, pH 6.5 and 2 h (Alkaram et al., 2009). Another study on model wood-based polymers reported that, under optimal conditions of 22 °C and 1 h, the adsorptions of sulfonated kraft lignin and blue dextran were almost 50 and 150 mg/g on bentonite, respectively (Asselman & Garnier, 2000). Economically, bentonite costs US$ 107 per ton (Carmignano & Carvalho, 2014), which is almost 500 times less than that of activate carbons. Consequently, bentonite and fly ash have the potentiality to be considered as adsorbents for isolating lignocelluloses from SL from economic point of view.

Table 2.2 also listed the application of some fillers (i.e. calcium carbonate and calcium oxide) as adsorbents for lignocellulose removals. It is evident that the adsorption of lignocelluloses on such adsorbents was less than that of activated carbons. This phenomenon might be due to the smaller surface area and charge density of fillers than those of activated carbons. It was stated that the product of such adsorption can be used as modified fillers in a variety of applications such as papermaking and composites (i.e. corrugated paper) (Fatehi et al., 2013a; Liu et al., 2011a; Shen et al., 2011a; Shen et al., 2011b).

Table 2.2. Adsorption of lignin and hemicelluloses from different liquors on various adsorbents

Adsorbent	**Type of liquor**	**Process condition**	**Adsorption**	**Reference**
Activated carbon	Model PHL (MPHL) $C_{L,0}$[1] = 20 g/l $C_{Xylan,0}$ = 20 g/l	pH 7, room temperature, 120 rpm and 50 wt. AC/MPHL for 360 min.	Q_L[2]= 194 mg/g Q_{Xylan} = 140 mg/g	(Fatehi et al., 2013b)
Calcium carbonate	PHL treated by 0.03 wt.% dodecyltrimethyl ammonium chloride (DTAC) $C_{L,0}$ = 15.1 g/l $C_{H,0}$ = 31.6 g/l	pH 7, 40 °C, 120 rpm and wt. ratio of 40 for 5 h.	Q_L = 80 mg/g Q_H = 200 mg/g	(Fatehi et al., 2013a)
Lime	PHL $C_{L,0}$ = 9.22 g/l	Lime was added at the dosage of 1.7 %, pH 11.5, 150 rpm and 78 °C for 1 h.	Q_L = NR (25 % removal)	(Shen et al., 2011a)
Lime mud	PHL $C_{L,0}$ = 5.35 g/l $C_{H,0}$ = 31.6 g/l	Lime mud was added at 5 wt.%, 26 °C and 150 rpm for 1h	Q_L = 16 mg/g Q_H = 7.8 mg/g	(Shen et al., 2011b)

[1] Subscripts "L" and "H" correspond to lignin and hemicelluloses
[2] "Q" represents the amount of adsorption

Continued on next page

Table 2.2 continued

Adsorbent	**Type of liquor**	**Process condition**	**Adsorption**	**Reference**
Modified activated carbon (treated with PDADMAC)	PHL $C_{L,0}$ = 5.35 g/l $C_{H,0}$ = 31.6 g/l	1 g modified activated carbon (treated with 0.2 mg/g PDAMAC) was added to 20 g of PHL at room temperature, 150 rpm and pH 7 for 24 h.	Q_L = 340 mg/g Q_H = 440 mg/g	(Liu et al., 2011b)
Modified activated carbon (treated with chitosan)	PHL $C_{L,0}$ = 11.78 g/l $C_{H,0}$ = 23.11 g/l	1 g modified activated carbon (treated with 2.4 mg/g chitosan) was added to 20 g of PHL at room temperature, 150 rpm and pH 7 for 24 h.	Q_L = 280 mg/g Q_H = 390 mg/g	(Liu et al., 2011b)
Oxidized activated carbon (treated with H_2SO_4)	PHL $C_{L,0}$ = 11.78 g/l $C_{H,0}$ = 23.11 g/l	1 g oxidized activated carbon (treated with 20% H_2SO_4) was added to 120 ml PHL at room temperature and pH 7 for 6 h.	Q_L = 300 mg/g Q_H = 700 mg/g	(Liu et al., 2011a)
Steam boiler fly ash	Bleaching effluent of TMP $C_{L,0}$ = 1.4 g/l	Fly ash was added at the dosage of 50 g/l to the bleaching effluent at pH 7, 200 rpm and room temperature for 6 h.	Q_L = 5 mg/g	(Andersson et al., 2012)
Coal fly ash	Calcium lignosulfonates (CLS) $C_{L,0}$ = 1 g/l	20 g/l coal fly ash was added to CLS solution at 30 °C, pH 7.6 and 150 rpm for 2 h.	Q_L = 34.2 mg/g	(Li et al., 2012)

2.4.7 Flocculation

The flocculation process has been applied in wastewater treatments for decades. The separation of lignocelluloses can be performed by charge interaction, patching or bridging phenomena which are followed by precipitation. The charge density of polymers participating in flocculation plays a significant role (Barany et al., 2011; Gregory & Barany, 2011; Zavgorodnya & Serpe, 2011). The removal of lignocelluloses from prehydrolysis liquor and hydrolyzate of wood (treating wood chips with hot water at 160 °C for 15 min) through various flocculants and surfactants was summarized in Table 2.3. As can be seen, flocculation is a fast process, it is mostly completed in 10-15 min. Hence, among all reported alternatives, flocculation was the fastest method to remove lignocelluloses. Also, in all studies that have been conducted on the removal of lignocelluloses from pulping liquors, the flocculant was cationic. It was stated that lignin and hemicelluloses contain anionic charge which accounts for sulfonate, carboxylate and carbonyl groups (Saeed et al., 2011). The shorter the time of treatment, the smaller the size of plant and subsequently the lower the investment will be. Flocculation has be mostly conducted on PHL rather than other types of liquors. The dosage of added flocculant or surfactant to PHL varied from 0.07 to 0.3 % depending on charge density and molecular weight of flocculant or surfactant. It is also evident that the maximum removal of lignocelluloses was not exceeded from 40 %. Subsequently, the treated liquor can further be processed to produce value-added products.

Table 2.3. Isolation of lignin and hemicelluloses from different liquors via flocculation

Flocculant/ Surfactant	**Type of liquor**	**Process condition**	**Removal**	**Reference**
Polyethylene oxide (PEO)	Pre-hydrolysis liquor (PHL) $C_{L,0}{}^{1}$ = 11.3 g/l	350 mg/l (PEO/PHL), at room temperature, 120 rpm, for 10 min.	R_L = 1.2 %	(Liu et al., 2013)
Dodecyltrimethyl ammonium chloride (DTAC)	PHL $C_{L,0}$ = 11.32 g/l $C_{H,0}$ = 30.02 g/l	0.06 g DTAC was added to 20 g PHL at pH 3.5, room temperature, 100 rpm for 10 min.	R_L = 17.5 % R_H = 12.1 %	(Shi et al., 2012)
Dodecyltrimethyl ammonium bromide (DTAB)	PHL $C_{L,0}$ = 11.32 g/l	0.06 g DTAB was added to 20 g PHL at pH 3.5, room temperature, 100 rpm for 10 min.	R_L = 13.6 %	(Shi et al., 2012)
Cationic alkoxylated amine surfactant (CAAS)	PHL $C_{L,0}$ = 11.32 g/l	0.06 g CAAS was added to 20 g PHL at pH 3.5, room temperature and 100 rpm for 10 min.	R_L = 4 %	(Shi et al., 2012)
Chitosan	PHL $C_{L,0}$ = 9.3 g/l $C_{H,0}$ = 15.9 g/l	0.7 mg/g low molecular weight chitosan was added to PHL at room temperature.	R_L = 40 % R_H = 20 %	(Saeed et al., 2011)
Polydiallyldimethyl-ammonium chloride (PDADMAC)	Hydrolyzate of wood (hot-water extraction) $C_{L,0}$ = 12.8 g/l $C_{H,0}$ = 31.1 g/l	PDADMAC was added to hydrolyzate at the dose of 47.3 ppm and pH 4.5 for 15min.	R_L = 36 % R_H= 4 %	(Duarte et al., 2010)

[1] Subscripts "L" and "H" correspond to lignin and hemicelluloses

[2] "R" represents the amount of removal

2.4.8 Modified processes; combination of processes

As previous discussed, various combinations of processes can be applied to isolate the lignocelluloses from pulping liquors, and they are listed in Table 2.4. In one study, by adding calcium carbonate to PHL at a dosage of 0.8 mg/g, lignin and hemicelluloses reached the adsorption equilibrium of 58 mg/g and 125 mg/g on calcium carbonate, respectively (Fatehi et al., 2013c). In the current study, 0.8 mg/g polydiallyldimethylammonium chloride (i.e. flocculation concept) was added to PHL and the adsorption of lignin and hemicelluloses were improved from 0.2 mg/g to 0.53 mg/g (Fatehi et al., 2013c). The aim of combing processes is not only to achieve a higher removal but also to make precipitated fillers or flocs with valuable characteristics (i.e. high charge density and/or heating value). It was suggested that the final product of such process can be used in composites (Fatehi et al., 2013c). Alternatively, PHL was initially treated with a surfactant (mostly dodecyltrimethylammonium (DTAC)) in another study (Shi et al., 2012). It was stated the surfactants mostly interacted with lignin rather than hemicelluloses (Shi et al., 2012). Also, the complex, which would be made from lignin and surfactant, is larger in size. Therefore, a combined process of flocculation and adsorption helps not only remove more hemicelluloses and lignin from spent liquors, but makes complexes with different sizes. It is also well known that polymers with a large hydrodynamic diameter has stronger steric hindrance effect, which results in higher dispersion (Ran et al., 2009). It was stated that small polymers would diffuse more than large ones into pores of an adsorbent (Bjelopavlic et al., 1999). Therefore, if used as a surface modifier of a filler (i.e. adsorbent), more of small polymers will be diffused into the filler structure and thus its surface modifying performance will be weakened (Fatehi et al., 2013a). Instead, more of large polymers will adsorb on the surface of filler and modify its surface properties (Huang et al., 2013).

Table 2.4. Separation of lignocelluloses from various liquors via modified adsorption/ flocculation

Method	Type of liquor	Process condition	Removal or adsorption	Ref.
Acidification and flocculation	PHL $C_{L,0}$ [1]= 11.3 g/l	First PHL acidified at pH 2 then polyethylene oxide (PEO) was added to the supernatant at the dosage of 350 mg/L, room temperature and 120 rpm for 10 min	R_L[2]= 22.75 %	(Liu et al., 2013)
Adsorption and flocculation	PHL treated by 0.03 wt.% dodecyltrimethyl ammonium chloride (DTAC) $C_{L,0}$ = 15.1 g/l $C_{H,0}$ = 31.6 g/l	First adsorption on calcium carbonate: pH 7, 40 °C, 120 rpm, wt. ratio of 40 ($PHL/CaCO_3$) for 24 h then cationic polyacrylamide (CPAM) was added (flocculant) at the dosage of 8 mg/g, pH 7 for 90 min	Q_L[3] = 0.28 g/g Q_H = 0.019 g/g	(Fatehi et al., 2013a)
Adsorption and flocculation	Model PHL (MPHL) $C_{L,0}$ = 20 g/l $C_{Xylan,0}$ = 20 g/l	First adsorption on activated carbon (50 wt. MPHL/AC), pH 7, room temperature for 360 min, then 0.5 g/l PDADMAC (polydiallyldimethylammonium chloride) was added at 120 rpm for another 2 h.	Q_L = 0.35 g/g Q_{Xylan} = 0.19 g/g	(Fatehi et al., 2013b)

[1] Subscripts “L” and “H” correspond to lignin and hemicelluloses

[2] “Q” and “R” correspond to the amount of adsorption and removal, respectively.

Continued on next page

Table 2.4 continued

Method	**Type of liquor**	**Process condition**	**Removal or adsorption**	**Ref.**
Adsorption and flocculation	Treated PHL with DTAC and CaO $C_{L,0}$ = 8 g/l $C_{H,0}$ = 29.2 g/l	First adsorption on precipitated calcium carbonate (50 wt. treated PHL/$CaCO_3$), 40 °C and 120 rpm for 90 min. Then 0.8 g/l PDADMAC was added at 120 rpm for another 90 min.	Q_L = 0.203 g/g Q_H = 0.53 g/g	(Fatehi et al., 2013c)
Adsorption and flocculation	PHL $C_{L,0}$ = 5.35 g/l $C_{H,0}$ = 31.6 g/l	First adsorption on Lime mud at the dosage of 5 wt.%, 26 °C, 150 rpm for 1h . Then 0.1 wt. % PDADMAC (based on the weight of PHL) was added at the same condition of adsorption but for 1 h.	Q_L = 36 mg/g Q_H = 16 mg/g	(Shen et al., 2011b)

2.5 UTILIZATION OF FLY ASH

Fly ash is generated in power generating boilers by burning wood residues, bark coals and has been employed as an adsorbent recently. The disposal of fly ash produced in power generators will soon be too expensive if not prohibited (Ahmaruzzaman, 2010). Consequently, the utilization of fly ash reduced the environmental concerns and has industrial applications. The application of fly ash will be discussed in the following sections.

2.5.1 Construction

Addition of modified gypsum with fly ash in cement and modifying cement with ash in Portland cement are the main applications that have been studied for fly ash in the construction field (Mehta & Gjørv, 1982; Poon et al., 2001). It was stated that the addition of fly ash to admixture would intensify compressive strength and corrosion resistance of the concrete (Maslehuddin et al., 1989).

2.5.2 Removal of dyes from wastewater

Pigments and dye are mostly released into wastewater from various industrial sources. Among all attempts that have been conducted on dye removal (i.e. flocculation), adsorption has been considered as a favourable alternative especially when the adsorbent does not require any pretreatment and is inexpensive (Ramakrishna & Viraraghavan, 1997). Fly ash has been used as an adsorbent for different dyes such as methylene blue (Janoš et al., 2003; Ramakrishna & Viraraghavan, 1997; Wang & Wu, 2006), crystal violet (Dizge et al., 2008; Mohan et al., 2002), rosaline hydrochloride (Mohan et al., 2002), rhodamine B (Janoš et al., 2003), egacid orange II (Janoš et al., 2003), acid blue (Ramakrishna & Viraraghavan, 1997), malachite green (Mall et al., 2005a) and congo red (Acemioğlu, 2004). Table 2.5 shows the amount of aforementioned dye adoptions on fly ash. It should be highlighted that, rather than temperature, other operating conditions were not reported in the literautres. As can be seen, the pretreatment of fly ash with NaOH improved the adsorption of methylene blue from 6.0×10^{-6} to 8.0×10^{-6} mol/g. Also, Table 2.5 shows that the amount of adsorption of dye on fly ash (FA) is a function of its origin. For instance, the adsorption of methylene blue on Colombian FA and Thai FA were almost 2×10^{-5}

and 1.6 × 10^{-5} mol/g, respectively. Table 2.5 also illustrates that FA with a high carbon content adsorbed 100 times more crystal violet than carbon-free FA, as their adsorptions were 10^{-4} and 10^{-6} mol/g, respectively. It is evident that bagasse FA was more effective for malachite green than cogno red and orange-G. This might be due to the various functional groups and charge density that associated with the aforementioned dyes.

Table 2.5. Utilizations of fly ash in dye removal reprinted with permission (Ahmaruzzaman, 2010). Copyright 2010 Elsevier.

Dye	Fly ash type	Adsorption (mol/g)	Temperature (°C)	Reference
Methylene blue	Coal FA	14.4×10^{-5}	25	(Viraraghavan & Ramakrishna, 1999)
Methylene blue	FA-HNO_3	2.2×10^{-5}	30	(Wang & Wu, 2006)
Methylene blue	FA	6.0×10^{-6}	30	(Wang & Zhu, 2005)
Methylene blue	FA-NaOH	8.0×10^{-6}	30	(Wang & Zhu, 2005)
Methylene blue	FA	1.4×10^{-5}	NR	(Wang & Wu, 2006)
Methylene blue	FA-HNO_3	2.4×10^{-5}	NR	(Wang & Wu, 2006)
Methylene blue	Carbon enriched FA	1.2×10^{-4}	NR	(Wang & Wu, 2006)
Methylene blue	Colombian FA	$> 2 \times 10^{-5}$	25	(Yamada et al., 2003)
Methylene blue	Thailand FA	$>1.6 \times 10^{-5}$	25	(Yamada et al., 2003)
Methylene blue	FA	2.2×10^{-5}	NR	(Wang & Wu, 2006)
Methylene blue	FA	2×10^{-5}	NR	(Gupta et al., 2000)
Crystal violet	Coal FA	9.76×10^{-5}	25	(Mohan & Gandhimathi, 2009)
Crystal violet	Carbon-free FA	1.0×10^{-6}	NR	(Wang & Wu, 2006)

Continued on next page

Table 2.5 continued

Dye	Fly ash type	Adsorption (mol/g)	Temperature (°C)	Reference
Crystal violet	Carbon-enriched FA	1.0×10^{-4}	NR	(Wang & Wu, 2006)
Crystal violet	FA	9.13×10^{-5}	NR	(Dizge et al., 2008)
Rosaniline hydrochloride	Coal FA	1.35×10^{-5}	25	(Mohan et al., 2002)
Rhodamine B	Colombian FA	8.0×10^{-6}	25	(Yamada et al., 2003)
Rhodamine B	Thailand FA	2.5×10^{-7}	25	(Yamada et al., 2003)
Acid blue 29	FA	3.25×10^{-6}	NR	(Ramakrishna & Viraraghavan, 1997)
Acid blue 9	FA	5.43×10^{-6}	NR	(Ramakrishna & Viraraghavan, 1997)
Acid red 91	FA	2.34×10^{-6}	NR	(Ramakrishna & Viraraghavan, 1997)
Congo red	Baggase FA	1.7×10^{-5}	NR	(Mall et al., 2005b)
Malachite green	Baggase FA	4.67×10^{-4}	NR	(Mall et al., 2005a)
Orange-G	Baggase FA	4.15×10^{-6}	NR	(Mall et al., 2006)

2.5.3 Removal of organic compounds from wastewater

Phenolic compounds are important organic pollutants in wastewater, which must be removed due to their toxicity (Dąbrowski et al., 2005; Mall et al., 2002). Previously, it was extensively studied that fly ash has an efficient affinity for removing these phenolic compounds (Dutta et al., 2003; Gupta & Ali, 2001; Kao et al., 2000; Viraraghavan & de Maria Alfaro, 1998). In one study, at the dosage of 55 mg/g fly ash/SL, lignin removal reached the maximum amount (53%), which corresponded to the lignin adsorption of 67 mg/g on fly ash. In another study, 67 mg of phenolic compounds (with various initial concentrations (C_0)) was adsorbed per gram of fly ash generated by a power generator in the effluent treatment of phenol, 3-chlorophenol and 2,4-dichlorophenol (Akgerman & Zardkoohi, 1996). Phenols have a strong hydroxyl functional group, which interacts with the active sites of active surface (i.e. activated carbon) (Dąbrowski et al., 2005). In most studies on phenol removal, fly ash was introduced as a substitute for activated carbon (Aksu & Yener, 2001; Aksu & Yener, 1999). Also, fly ash was utilized to remove o-xylene from wastewater (Banerjee et al., 1997). It was also reported that factors such as washing the fly ash and the carbon amount of fly ash may influence on the adsorption of organic materials (Ahmaruzzaman, 2010).

2.5.4 Synthesis of zeolite

Zeolites are crystalline aluminum-silicates, which can mostly be found in natural deposits such as volcanic rocks (Juan et al., 2002). They can also be synthesized from a variety of materials that contain significant amount of Si and Al (Xie et al., 2013). In this regard, numerous studies have been conducted on the utilization of fly ash in synthesizing zeolite (Goswami & Das, 2000; Hui et al., 2005; Shawabkeh et al., 2004; Wajima et al., 2007; Xie et al., 2013; Zhang et al., 2011). The similarity in compositions of some fly ash and volcanic materials has motivated researchers to synthesize zeolites from fly ash (Querol et al., 1995). Zeolites, which is synthesized by the hydrothermal treatment of fly ash, has a low Si content, but a high ion exchange capacity and a large pore volume (Holler & Wirsching, 1985). Zeolites have plenty of industrial applications. They can exchange inherent Na^+, Ca^{2+} and k^+ for other cations based through the concept of ion exchange (Holler & Wirsching, 1985). They can adsorb specific gas molecules (Ahmaruzzaman, 2010). Therefore, they can be applied as adsorbents in wastewater treatment processes and air emission control and as replacement for phosphate in detergents (Gianoncelli et al., 2013).

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3 CHAPTER THREE: ISOLATING LIGNIN FROM SPENT LIQUOR OF THERMOMECHANICAL PULPING PROCESS VIA ADSORPTION

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3.1 ABSTRACT

Wood chips are pretreated with steam prior to refining in the thermomechanical pulping (TMP) process. The steam treatment dissolves part of lignin of wood chips in the spent liquor (SL) of this process, and subsequently the SL is sent to the waste water system of the process. However, the lignin of SL can be used in the production of value-added chemicals, but it should be first separated from the SL in order to have a feasible downstream process. In this study, activated carbon (AC) was considered as an adsorbent to isolate lignin from SL. The results showed that the maximum adsorption of lignin on AC was166 mg/g under the optimal conditions of pH 5.2, 30ºC and 3 h treatment. Furthermore, the separation of lignin from SL was improved from 45% to 60% by having a two-stage adsorption process at pH 5.2, which also reduced the turbidity and COD of SL by 39 % and 32 %, respectively.

KEYWORDS: Lignin, TMP spent liquor, Adsorption, Biorefinery, Activated carbon

3.2 INTRODUCTION

The depletion of fossil fuel and environmental concerns associated with the use of fossil fuel have made a great incentive for producing bio-based chemicals and biofuels (Zhu & Pan, 2010). Forest biomass can be a valuable resource for producing bio-based chemicals and biofuels.

In thermomechanical pulping (TMP) process, wood chips are pretreated with steam, which dissolves part of lignocelluloses of wood chips. The spent liquor (SL) of this process is directly treated in the wastewater treatment plant of the mill, but the SL contains some lignocelluloses. The production of value-added chemicals from the lignocelluloses of SL will help the overall economy of the TMP process. Currently, the TMP processes are financially struggling, thus the utilization of their wasted lignocelluloses will help the process to be more cost effective (Olsson et al., 2006). However, the SL is very dilute and hence a process for directly accommodating SL is not feasible.

The isolation of lignocelluloses from the SLs of various pulping processes via acidification was investigated in the past (Alén et al., 1979; Fatehi et al., 2013; Shen et al., 2011; Yu et al., 2012). However, acidification may not be a feasible option for the SL of the TMP process, as the SL is a very dilute solution. Ultrafiltration was also introduced for isolating lignin from black liquor (Holmqvist et al., 2005). Although ultrafiltration can be advocated in a wide range of temperatures and pHs, the required flux and energy strongly depend on pressure gradient in the membrane (Nordin & Jönsson, 2009). Adsorption was recently introduced as a means to isolate lignocelluloses from SLs (Fatehi et al., 2013; Wang et al., 2010). Adsorption is a fast and economical process with a high selectivity. Previous studies on pre-hydrolysis liquor (PHL) of a kraft- based dissolving pulp process showed that lignocelluloses could be extracted from liquor through adsorption (Fatehi et al., 2013; Liu et al., 2011a; Liu et al., 2012). For the first time, the feasibility of an adsorption process for isolating lignin from the SL of a TMP process was investigated in this work.

Activated carbon (AC) with a large specific surface area and porous medium is one of the most effective and widely used adsorbents in various industries (Lin et al., 2008). AC could be easily recovered for reuse (Gütsch & Sixta, 2012; Palomar et al., 2012). In this work, AC was considered as an adsorbent, and the adsorption behavior of lignin of an industrially produced SL of a TMP process was assessed on AC under various conditions. Also, the effectiveness of a two-stage adsorption process for isolating the lignin of SL was investigated. Furthermore, the impact of lignin removal on the COD of the SL was assessed, which would help reduce the load to waste water treatment of the TMP process.

3.3 MATERIALS AND METHODS

3.3.1 Materials

Spent liquor (SL) sample was collected from a TMP mill located in Ontario, Canada, in Jan. 2013. In this TMP process, wood chips (hardwood) are treated with steam at 130 ºC for 30 min prior to refining, which dissolves some lignin and hemicelluloses of wood chips in the SL.

Coconut based charcoal (AC1) was purchased from Fisher Scientific and peat bog charcoals with the mesh sizes of 4-8 (AC2) and 8-20 (AC3) were purchased from Sigma-Aldrich Company. The SL and ACs were used as received.

The standard solutions (0.001 M) of polydiallyldimethylammonium chloride (PDADMAC) and potassium polyvinyl sulfate (PVSK) were purchased from Sigma-Aldrich Company and used for a charge density analysis. Chemical oxygen demand (COD) kit (K-73663) was purchased from CHEMetrics Company and used for COD analysis of SL.

3.3.2 Charge density and surface area of AC

The charge density of ACs was determined by using Mütek PCD04 charge detector. The standard solutions of PVSK and PDADMAC were used as titrants according to the method described in the literature (Saeed et al., 2011). The BET surface area of all ACs was measured via using a NOVA-2200e Autosorb with N_2 according to a previously established method (Yang et al., 2010).

3.3.3 One-stage adsorption process

In this work, the SL was first centrifuged at 1000 rpm for 10 min prior to analysis. The filtrate of this process was collected for analysis in this research. Initially, each AC was dried at 105 °C for 24 h. Then, 1 g of dried ACs was added to 30 g of SL samples in 125ml Erlenmeyer flasks. In one set of experiments, all three types of ACs were mixed with the SL, and the flasks were sealed and incubated in a Boekel water bath shaker at 30 °C and 100 rpm for 3 h. Subsequently, all samples were filtered using Whatman filter (No 5) and the filtrates were collected for lignin, hemicelluloses and COD analyses. This set of experiment was conducted to identify the most effective AC for adsorbing lignocelluloses of SL. It should be stated that the same analysis was conducted for control samples (SL without ACs) under the same conditions. The analysis of control sample showed that the filtration of SL (using Whatman paper) had no significant effect on the lignin and sugar contents of SL. To obtain the maximum adsorption of lignocelluloses on AC3 (i.e. the most effective AC), the process conditions of adsorption was optimized via conducting adsorption at different temperatures in another set of experiments. Furthermore, the pH of SL was adjusted to different levels, and the adsorption experiment was repeated. At last, the adsorption was investigated as a function of time at optimal pH and temperature. Each test was repeated three times and the experimental isotherm and kinetic results were compared with those of model analyses. It should be highlighted that the errors within 2% errors were reported in this work.

3.3.4 Two-stage adsorption process

To improve the recovery of lignocelluloses from SL, the SL that was already treated with the selected AC (AC3) was retreated with the same type of AC (but unused) under the optimal adsorption conditions. In this case, the treatment was conducted at original pH in order to have a simple adsorption process. It should be noted that treated AC has less active sites than untreated one, as its surface will be covered by lignin via adsorption. Therefore, untreated AC was used in the second stage and in fact a thermal regeneration of AC, for example at 850 °C for 30 min, is required for reusing the treated AC as an adsorbent in the second stage (Gütsch & Sixta, 2012). The filtrates of this test were collected for sugar, lignin, COD and turbidity analyses.

3.3.5 Lignin and sugar analyses

The lignin amount of all solutions was determined by UV/VIS spectrophotometry, Genesys 10S, at the wavelength of 205nm according to TAPPI UM 250 (Fatehi et al., 2013). The DNS method was applied to determine the sugar concentration of samples (Dashtban et al., 2011; Ge et al., 2013). In this method, 4 g of 4 % sulphuric acid was initially added to 1 g of SL sample, and then the solution was incubated at 121 ºC for an hour. Afterwards, 360 µl of 3, 5- dinitrosalicylic acid (DNS) and 120 µl of deionized water were added to 60 µl of acid hydrolyzed samples, and subsequently the produced solution was boiled at 100 ºC for 5 min. Subsequently, samples were cooled down to room temperature, and the total sugar content was measured by UV/VIS spectrophotometry at the wavelength of 540nm. Calibration curves were generated and the average of three testing results was reported.

3.3.6 COD and turbidity analyses

The chemical oxygen demand (COD) of SL samples before and after AC treatments was assessed according to ASTM D12552-06. In each test, 2 ml of diluted sample was added to COD vials and incubated at 150 ºC in COD CR 2200 WTW thermoreactor for 2 h. Subsequently, the intensity of solutions was measured using the UV/VIS spectrophotometry at the wavelength of 620 nm. A calibration curve was taken into account for determining the COD of samples. On the other hand, the turbidity of samples was assessed before and after the adsorption experiments using a Hach 2100AN turbidity meter (Fatehi et al., 2013). This procedure was repeated three times and the average value was reported.

3.4 RESULTS AND DISCUSSION

3.4.1 Characterization of AC

Table 3.1 lists the properties of ACs. As can be seen, AC1 had no surface charge, and AC3 had higher anionic and cationic charges than AC2 did. Generally, the cationic charges are attributed to nitrogen or phosphor containing groups associated with the AC, while anionic charges are ascribed to sulphonated or carboxylic groups attached to AC (Takahashi et al., 2012). Various surface charge densities (i.e. +0.03 mmol/g (Bjelopavlic et al., 1999) and -0.07 mmol/g (Newcombe, 1999)) were reported for different ACs. Table 3.1 also lists the BET (Brunauer-Emmett-Teller) surface area of ACs. As can be seen, AC1 had the highest surface area, but AC2 and AC3 had a similar surface area of 623 m^2/g and 647 m^2/g, respectively. In earlier studies, BET surface areas of 702 m^2/g (Yang et al., 2010) and 1107 m^2/g (Ruiz et al., 2009) were reported for different ACs.

Table 3.1. Charge Density and Surface Area of ACs

Sorbent	Anionic **charge density (μeq/g)**	**Cationic charge density (μeq/g)**	**BET surface area (m²/g)**
AC1	0.00 ± 0.00	0.00 ± 0.00	1197
AC2	0.00 ± 0.00	0.44 ± 0.01	623
AC3	2.96 ± 0.25	1.02 ± 0.02	647

Table 3.2 lists the lignocelluloses content of SL. Evidently, it contained 4.48 g/l lignin, 1.53 g/l hemicelluloses and 0.51 g/l ash. These results imply that the steam to wood ratio of the steaming process was probably so high that the SL with very dilute concentration was generated. Also, the COD of original SL was approximately 5300 mg/l, which is mainly attributed to the organic compounds of SL.

Table 3.2. Concentration of Lignocelluloses as well as COD and the Turbidity of Original and Treated SL after the First and Second Adsorption Stages Conducted under Optimal Conditions of pH 5.2, 30 ºC for 3 h

	Lignin, g/l	Hemicelluloses, g/l	COD, mg/l	Turbidity, NTU
Original	4.48 ± 0.02	1.53 ± 0.05	5311 ± 12	486 ± 2
After adsorption I	2.48 ± 0.01	1.38 ± 0.06	4115 ± 4	380 ± 3
After adsorption II	1.80 ± 0.01	1.24 ± 0.06	3617 ± 8	295 ± 2

Table 3.3 also lists the adsorption of lignocelluloses on ACs and the COD reduction of SL as a result of lignocellulose removal. Generally, all ACs absorbed more lignin than hemicelluloses on their surfaces. This phenomenon was observed in other studies, and is attributed to the higher affinity of lignin than hemicelluloses for separation from aqueous solutions (Sulaymon & Ahmed, 2007). It is well known that hydrophobic compounds in a solution have a great tendency to be

isolated from aqueous solution (Chinn & King, 1999). Therefore, the higher adsorption of lignin than hemicelluloses could be due to the higher hydrophobic properties of lignin than hemicelluloses. Another reason for the lower adsorption of hemicelluloses on AC was the fact that the SL had lower hemicellulose content, thus its adsorption on ACs was less (than lignin). As can be seen, AC3 was the most effective adsorbent for lignocelluloses and COD removals, and thus was selected for further analysis. This higher adsorption was attributed to the higher cationic and anionic charges of AC3 than AC2 (Table 3.1). In previous studies, it was reported that both cationic and anionic charges on the surface of AC played important roles in the adsorption of lignocelluloses (Fatehi et al., 2013; Liu et al., 2011a; Liu et al., 2011b). The presence of carboxylic, carbonyl and sulfonated groups on the structure of lignocelluloses make lignocelluloses anionic oligomers (Liu et al., 2011a; Takahashi et al., 2012). Therefore, there would be an electrostatic interaction between lignocelluloses of SL and AC with cationic surface charge (Liu et al., 2011b), and hydrogen bonding between lignocelluloses of SL and AC with anionic charges (Liu et al., 2011a). It was claimed that the higher anionic and/or cationic charges on the surface of AC, the higher adsorption of lignocelluloses on AC could occur (Liu et al., 2011a; Liu et al., 2011b). Furthermore, these results suggest that surface charge of AC was a more influencing factor than surface area in adsorbing lignocelluloses.

Table 3.3. Influence of Various ACs on the Adsorption of Lignocelluloses of SL (1 g of dried AC was mixed with 30 g of SLs at 30 ºC and Shaken at 100 rpm for 3 h)

AC	Lignin		Hemicelluloses		COD
	Adsorbed, mg/g	Removal, %	Adsorbed, mg/g	Removal, %	mg/l
AC1	25.3 ± 0.5	27.0 ± 0.6	2.4 ± 0.2	5.9 ± 0.4	3711 ± 48
AC2	57.9 ± 0.3	61.6 ± 0.4	4.2 ± 0.2	10.4 ± 0.5	2839 ± 50
AC3	91.3 ± 0.3	78.0 ± 0.4	5.0 ± 0.2	11.9 ± 0.4	2423 ± 50

3.4.2 Kinetics of adsorption

Figure 3.1 shows the adsorption of lignin on AC3 as a function of time. As can be seen, lignin reached equilibrium in 3 h. In the literature, the adsorptions of lignin from PHL on oxidized AC reached its maximum in 2 h (Liu et al., 2011a). Similarly, it was stated that the adsorption of phenols on AC was constant after 2 h (Liu et al., 2011b). The results imply the slow adsorption of lignin on AC in the first 3 hours, which is probably due to the gradual diffusion of lignin into AC pores.

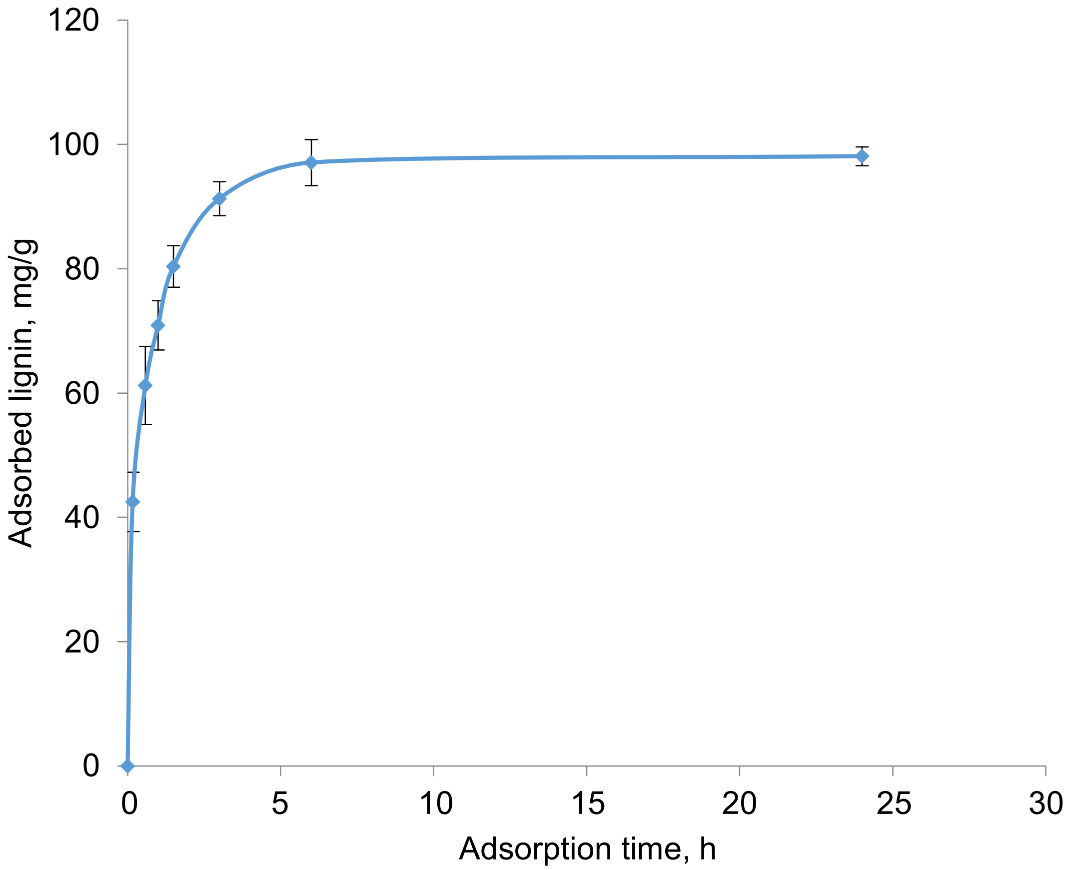

Figure 3.1. Adsorption of lignin of SL on AC3 versus the time of adsorption (1 g of AC3 was added to 30 g of SL at 30 ºC and shaken at 100 rpm).

The experimental data shown in Figure 3.1 was employed to model the lignin adsorption on AC. In this regard, pseudo- first order (Eq. 3.1), pseudo-second order (Eq. 3.2) and Elovich's equation (Eq. 3.3) were employed to predict the isotherm behavior of lignin on AC3 (Fatehi et al., 2013; Zuo et al., 2013):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (3.1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3.2)$$

q��$_{ee}$

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \qquad (3.3)$$

where k (1/min) and k' (g/ (mg.min)) represent kinetic constants, q_t and q_e (mg/g) are related to adsorption amount at time *t* (min) and equilibrium, respectively (Fatehi et al., 2013; Fierro et al., 2008). Other parameters such as *a* (mg/ (g.min)) and *1/b* (mg/g) resemble initial adsorption rate and available active sites, respectively (Fatehi et al., 2013; Zuo et al., 2013). Table 3.4 lists kinetic model parameters determined by fitting the experimental data into the models. These results are in harmony with results reported about the adsorption of lignin of PHL on AC in a previous work (Fatehi et al., 2013). It is concluded from the results that pseudo- second order model predicted the experimental results most accurately (Fatehi et al., 2013; Fierro et al., 2008; Liu et al., 2010; Zuo et al., 2013). Consequently, on the basis of pseudo second order model, chemical sorption may be the rate-restricting step due to valency forces and sharing or exchanging electrons between lignin and AC (Ho & McKay, 1999). Since all models represents the behaviour of lignin adsorption, SL samples with different dilution levels should be taken into account for model adsorption analysis, and the analysis should be conducted using more data points to have more reliable model analysis in future.

Table 3.4. Kinetic parameters of adsorption by fitting the experimental results of Figure 3.1 into models

component	Pseudo- first order model		Pseudo- second order model		Elovich's equation	
	K × 10^4 (1/min)	R^2	K' × 10^3 (g/ (mg. min))	R^2	1/b (mg/g)	R^2
Lignin	118	0.98	0.2	0.99	12	0.89

3.4.3 Impact of temperature

Figure 3.2 depicts the impact of temperature on the adsorption of lignin on AC3. It is evident that the maximum adsorption was achieved at 30 ºC. It was claimed that the entropy of lignin would decrease by its adsorption on AC (Petzold et al., 1996). According to the second law of thermodynamics, the enthalpy of the system must also decrease to have an adsorption phenomenon, which implies that the adsorption of lignin on the surface of AC3 is an exothermic process (i.e. the lower the temperature, the higher the adsorption). A similar behavior was observed for the adsorption of phenolic compounds on AC at various temperatures (Andriantsiferana et al., 2012; Zuo et al., 2013).

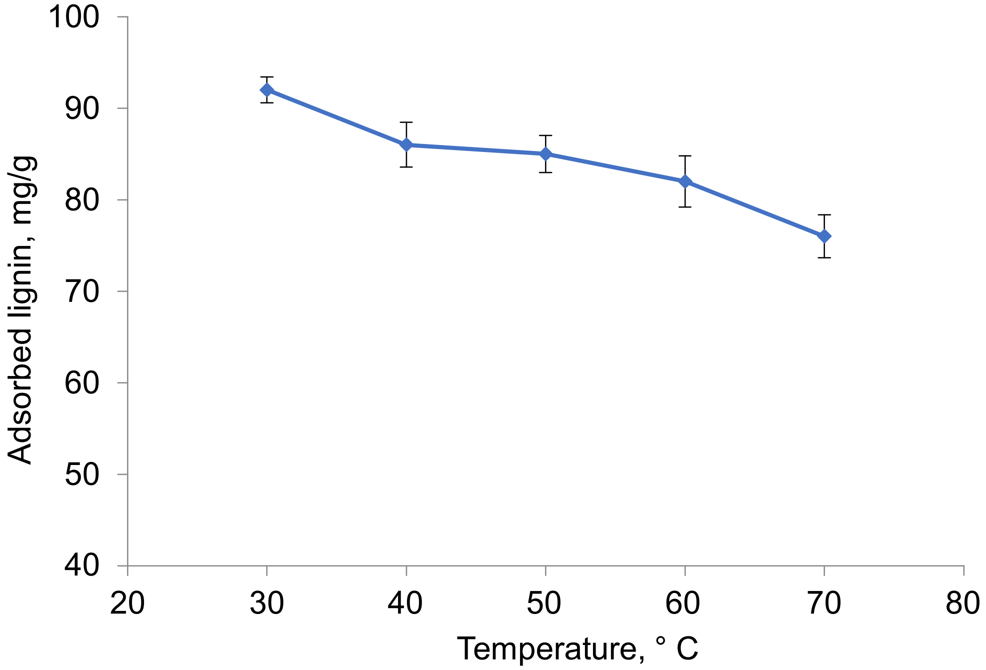

Figure 3.2. Adsorption of lignin of SL on AC3 at different temperatures (1 g of AC3 was added to 30 g of SL and shaken for 3 h).

3.4.4 Adsorption isotherm

Figure 3.3 depicts the adsorption isotherm of lignin of SL at 30 ºC on AC3. The results showed that, by increasing the ratio of SL to AC3, more lignin was adsorbed on AC3, and the highest adsorption was 166 mg/g. In another study, the adsorption of lignin of PHL on AC was 194 mg/g via mixing 50 ml PHL with 1 g AC (Fatehi et al., 2013). Under similar operating conditions (30 ºC, pH 4 and 24 h operation), it was observed that 70 mg/g of phenols of anaerobic sludge, which contained 50 mg/l of phenol, was adsorbed on AC (Sulaymon et al., 2013).

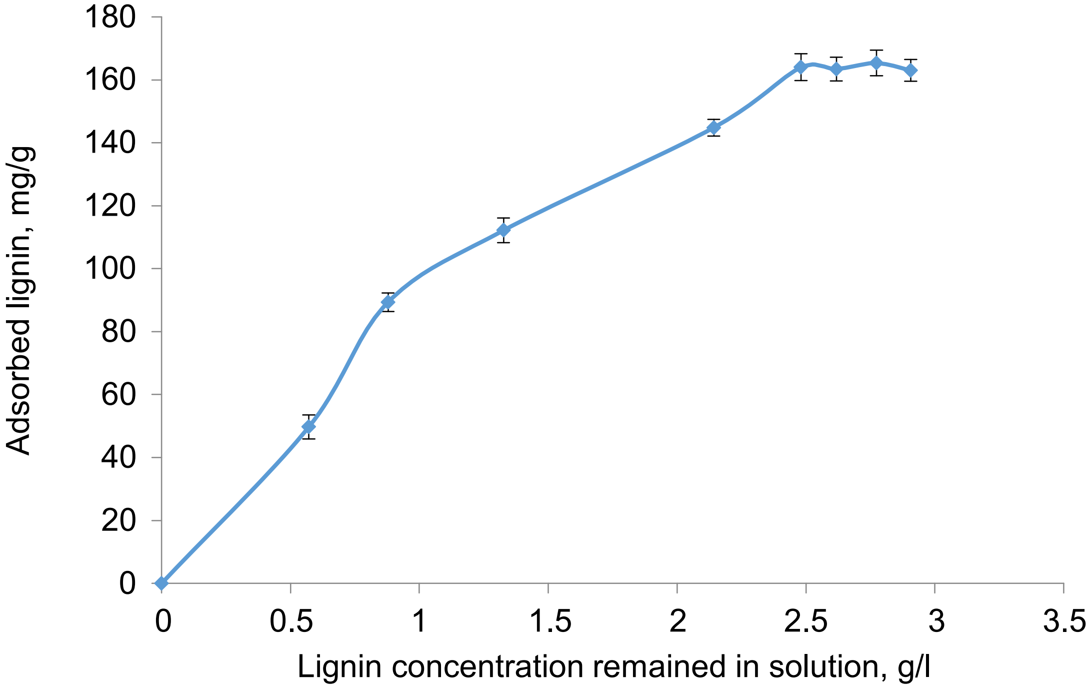

Figure 3.3. Adsorption of lignin of SL on AC3 (1 g of AC was added to various amounts of SL at 30 ºC and was shaken at 100 rpm for 3 h).

The plotted data in Figure 3.3 was hired to model the adsorption isotherm of lignin on AC3. In this regard, Tempkin and Pyzhev (Eq. 3.4), Langmuir (Eq. 3.5) and Freundlich (Eq. 3.6) isotherms were considered for the analysis (Fatehi et al., 2013). In all equations C_e (g/l), q_e (mg/g) correspond to the concentration and adsorption at equilibrium, respectively (Fierro et al., 2008).

$$q_e = k_1 . \ln(k_2) + k_1 . \ln(C_e) \quad (3.4)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . \beta} + \frac{C_e}{Q_0} \quad (3.5)$$

$$q_e = K_f . C_e^{1/n} \quad (3.6)$$

The experimental results of isotherms showed that k_1, k_2 (heat of adsorptions), Q_0 (maximum possible adsorption), β (Langmuir constant), k_f (Freundlich constant) and n were 71.4 l/g), 3.7 l/g, 336.7 mg/g, 0.36 l/mg, 85 and 1.44, respectively. A comparison between the R^2 values of Tempkin and Pyzhev equation ($R^2 = 0.99$), Langmuir model ($R^2 = 0.92$) and Freundlich isotherm ($R^2 = 0.95$) depicted that experimental results fitted well into all models. However, Tempkin and Pyzhev isotherm predicted the results more precisely, indicating that the interaction of lignin (sorbate) /AC (sorbent) may occur and the heat of adsorption would reduce linearly as the active sites of AC occupied by the lignin (Fierro et al., 2008).

3.4.5 Impact of pH

The adsorption of lignin of SL on AC3 at different pHs are presented in Figure 3.4. As can be seen, the adsorption was the maximum (120 mg/g) at pH 5.2 (i.e. original pH of the SL). Lignin is more soluble under alkaline conditions, and thus does not tend to be isolated from SL. Therefore, less lignin would interact with AC for adsorption at high pHs. On the other hand, it was claimed that, under strong acidic conditions (i.e. pH 2), lignin could precipitate in a 4 % diluted pulp slurry (Koljonen et al., 2004). Therefore, less lignin is present in solution for adsorption on AC at a low pH. Also, the surface of AC3 is protonated under strong acidic conditions, which reduces the interaction of lignin and AC and eventually hinders the adsorption of lignin. However, by acidifying the SL to pH 2, a part of lignin was precipitated; thus by including lignin removal via acidification, the overall lignin removal from SL at pH 2 was 89 % in this work. However, as acidification results in more dilution of SL and the lignin adsorption on AC was less effective under acidic conditions; original pH (5.2) of the SL was selected as optimal pH for further research.

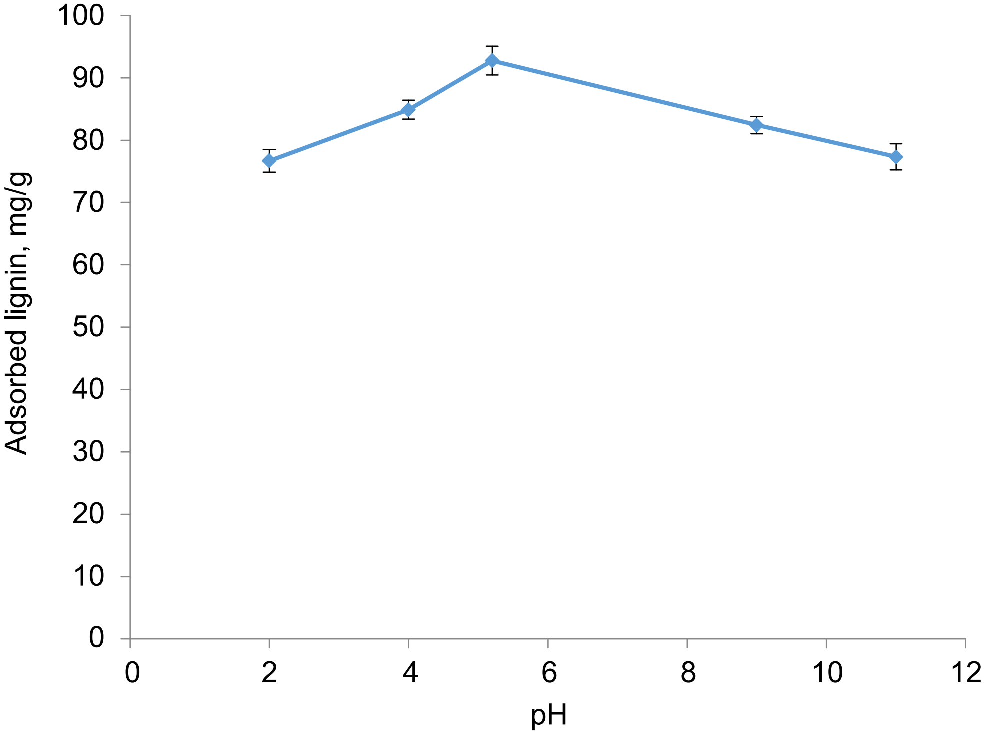

Figure 3.4. Adsorption of lignin of SL on AC versus pH (1 g of AC3 was added to 30 g of SL at 30 ºC and shaken at 100 rpm for 3 h).

3.4.6 Two-stage adsorption process

Table 3.2 also lists the adsorption performance of lignin of SL on AC3 in the two-stage process. Evidently, 45 % (166 mg/g) and 27 % (81 mg/g) of lignin was removed in the first and second stage of adsorption, respectively. As was discussed earlier, the sugar content of SL was low, which resulted in 10 % hemicelluloses removal in each stage. The results also depicted that the COD and turbidity of SL were removed by 1196 mg/l and 106 NTU in the first and 498 mg/l and 85 NTU in the second stage of adsorption, which is mainly due to the lignin removal of SL. Overall, the lignin, hemicelluloses, COD and turbidity of SL were decreased by 2.68 g/l (60 % removal), 0.29 g/l (19 % removal), 1694 mg/l (32 % removal) and 191NTU (39 % removal) with the aim of the two-stage process, respectively.

3.5 CONCLUSIONS

In this work, the removal of lignin from SL of a TMP process was successfully achieved with the help of activated carbon adsorption. The process was optimized under the conditions of 5.2 pH, 30 ºC for 3h adsorption treatment, which resulted in 45 % lignin removal (166 mg/g of lignin was adsorbed on AC). However, the acidification (to pH 2) and a subsequent adsorption treatment (using AC) resulted in an overall lignin removal of 89 %. Additionally, 60 % of lignin, 19 % of hemicelluloses, 32 % of COD and 39 % of turbidity were removed in the two-stage process at pH 5.2. These results show that the adsorption process can help reduce the load of SL to waste water system of the mill.

3.6 ACKNOWLEDGMENT

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4 CHAPTER FOUR: IMPACT OF POWER BOILER FLY ASH ON PROPERTIES OF SPENT LIQUOR OF THERMOMECHANICAL PULPING PROCESS

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4.1 ABSTRACT

The spent liquor (SL) of thermomechanical pulping (TMP) process introduces a high load to the wastewater system of this process. In this work, fly ash from a biomass boiler was used not only for removing lignin from SL, but also for decreasing the COD and turbidity of SL. The results showed that the maximum adsorption of lignin on fly ash was 67 mg/g by treating SL with fly ash at room temperature for 3 h in one stage adsorption. The results showed that adjusting the pH of adsorption before or after the process had an insignificant influence on the adsorption of lignin, but affected the turbidity of SL. Additionally, the lignin removal was improved from 53 % to 68 % in a two stage process (rather than one), while the COD and turbidity reductions were increased from 49 % to 70 % and from 89 % to 94 %, respectively.

KEYWORDS: Lignin, TMP spent liquor, Adsorption, COD, Fly ash

4.2 INTRODUCTION

The pulp and paper industry is one of the main industries contributing to the gross domestic products (GDP) of Canada and the USA due to their enormous forest resources (Sinclair, 1991; Van Heiningen, 2006). However, the pulp and paper industry is currently struggling financially due to strong competition from countries with low labor costs. One strategy to reduce the production costs, and thus to increase the economic benefits of the pulp and paper industry is to utilize their wasted materials more effectively.

The amount of wastewater generated in the pulp and paper industry was estimated as half of all waste effluents released to surface water in Canada (Pokhrel & Viraraghavan, 2004). Recently, the capital cost for a lignocellulosic-based wastewater plant with a hydraulic load of 2.15 MMgal/d was estimated to be $49.4 million and the annual chemical cost for this plant was predicted to be $2.83 million (Humbird et al., 2011).

In the thermomechanical pulping (TMP) process, wood chips are pretreated with steam, which extracts some organic materials including lignin from wood and dissolves it in pressate (i.e. the spent liquor (SL) of this process). This extract is sent to a wastewater treatment plant in order to remove the suspended solids and dissolved organic material prior to its discharge. Lignin of SL can be used in the production of value-added products such as carbon fiber, epoxy resins and adhesives (Kumar et al., 2009; Lora & Glasser, 2002). Alternatively, lignin has a heating value of 27 MJ/kg, which equivalently worth $99 per oven dry metric ton (Van Heiningen, 2006). Possessing such a high heating value would make lignin as an alternative fuel.

It was stated that the main source of chemical oxidation demand (COD) of SL is dissolved lignin and its derivatives (Andersson et al., 2008; Andersson et al., 2012; Kavanagh et al., 2011). In this regard, the COD reduction of lignocellulosic-based wastewater effluent was the subject of several research projects (Liu et al., 2011a; Yu et al., 2004; Yuliani et al., 2013; Zhou et al., 2008). It was claimed that, within two stages of anaerobic reactors, 90 % of COD from SL was removed at hydraulic retention time of 21h (Vinas et al., 1993). Although biological methods are efficient in removing COD, the treated wastewater has color as not all lignocelluloses will decompose by biological treatments (Yuliani et al., 2013). To improve the COD removal from TMP wastewater, the co-digestion of lignocelluloses with glucose using thermophilic acidogens was suggested in anaerobic reactors (Yu et al., 2004). The main disadvantage of such process is the decomposition and thus wasting of the dissolved lignocelluloses in wastewater. In other words, the biological treatment improved the COD removal from wastewater at the expense of decomposing lignocelluloses. Coagulation with metal salts and polymers (mostly anionic) was proposed to improve the removal of lignocelluloses and COD from SL. In one study, the aerobic fermentation of effluent of alkaline peroxide mechanical pulping (APMP) with A*spergillus niger* showed 30 % COD reduction via adding 1000 mg/l alum, as a coagulant, and 2 mg/l cationic polyacrylamide (CPAM), as a flocculant (Liu et al., 2011a). In a similar study, almost 90 % of COD was removed by adding 4.5 mg/l aluminium sulfate and 2 mg/l CPAM from the secondary treatment of a wastewater effluent (Zhou et al., 2008). Although coagulation and flocculation treatments are more effective than biological processes for removing lignocelluloses and COD, their operating cost is significant.

Adsorption was regarded as a fast, selective and economical method for lignin removal from spent liquors. In one study, a two stage adsorption process (using activated carbon with the dosage of 1 g activated carbon per 90 g of SL) reduced the lignin, COD and turbidity of SL of TMP by 60 %, 32 %, 39 %, respectively (Oveissi & Fatehi, 2014). Fly ash is produced in solid fuel boilers by burning wood residuals, bark or coal. In the literature, the utilization of fly ash for adsorption of NO_x, SO_x and several organic compounds (i.e. phenols) from wastewater effluents and air was discussed (Ahmaruzzaman, 2010). It was stated that up to 90 % of lignin was removed from a bleaching effluent of a TMP process by treating with 50 g/l fly ash generated in a steam-producing boiler (Andersson et al., 2012).

This is the first study on the application fly ash to the SL of a TMP process (Oveissi & Fatehi, 2014). The main focus of this study is on the changes in the COD, turbidity and lignin removals of pulping spent liquor via treatment with fly ash. In this work, operating conditions (treatment time and dosage of fly ash) for removals of lignin, COD and turbidity was optimized. Subsequently, the impact of a two stage process on treating SL was studied under various conditions. Based on the results, an integrated process was proposed not only for decreasing the load to wastewater system, but also for using treated fly ash as a fuel source in the biomass boiler in an effort to improve the energy balance of the TMP process.

4.3 MATERIALS AND METHODS

4.3.1 Materials

Fly ash was collected from a bark boiler of a pulp mill in Northern Ontario, Canada, and ground to be homogeneous. The spent liquor (SL) of a thermomechanical pulping (TMP) process was received from the same mill and used as received.

4.3.2 Elemental analysis

The metal content of fly ash was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with CETAC ASX-510 Auto Sampler (Canada). The ICP-AES analysis was conducted via using Varian Vista Pro CCD (Canada) according to the method established in the literature (Yuan et al., 2010). Elemental (ultimate) analysis was performed using a Vario EL cube instrument (Germany), according to the procedure described in the literature (Fadeeva et al., 2008).

4.3.3 Surface area and charge density

The BET surface area of fly ash was determined using a NOVA-2200e Autosorb under N_2 atmosphere according to a previously established method (Yang et al., 2010). The charge density of fly ash was determined by using Mütek PCD04 charge detector as previously described (Liu et al., 2011b; Oveissi & Fatehi, 2014).

4.3.4 Single stage adsorption process

In one set of experiments, different amounts of fly ash were added to 45g of SL samples in 125 ml Erlenmeyer flasks. Then, all flasks were sealed and incubated in a Boekel water bath shaker at 30 °C and 100 rpm for 3 h. This set of experiments helped optimize the dosage of fly ash in SL (i.e. the dosage that induced the maximum removals of lignin, COD and turbidity). Based on these results, the treatment time of adsorption was investigated at various time intervals at 100 rpm. In this set of experiments, control samples were prepared under the same conditions as treated SL, but without fly ash. The temperature of this experiment was fixed at 30°C, as an earlier study showed that the adsorption of lignin on activated carbon was the maximum at 30°C (Oveissi & Fatehi, 2014). Subsequently, the treated SLs were centrifuged at 1000 rpm for 10 min using Survall ST16 centrifuge. The filtrates were collected for lignin, COD and turbidity analyses. To satisfy statistical consistency, all tests repeated three times and the average of three repetitions was reported in this study. The error bars in all figures accounts for standard deviations of each triplicate.

Alternatively, fly ash was washed with deionized water (incubated at 30°C, 100rpm for 24h), then dried. Different amounts of washed fly ash were added to SL and samples were centrifuged at 1000 rpm for 10 min. This set of experiments was conducted to investigate the effect of fly ash impurity (e.g. metal ions) on lignin, COD and turbidity removals.

4.3.5 Removal alternatives

To find the maximum removals of lignin, COD and turbidity from SL, various processes were studied as depicted in Figure 4.1. In option a, 2.5 g of fly ash were added to 45 g of SL and shaken at 100 rpm and room temperature for 3 h. In option b, the pH of SL samples were set to 5.3 (i.e. pH of original SL) after addition of fly ash, but before incubation. In option c, sulfuric acid (4 wt.%) was added after adsorption treatment to adjust the pH of the treated effluent after separation addition. It should be stated that for comparing various treated SL samples, the adjusted pH was considered as the same pH of original SL (pH 5.3).

In option d, the SL that was already treated with fly ash was re-treated with the fresh fly ash under the same optimal conditions to further reduce the organic material from the effluent without any pH adjustment. In option e, the two stage adsorption was performed with the pH adjustment step after the treatment, as depicted in Figure 4.1. The filtrates of these processes were analysed and compared with original effluent.

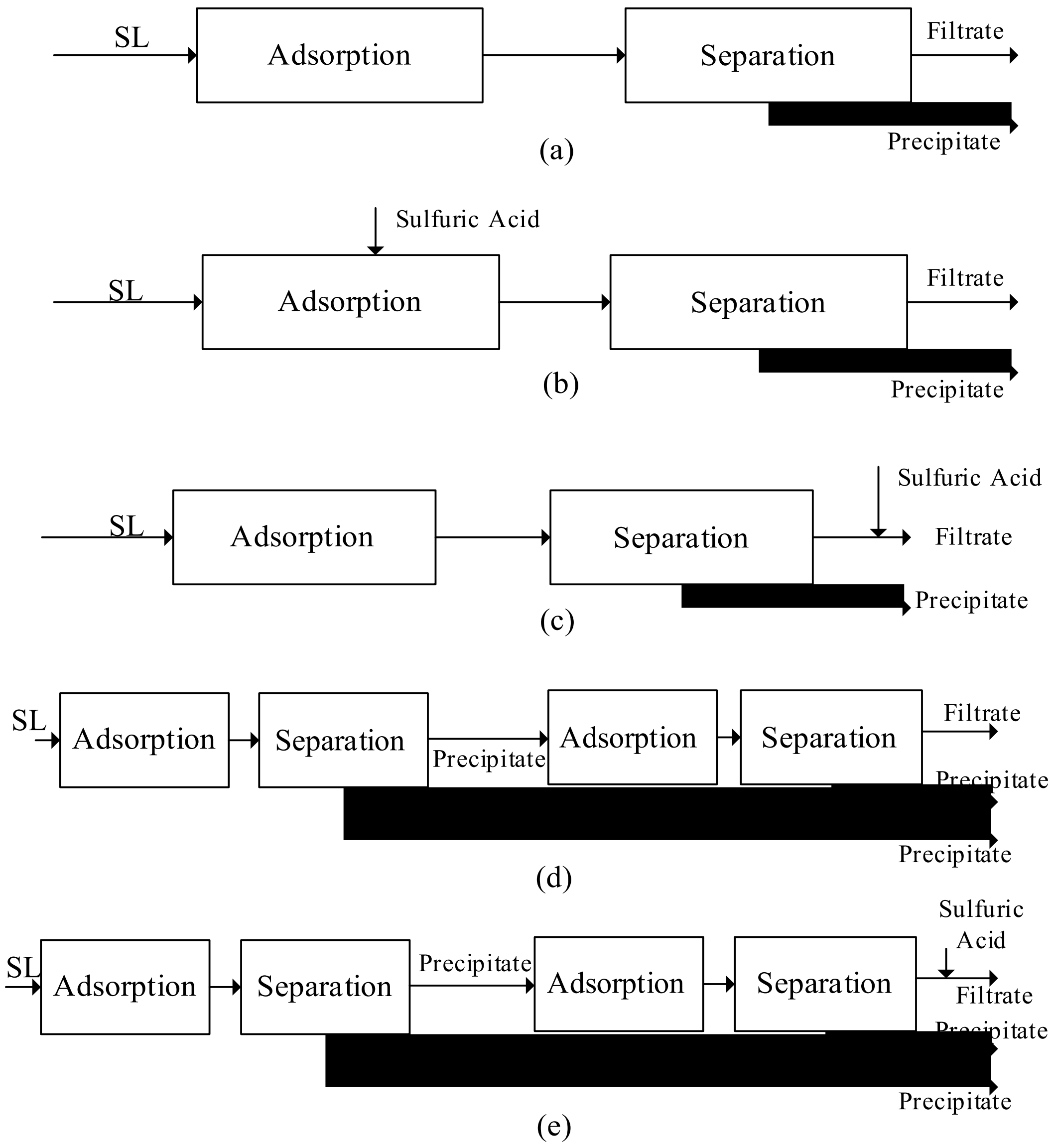

Figure 4.1. Process alternatives: (a) one stage adsorption (b) one stage with pre-pH adjustment (c) one stage adsorption with post pH adjustment (d) two-stage adsorption (e) two-stage adsorption and post pH adjustment

4.3.6 Lignin analysis

The lignin content of all solutions was determined by UV/VIS spectrophotometry, Genesys 10S, at the wavelength of 205nm according to TAPPI UM 250 (Dashtban et al., 2014). Calibration curves were generated and the average of three testing results was reported. Also, in order to confirm that there is no interaction between fly ash and water, 2.5g of fly ash was added to 45g of deionized water and incubated overnight at 30°C, 100rpm (i.e. control sample). After separation, the filtrate was collected and its UV adsorption was scanned at the wavelength of 205 nm in order to confirm that there was no interference from fly ash in lignin analysis using UV/VIS spectrophotometry.

4.3.7 Analysis of turbidity and chemical oxygen demand (COD)

The turbidity of SL samples was assessed before and after the adsorption experiments using a Hach 2100AN turbidity meter (Fatehi et al., 2013). This procedure was repeated three times and the average values were reported. The chemical oxygen demand (COD) of SL samples before and after fly ash treatment was measured as previously described, and the average values of three repetitions were reported in this work (Dashtban et al., 2014).

4.3.8 Calorific value

Gross calorific heating value was measured by a PARR 6200 oxygen bomb calorimeter, according to ASTM E711-87 (ASTM, 2004).

4.4 RESULTS AND DISCUSSION

4.4.1 Ash characterization

Table 4.1 shows the properties of unwashed and washed fly ash. Evidently, fly ash contained 30 wt. % metals, such as calcium, potassium, magnesium and aluminium, which may create fly ash as a potential coagulant for effluent treatment. These metals were also reported as the most common constituents of fly ash in the literature (Furuya et al., 1987). By washing fly ash, the weight percentage of potassium, sodium, sulfur in fly ash decreased by 3.36 %, 0.55 % and 2.16 %, respectively. However, weight percentages of carbon and oxygen increased by 2.12 % and 2.58 %, respectively. The shares of other constituents in fly ash were not significantly changed by washing.

Table 4.1. Elemental Analysis of Fly Ash

Element	Unwashed fly ash, wt.%	Washed fly ash, wt.%	Element	Unwashed fly ash, wt.%	Washed fly ash, wt.%
Calcium	14.60	14.51	Phosphorus	0.87	0.92
Potassium	4.06	0.70	Manganese	0.33	0.38
Magnesium	1.96	2.01	Zinc	0.19	0.21
Aluminum	0.99	1.03	Silicon	0.08	0.13
Sodium	0.93	0.38	Sulfur	4.60	2.44
Iron	0.89	0.84	Carbon	34.60	36.72
Oxygen	26.33	28.91	Hydrogen	1.59	1.79
Nitrogen	0.14	0.14			

Table 4.2 lists the surface area and charge density of unwashed and washed fly ash samples. As can be seen, unwashed fly ash had 35 μeq/g of cationic charge density, while washed fly ash

had 17.2 μeq/g of cationic charge density. The anionic charge density of fly ash was negligible before and after washing. Decrease in cationic charge density of fly ash through washing might be due to the decrease in the metal component of fly ash such as potassium and sodium.

Based on the Brunauer-Emmett-Teller equation, the surface area for unwashed and washed fly ash was determined as 63.72 and 90.2 m^2/g, respectively. It can be inferred that washing either removed the large metal components from fly ash or opened the structure of fly ash (i.e. improved the porosity of fly ash). In the literature, it was claimed that fly ash, obtained from Obra thermal power station, had a surface area of 4.87 m^2/g (Kumar et al., 1987). In another study, 1.5-1.7 m^2/g was as the surface area of fly ash received from Poplar River power station operated by the Saskatchewan Power Cooperation (Viraraghavan & de Maria Alfaro, 1998).

Table 4.2. Charge Density and Surface Area of Fly Ash

	Unwashed fly ash	**Washed fly ash**
Anionic charge density (μeq/g)	0.00 ± 0.00	1.83 ± 0.01
Cationic charge density (μeq/g)	35.01 ± 0.02	17.17 ± 0.01
BET surface area (m^2/g)	63.7	90.2

4.4.2 Adsorption on unwashed fly ash

Figure 4.2 shows the change in the lignin, COD, turbidity and pH of SL after treating with fly ash as a function of the ratio of fly ash to SL. It is evident that, as fly ash content increased, the lignin removal from the SL increased. The increase in lignin removal was due to the adsorption of lignin on fly ash (Ahmaruzzaman, 2010).

At the dosage of 55 mg/g fly ash/SL, lignin removal reached the maximum amount (53%), which corresponded to the lignin adsorption of 67 mg/g on fly ash. In another study, 67 mg/g of phenolic compounds (with various initial concentrations (C_0)) was adsorbed on fly ash generated by a power generator in the effluent containing phenol, 3-chlorophenol and 2,4-dichlorophenol(Akgerman & Zardkoohi, 1996). In another study, by adding 100 mg of fly ash generated by a steam boiler to 50 g/L of bleaching effluent of a TMP process (stirred at 200 rpm for 6h), 5 mg/g of lignin was adsorbed on fly ash(Andersson et al., 2012).

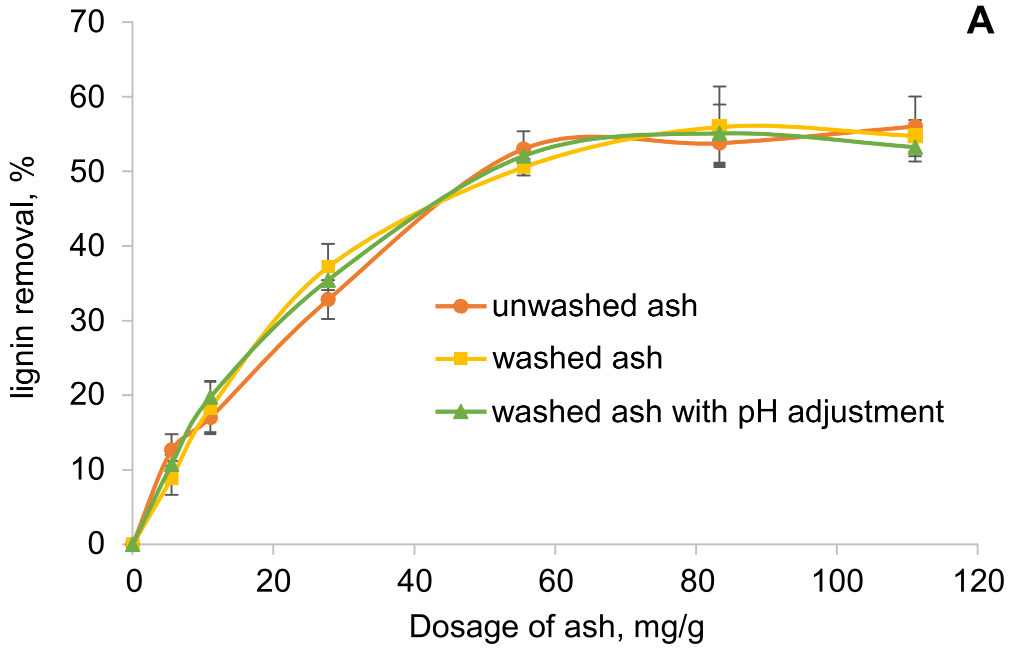

Figure 4.2. Effect of dosage of fly ash (unwashed, washed and washed fly ash with post-pH adjustment) to SL ratio on removals of (A) lignin (B) COD (C) turbidity and (D) pH of SL (conducted via adding 1 g of unwashed and washed fly ash to 45g of SL at 30 °C, 100 rpm for 3h)

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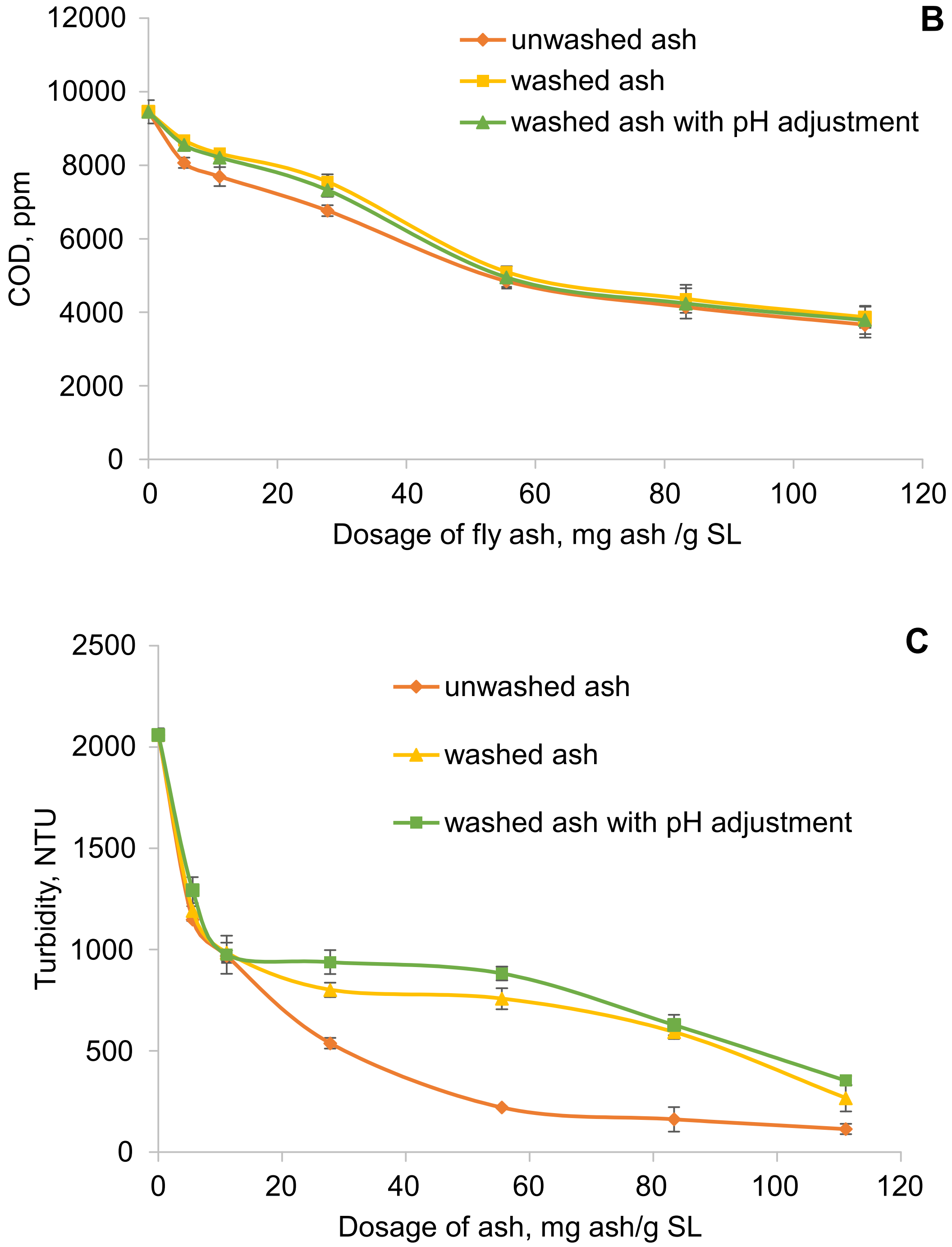

Figure 4.2 continued

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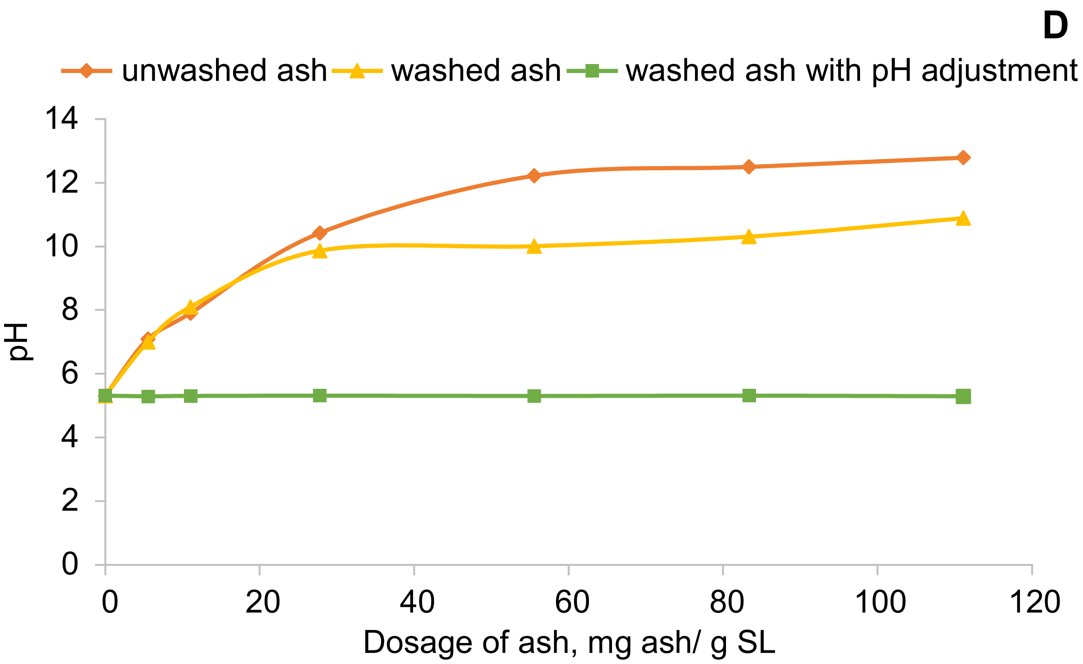

Figure 4.2 continued

Figure 4.2B presents the COD reduction of SL as a function of fly ash/SL weight ratio. It is apparent that the COD level of SL decreased by increasing fly ash ratio. As can be observed, at 55 mg/g fly ash/SL ratio, almost 50% (4728 ppm) of COD was removed. It was claimed that lignin-related substances significantly contributed to COD content of pulping effluent (Andersson et al., 2008; Kavanagh et al., 2011). Hence, decrease in COD amount could be attributed to the reduction in lignin content of SL.

Figures 4.2C and 4.2D show the change in the turbidity and pH of SL as a function of fly ash/SL ratio, respectively. As can be seen, by increasing the dosage of fly ash, turbidity of SL significantly decreased and it reached a plateau of 220 NTU (89% turbidity removal). The decrease in turbidity removal can probably be attributed to two phenomena of adsorption and coagulation. 1) Lignin concentration in SL decreased as it was adsorbed on fly ash (i.e. adsorption); 2) It was claimed that lignin of pulping effluent had carboxylic groups, which implies that lignin had an anionic charge density (Chen et al., 1983; Nakagame et al., 2011; Saeed et al., 2011). Lignin and other anionic components of SL would be neutralized by fly ash metals (such as Ca^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+}). The hydrolysis of metals and subsequent precipitation of metal hydroxides and other metal- lignocellulosic compounds would contribute to the decrease in the turbidity of SL (i.e. coagulation) (Duan & Gregory, 2003; Gregory & Duan, 2001).

Additionally, the pH of samples increased by adding fly ash. It was discussed that most fly ashes are alkaline due to their alkali and alkaline earth metal compounds (Ahmaruzzaman, 2010). Increasing pH of the SL may be due to the hydrolysis of fly ash constituents (mainly metals) in SL (Gregory & Duan, 2001).

4.4.3 Adsorption on washed fly ash

Figure 4.2 also shows lignin removal, turbidity and COD as a function of the dosage of washed fly ash (mg/g) with and without pH adjustment. As can be seen, washing fly ash insignificantly affected the removal of lignin. In this case, an increase in the surface area of fly ash through washing (Table 4.1) compensated for the decrease in cationic charge density of fly ash. In other words, the overall adsorption might have been increased, while the overall coagulation might have been decreased in the treatment of washed fly ash compared with that of unwashed fly ash, which implies that washing fly ash had inconsiderable effect on adsorption of lignin.

The COD and turbidity analyses showed that washed fly ash treatment had less COD and turbidity reductions compared with unwashed fly ash treatment. As explained earlier, by washing fly ash, the metal components of fly ash decreased, and thus its coagulating performance was reduced. The reduction in coagulating performance of fly ash would reduce its affinity in removing other components of effluent (i.e. extractives and fatty acids).

It should be highlighted that the difference in end pH of SL between unwashed and washed fly ash is due to the reduction in metal ions (mainly sodium and potassium) and thus alkalinity of fly ash through the washing process.

4.4.4 Kinetics of adsorption

Figure 4.3 shows the impact of unwashed fly ash treatment time on lignin, COD and turbidity contents of SL samples. It is observable that lignin reached the saturation level of 67 mg/g adsorption in 3 h. However, COD and turbidity reached the plateau in 45 min and 90 min, respectively. These results are in harmony with earlier study on adsorption of lignin from SL on activated carbon (Oveissi & Fatehi, 2014). This hypothesis is in harmony with literature results (Andersson et al., 2011; Mohan & Gandhimathi, 2009; Ugurlu et al., 2005). In the literature, it was claimed that the maximum adsorption of calcium lignosulfonate (34.20 mg/g) onto coal fly ash obtained in 2 h under the conditions of 30 °C and 150 rpm (Li et al., 2012). These results may imply that the coagulation of metals with components of SL was a fast process, while adsorption of lignin on fly ash was a slower process in the overall removal of lignin, COD and turbidity analyses.

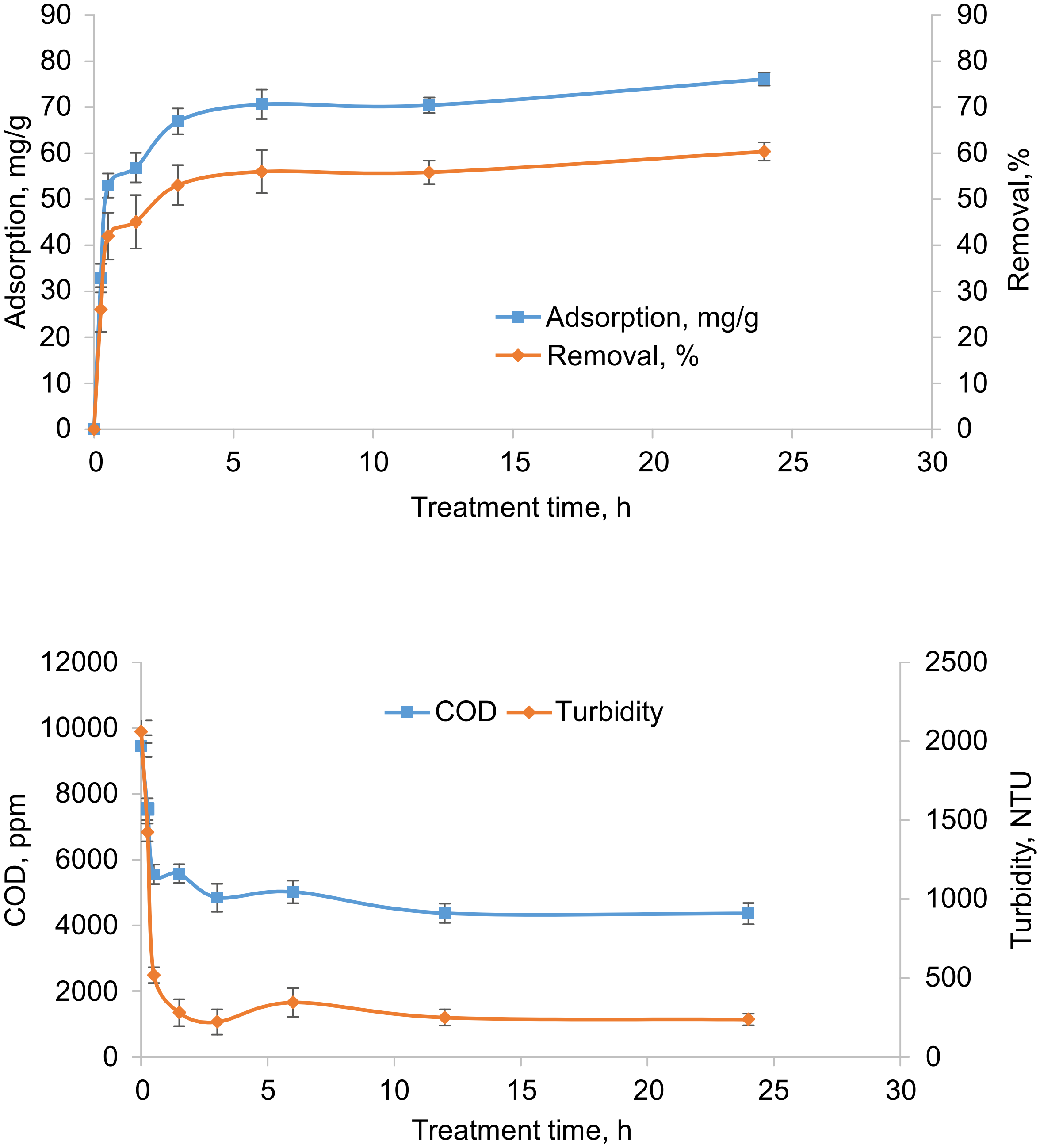

Figure 4.3. Effect of treatment time on properties of SL: (top) adsorption of lignin on fly ash and removal of lignin from SL (bottom) COD and turbidity removals from SL (incubated at the fly ash/SL ratio of 55mg/g 30 °C and 100 rpm)

4.4.5 Process modification

As illustrated in the experimental section, five alternatives were assessed under the optimized conditions (3 h and dosage of 55mg fly ash per gram of SL) and the experimental data were listed in Table 4.3. The results showed that a single stage adsorption resulted in 53 % of lignin, 49 % of COD and 89 % of turbidity removals from SL (option A). However, the pH of sample increased to 12.1, which is unfavorable as biological wastewater treatment are mostly performed at 5-8 pH (Kavanagh et al., 2011). Therefore, pH was adjusted before and after incubation in options B and C, respectively, and the results were listed in Table 4.3. As can be seen, the pH adjustment before incubation (option B), caused 53 % lignin removal, but the turbidity and COD were less reduced compared with option A. This analysis indirectly implies that lignin removal was somehow independent of pH of the process (adsorption was independent), but the removal of other compounds from SL (via coagulation) was pH dependent. In the literature, it was reported that the metal-lignocellulosic compounds were more effectively formed under alkaline pH, which indirectly confirms the dependency of coagulation with pH (Mourant et al., 2011).

In option C, the addition of acid after adsorption slightly improved the removal of lignin and COD, but not turbidity. The small decrease in lignin content of SL is attributed to the adsorption of more lignin on fly ash, which resulted in a further COD reduction. However, addition of acid affects the overall ionic strength of the SL. Under acidic condition, the hydrogen ion will replace the metal ion on the metal-lignocellulosic compounds. The solubility of hydrogen-based compound might be higher than that of metal-based compounds, which resulted in its dissolution in SL after readjusting the pH to 5.3 (Fu & Wang, 2011). It should be highlighted that the adsorption of lignin in single-stage adsorption (option A) and single-stage adsorption with post pH adjustment (option C) is similar.

An earlier study showed that a two stage adsorption was a more efficient option than one stage adsorption for lignin removal from SL (lignin removal increased from 45% to 60 %)(Oveissi & Fatehi, 2014). The results of option D depicted that after two stages of adsorption, lignin, COD and turbidity removal were 66 %, 68 % and 94 %, respectively. In this case, the lignin adsorption on fly ash corresponded to 67 mg/g and 17 mg/g in the first and second stages, respectively. In option E, the two stage adsorption was followed by a neutralization step, which led to 68 % of lignin, 70 % of COD and 94 % of turbidity reductions.

Table 4.3. Concentration of lignin, COD, turbidity and pH of SL under different process options that were conducted under the optimal conditions of 55 mg fly ash/g SL, 3 h and 30 °C.

Process	Fly ash	Lignin concentration, g/l	COD, mg/l	Turbidity, NTU	End pH
control	-	7.05 ± 0.12	9456 ± 510	2060 ± 82	5.3 ± 0.1
A	unwashed	3.29 ± 0.09	4840 ± 246	221 ± 90	12.1 ± 0.1
A	washed	3.45 ± 0.10	5100 ± 324	758 ± 47	10.0 ± 0.0
B	unwashed	3.32 ± 0.08	6085 ± 489	620 ± 73	5.3 ± 0.0
C	unwashed	3.06 ± 0.11	4508 ± 341	301 ± 65	5.3 ± 0.1
C	washed	3.36 ± 0.12	4950 ± 487	882 ± 74	5.3 ± 0.0
D	unwashed	2.37 ± 0.14	2985 ± 342	126 ± 13	12.3 ± 0.2
E	unwashed	2.28 ± 0.16	2873 ± 358	121 ± 18	7.1 ± 0.1

4.4.6 High Heating Value (HHV) of treated fly ash.

Figure 4.4 shows the calorific value of the fly ash treated with SL in a single adsorption step (option A). As can be seen, an increase in the adsorption of lignin on fly ash escalated the calorific value of the lignocellulosic-treated fly ash. This would indicate that the lignocellulosic-treated fly ash can be introduced as a source of energy in the boiler.

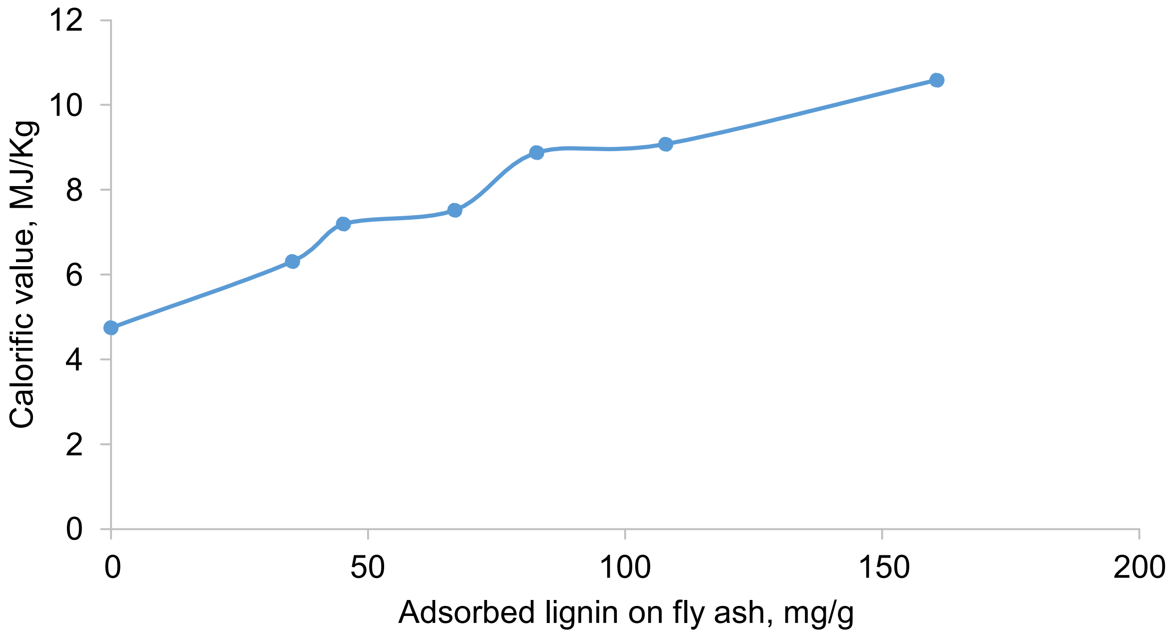

Figure 4.4. High heating values of lignocellulose-treated fly ash as a function of lignocellulose adsorption on fly ash.

Based on the results in Table 4.3, a process was proposed in Figure 4.5 to treat the SL of a TMP process with fly ash. In this process, the SL of TMP would be treated via two step adsorption stages. Then, the treated fly ash will be separated with a filtrate in each adsorption stage, then combined together and sent to a mechanical press to increase its dryness. Once the water content of the treated fly ash is reduced, it will be sent to the power boiler. Afterwards, it will be recirculated to the adsorption stages after incineration. The lignocellulosic materials attached to fly ash will ideally generate a net heat in the power boiler, hence it will help the overall economy of the plant. Consequently, not only the power boiler is integrated into the process (and lignocelluloses will be more effectively utilized), but also the load to wastewater treatment will be reduced significantly. This is important as the current anaerobic, aerobic and polymers treatments are expensive. The developed process is environmentally friendly, simple and well integrated into the existing facilities of pulping processes.

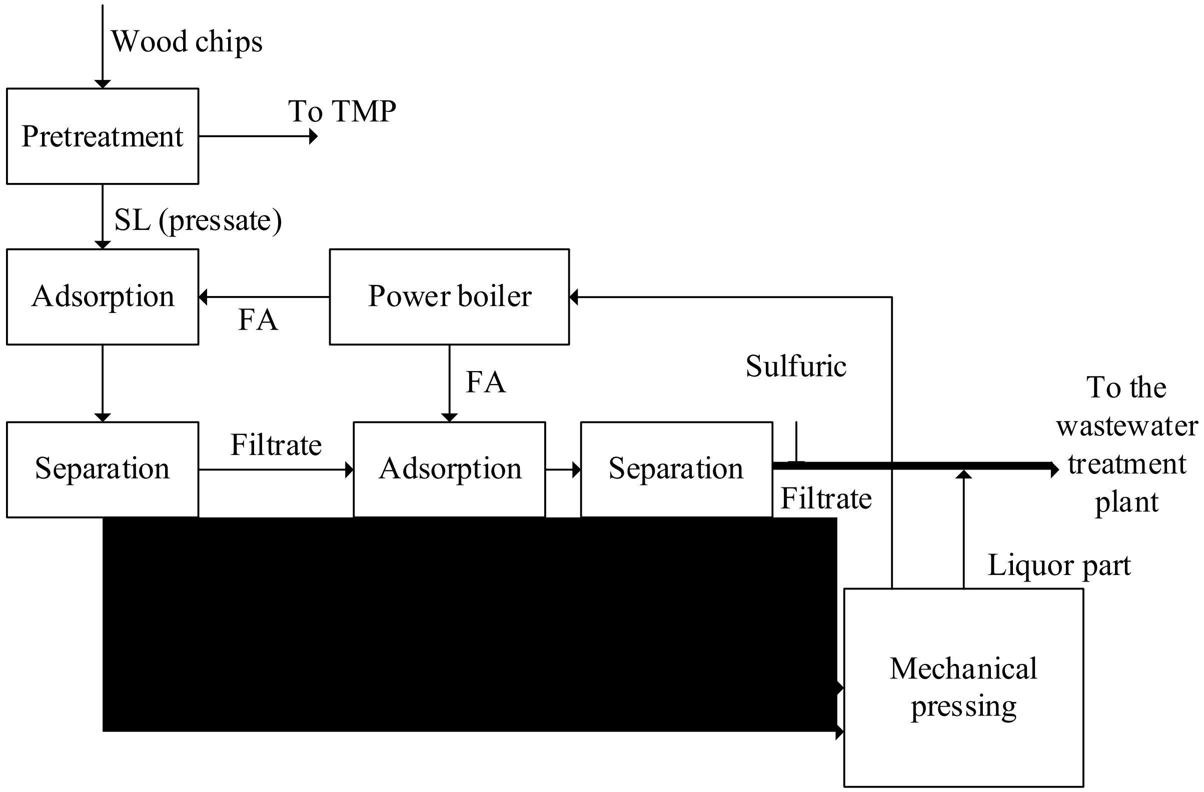

Figure 4.5. Proposed process for SL of TMP

4.5 CONCLUSIONS

The adsorption of lignin from SL of TMP process via fly ash was investigated. The results suggest that adsorption of lignin on fly ash was insensitive to pH and slow, but the coagulation of other constituents of SL with fly ash components was pH sensitive and fast. Also, decreasing the pH slightly increased the turbidity of SL. The results showed that the adjustment of pH after the treatment was better for COD removal. It was observed that within the optimum condition (fly ash/SL ratio of 55 mg/g for 3h), 53 % of lignin, 49 % of COD and 89 % of turbidity was removed.

The maximum removals of lignin and COD were achieved via adjusting pH after adsorption while the maximum turbidity removal was obtained without pH adjustment. The process was modified by adding another stage of adsorption and neutralizing the pH. The two stage adsorption process had 68 %, 70 % and 94 % lignin, COD and turbidity removals, respectively. These results show that the adsorption process with fly ash can be applied to decrease the load of wastewater in the TMP pulping process.

4.6 ACKNOWLEDGMENT

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5 CHAPTER FIVE: PRODUCTION OF MODIFIED BENTONITE VIA ADSORBING LIGNOCELLULOSES FROM SPENT LIQUOR OF NSSC PROCESS

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5.1 ABSTRACT

In this work, the adsorption of lignocelluloses from spent liquor (SL) of neutral sulfite semi chemical (NSSC) pulping process on bentonite was investigated. It was observed that 0.26 g/g of lignin and 0.27 g/g of hemicelluloses from SL were adsorbed on bentonite under the conditions of 50 °C, 100 rpm and 40 g/g SL/bentonite after 3 h of treatment. The adsorptions of lignin and hemicellulose were increased to 1.8 g/g and 0.5 g/g, respectively, via adding 15 mg/g of polydiallyldimethylammonium chloride (PDADMAC) in the system of SL/bentonite. The turbidity and COD removals were improved from 69 % to 93 % and from 25 % to 38 % by adding PDADMAC to the SL/bentonite, respectively. The increase in the heating value of bentonite (from 0 to 15.4 MJ/kg) confirmed the adsorption of lignocelluloses. The modified bentonite can be used as filler in corrugated medium paper production or as fuel.

KEYWORDS: Lignocelluloses, NSSC spent liquor, Adsorption, Bentonite, Biorefinery.

5.2 INTRODUCTION

The tight competition in the market of traditional forest products and a dramatic decrease in the price of pulp and paper products have been a strong driving force for seeking novel forest-based business strategies (Van Heiningen, 2006). In this regard, several scenarios of biorefinery were suggested over the past decade in order to reduce the energy costs or to generate value-added products rather than traditional pulp and paper products in forest industry (Huber and Dumesic, 2006; Oveissi and Fatehi, 2014; Sitter et al., 2014).

Neutral sulfite semi-chemical (NSSC) pulping process is used for producing corrugated medium papers. In this process, wood chips are initially treated with sodium bicarbonate and sodium sulfite. Subsequently, the soften woodchips are mechanically fragmented and are used to produce corrugated paper boards (Navaranjan et al., 2013). However, the spent liquor (SL) of this process contains lignin and hemicelluloses that are separated from wood chips during chemical pretreatment, but lignin and hemicelluloses could be considered for producing energy or value-added products.

However, these lignocelluloses should be extracted from SL so that their use in the production of value-added chemicals or energy becomes cost effective. It was previously discussed that ultrafiltration, acidification and evaporation would not be economically feasible for extracting lignocellulose from SL due to the dilute concentration of dissolved lignocelluloses in spent liquors (Oveissi and Fatehi, 2014; Sitter et al., 2014). However, adsorption was suggested as feasible and economical alternative for the isolation of lignocelluloses from pulping liquors, e.g. SL and pre hydrolysis liquor (Dashtban et al., 2014b; Fatehi et al., 2013a; Liu et al., 2011a; Oveissi and Fatehi, 2014). In the literature, 0.33 g/g of lignin and 0.25 g/g of hemicellulose (from SL of NSSC pulping process) were adsorbed on activated carbon under the conditions of 30 °C, 100 rpm, pH 5.7, SL/activated carbon weight ratio of 30 after 360 min of treatment (Dashtban et al., 2014b). Another study showed that the maximum adsorptions of 0.2 g/g of oligomeric sugars and 0.08 g/g of lignin from PHL were achieved on calcium carbonate at 40 °C, 120 rpm, pH 7, 40 g/g PHL/$CaCO_3$ for 5 h (Fatehi et al., 2013a).

Bentonite is a natural mineral with a three-layer structure: two silicate layers surrounding an aluminate layer (Tahir & Rauf, 2006). Recently, bentonite was subjected for the removals of phenols and toxic metals from aqueous solutions (Fernández-Pérez et al., 2005; Lee and Tiwari, 2012; Richards and Bouazza, 2007). Another study showed that 8 mg/g of phenol (from a concentration of 60 mg/l) adsorbed on bentonite at 25 °C, pH 6.5 and 2 h (Alkaram et al., 2009). Furthermore, a study on model wood-based polymers reported that the adsorptions of sulfonated kraft lignin and blue dextran were 50 and 150 mg/g on bentonite at 22 °C after 1 h of treatment, respectively (Asselman and Garnier, 2000). Economically, bentonite costs US$ 107/ton (Carmignano and Carvalho, 2014), which is almost 500 times lower than that of activate carbons ($US 1,650-9,900/ton) (Zhi et al., 2014). Accordingly, bentonite has the potentiality to be considered as an adsorbent for isolating lignocelluloses from SL from economical point of view.

To the present day, no work was reported on the adsorption of lignin and hemicelluloses from pulping liquors on bentonite. The first stage of the current work aimed at investigating the adsorption behaviour of lignin and hemicelluloses on bentonite. Furthermore, it is well know that the addition of cationic polymers can improve the adsorption efficiency of polymers on adsorbents (Dashtban et al., 2014a; Fatehi et al., 2013a; Liu et al., 2012). It was previously reported that the adsorption of lignin (from the SL of NSSC process) on activated carbon was significantly improved from 0.9 g/g to 2.5 g/g by adding polydiallyldimethylammonium chloride (PDADMAC) (Dashtban et al., 2014a). Hence, the second objective of the present study was to investigate the effect of PDADMAC on the adsorption of lignocelluloses on bentonite. Finally, a process was proposed not only for isolating the lignocelluloses from SL, but also for decreasing the organic load of SL to wastewater treatment system of an NSSC process. It should be highlighted that the product of such process can be directly applied as a filler (value-added product) in corrugated medium papers or the adsorbed lignocelluloses on bentonite can be desorbed and considered as a raw material for producing other value-added products in a downstream process.

5.3 MATERIALS AND METHODS

5.3.1 Materials

The spent liquor (SL) of an NSSC pulping process was obtained from a mill located in eastern Canada. In this process, wood chips were pretreated with sodium sulfite and caustic for 15-18 min at 180 °C. The SL samples were received from the company and centrifuged at 1000 rpm for 10 min prior to use. Bentonite was purchased from Sigma-Aldrich Company and used as received. Solutions (20 wt. %) of low molecular weight (MW) 100,000-200,000 g/mol of polydiallyldimethylammonium chloride (PDADMAC1), and high MW 400,000-500,000 g/mol PDADMAC (PDADMAC2) were purchased from Sigma-Aldrich Company.

5.3.2 Adsorption

In one set of experiments, various amounts of bentonite were added to 45 g of SL in 125 ml Erlenmayer falsks. Then, the flasks were sealed and incubated in a C76 New Brunswick water bath shaker at 50 °C, and 100 rpm for 24 h. This set of experiments aimed to optimize the ratio of bentonite to SL for the maximum adsorption of lignin and hemicelluloses. Based on these results, the kinetics of adsorption was investigated at various time intervals. Under the optimum conditions (i.e. the dosage of bentonite/SL and the time that maximum adsorption of lignin and hemicelluloses were achieved), another set of experiments was conducted at different temperatures. In all sets of experiments, control samples of SL were incubated at the same operating conditions, but without the bentonite addition. Afterwards, the treated SLs were centrifuged at 2000 rpm for 10 min using a Survall ST16 centrifuge. The supernatants were collected for lignin, sugar, COD and turbidity analyses. Also, the precipitates were oven dried at 60 °C for a week and subsequently were used for elemental, calorific value and thermogravametric analyses. To satisfy statistical aspects of this work, all experiments were triplicated and the average of the three was reported. The error bars in all graphs account for the standard deviations of three measurements.

5.3.3 Combined process of adsorption/flocculation

In another set of experiments, PDADMACs were added to SL/bentonite system in order to improve the adsorption of lignin and hemicelluloses on bentonite. In this regard, after conducting the adsorption under the optimal conditions (obtained in section 2.2), different dosages of PDADMAC (in solution) were added to SL/bentonite systems after treating SL with bentonite for 3 h and without any intermediate filtration stage, and then the systems were incubated for another 90 min in the water bath shaker. Afterwards, samples were centrifuged at 2000 rpm for 10 min and the supernatants and the precipitates were used for further analyses. This analysis helped optimize the dosage of PDADMAC in SL/bentonite systems for better adsorptions of lignin and hemicelluloses. In another set of experiments, the effect of molecular weight of PDADMAC on its adsorption performance on bentonite was investigated by conducting the dosage experiment with two different MWs of PDADMAC (PDADMAC1 and PDADMAC2). Control samples were incubated under the same operating conditions, but deionized water was added instead of PDADMAC solution in the SL/bentonite systems. All tests were conducted three times and the average of the three was reported.

5.3.4 Charge density and surface area analyses

The charge density of bentonite was measured by Mütek PCD04 charge detector as previously described (Liu et al., 2011b; Oveissi and Fatehi, 2014). The BET surface area of bentonite was also determined by a NOVA-2200e Autosorb under N_2 medium according to the procedure described in the literature (Yang et al., 2010).

5.3.5 Precipitate analyses

The elemental (ultimate) analysis of precipitates was conducted using a Vario EL cube instrument (Germany), according to the previously established method (Fadeeva et al., 2008; Sitter et al., 2014). The thermal stability of precipitates was assessed by a thermo-gravimetric analyzer (TGA)-i1000 series (instrument Specialist Inc., U.S.A.) under N_2 atmosphere (30 mlit/min) and increment rate of 10 °C/min (Dashtban et al., 2014a; Wang et al., 2009). The gross calorific values (high heating values) of precipitates were measured according to ASTM E711-87 using a Parr 6200 oxygen bomb calorimeter. Prior to this analysis, 0.8–1.2 g of the dried precipitates was pulverized by a Wiley mill and subsequently pelletized with a Parr Pellet press (Dashtban et al., 2014a).

5.3.6 Lignin, ash and hemicelluloses analyses

The lignin content of SL was assessed before and after adsorption treatment according to TAPPI UM 250 using a UV/VIS spectrophotometry (Genesys 10S, Thermo Scientific) at the wavelength of 205nm (Liu et al., 2011b; Oveissi and Fatehi, 2014). The ash content of SL was measured according to TAPPI T412 (Dashtban et al., 2014a). The hemicelluloses concentration of SLs before and after the treatment was determined according to the previously established DNS method using 3,5-dinitrosualicylic acid (DNS reagent) (Sitter et al., 2014). Prior to hemicelluloses analysis, all samples were acid hydrolyzed with 4 % sulfuric acid at 121 °C for 1 h in a Haake-S45 oil bath. This pretreatment aimed to break all oligomeric sugars to mono-sugars as DNS reagent can only identify the monomeric sugars.

5.3.7 Turbidity and COD analyses

The turbidity of SL samples was measured before and after the adsorption experiments using a Hach 2100AN turbidity meter (Fatehi et al., 2013b; Oveissi and Fatehi, 2014). This procedure was repeated three times and the average of three repetitions was reported. The chemical oxygen demand (COD) of SL samples before and after adsorption was measured as previously described, and the average values of three measurements were reported in this work (Dashtban et al., 2014b; Oveissi and Fatehi, 2014).

5.4 RESULTS AND DISCUSSION

5.4.1 SL and bentonite characterizations

It was illustrated that SL had 66.67 g/l lignin, 14.20 g/l hemicelluloses (included both monomeric and oligomeric sugars), 26.50 g/l acetic acid, 0.52 g/l furfural and 59.43 g/l ash. The ash content of SL is originated from chemicals, such as bicarbonates and sodium sulfite used in the chemical pretreatment stage of NSSC pulping process. The removals of acetic acid and furfural from SL were excluded from the present work due to the 1) weak adsorption of acetic acid on adsorbents, 2) weak interaction of acetic acid with cationic polymers (i.e. PDADMAC) and 3) low concentration of furfural in SL and hence its low adsorption on adsorbents (e.g. bentonite) (Saeed et al., 2011; Sitter et al., 2014).

Bentonite had a surface area of 13.49 m^2/g and charge density of -0.067 μeq/g. In the literature, it was stated that bentonite had a neutral charge density (Hu et al., 2006). However, the excess negative charge density of bentonite may be due to isomorphous substitution (Hu et al., 2006). In other words, when bentonite is placed in water, the tetravalent silica would partially exchange with trivalent aluminum, which may lead to the replacement of trivalent aluminum with other cations in bentonite (i.e. divalent calcium or monovalent sodium) and produce a slight negative charge density (Hu et al., 2006; Tahir and Rauf, 2006).

5.4.2 Effect of temperature

Figure 5.1 shows the effect of temperature on the adsorption of lignin and hemicelluloses from SL on bentonite. As can be seen, lignin and hemicellulose had peaks of adsorption at two different temperatures. A study on the adsorption of chlorobenzenes on the surface of modified silica showed that equilibrium adsorption increased by increasing the temperature from 3 °C to 11°C, then decreased by increasing the temperature from 11°C to 50 °C (Szecsody and Bales, 1991). However, the reason for such behavior is still under investigation. It is well know that lignin has higher tendency to be adsorbed than do hemicelluloses in aqueous solution due to the higher amounts of carboxylic and sulfonated groups attached to lignin and the more hydrophobic nature of lignin (compared with hemicellulose) (Oveissi and Fatehi, 2014; Dashtban et al., 2014a) that can develop interaction with the surface of bentonite.

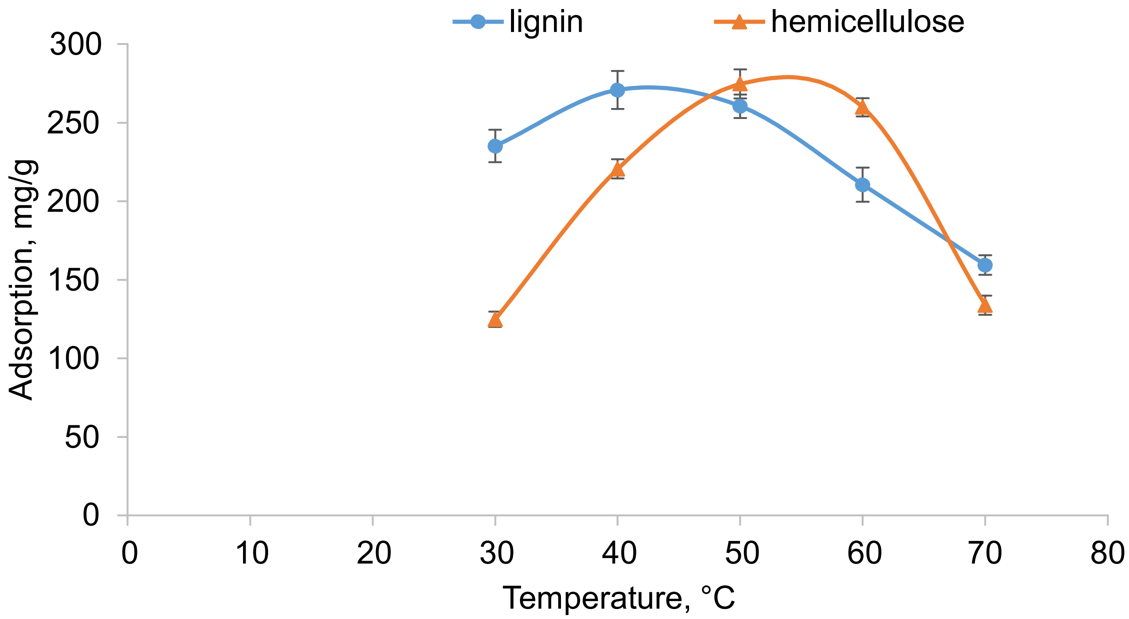


Figure 5.1. Effect of temperature on the adsorptions of lignin and hemicelluloses from SL on bentonite (1 g of bentonite in 40 g of SL, 100 rpm for 24 h).

5.4.3 Adsorption isotherms

Figure 5.2 shows the adsorption isotherms of lignin and hemicelluloses from SL on bentonite. C_{eq} is the equilibrium adsorbate (i.e. lignin or hemicelluloses) concentration (mg/l) and C_{bent} is the bentonite concentration (mg/l) in the SL. As can be seen, the adsorption of lignin increased initially and reached to the equilibrium of 0.26 g/g on bentonite. However, no plateau was found for the adsorption of hemicelluloses. At the ratio of 1/40 bentonite/SL ratio, 0.27 g/g of hemicelluloses was adsorbed on bentonite. A similar study on the adsorption of lignocelluloses from SL on activated carbon showed that adsorptions of 0.9 g/g lignin and 0.43 g/g of hemicelluloses were achieved via treating activated carbon with SL at 30 °C, 100 rpm, 3 h and the ratio of 1/90 g/g activated carbon/SL (Dashtban et al., 2014a). Another study showed that 150 mg/g of sulfonated kraft lignin and 150 mg/g of dextran were absorbed on bentonite at 22 °C and 1 h treatment (Asselman and Garnier, 2000). The main driving force for the adsorption of lignin and hemicelluloses on bentonite could be the development of hydrogen bonding between lignin and hemicellulose on one hand and bentonite on the other hand (bentonite contains oxygen atoms on its lamellar plate structure). In addition, the diffusion of lignin and hemicelluloses in silicate sheets of bentonite could weaken the attraction forces between the sheets of bentonite and would subsequently increase the interlayer spacing in bentonite structure (Al-Asheh et al., 2003; Lee and Tiwari, 2012), which would increase the surface area of bentonite. Consequently, the small size molecules of hemicelluloses (mostly monomeric sugars) could diffuse into the bentonite structure. In this work, the adsorption of monomeric and oligomeric sugars were reported as hemicelluloses on bentonite, thus the increase in the adsorption of monomeric sugars leads to the higher overall adsorption of hemicelluloses on bentonite, which was observed in Figure 5.2.

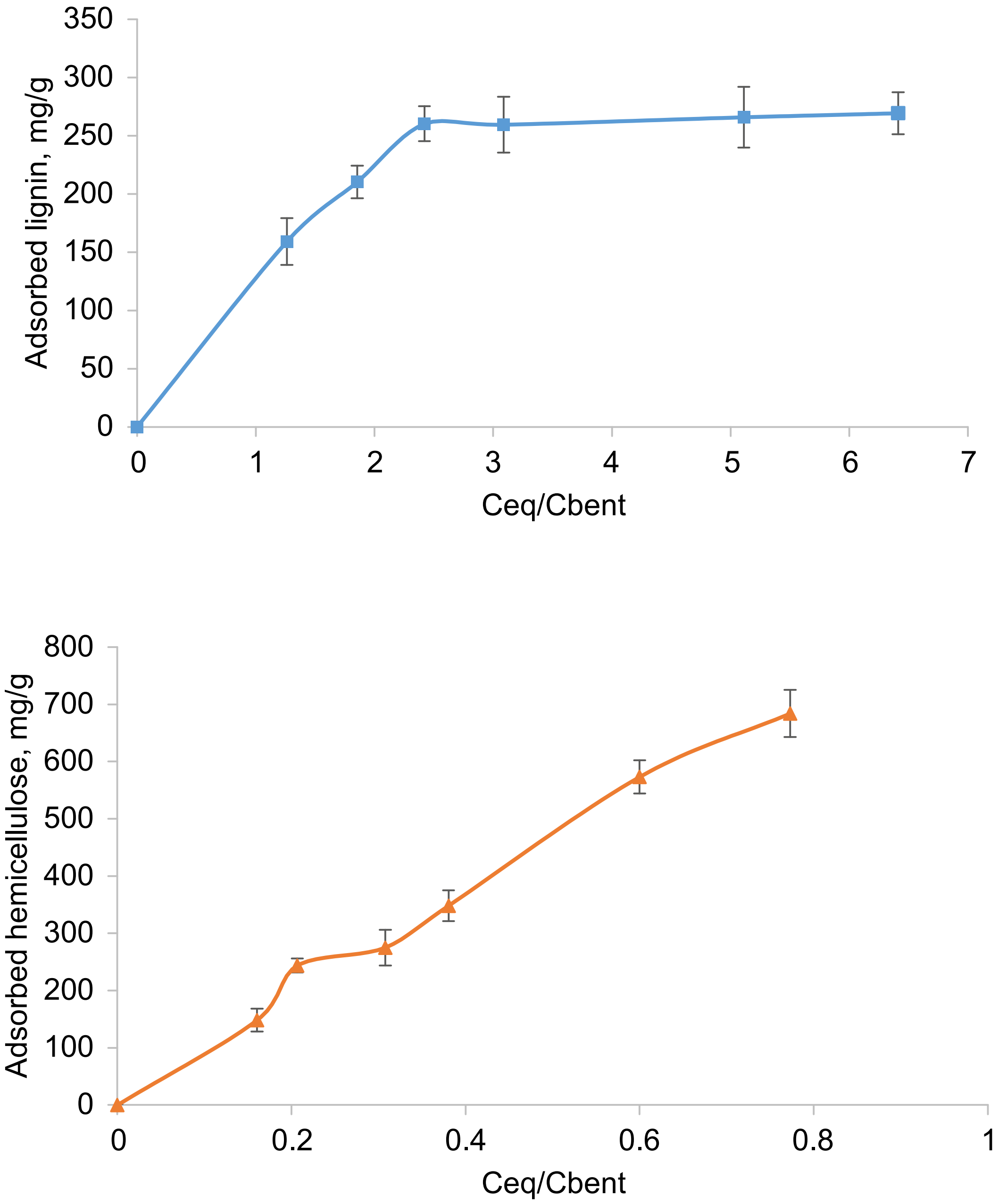


Figure 5.2. Adsorption isotherms of lignin (top) and hemicelluloses (bottom) from SL on bentonite (50 °C and 100 rpm for 24 h)

The experimental results were fitted into Langmuir (5.1) and Freundlich (5.2) isotherm models (Asselman and Garnier, 2000; Fatehi et al., 2013a):

$$\Gamma_{ads} = \frac{\Gamma_{max} C_e}{K + C_e} \tag{5.1}$$

$$\Gamma_{ads} = K_f C_e^{1/n} \tag{5.2}$$

where Γ_{ads} (g/g), Γ_{max} (g/g), C_e (g/g) and K (g/g) were the adsorbed amounts on bentonite, maximum adsorption on bentonite, the adsorbate concentration per unit mass of bentonite and the ratio of desorption/adsorption rate constants, respectively (Asselman and Garnier, 2000). In Freundlich model, K_f and n are known as Freundlich constants (Foo and Hameed, 2010). Table 5.1 summarized the modeling parameters that were obtained from experimental results of Figure 5.1. As can be seen, the adsorption isotherm of lignin fitted better in Langmuir model (R^2= 0.983) than Freunlich model. This indicates that the adsorption of lignin on bentonite was homogenous (each molecules had constant enthalpy and sorption activation energy) and monolayer, and the adsorbed layer was one molecule in thickness (Foo and Hameed, 2010). Also, based on Langmuir's assumptions, there was no lateral interaction between the adsorbed lignin molecules on adjacent sites (Foo and Hameed, 2010). Interestingly, the adsorption isotherm of hemicelluloses fitted well into Freundlich. It can be concluded that the adsorption of hemicelluloses on bentonite was multilayer and the distribution of adsorption heat and tendency for adsorption were not uniform over the bentonite surface (Foo and Hameed, 2010).

Table 5.1. The measured parameters for Langmuir and Freundlich adsorption isotherms of lignin and hemicelluloses on bentonite (generated using experimental results of Figure 1)

Component	**Langmuir isotherm**			**Freundlich isotherm**		
	Γ_{max} (g/g)	K (g/g)	R^2	K_f	n	R^2
Lignin	0.310	0.822	0.983	0.172	3.48	0.711
Hemicelluloses	5.317	5.195	0.182	0.744	1.08	0.971

5.4.4 Kinetics of adsorption

Figure 5.3 depicts the adsorption kinetics of lignin and hemicelluloses on bentonite. As can be seen, the adsorptions of lignin and hemicelluloses were fast. In other words, lignin adsorption reached to equilibrium in 2 h, while hemicellulose adsorption reached to its maximum value in 3 h. It can be concluded that the adsorption of hemicelluloses is slower than that of lignin. This is due to the gradual diffusion of monosugars into the structure of bentonite, as explained earlier. These results are in harmony with the results of previous studies on the adsorption of lignocelluloses from pulping liquors on calcium carbonate and activated carbon (Dashtban et al., 2014a; Fatehi et al., 2013a; Oveissi and Fatehi, 2014).

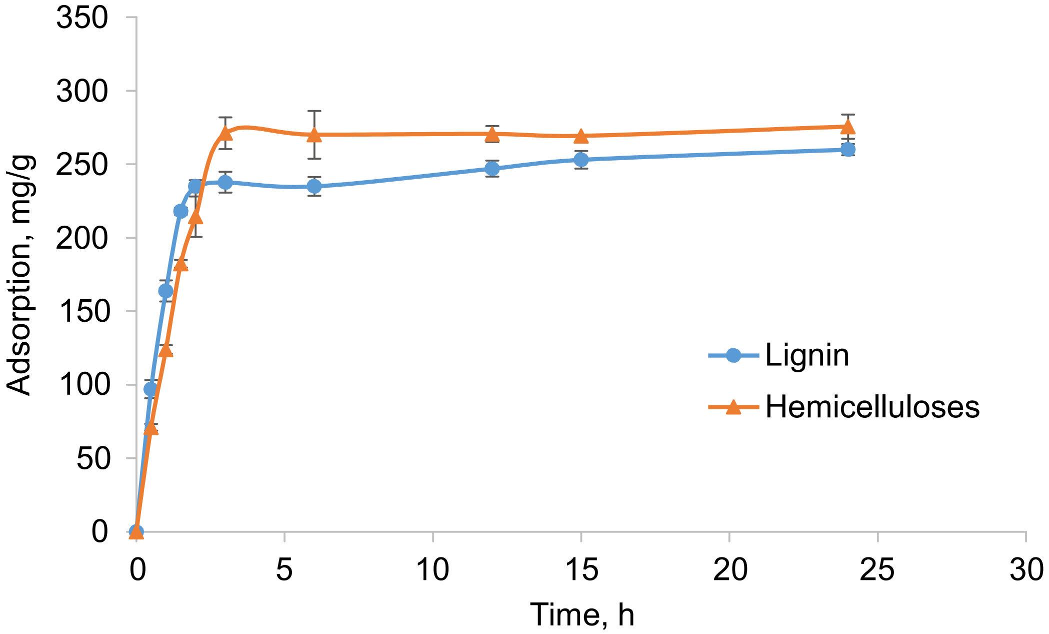


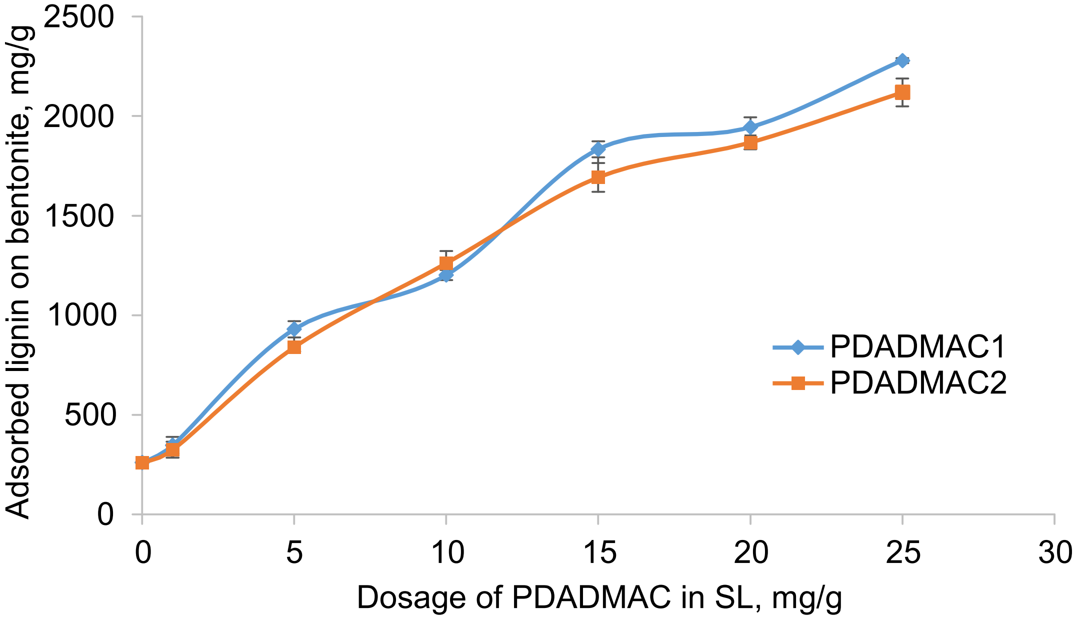
Figure 5.3. Effect of time on the adsorption of lignin and hemicelluloses on bentonite (50 °C, 100 rpm).

5.4.5 Impact of PDADMAC on adsorption

In the literature, it was stated that the addition of cationic polymer would improve the adsorption of lignocelluloses on different adsorbents (Liu et al., 2012). It is well known that lignin and hemicelluloses of pulping liquors has anionic charge densities (Liu et al., 2011a,2012). Consequently, a part of PDADMAC (cationic polymer) would interact with lignocelluloses in SL, and form complexes in the SL solution. These complexes would adsorb on the surface of bentonite. Furthermore, another part of PDADMAC would adsorb on the surface of bentonite and form a layer-by-layer assembly of PDADMAC and lignocelluloses on bentonite (Dashtban et al., 2014a; Fatehi et al., 2013b). In another set of experiments, different dosages of PDADMAC solutions were added to bentonite/SL system and the results are presented in Figure 5.4. It is observable that the adsorption of lignin on bentonite increased by increasing the dosage of PDADMAC in bentonite/SL system. However, the adsorption of hemicelluloses on bentonite reached the maximum at 15 mg/g PDADMAC/SL. A similar trend was observed for the adsorption of hemicelluloses on activated carbon in another study (Liu et al., 2012). It was discussed in the literature that lignin has more negative charge density than do hemicelluloses. As explained earlier, this is due to presence of more carboxylic, carbonyl and sulfonated groups on its structure (Saeed et al., 2011; Zhu et al., 2009). Therefore, the interaction of lignin with PDADMAC would be stronger than that of hemicellulose and PDADMAC. Therefore, by increasing the dosage of PDADMAC in the SL, more of lignin-PDADMAC complexes would be developed and adsorbed on bentonite. It was hypothesized that an increase in the adsorption of lignin-PDAMAC on bentonite would restrict the available surface area of bentonite for the adsorption of hemicelluloses. However, more studies on this topic are required to prove the aforementioned hypotheses.

Figure 5.4 also depicts the influence of molecular weight of PDADMAC on the adsorption of lignocelluloses on SL. As can be seen, PDADMAC1 slightly adsorbed more lignin and less hemicellulose than did PDADMAC2. A similar trend was observed in another study, and this behavior was related the fact that lignin had more affinity to interact with low MW polymers than with high MW polymers (Dashtban et al., 2014a). It was claimed that smaller polymers makes smaller complexes than do large polymers (Saeed et al., 2011). Subsequently, the smaller complexes of lignin/PDADMAC1 can diffuse more into the pores of bentonite than large complexes of lignin/PDADMAC2. Therefore, by increasing the dosage of PDADMAC1, more complexes of lignin/PDADMAC1 can be made and diffuse in the pores. However, at higher dosage of polymers, the adsorption of hemicelluloses decreased (Figure 5.4). It was hypothesised that by increasing the dosage of PDADMAC, more lignin/PDADMAC complexes would be formed and hence they fill the pores so that there is less chance for larger complexes of hemicelluloses/PDADMAC to diffuse into the bentonite (Dashtban et al., 2014a).

At the dosage of 15 mg/g PDADMAC1/SL, approximately 1.8 g/g lignin and 0.5 g/g hemicelluloses were adsorbed on bentonite, which corresponded to 56 % and 67 % of lignin and hemicellulose removals from the SL, respectively. Also, at the dosage of 15 mg/g PDADMAC2/SL, the adsorptions of lignin and hemicelluloses were 1.7 g/g and 0.5 g/g, which corresponded to 52 % and 72 % removals, respectively.



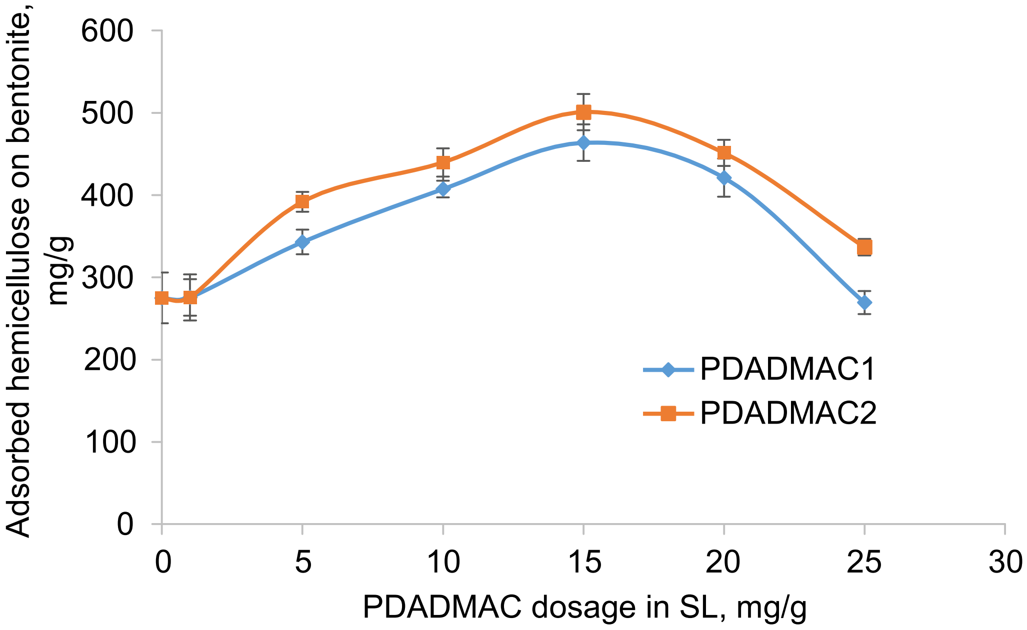


Figure 5.4. Adsorption of lignin (top) and hemicelluloses (bottom) of SL on bentonite as a function of PDADMAC dosage in the SL/bentonite system (SL was treated with bentonite under the conditions of 40 g/g SL/bentonite, 50 °C, 100 rpm for 3 h, then PDADMAC was added to SL/bentonite system at 50 °C, 100 rpm and the system was incubated for another 90 min)

5.4.6 Turbidity and COD analyses

It was previously stated that lignocelluloses have a great contribution in the chemical oxygen demand (COD) of SL (Andersson et al., 2008, 2012; Kavanagh et al., 2011). The turbidity and COD content of original SL and that after treatments are listed in Table 5.2. It is evident that the turbidity and COD of SL decreased from 6980 to 2186 NTU and from 1.59×10^5 to 1.19×10^5 ppm via treating SL with bentonite under the optimal conditions of 50 °C, 100 rpm and 40 g/g SL/bentonite for 3 h, respectively. The turbidity and COD content of SL were 480 NTU and 0.99×10^5 ppm after treating SL with bentonite/PDADMAC1 and they were 1000 NTU and 1.08×10^5 after treating SL with bentonite/PDADMAC2 (conducted under optimized conditions of 40 g/g SL/bentonite, 50 °C, 100 rpm for 3, then 15 mg of PDADMAC was added to 1g SL/bentonite system at 50 °C, 100 rpm and the system was incubated for another 90 min), respectively. Overall, 69, 93 and 86 % of turbidity were removed through SL/bentonite, SL/bentonite/PDADMAC1 and SL/bentonite/PDADMAC2, respectively. Also, the COD of SL was reduced by 25, 38 and 32 % via SL/bentonite, SL/bentonite/PDADMAC1 and SL/bentonite/PDADMAC2 treatments, respectively. Consequently, SL/bentonite/PDADMAC1 was the most efficient system for COD and turbidity removals. Furthermore, as PDADMAC1 slightly removed more lignin and less hemicellulose than did PDADMAC2, it may be concluded that lignin had more contribution than hemicelluloses in turbidity and COD content of SL.

Table 5.2. CHNSO, COD, turbidity and high heating values of different samples used/generated in this study (all samples were oven dried at 60 °C for 7 days prior to CHNSO and heating value analyses).

Sample	N	C	H	S	O	High heating value	Turbidity	COD
	wt. %	wt. %	wt. %	wt. %	wt. %	MJ/Kg	NTU	ppm
Bentonite	0.00	0.36	0.66	0.27	8.39	0.00	-	-
PDADMAC1	6.99	47.59	9.32	0.00	36.00	27.99	-	-
PDADMAC2	7.12	48.52	8.50	0.00	35.87	30.27	-	-
SL	0.17	34.12	4.15	3.56	41.75	13.43	6980 ± 87	1.59×10^5 ± 515
SL/bentonite	0.10	15.34	2.12	1.24	21.74	5.01	2186 ± 65	1.19×10^5 ± 621
SL/bentonite/ PDADMAC1	1.45	29.18	4.26	2.44	26.49	15.39	480 ± 46	0.99×10^5 ± 366
SL/bentonite/ PDADMAC2	1.56	31.06	4.66	2.43	27.25	13.51	1000 ± 93	1.08×10^5 ± 458

5.4.7 Elemental and high heating value analyses

Table 5.2 also lists the elemental analysis of precipitates. Bentonite had 0.36 wt.% carbon, 0.66 wt.% hydrogen, 8.39 wt.% oxygen and 90.32 wt.% other components (i.e. silica-based components), which led to a poor heating value (0.00 MJ/Kg). However, the SL-treated bentonite contained 0.1 wt.% nitrogen, 15.34 wt.% carbon, 2.12 wt.% hydrogen, 1.24 wt.% sulfur, 21.74 wt.% oxygen and 59-60 wt.% of other components. The increase in organic (especially carbon) contents of bentonite accounts for the adsorption of lignin and hemicelluloses on bentonite. The precipitates of PDADMAC in SL/PDADMAC-treated bentonite have almost 1-2 wt.% nitrogen, 6 wt.% hydrogen, sulfur, 29-31 wt.% carbon, 26-27 wt.% and 33-36 wt.% of other elements. The increase in nitrogen content was most likely due to the presence of PDADMAC in the SL/PDADMAC-treated bentonites. Comparing the elemental analysis of PDADMACs with that of precipitates revealed that PDADMACs had higher carbon and hydrogen contents, which resulted in their higher calorific values (compared with that of precipitates). As explained earlier, lignocellulose might have had sulfonated groups on their structures (Liu et al., 2011a, 2011b; Sitter et al., 2014). Thus, the increase in the sulphur content of the treated bentonite is most probably due to the adsorption of lignin on bentonite. Table 5.2 also lists the heating values of precipitates. The high heating values (HHV) of precipitates were 5.0, 15.4 and 13.5 MJ/Kg for the bentonite that was treated with SL, SL/PDADMAC1 and SL/PDADMAC2, respectively. The HHV of kraft lignin and wood pellets are in the range of 19-21 MJ/kg (Bu et al., 2014; Telmo and Lousada, 2011), which implies that the treated bentonite could be used as a heating source. The increase in heating value of bentonite treated with PDADMAC is due to the adsorption of PDADMAC and more lignocelluloses on bentonite. Generally, lignin has a higher heating value than hemicelluloses (Jablonský et al., 2013). Consequently, the slightly higher heating value of precipitates made of SL/bentonite/PDADMCA1 than that of precipitates made of SL/bentonite/PDADMAC2 could be due to the slightly higher lignin adsorption on bentonite in the SL/bentonite/PDADMAC1 system.

5.4.8 Thermogravimetric analysis (TGA)

Figure 5.6 depicts the thermal stability of the bentonite samples. It is evident that bentonite did not have a significant weight loss via increasing the temperature, and only 7 % of bentonite incinerated at 690 °C. The SL-treated bentonite had 15% and 30 % of weight losses at 272 and 540 °C. It was previously reported that the pyrolysis of hemicelluloses and lignin happened at the temperature range of 220-300 °C and 500-650 °C, respectively (Lv et al., 2010; Yang et al., 2004). Thus, the two major peaks developed on SL/bentonite curves (Figure 5.6b) accounts for the incineration of adsorbed lignocelluloses on bentonite. The addition of PDADMAC made two peaks at the temperature range of 270-280 °C and 575-590 °C. These results also showed that the molecular weight of PDADMAC did not have a significant impact on the incineration of precipitates. After incinerating samples up to 730 °C, 93, 65, 36 and 35% of bentonite, SL/bentonite, SL/bentonite/PDADMAC1 and SL/bentonite/PDADMAC2, respectively, remained as ash.

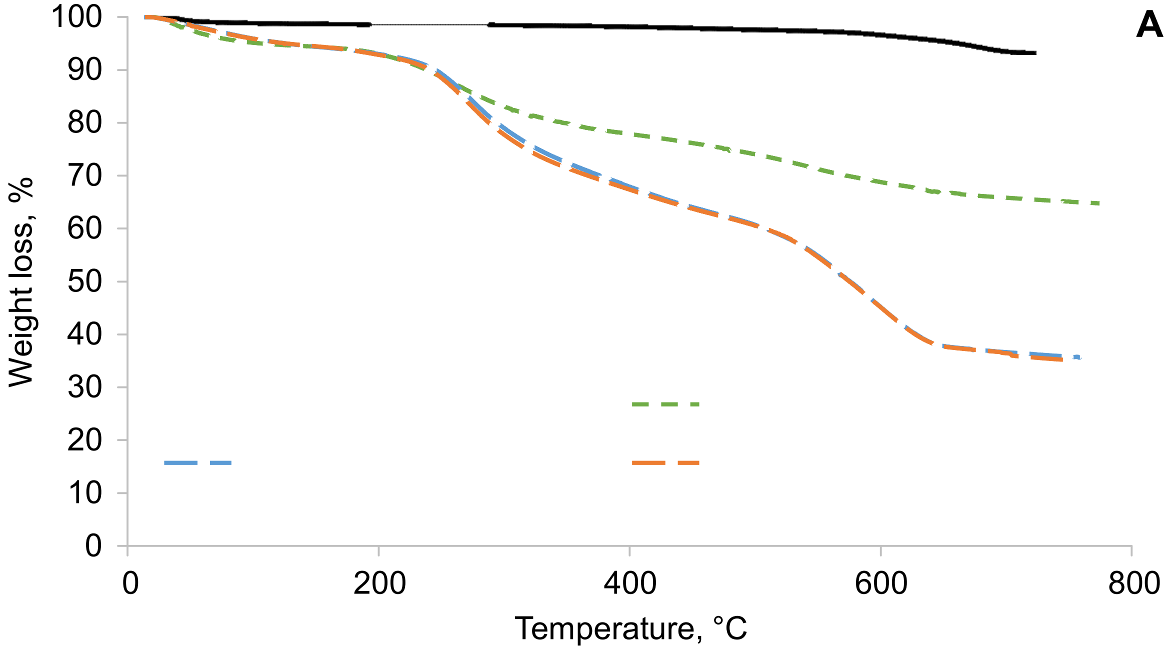


Figure 5.6. Weight loss (A), and weight loss rate (B) of bentonites samples (conducted at 30 ml/min N_2 and heated at 10 °C/min)

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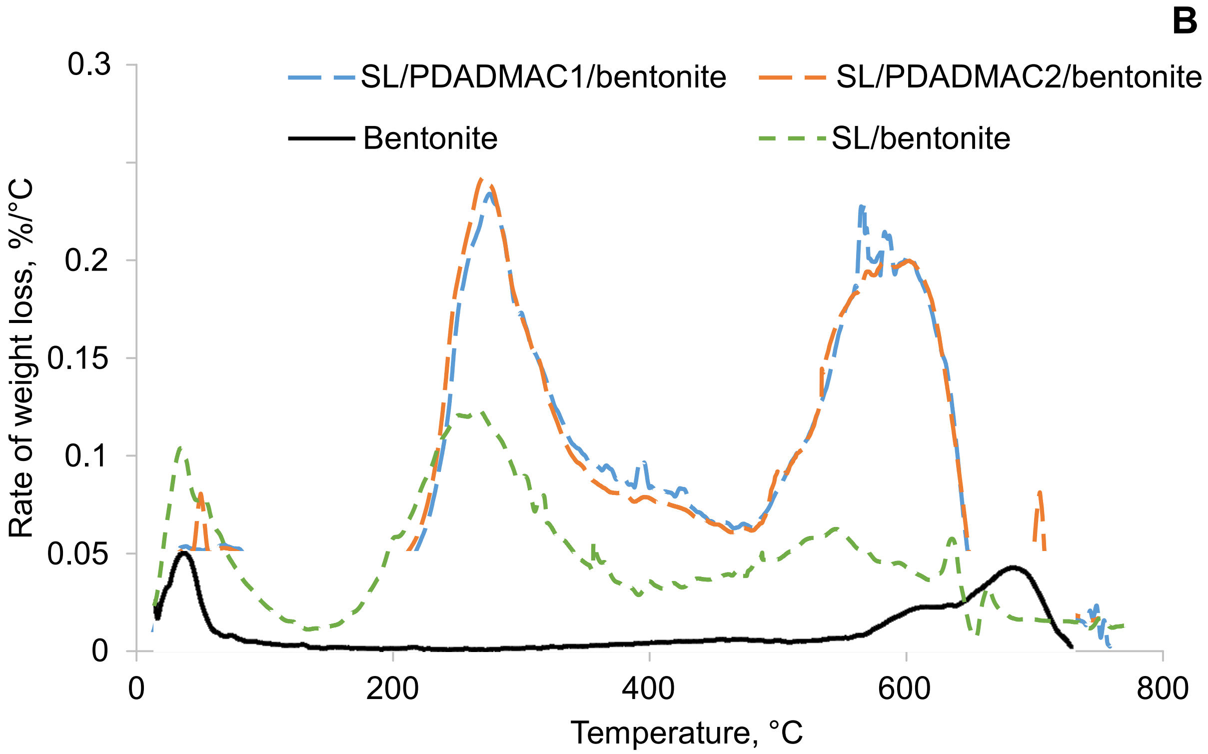

Figure 5.6 continued

5.4.9 Application

The small weight loss of bentonite (Figure 5.6) implies that bentonite can be recycled for reuse. As a significant amount of lignocelluloses were adsorbed on bentonite (Figure 5.4) (which can develop hydrogen bonding with other lignocelluloses in the matrix of corrugated paper) and the weight loss was generally minimal when the temperature was below 200 °C (Figure 5.6), the modified bentonite can be used as an additive in corrugated paper as the production process of corrugated medium paper is followed at a temperature that is below 200 °C. The significant weight loss of the treated bentonite at a high temperature is most probably due to the incineration of lignocelluloses and PDADMAC. Considering the heating value and ash content of the

SL/PDADMAC treated bentonite, it can be concluded that the treated bentonite can also be used as a fuel source, and the incinerated bentonite can be recycled for reuse.

5.5 CONCLUSIONS

It was generally observed that lignin was adsorbed more than hemicellulose on bentonite. By adding PDADMAC to the SL/bentonite system, the maximum of 1.8 g lignin and 0.5 g/g hemicellulose were adsorbed on bentonite. These adsorption levels corresponded to 57% lignin and 67 % hemicellulose, 93% turbidity and 38% COD removals from the SL. The high heating value of bentonite was increased from 0 to 15.4 MJ/kg for the precipitates made from SL/bentonite/PDADMAC1 treatment. The final product of this process can be used as filler in the production of corrugated medium papers or as fuel.

5.6 ACKNOWLEDGMENT

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6 CHAPTER SIX: EFFICIENCY OF VARIOUS ADSORBENTS IN ADSORIBING LIGNOCELLULOSES FROM THE SPENT LIQUORS OF NSSC AND THERMOMECHANICAL PULPING

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6.1 ABSTRACT

The applications of lignin and hemicelluloses in the production of value-added products have attracted attention these days. In this study, kaolin, kaolinite, calcium carbonate (two grades), aluminum silicate and talc were added to spent liquors of thermomechanical pulping (TMP) and neutral sulfite semi-chemical (NSSC) pulping processes and the removals of lignin, hemicelluloses, COD and turbidity were studied under the conditions of 30 °C, 90 g/g SL/adsorbent ratio and 100 rpm for 24 h. It was observed that calcium carbonate (puriss) and kaolinite were more efficient than the other tested adsorbents with removing 53 and 49 wt.% of lignin, 30 and 32 % of COD and 63 and 60% of turbidity from SL of TMP, respectively. Similarly, calcium carbonate (puriss) and kaolinite removed 12 and 11 % of lignin, 15 and 13 % of hemicelluloses, 5 and 4 % of COD and 27 and 7% of turbidity from SL of NSSC, respectively. The second part of this study focused on the adsorption of lignocelluloses from the SL of NSSC pulping on various fly ashes (FA)s. The maximum adsorptions of 129 mg/g lignin and 194 mg/g hemicellulose were achieved on FA4 at 30 °C, 90 g/g SL/FA4 ratio and 100 rpm for 24 h. Using the same FA4 and under the same adsorption conditions, 69 % of original turbidity and 24 % of original COD were removed from the SL of NSSC process. In addition, an equation was developed in this work in order to estimate the adsorption amount of lignocelluloses on FA as a function of charge density and surface area of FAs.

KEYWORDS: Adsorption, Lignin, Hemicelluloses, Fly ash, Kaolinite, Calcium carbonate, Biorefinery.

6.2 INTRODUCTION

Recent studies on the generation of fuel and value-added products from lignocelluloses have shown potential to extract lignocelluloses from pulping spent liquors and to use them in the production of value-added products (Dashtban et al., 2014b; Kumar et al., 2009; Olsen et al., 2011; Thakur et al., 2014; Yang et al., 2014). In this regard, the spent liquors of sulfite, kraft and NSSC pulping processes have been the subject of many studies (Dashtban et al., 2014a; Oveissi & Fatehi, 2014; Sitter et al., 2014).

In thermomechanical pulping (TMP) process, wood chips are treated with steam at 130 °C prior to pulping. The spent liquor of this process, which is also called pressate, dissolves some of the lignocelluloses of wood chips, but is presently sent to the wastewater treatment process of the mills. In neutral sulfite semi-chemical (NSSC) pulping process, wood chips were treated by caustic, sulfite and steam prior to refining. Similar to SL of TMP, the SL of the NSSC process contains lignocelluloses, and they are treated in the wastewater of the mill.

However, these lignocelluloses can be recovered from the SLs to be used in the production of value-added products. Different processes, such as ultrafiltration, acidification and solvent extraction were suggested in the literature for conducting this task, but they would not be feasible and economical due to the dilute concentration of lignocelluloses in these liquors (Oveissi & Fatehi, 2014). Adsorption concept was considered as a feasible process for separating these lignocelluloses from SLs (Fatehi et al., 2013a; Fatehi et al., 2013b; Liu et al., 2012). A pervious study showed that 166 mg/g lignin and 13.5 mg/g hemicelluloses from SL, which was obtained from the pre-treatment of TMP, were adsorbed on activated carbon under optimal operating conditions of 30 °C, pH 5.3, 100 rpm and SL/activated carbon ratio of 90 g/g for 3 h (Oveissi &

Fatehi, 2014). Another study illustrated that 330 mg/g lignin and 250 mg/g hemicelluloses were adsorbed on activated carbon from the SL of NSSC pulping process under the optimal conditions of 30 °C, pH 5.7, 100 rpm and SL/activated carbon ratio of 30 g/g for 6 h (Dashtban et al., 2014c). However, depending on the AC origin, the price of $US 1,650-9,900/ton was reported for activated carbon (Zhi et al., 2014). Therefore, adsorption on inexpensive materials such as kaolinite, kaolin, lime and fly ash could be more economical and preferred. Previously, 16 mg/g lignin and 7.8 mg/g hemicelluloses were adsorbed from pre-hydrolysis liquor (PHL) on lime mud under the conditions of lime/PHL ratio of 5 wt.%, 26 °C and 150 rpm for 1 h (Shen et al., 2011). Another study showed that 80 mg/g lignin and 200 mg/g hemicelluloses from PHL were adsorbed on calcium carbonate under the conditions of pH 7, 40 °C, 120 rpm and the PHL/calcium carbonate ratio of 40 g/g for 5 h (Fatehi et al., 2013a). However, it is not clear how the lignin of TMP spent liquor would be adsorbed on other inexpensive adsorbents such as fly ash, kaolinite and kaolin.

It was claimed that COD and turbidity of pulping spent liquors were attributed to the presence of lignocelluloses and extractives (Andersson et al., 2008; Andersson et al., 2012; Sitter et al., 2014). Therefore, it is also important to see how COD of the SLs would be affected by the adsorption treatments. Recent studies showed that fly ash can be utilized in removing lignocelluloses and subsequently turbidity and COD from lignocellulosic wastewater (Andersson et al., 2012; Andersson et al., 2011).

In this study, the efficiency of various adsorbents for the separating lignocelluloses and subsequently removing the turbidity and COD of SLs is assessed. The second part of this study aims to compare the impacts of fly ash on the properties of SL of NSSC process. Based on results, a model was fitted to estimate the value of adsorption of lignocelluloses as a function of charge density and surface area of fly ash. The results of this modeling would help identify the impact of

FA characteristics on adsorbing lignocelluloses. The novelty of this work is the investigation on the efficiency of various inexpensive adsorbents, which consists of two objectives: 1) determining an economical and efficient adsorbent for lignin and hemicelluloses removals and 2) estimating the adsorption behaviour based on adsorbent's properties.

6.3 MATERIALS AND METHODS

6.3.1 Materials

Aluminium silicate, calcium carbonate puriss (PCC1), calcium carbonate reagent (PCC2), kaolin and kaolinite were purchased from Sigma-Aldrich Company and used as received. Fly ash samples FA1 and FA2 were received from mills in NB, Canada and FA3, FA4 and FA5 were received from a pulp mill in Northern Ontario, Canada. FAs were residuals of incinerating bark and branches of trees and some organic materials, e.g. wastewater sludge in the boilers of aforementioned mills. All samples were grinded to be homogenized. The spent liquor (SL1) of a thermomechanical pulping (TMP) process was received from a mill in Northern Ontario. Also, the spent liquors (SL2 and SL3) of an NSSC process were received from a mill in NB, Canada. To remove large particles (i.e. small wood species), SL2 was initially centrifuged at 1000 rpm for 10 min using Survall ST16 centrifuge. It should be noted that the SL2 and SL3 received in August 2013 and March 2014, respectively.

6.3.2 Adsorption

6.3.2.1 Adsorption of lignocelluloses on fillers

To compare the adsorption efficiency of lignocelluloses from SLs on various adsorbents, 1 g of an adsorbent was added to 45 g of SL1 and SL2 in 125 ml Erlenmeyer flasks and sealed. Afterwards, samples were incubated in a Boekel water bath shaker at 30 °C and 100 rpm for 24 h. Then, samples were centrifuged at 1000 rpm for 10 min using Survall ST16 centrifuge. The filtrates were collected for lignin, hemicelluloses, pH, COD, and turbidity analyses. All tests were triplicated and the average of three with its standard deviation was reported. The control samples in all experiments were incubated under the same conditions but without adsorbent. This test was repeated for all adsorbents included in this study under the same conditions specified above.

6.3.2.2 Adsorption of lignocelluloses on FAs

In another set of experiments, 1 g of different FA was added to 45 g of SL3. Samples were incubated at 30 °C and 100 rpm for 24 h using a Boekel water bath shaker. The filtrates were collected after centrifugation at 1000 rpm for 10 min using Survall ST16 centrifuge. Lignin, hemicelluloses, COD, pH and turbidity of SL3 before and after ash treatment were measured. To have statistically meaningful results, three repetitions were conducted for each test and the average of the three and its standard deviation were reported. Also, control samples were incubated under the same conditions but without FA.

6.3.3 BET surface area and charge density analyses

The BET surface areas of all adsorbents were measured using NOVA-2200e Autosorb under N_2 atmosphere according to the method described in the literature (Yang et al., 2010). The charge densities of all adsorbents were determined using Mütek PCD04 charge detector (Germany) as previously described (Liu et al., 2011; Oveissi & Fatehi, 2014).

6.3.4 Elemental and ash and dry matter analyses

Elemental (ultimate) analysis on fly ash samples was conducted using a Vario EL cube instrument (Germany), according to the procedure described in the literature (Fadeeva et al., 2008). The metal content of fly ash samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with CETAC ASX-510 Auto Sampler (Canada). The ICP-AES analysis was performed using Varian Vista Pro CCD (Canada) according to the previously described method in the literature (Yuan et al., 2010). The ash content of SLs was determined according to TAPPI T412 (Dashtban et al., 2014a). For measuring the dry matter, SLs were dried overnight at 105 °C. Subsequently, dry contents of SLs were determined by measuring the weight of SLs before and after drying.

6.3.5 Lignin and hemicelluloses analyses

Lignin analysis was performed on all solutions using UV/VIS spectrophotometry, Genesys 10S, at the wavelength of 205nm according to TAPPI UM 250 (Dashtban et al., 2014c). It should be highlighted that calibration curves for SL1 and SL2 were generated individually due to the different nature of lignin in both liquors. The hemicelluloses content of all solutions was determined via DNS (3, 5- dinitrosalicylic acid) method as previously described (Dashtban et al., 2014c; Sitter et al., 2014). All samples were acid hydrolyzed with 4 % sulfuric acid at 121 °C for 1 h in a Haake-S45 oil bath to break all oligomeric sugars to monomeric sugars as DNS reagent can only react with monomeric sugars. Both analyses repeated three times and the average of three was reported. Also, 1g of adsorbent was added to 45g of deionized water and incubated overnight at 30°C, 100rpm (i.e. control sample) then centrifuged at 1000 rpm for 10 min. Subsequently, The UV absorption of the filtrates was measured at 205 and 540 nm to confirm there was not any interference from adsorbent in lignin and hemicellulose analyses, respectively.

6.3.6 Turbidity and COD analyses

The turbidity of SL samples was measured before and after the treatment experiments using a Hach 2100AN turbidity meter (Fatehi et al., 2013c; Oveissi & Fatehi, 2014). The chemical oxygen demand (COD) of SL samples before and after treatment was also measured according to the previously established method. (Dashtban et al., 2014c; Oveissi & Fatehi, 2014). The tests were repeated three times and the average of three was reported.

6.3.7 Data analysis

The results of lignin and hemicelluloses adsorption from SL3 on FAs were modeled by a polynomial function of the independent variables (Montgomery, 2013) based on equation 6.1:

2 2 2

$yy = \beta��_0 + \sum_{i��=1} \beta��_{ii}$ $+$ (6.1)

$x��_{ii} + \sum_{i��=1} \beta��_{iiii} x��_{ii}$ $\beta��_{12} x��$

${}_1 x��_2$

where y is the amount of adsorption and x_1 and x_2 are the independent parameters of cationic charge density and surface area in this study, respectively. Also, β values correspond to the effect of each parameter. Using the least square method, the parameters of polynomials were determined using MATLAB® software (version R2014a).

6.4 RESULTS AND DISCUSSION

6.4.1 Characterizations of SLs

Table 6.1 lists the properties of SLs. As can be seen, lignin and sugar contents of SL2 and SL3 are almost 10 times greater than that of SL1. The low concentration of lignocelluloses in SL1 is due to the fact that the pretreatment stage in the TMP and NSSC process are considerably different, and thus their SLs would have altered characteristics (Oveissi & Fatehi, 2014). It is also evident that SL2 and SL3 had almost 7000 NTU turbidity and 110-160 g/l COD, which were 3.5 and 10 times greater than those of SL1, respectively. It was claimed that a large portion of COD and turbidity of SL accounts for dissolved lignocelluloses in SLs (Andersson et al., 2008; Andersson et al., 2012). Therefore, higher COD and turbidity of SL2 and SL3 is due to the higher concentration of lignocelluloses in SL2 and SL3. However, the COD of SL3 is higher than that of SL2. This might be due to the higher content of other components dissolved in SL3 (i.e. extractives and fatty acids). This is indirectly confirmed by the higher dry matter content of SL3. All SLs had almost the same pH (5.3-5.7). The higher ash content of SL2 and SL3 than SL1 illustrates the higher concentration of inorganic materials dissolved in SL2 and SL3. In pretreatment of NSSC process, woodchips are treated with caustic and sulfite, while in the pretreatment of TMP processes woodchips are just pretreated with steam. Hence, the SL of the former contains more inorganic than the SL of the latter.

Table 6.1. Characterizations of SLs

SL	*Lignin conc.* *g/l*	*Hemicelluloses conc.* *g/l*	*COD* *g/l*	*Turbidity* *NTU*	*Dry matter content,* *%*	*pH*	*Ash* *g/l*
SL1	7.3 ± 0.2	1.5 ± 0.3	9.46 ± 0.18	2060 ± 141	0.08 ± 0.01	5.3 ± 0.2	0.58 ± 0.06
SL2	76.0 ± 2.8	11.3 ± 0.9	109.57 ± 1.01	7010 ± 119	0.19 ± 0.00	5.7 ± 0.1	64.52 ± 1.93
SL3	67.0 ± 4.1	12.6 ± 0.7	159.23 ± 0.95	6980 ± 105	0.17 ± 0.01	5.7 ± 0.2	59.67 ± 1.47

6.4.2 Adsorption of lignocelluloses on adsorbents

6.4.2.1 Adsorbent characterisations

Table 6.2 tabulates the charge densities and surface areas of various adsorbents. As can be seen, the overall charge density of all tested adsorbents (except PCCs) was negative. Talc involves octahedral magnesium hydroxide, which is surrounded between silicon-oxygen tetrahydra sheets with weak van der Waals forces (Burdukova et al., 2007). The covalent bonds might be broken in the brucite layer and gives the edges of talc some negative charge density (Burdukova et al., 2007; Morris et al., 2002). Kaolinte (or kaolin) has tetrahedral Si-O and the octahedral Al-OH basal planes (Carty, 1999). Substitution of Si^{4+} with Al^{3+} in silicon-oxygen tetrahedral gives the basal planes a negative charge density (Burdukova et al., 2007). This substitution may not occur in aluminium silicate which results in less charge density than that of kaolin and kaolinite. Although PCC had a cationic charge density, the net charge density of PCC was negative. This might be due to the fact that the dissolution of PCCs in aqueous solution helps Ca^{2+} ions leave the crystalline structure of PCC (Nilsson & Sternbeck, 1999). All in all, kaolinite had the highest and talc had the lowest anionic charge densities among all tested samples.

The surface area of samples were also measured and listed in Table 6.2. As can be seen, PCC2 and aluminium silicate had the highest surface area among all test samples. The surface area (S) of tested samples from the largest to the lowest was: $S_{PCC2} > S_{aluminum\ silicate} > S_{talc} > S_{kaolin} > S_{PCC1} > S_{kaolinite}$.

Table 6.2. Properties of various adsorbents

Adsorbent	*Charge density (µeq/g)*		*Surface area (m²/g)*
	Anionic	*Cationic*	
Talc	5.83 ± 0.12	0.00 ± 0.00	67.1
PCC1	10.50 ± 0.11	16.30 ± 0.04	38.0
PCC2	6.17 ± 0.12	7.19 ± 0.11	77.1
Aluminium silicate	8.32 ± 0.09	0.00 ± 0.00	76.8
Kaolinite	15.21 ± 0.11	0.00 ± 0.00	11.2
Kaolin	12.51 ± 0.10	0.00 ± 0.00	50.6

6.4.3 Adsorption of lignocelluloses on adsorbents

To compare the impact of various adsorbents on COD, turbidity, pH, lignin and hemicelluloses removals; 1 g of each adsorbent was added to SL1 and SL2 at 30 °C, 90 g/g SL/adsorbent ratio and 100 rpm for 24 h and the obtained results were summarized in Table 6.3. It is evident that adsorbents were not effective in removing hemicelluloses from SL1. This might be due to the fact that hemicellulose content of SL1 was low and the charge density of adsorbents was insufficient for the adsorption of hemicelluloses. It was previously observed that 166 mg/g of lignin and 13.5 of mg/g hemicellulose from SL of TMP was adsorbed on activated carbon under the conditions of 30 °C, 100 rpm, pH 5.3 for 3 h (Oveissi & Fatehi, 2014). It is also evident in Table 6.3 that the adsorption of lignin was higher than that of hemicelluloses from SL2. It was claimed that the molecular weight of lignin was generally smaller than that of hemicelluloses in SL (Dashtban et al., 2014a). Therefore, more of lignin molecules may diffuse into the pores of adsorbents. Another reason might be the higher concentration of lignin than that of hemicelluloses in SLs, which would increase the chance of lignin adsorption. The mechanism of adsorption on aluminum silicate, talc, kaolin and kaolinite might be similar and be through hydrogen bonding development between the oxygen in the structure of all adsorbents and adsorbing lignocelluloses (Aguzzi et al., 2007; Miller et al., 2007). It is evident that PCC1 and kaolinite had the highest adsorption of lignocelluloses comparing to the other samples. Also, kaolinite adsorbed more lignocelluloses than kaolin from SL1 and SL2. This might be due to the fact that kaolin has more impurities than kaolinite (Andreola et al., 2004). A pervious study showed that 80 mg/g of lignin and 200 mg/g of hemicelluloses from pre-hydrolysis liquor were adsorbed on PCC at pH 7, 40 °C, 100 rpm, PHL/PCC 40 g/g and 5 h of time (Fatehi et al., 2013a). Although PCC2 had a larger surface area than PCC1, PCC1 adsorbed more lignocelluloses than did PCC2. It was stated that lignocelluloses general possess anionic charge density (Saeed et al., 2011). Therefore, the charge interaction between lignocelluloses and PCC1 might be the reason of highest adsorption on this adsorbent. Interestingly, aluminium silicate adsorbed 331 and 459 mg/g lignin, and 0 and 80 mg/g hemicelluloses from SL1 and SL2, respectively. The relatively high adsorption on aluminum silicate might be due to its large surface area in comparison with other tested adsorbents.

In the literature, it was claimed that the COD content of lignocellulosic wastewater effluents mainly accounts for lignin, hemicelluloses and extractives (Andersson et al., 2012). As can be seen, PCC1 removed 30 and 4.5 % and kaolinite removed 32 and 4 % of original COD from SL1 and SL2, respectively. The COD removals from SL2 were less than that of SL1, while the lignocelluloses removals were higher under the same adsorption conditions. One possible reason for this phenomenon is the significant concentration of extractives and fatty acids in SL2, which had a great contribution in COD of SL2. However, more studies are required to confirm this hypothesis.

The turbidity removals from SL1 and SL2 were 63 and 27 % via PCC1, 52 and 7 % through kaolinite treatment, respectively. Although the lignocellulosic removals from SL2 were higher than SL1, the turbidity removals of SL1 were more than that of SL2. The higher concentration of metal ions in SL2 (Table 6.1) may be an obstacle for neutralizing the charged particles in the SL. Interestingly, aluminium silicate removed 58 % of the turbidity from the SL1. It was claimed that Ca^{2+} and Al^{3+} had a significant role in neutralizing charged particles in aqueous solution (Abdel-Shafy & Emam, 1991).

The end pH of the SLs did not change after adsorption except the SLs that were treated by PCCs. It is well known that dissolution of metals (i.e. Ca^{2+} ion) increases the pH of aqueous solutions (Berner & Morse, 1974). However, the increase in the pH of SL1 was higher than that of SL2. This might be due to more dissolution of PCC in SL1, as more of lignocelluloses were adsorbed from SL2.

Table 6.3. Impact of treating on SLs with adsorbents (conducted at 90 g/g SL/filler, 30 °C and 100 rpm for 24 h)

SL	Adsorbent	Lignin		Hemicelluloses		COD		Turbidity		End pH
		Adsorption	Removal	Adsorption	Removal	End COD	Removal	End Turbidity	Removal	
		mg/g	%	mg/g	%	g/l	%	NTU	%	pH
SL1	Talc	18 ± 1	2.79 ± 0.05	0 ± 0	0.00 ± 0.00	7.67 ± 0.03	18.90 ± 0.07	1191 ± 43	42.18 ± 0.21	5.2 ± 0.2
	PCC1	331 ± 8	52.52 ± 1.85	0 ± 0	0.00 ± 0.00	6.65 ± 0.45	29.69 ± 2.01	757 ± 62	63.25 ± 1.31	7.3 ± 0.0
	PCC2	305 ± 11	48.21 ± 1.91	0 ± 0	0.00 ± 0.00	7.62 ± 0.10	19.47 ± 0.25	1097 ± 30	46.73 ± 1.84	6.9 ± 0.1
	Aluminiu n silicate	59 ± 3	9.36 ± 1.03	0 ± 0	0.00 ± 0.00	6.81 ± 0.75	27.94 ± 3.12	873 ± 78	57.62 ± 9.23	5.4 ± 0.1
	Kaolinite	310 ± 10	49.08 ± 1.48	0 ± 0	0.00 ± 0.00	6.44 ± 0.30	31.93 ± 1.98	991 ± 61	51.9 ± 7.49	5.3 ± 0.0
	Kaolin	300 ± 14	47.50 ± 1.91	0 ± 0	0.00 ± 0.00	6.48 ± 0.25	31.48 ± 1.19	1112 ± 36	46.04 ± 2.06	5.4 ± 0.0
SL2	Talc	233 ± 21	3.40 ± 0.31	119 ± 12	11.00 ± 0.84	105.80 ± 2.46	3.45 ± 0.08	6831 ± 271	2.13 ± 0.51	5.7 ± 0.1
	PCC1	837 ± 16	12.22 ± 0.21	161 ± 4	14.85 ± 1.21	104.60 ± 0.69	4.53 ± 0.03	5121 ± 212	26.63 ± 7.31	6.5 ± 0.0
	PCC2	770 ± 33	11.24 ± 0.42	17 ± 7	1.55 ± 0.51	105.73 ± 2.12	3.50 ± 0.07	6532 ± 124	6.42 ± 2.23	6.1 ± 0.2
	Aluminiu n silicate	459 ± 38	6.70 ± 0.55	80 ± 4	7.43 ± 0.47	105.33 ± 0.81	3.87 ± 0.03	6892 ± 159	1.26 ± 0.08	5.7 ± 0.0
	Kaolinite	745 ± 11	10.88 ± 0.18	137 ± 9	12.69 ± 0.04	105.18 ± 2.63	4.01 ± 0.10	6495 ± 248	6.94 ± 1.29	5.7 ± 0.0
	Kaolin	573 ± 26	8.37 ± 0.39	118 ± 11	10.88 ± 0.03	105.35 ± 1.09	3.85 ± 0.04	6888 ± 207	1.32 ± 0.14	5.7 ± 0.1

6.4.4 Adsorption of lignocelluloses on FAs

6.4.4.1 FA characterization

Table 6.4 lists the properties of FAs. As can be seen, except FA1 which was neutral, all FAs had a cationic charge density. A great portion of this charge density might be due to the existence of metal ions (Table 6.4). It is observable that the majority of metals in FAs were calcium, potassium, magnesium and aluminium. These metals were reported as the most common constituents of FA in the literature (Furuya et al., 1987). Among all FAs, FA4 had the highest cationic charge density of 69.33 μeq/g and surface area of 223.5 m^2/g. As can be seen, the surface areas of FAs were 16-223 m^2/g. In the literature, it was reported that fly ash, received from Obra thermal power station and FA collected from Poplar River power station (in Saskatchewan) had the surface areas of 4.87 m^2/g (Kumar et al., 1987) and 1.5- 1.7 m^2/g (Viraraghavan & de Maria Alfaro, 1998), respectively. Consequently, the surface of FA depends on FA origin.

Table 6.4. Properties of various FAs

Constituents	**FA1**	**FA2**	**FA3**	**FA4**	**FA5**
Element (wt.%)					
K	8.75	2.18	0.97	2.93	4.06
Al	2.00	1.58	0.25	0.07	0.99
Mg	1.83	0.60	0.27	1.05	1.96
Fe	1.59	1.11	0.28	0.03	0.89
S	1.50	1.59	0.10	4.27	4.60
Mn	1.33	0.67	0.10	0.03	0.33
Na	0.79	0.84	0.13	0.08	0.93
P	0.78	0.35	0.13	0.09	0.87
Ba	0.25	0.12	0.03	0.01	0.00
Zn	0.23	0.05	0.00	0.01	0.19
Ti	0.12	0.07	0.02	0.00	0.00
Sr	0.09	0.03	0.01	0.00	0.00
Si	12.04	0.06	0.08	0.00	0.08
Cu	0.01	0.00	0.00	0.01	0.00
Ca	0.00	6.41	2.84	0.00	14.60
C	32.20	52.46	66.20	37.90	34.60
H	0.43	0.76	1.00	1.03	1.59
N	0.01	0.29	0.50	0.15	0.14
O	27.60	18.50	14.67	28.46	26.33
Charge density (μeq/g)					
Anionic	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Cationic	0.00 ± 0.00	23.50 ± 1.13	9.50 ± 1.01	69.33 ± 3.08	35.01 ± 2.10
Surface area (m^2/g)	16.4	102.0	179.0	223.5	63.7

6.4.5 Adsorption on FAs

Table 6.5 summarized the effect of various FAs on lignin, hemicelluloses, turbidity, COD and final pH of SL3 at 30 °C, 90 g/g ratio of SL3/FA and 100 rpm for 24 h. As can be seen, FA4 adsorbed 129 mg/g of lignin and 194 mg/g of hemicelluloses. The highest adsorptions of lignocelluloses on FA4 would be due to its higher surface area and cationic charge density compared to other FAs. As explained earlier, lignocelluloses possess anionic charge density due to the sulfonated, carboxylic or carbonyl groups attached on their structures (Liu et al., 2012; Nakagame et al., 2011; Saeed et al., 2011). Therefore, the main mechanism for the adsorption of lignocelluloses on FAs (except FA1) would be the electrostatic charge interaction. Interestingly, FA1 had 89 mg/g lignin and 155 mg/g hemicelluloses adsorption, whereas FA1 was neutral and had the least surface area. As is well known, metal ions can form ligands with lignocelluloses in solutions (Guo et al., 2008), and these complexes would be precipitated on fly ash. In other words, coagulation also occurs simultaneously with adsorption in the treatment of SL with fly ash. However, more detailed studies are required to prove this hypothesis.

The decrease in the concentration of lignocelluloses results in a decrease in COD and turbidity of SLs (Sitter et al., 2014). Although FA5 adsorbed less lignocellulose than FA4, its turbidity removal was higher than that of FA4. It is observable that the concentrations of metal ions (especially those with high oxidation number such as Al^{3+}) in FA5 were significantly higher than those in other FAs. This may assist FA4 in neutralizing more suspended charged particles via complex formation. The pH of SL3 after treatment with FA2, FA3 and FA4 was almost the same (pH 6). However, the pH of SL3 after FA1 and FA5 treatments were 7.8 and 6.6, respectively. It is well known that dissolution of metal ions (especially alkali and alkali earth metals) in aqueous solution increases the pH (Seida & Nakano, 2002). Therefore, the higher pH of SL3 treated by FA1 and FA5 would be due to the higher concentration of alkali metals. Overall, the lignin, hemicelluloses, COD and turbidity removals of SL3 via FA4 were 4, 33, 24 and 69%, respectively.

Table 6.5. Impact of treating SL3 with FAs (incubated at 30 °C, 90 g/g SL3/FA and 100 rpm for 24 h).

Adsorbent	Lignin		Hemicelluloses		COD		Turbidity		End pH
	Adsorption mg/g	Removal %	Adsorption mg/g	Removal %	End COD g/l	Removal %	End Turbidity NTU	Removal %	
FA1	89 ± 4	2.80 ± 0.11	155 ± 7	26.00 ± 1.21	133.27 ± 8.10	16.52 ± 1.01	5035 ± 60	27.87 ± 0.33	7.8 ± 0.1
FA2	20 ± 3	0.62 ± 0.08	163 ± 17	27.35 ± 2.89	129.02 ± 9.71	19.22 ± 1.52	6789 ± 173	2.74 ± 0.07	6.1 ± 0.0
FA3	58 ± 4	1.81 ± 0.13	134 ± 6	22.48 ± 1.04	118.08 ± 10.04	25.64 ± 2.13	6810 ± 112	2.44 ± 0.04	5.7 ± 0.1
FA4	129 ± 2	4.07 ± 0.04	194 ± 10	32.63 ± 1.65	120.16 ± 6.23	24.38 ± 1.34	2143 ± 91	69.30 ± 2.93	6.1 ± 0.2
FA5	11 ± 2	0.34 ± 0.05	139 ± 12	23.43 ± 2.07	113.11 ± 10.26	28.8 ± 2.61	1947 ± 39	72.11 ± 1.46	6.6 ± 0.1

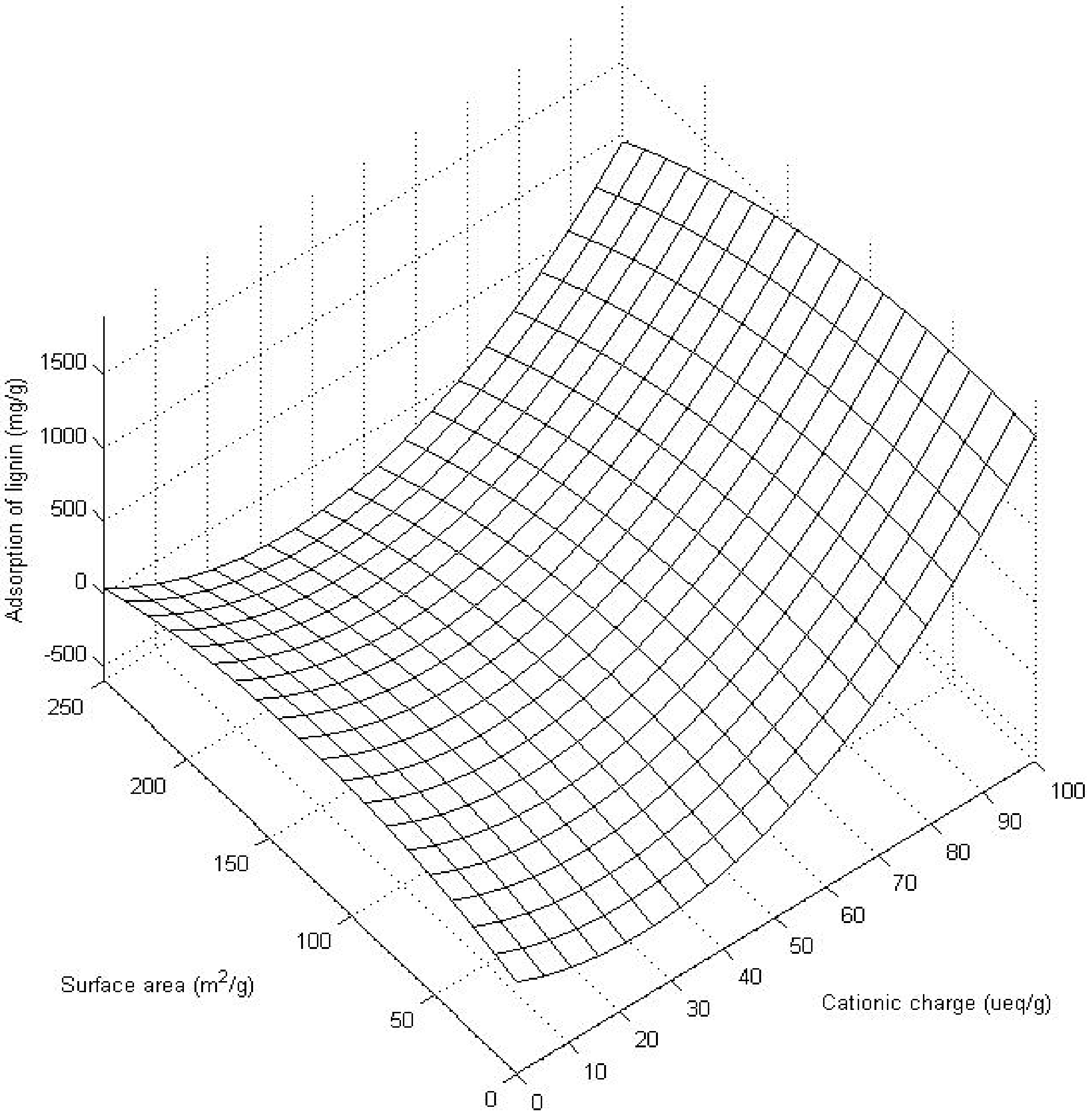
6.4.6 Modeling analysis

The obtained data from Tables 6.4 and 6.5 were modeled using equation (1), which generated equations 2 and 3:

$y_{lignin} = 27.1028 - 14.9781\, x_1 + 4.0266\, x_2 + 0.3098\, x_1^2 - 0.0165\, x_2^2 - 0.0273\, x_1 x_2$ and

$y_{hemicelluloses} = 119.3153 - 6.0600\, x_1 + 2.344\, x_2 + 0.0955\, x_1^2 - 0.0114\, x_2^2 + 0.0052\, x_1 x_2$

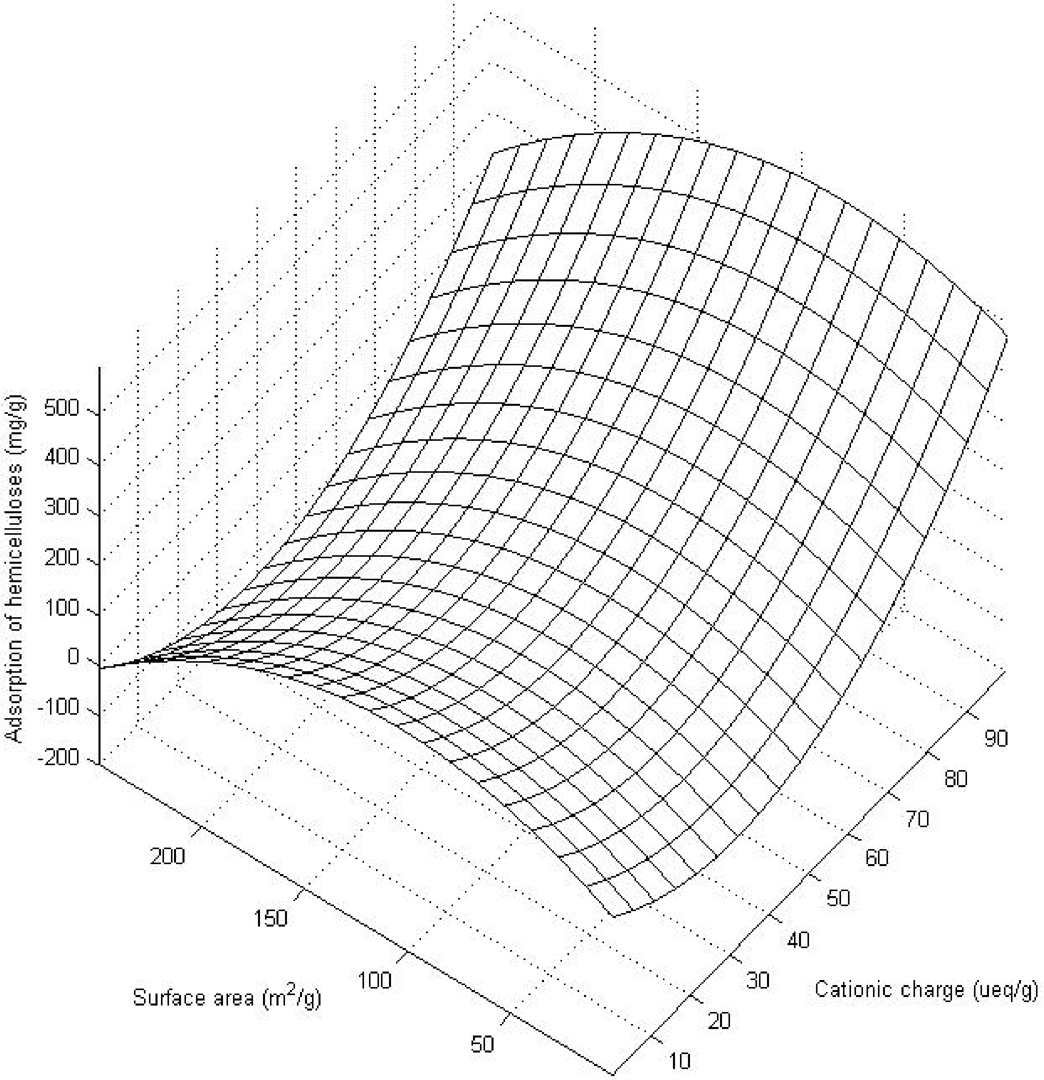
The sum of squares of the difference between the model value and the experimental values were zero in both models, which showed the accuracy of both expressions. The aforementioned equations were plotted in Figure 6.1. As can be seen, at the same surface area, by increasing the cationic charge density the amount of adsorption increased. At the same cationic charge density, the increase in the surface area (up to 175 m^2/g) increased the adsorption, but further increase in surface area resulted in less adsorptions. The reason for such behaviour is not known. As is generally accepted, the larger the surface area, the higher adsorption would be. Therefore, the results in Figure 6.1 shows that other characteristics of FA (e.g. those listed in Table 6.4) should have played an important role in the adsorption, and surface area analysis cannot be a factor in determining its adsorption performance. The obtained equations can be used for identifying the impact of FA characteristics on its adsorption performance.



(a)

Figure 6.1. Adsorption of lignin (a) and hemicelluloses (b) versus surface area and cationic charge density

Continued on next page



(b)

Figure 6.1 continued

6.5 CONCLUSIONS

In this study, aluminium silicate, calcium carbonates (PCC1 and PCC2), kaolin, talc and kaolinite were added to spent liquors of TMP (SL1) and NSSC pulping (SL2) at 30 °C, 90 g/g SL/adsorbent ratio and 100 rpm for 24 h. It was observed that PCC1 adsorbed 331 and 837 mg/g of lignin and 0 and 161 mg/g of hemicelluloses from SL1 and SL2, respectively. Also, COD and turbidity removals via adding PCC1 were 30 and 63 % from SL1 and 5 and 27 % from SL2, correspondingly. The study on the impact of FAs on lignocelluloses of SL3 revealed that, under the conditions of 30 °C, 90 g/g SL/FA ratio and 100 rpm for 24 h, FA4 were the most effective one with lignin and hemicellulose adsorptions of 129 and 194 mg/g, respectively. The turbidity and COD removals via FA4 treatment were 69 and 24 %, correspondingly. Consequently, these data showed that adsorption of lignocellulose via kaolinite, PCC1 and FA could decrease the load of wastewater treatment.

6.6 ACKNOWLEDGMENT

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7 CHAPTER SEVEN: CHARACTERISTICS OF VARIOUS LIGNIN SAMPLES GENERATED IN PULPING PROCESSES

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7.1 ABSTRACT

Lignin present in the spent liquor of neutral sulfite semichemical (NSSC) pulping and prehydrolysis (PHL) of kraft-based dissolving pulp process can be utilized in many applications. However, the surface and thermal properties of lignin have not been investigated yet. The main aim of this work was to study the structural, surface and thermal behavior of lignin separated from pulping spent liquors of NSSC as well as prehydrolysis-based and traditional kraft processes. In this work, lignin of spent liquor and of pre-hydrolysis liquor were isolated and compared to two commercial lignosulfonates (LS1 and LS2) and softwood kraft lignin (KL). It was illustrated that kraft lignin (KL), lignin of prehydrolysis liquor (LPHL), lignosulfonate of NSS process (LSL), and commercial lignosulfonates (LS)s had 0.67, 0.25, 0.90 and 1.52-2.25 meq/g of anionic charge densities; 0.54, 0.22, 0.14 and 0.11-0.23 meq/g of carboxylic group and 0.00, 0.01, 0.70 and 1.33-1.92 meq/g of sulfonated group attached to them, respectively. Also, the hydrodynamic diameter and charge density analyses suggested that LSL, LSs would be more efficient filler modifier, flocculants and dispersants than would be KL and LPHL. The combustion studies of these lignin samples revealed that KL and LPHL combusted more efficiently than other samples, as they had high heating (calorific) values of 27.02 and 19.2 MJ/kg, apparent activation energy of 126.64 and 99.14 kJ/mol (based on Flynn-Wall-Ozawa method) and 122.16 and 94.73 kJ/mol (based on Kissinger-Akahira-Sunose) and no ash, respectively.

KEYWORDS: Lignin, NSSC spent liquor, PHL, lignosulfonate, kraft lignin, Biorefinery

7.2 INTRODUCTION

Forest biorefinery has been an alternative approach for revising traditional pulp and paper industry (Dansereau et al., 2014; Saeed et al., 2011; Van Heiningen, 2006). Forest biorefinery concept aims not only to reduce the production cost of energy, but also to produce value-added products from lignocelluloses (Van Heiningen, 2006). One scenario of biorefinery is to produce value-added products from lignin and hemicelluloses that are generated, but wasted, in pulping processes. In this regard, various strategies were proposed recently in order to isolate lignin and hemicellulose from pulping spent liquors. In these strategies, isolated lignocelluloses can be used as an energy source or in production of value-added products (Holmqvist et al., 2005; Liu et al., 2011; Oveissi & Fatehi, 2014).

In neutral sulfite semichemical (NSSC) pulping process, wood chips are treated with sodium sulfite and carbonate to soften the structure of wood chips prior to NSSC pulping. The spent liquor (SL) of this process contains a portion of lignocelluloses, which is currently wasted in the wastewater of the mill (Dashtban et al., 2014; Sitter et al., 2014). In the kraft-based dissolving pulp process, hemicelluloses and lignin are partially separated from wood chips and dissolved in prehydrolysis liquor of the process. These lignocelluloses are mixed with black liquor and incinerated in the recovery cycle of the mill (Liu et al., 2011; Saeed et al., 2011). In addition, although PHL is incinerated in the recovery process, it is a dilute stream, which increases the load to the recovery cycle of the process. SL and PHL have been recently subjected to several studies in order to produce value-added products from their lignocelluloses (Dashtban et al., 2014; Fatehi et al., 2013; Sitter et al., 2014).

In the past, lignosulfonates were used as adhesive (Mansouri & Salvadó, 2006), plasticiser in concrete (Pelisser et al., 2011) and dye dispersant (Yang et al., 2014). Moreover, lignin was used in a variety of polymer applications such as lubricant, stabilizer (Kumar et al., 2009), surfactants (Olsen et al., 2011), epoxy resins (Sasaki et al., 2013) and superabsorbent hydrogel (Thakur et al., 2014). The lignin of PHL was also used as a filler modifier (Fatehi et al., 2013), fuel source in the past (Saeed et al., 2011; Van Heiningen, 2006). Kraft lignin can be used in production of carbon and composite fibers via pyrolysis or used as fuel (Kadla et al., 2002; Thakur et al., 2014). However, the most suitable applications of lignin generated from the SL of NSSC process and the PHL of kraft-based dissolving pulp process have been unidentified yet.

Lignin has a three dimensional structure with many aromatic and aliphatic groups, which makes its modification and end use application challenging. In the literature, it was claimed that lignin have various functional groups (i.e. carboxylic and sulfonated) depending on its type and origin (El Mansouri & Salvadó, 2007; Mansouri & Salvadó, 2006). However, no study was conducted on analyzing the chemical, thermal and incineration behavior of lignin generated in the spent liquors of PHL and NSSC processes. This study aims to characterize lignin separated from industrially produced SL and PHL of NSSC and kraft-based dissolving pulp processes, respectively, and to compare their properties with those of commercial lignosulfonates and kraft lignin. The surface, chemical and thermal assessments of lignin are important parameters that affect the properties of end use lignin-based products (Lora & Glasser, 2002). The main novelty of this work is the surface, chemical, structural and thermal analyses of various lignins to identify suitable end use applications for them.

7.3 MATERIALS AND METHODS

7.3.1 Materials

Tego@trant A100, 1,3-didecyl-2-methylimidazolium (TEGO), was purchased from Metrohm (Canada) and used for the determination of carboxylated and sulfonated groups attached to lignin. Also, the solution (0.005 N) of polydiallyldimethylammonium chloride (PDADMAC) was purchased from Sigma-Aldrich and used as received to measure the total anionic charge density of lignin samples. Washed and dried softwood kraft lignin (KL) was supplied by FPInnovations from its pilot facilities in Thunder Bay, ON. Lignosulfonic acid sodium salt (LS1) was purchased from Sigma-Aldrich, while sodium lignosulfonate powder (LS2) was received from Tembec (Temiscaming, Quebec, Canada) companies. Spent liquor (SL) of neutral sulfite semi chemical (NSSC) received from a mill located in New Brunswick, Canada. In this process, wood chips are treated at 180 °C for 15-18 min using caustic and sulfite prior to refining in the NSSC pulping process. Wood chips from maple, poplar and birch with the mass ratio of 7:2:1 are used in the kraft-based dissolving pulp production in a mill, located in New Brunswick, Canada (Saeed et al., 2012). The hemicelluloses and a part of lignin are separated in the pre-hydrolysis stage. The pre-hydrolysis liquor (PHL) of this process obtained from the aforementioned mill and used as received.

7.3.2 LPHL and LSL collection

Both SL and PHL samples were initially centrifuged at 1000 rpm for 10 min using a Survall ST16 centrifuge to remove large particles (i.e. solid woody components). Afterwards, SL and PHL samples were acidified using 60 wt % sulfuric acid to a pH of 1.5 and kept for 60 min under stirring. Then, the samples were centrifuged at 2500 rpm for 10 min and the precipitates were collected. This treatment aimed to isolate the lignin of SL and PHL. The isolated lignin of SL (LSL), of PHL (LPHL), LS1 and LS2 were oven dried at 60 °C for a week and used in this study.

7.3.3 Elemental and FTIR analyses

Elemental (ultimate) analysis was performed on all dried lignin samples using a Vario EL cube instrument (Germany) according to the previously described method (Fadeeva et al., 2008; Oveissi & Fatehi, 2014). For this analysis, less than 50 mg of sample was used with two CAHN C-31 microblances (7 pt) associated with HR-2021 top loader (5pt Fourier Transform Infrared Spectrophotometer (FTIR) and Tensor 37 (Bruker, Canada) was assessed for analyzing the functional groups associated with lignin samples. The FTIR spectra were developed by embedding less than 10 mg of sample on KBr disc. The resolution of spectroscopy was 2 cm^{-1} in a frequency range of 700-4000 cm^{-1}.

7.3.4 Sulfonated, carboxylic and total charge density analyses

Initially, aqueous solutions (1 wt. %) of lignin samples were made from dried samples and incubated in a C76 New Brunswick water bath shaker at pH 10, 30 °C, 100 rpm for 1 h. Then, 1 to 2 ml of lignin sample solutions were titrated against PDADMAC standard solution (0.005M) using a Mütek PCD04 charge titrator (Herrsching, Germany), and the charge density of lignin samples were measured (Eq.7.1).

$$\text{Charge Density } \left(\frac{\text{meq}}{\text{g}}\right) = \frac{\text{Volume of titrant} \times \text{concentration of titrant}}{\text{mass of lignin used in titration}} \qquad (7.1)$$

To determine the charge density of sulfonated group attached to lignin, 1 wt. % aqueous solutions of lignin was prepared and incubated at pH 10, 30 °C and 100 rpm, for 1 h in a C76 New

Brunswick water bath. Afterwards, all solutions were titrated against TEGO (0.004 mol/l) using a Metrohm 905 Titrando (Canada). The charge density of sulfonated group attached to lignin samples was determined according to equation 7.2:

$$\text{Charge density of sulfonated group } \left(\frac{\text{meq}}{\text{g}}\right) = \frac{\text{Volume of Point of inflection} \times \text{Tego concentration}}{\text{mass of sample tested}} \tag{7.2}$$

To measure the charge density of carboxylic group attached to lignin, the same protocol was followed, but at pH10. Consequently, the charge density of carboxylic group was measured based on equation 7.3:

$$\text{Charge density of carboxylic group } \left(\frac{\text{meq}}{\text{g}}\right) = \frac{\text{Volume of Point of inflection} \times \text{Tego concentration}}{\text{mass of sample tested}} - \text{the charge density of sulfonated group} \tag{7.3}$$

All measurements were conducted three times and the averages of the three were reported.

7.3.5 Hydrodynamic diameter analysis

The molecular diameter of all lignin samples was measured by a Dynamic Light Scattering (DLS) (Brookhaven BI200, USA) at 90° according to the method described in the literature (Li et al., 2006). Alkaline aqueous solutions of 1 wt.% of lignin samples were prepared at pH 10 (using NaOH) and room temperature. A scattering angle of 90° was applied for reading the hydrodynamic diameter of lignin fragments in solutions. Based on volume, the results were reported as the average and the standard deviation from more than five measurements was reported. pH 10 was selected for this measurement as KL is soluble in solutions with a pH higher than 10.

7.3.6 Calorific value and thermogravimetric analysis (TGA)

Calorific value or high heating value (HHV) of lignin samples was measured according to ASTM E711-87 (ASTM, 2004) using a Parr 6200 oxygen bomb calorimeter, as previously described (Dashtban et al., 2014). Thermogravimetric analysis was assessed for all oven dried samples by a thermogravimetric analyzer (TGA)-i1000 series (instrument Specialist Inc., U.S.A.) under air at 35 ml/min and increment rates of 10, 12.5, 15, 17.5 and 20 °C/min according to an establish method (Zhang et al., 2014).

7.3.7 Activation energy determination

Non-isothermal methods have been applied to calculate the effective activation energy as a function of conversion rather than temperature (Slopiecka et al., 2012). It was claimed that in non-isothermal solid state kinetic studies, the rate of conversion of biomass to char and volatiles (tar and gas) would follow equation 7.4 (Slopiecka et al., 2012):

$$\frac{d\alpha}{dt} = k(T) \times f(\alpha) \qquad (7.4)$$

In which *k(T)* is the temperature dependent rate constant, *f(α)* is temperature-independent function of conversion. *k(T)* and α can be replaced by Arrhenius equation according to equation 7.5 and equation 7.6, respectively, in equation 7.7:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \qquad (7.5)$$

$$\alpha = \frac{p_0 \quad -p_t}{}$$

$$\begin{array}{l} p\text{��}_0 \\ -p\text{��}_\infty \end{array} \qquad (7.6)$$

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (7.7)$$

where A, R, E, and α corresponded to frequency factor, the universal gas constant, activation energy and sample conversion, respectively. Also, m_0, m_∞ and m_t are the mass of sample before the reaction, after the reaction and at time t, correspondingly. Considering β as heating rate

$$\beta = \frac{dT}{dt} \qquad (7.8)$$ and

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \qquad (7.9),$$

the integration of equation 9 generates:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \qquad (7.10)$$

Equation 7.10 does not have any analytical solution. In the literature, it was stated that activation energy (E) could be determined without detailed information of *G(α)* (Li et al., 2012). Considering x = E/RT as reduced activation energy at the temperature T; Equation 7.10 would be rewritten as equation 7.11:

$$G(\alpha) = \frac{AE}{R\beta}\left(\frac{-\exp(-x)}{x} - \int \frac{\exp(-x)}{x}\,dx\right) = \frac{AE}{R\beta}\,p(x) \qquad (7.11)$$

Using appropriate approximations for p(x), two iso-conversional methods were developed by Flynn-Wall-Ozawa (FWO) (Eq.7.12) and Kissinger-Akahira-Sunose (KAS) (Eq.7.13)

(Slopiecka et al., 2012):

$$\ln(\beta) = \ln\left(\frac{0.0084\times A\times E}{R\times G(\alpha)}\right) - 1.0516\,\frac{E}{RT} \qquad (7.12)$$

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A \times R}{E \times G(\alpha)}\right) - \frac{E}{RT} \qquad (7.13)$$

Based on FWO and KAS methods, ln(β) versus 1/T and ln(β/T^2) versus 1/T would be straight lines at any constant α. Consequently, the slopes of these straight lines yield the apparent activation energy for the combustion of lignin samples.

7.4 RESULTS AND DISCUSSION

7.4.1 Structural characterization

Figure 7.1 depicts the FTIR spectra of lignin samples. All samples had a peak at 3360 cm^{-1}, however the intensity of this peak was greater in LPHL than other samples. This peak accounts for stretching of hydroxyl groups in lignin (Laurichesse & Avérous, 2013). KL and LPHL had a peak at 1713 cm^{-1}, which corresponded to the carboxylic group in lignin (Ishida et al., 2000). This peak was hardly observable in LS1 implying that LS1 did not have a noticeable amount of carboxylic group. In the literature, it was stated that aromatic skeletal vibrations present at the wavelength range of 1400-1600 cm^{-1} in the FTIR spectrum (El Mansouri & Salvadó, 2007; Maria et al., 2002). It was claimed that the major peak of lignin mirrored at 1032 cm^{-1} (Tucker et al., 2001). This peak (1032-1034 cm^{-1}) is corresponded to plane deformation of aromatic C-H in guaiacyl unit (El Hage et al., 2009; Xu et al., 2008). The peaks of sulfate groups were observed at 620-635 cm^{-1} and 1100-1137 cm^{-1} ranges (El Mansouri & Salvadó, 2007; Maria et al., 2002; Paul et al., 2005). Also, the decrease in LSL peak at 630 cm^{-1} was less than that in LS1 and LS2. From this analysis, it can be concluded that the sulfite content of KL and LPHL was less than that of others.

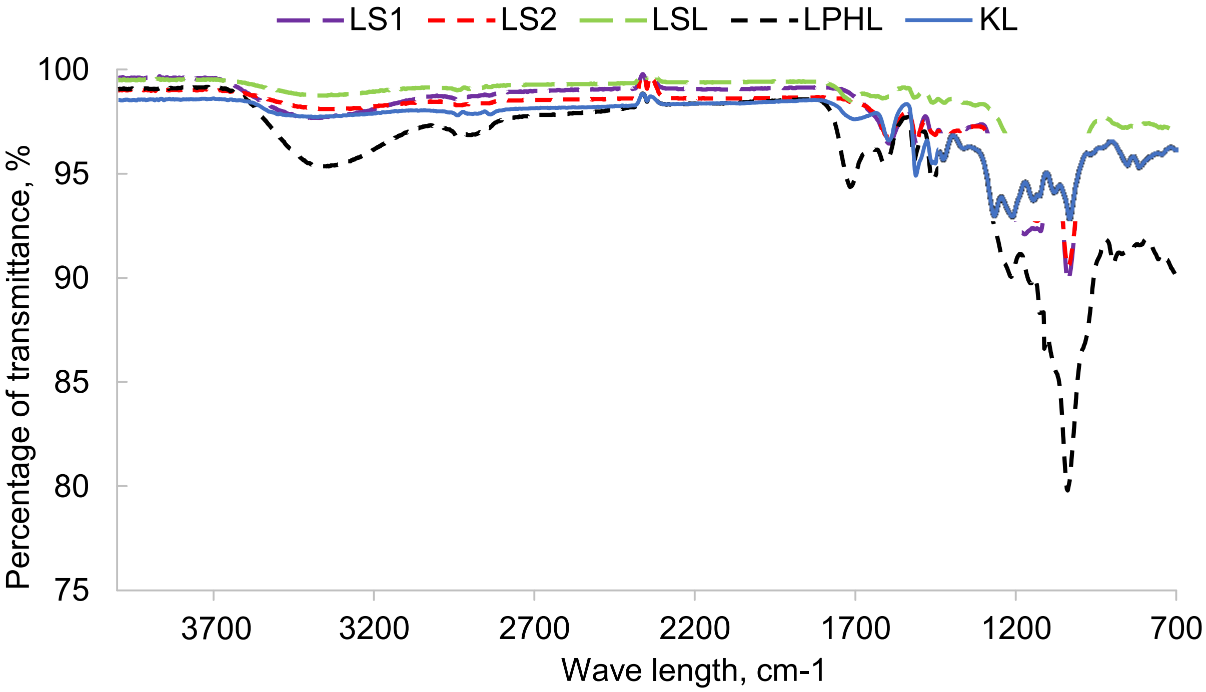

Figure 7.1. FTIR spectra of lignin samples

7.4.2 Charge density and hydrodynamic diameter characterization

It is well known that charge density plays a significant role in the adsorption and flocculation of macromolecules in polyelectrolyte solutions (Barany et al., 2011; Gregory & Barany, 2011; Zavgorodnya & Serpe, 2011). Generally, the adsorption of lignocelluloses on adsorbents occur via developing mainly hydrogen bonding, and thus the amount of anionic charged groups (i.e. carboxylic and sulfonated groups) attached to lignocelluloses is critical (Liu et al., 2011; Nakagame et al., 2011). Furthermore, lignocelluloses bond with other dissolved materials in polyelectrolyte solutions via developing hydrogen bonding and electrostatic forces (Yasarla & Ramarao, 2013). In this case, the charged groups of lignocelluloses will attract or repel the charged groups of other constituent in the solutions and hence form flocs or disperse dissolved materials in solutions (Nasser & James, 2006). Thus, determining the charge density of lignin is critical for evaluating its adsorption/flocculation performance. In this regard, charge density of lignin samples were measured and listed in Table 7.1. The overall charge density of all samples was negative. It is evident that the anionic charge density of LS2 (2.25 meq/g) and LS1 (1.52 meq/g) were more than that of LSL (0.9 meq/g), KL (0.67 meq/g) and LPHL (0.25 meq/g). In the literature, it was stated that anionic charge density of lignin was mainly attributed to sulfonated and carboxylic groups (Liu et al., 2011; Liu et al., 2012). The sulfonated and carboxylic groups of all samples were measured and listed in Table 7.1. As can be seen, 88% of anionic charge density of LPHL was related to carboxylic group and only 4 % of that corresponded to sulfonated group. The shares of sulfonated group in total charge density were 0, 87, 85 and 78 % and the shares of carboxylic group were 81, 7, 10 and 16 % in KL, LS1, LS2 and LSL, respectively.

It should be highlighted that the sulfonated and carboxylic groups and total charge density of LS2 were higher than that of other samples. These results are in harmony with observed peaks of carboxylic and sulfonated groups in FTIR analysis. Table 7.1 also lists the hydrodynamic diameter of lignin samples in 1 wt.% water solution at pH 10 and room temperature. As can be seen, the diameters of LSL and LS1 were the same (10.1 nm) and were higher than that of LS2, KL and LPHL. In the literature, it was claimed that commercial sodium lignosulfonate (obtained from Chemische Werke Zell-Wildshausen, Düsseldorf, Germany) had the hydrodynamic diameter of 5-6 nm (Tiemeyer et al., 2014). The hydrodynamic diameter is correlated to molecular weight of lignin samples. As lignin has a similar subunit structure, the larger the hydrodynamic diameter, the large the molecular weight of lignin would be. The results showed that the smallest lignin sample was LPHL. The size of lignin plays a significant role on its adsorption and flocculation performance. It was stated that small polymers would diffuse more than large ones into pores of an adsorbent (Bjelopavlic et al., 1999). Therefore, if used as a surface modifier of a filler (i.e. adsorbent), more of small polymers will be diffused into the filler structure and thus its surface modifying performance will be deteriorated (Fatehi et al., 2013). Instead, more of large polymers will adsorb on the surface of filler and modify its surface properties (Huang et al., 2013). In this regard, at the same dosage applied, LPHL would not be suitable as a surface modifier as it is the smallest, and LSL and LS1 would work more effectively on modifying the surface properties of fillers. In addition, it was claimed that the smaller the polymers, the smaller the flocs would be formed (Saeed et al., 2011). Hence, via interacting with a specific particle, LPHL or KL would form smaller flocs than LSL, LS1 or LS2 in solutions. Therefore, LS samples would be more effective flocculant than LPHL and KL. It is also well known that polymers with large hydrodynamic diameter has stronger steric hindrance effect, which results in higher dispersion (Ran et al., 2009). Consequently, LSL, LS1 and LS2 could be better dispersants than LHPL and KL. In fact, lignosulfonate was used as dispersant for various applications in the past (Wei et al., 2013; Xiao et al., 2014)

Table 7.1. Charge density characteristics and hydrodynamic diameter of lignin samples

sample ID	Total charge density (anionic) meq/g	Sulfonated group meq/g	Carboxylic group meq/g	Hydrodynamic diameter nm
LPHL	0.25 ± 0.01	0.01 ± 0.00	0.22 ± 0.01	2.1 ± 0.2
LSL	0.90 ± 0.03	0.70 ± 0.01	0.14 ± 0.02	10.1 ± 1.1
LS1	1.52 ± 0.02	1.33 ± 0.02	0.11 ± 0.01	10.1 ± 0.9
LS2	2.25 ± 0.01	1.92 ± 0.02	0.23 ± 0.02	8.8 ± 1.2
KL	0.67 ± 0.02	0.00 ± 0.00	0.54 ± 0.03	6.3 ± 0.7

7.4.3 CHNSO and HHV analyses

Table 7.2 lists the elemental analysis of lignin samples. As can be seen, KL and LPHL had less sulfur content than other lignin samples. Also, the inorganic content (i.e. other elements) of KL and LPHL were the least in comparison with that of other samples. The remaining elements that were not reported in this study are usually the residual of cooking/pulping chemicals and inorganics originated from wood. Table 7.2 also lists the HHV of lignin samples. It is evident that KL generated more energy (HHV of 27.02 MJ/kg) than other tested samples ($HHV_{KL} > HHV_{LPHL} > HHV_{LS2} > HHV_{LS1} > HHV_{LSL}$). One study reported that the lignosulfonate obtained from hydrolyzate of pine wood had an HHV of 25 MJ/kg (Retsina & Pylkkanen, 2008). In another study, it was reported that alkali lignin had an HHV of 19 MJ/kg (Bu et al., 2014). It was claimed that HHV of an organic materials is a function of its organic elements (ultimate) (DEMİRBAŞ, 2003; Sheng & Azevedo, 2005; Vargas-Moreno et al., 2012). A recent study on lignin of black liquor showed that HHV can be predicted based on the carbon content of lignin (Eq.7.14) (Jablonský et al., 2013).

$$HHV_{model} = 0.40659 \times X_C \qquad (7.14)$$

where X_c is the carbon content (wt.%) of the sample. Based on Eq.7.14, HHV_{model} of KL, LPHL, LSL, LS1 and LS2 were calculated and tabulated in Table 7.2. A comparison between the calculated and measured values revealed 7-9% difference (i.e. error).

Table 7.2. CHNSO and high heating value (HHV) of lignin samples

sample ID	N wt. %	C wt. %	H wt. %	S wt. %	O wt. %	Other elements wt. %	$HHV_{measured}$ (MJ/ kg)	HHV_{model} (MJ/ kg)
LPHL	0.14	43.58	5.49	2.62	48.09	0.09	19.20	17.72
LSL	0.43	36.30	4.49	7.65	46.90	4.23	16.03	14.76
LS1	0.22	41.15	4.70	5.32	43.21	5.41	17.92	16.73
LS2	0.86	41.33	4.65	6.06	39.64	7.47	18.45	16.80
KL	0.06	63.07	5.97	0.23	30.60	0.07	27.02	25.64

7.4.4 TGA analysis

TGA analysis not only helps understand the thermal behavior of lignin as fuel, but also indicates how lignin can behave under different thermal treatments in composites. The weight loss and the rate of weight loss of lignin samples versus temperature under air (35 ml/min) and incineration rate of 10 °C/min are depicted in Figure 7.2. It is apparent that the thermal decomposition of lignin occurred at different temperatures due to the heterogeneous and complex structure of lignin (Lemes et al., 2010). Volatile components would also be generated during the combustion of lignin, which mirrored in several peaks in Figure 7.2 (Lemes et al., 2010). It is evident that KL and LPHL showed less resistance to incineration than other samples. By incinerating the samples to 700 °C, 15 wt.% of LSL, 51 wt.% of LS1 and 27 wt.% of LS2 were remained. Interestingly, all LPHL and KL were combusted and no ash was remained at 700 °C. The peaks below 150 °C were due to the evaporation of moisture content of lignin samples (Singh et al., 2005). It is evident that a part of LSL decomposed at 214 °C (T_{p1}). This degradation may be due to the removal of terminal groups of LSL (Wang et al., 2009) or probably the degradation of lignin-hemicellulose complexes accompanied in LSL (Singh et al., 2005). Figure 7.2 also shows that the maximum incineration of KL and LPHL occurred at 469 and 375 °C, which corresponded to 6 and 19 % of remaining weight, respectively. This peak (T_{p2}) was observed at 383 °C in LSL, 297 °C in LS1 and 299 °C in LS2, which were related to 43, 71 and 73 % of weight loss, respectively. In the literature, it was stated that the maximum degradation of lignin occurred at 330-400 °C (Singh et al., 2005). In all samples (except LPHL), the second major increase in the rate of weight loss (T_{p3}) occurred at the temperature range of 439-479 °C, which might be due the conversion of lignin to phenols (Wang et al., 2009). At this peak, the remaining mass of LS1, LS2 and LSL were 54.8, 50.4 and 24.3 wt.%, respectively. Moreover, a portion of LS2 decomposed at 656.6 °C (T_{P4}), which may correspond to the degradation of phenols to carbonaceous structure (Chen et al., 2008; Wang et al., 2009).

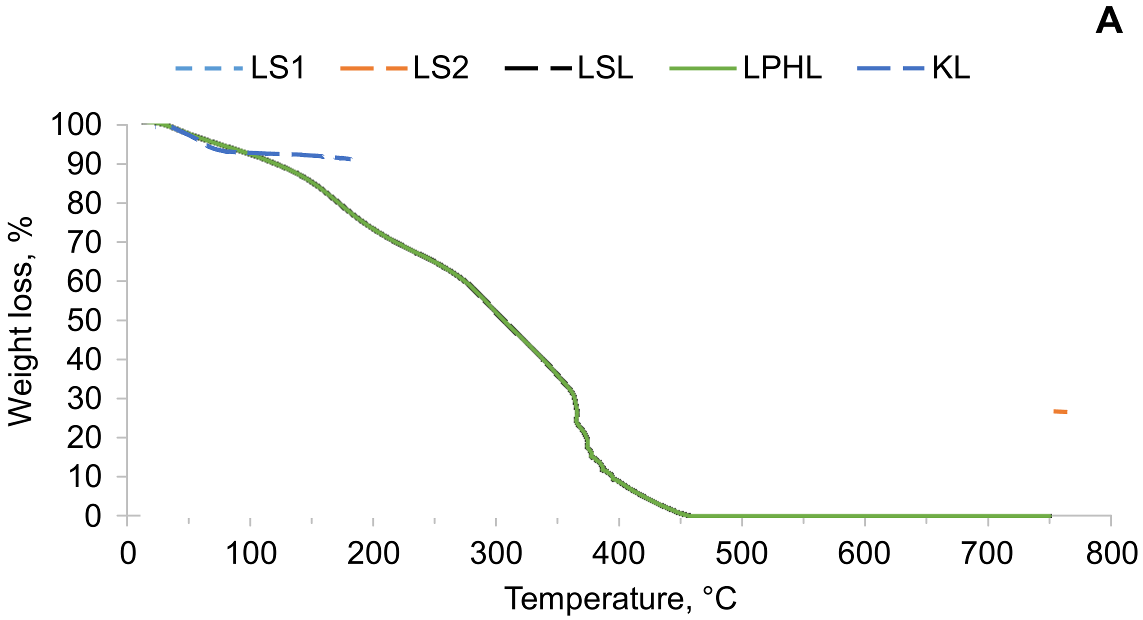

Figure 7.2. Thermogravimetric (A) and derivative of thermogravemetric (B) of LS1, LS2, LSL, LPHL and KL (conducted under air at 35 ml/min and heating rate of 10 °C/min)

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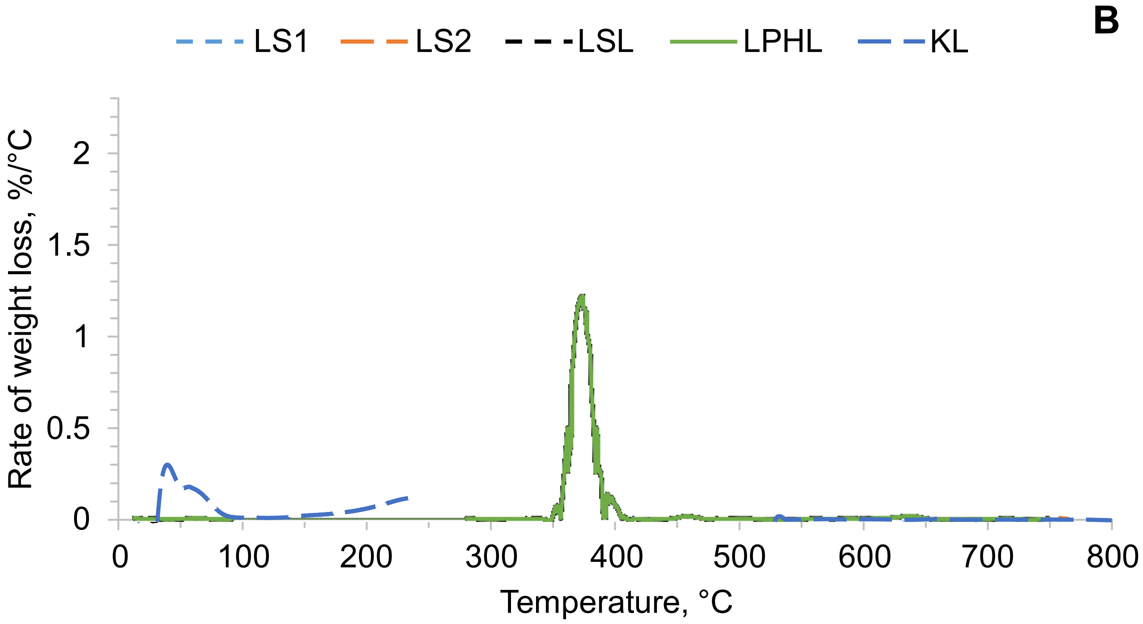


Figure 7.2 continued

Table 7.3 summarized the combustion parameters of lignin, which were obtained from Figure 7.2. Reactivity index was defined as the maximum rate in which the biomass or char combusted in oxidizing or reducing atmosphere (Gomes et al., 2006):

$$RR = \frac{1}{w_0} \times \left(\frac{dw}{dt}\right)_{max} \tag{7.15}$$

where w_0 is the initial mass of sample (kg) and $\left(\frac{dw}{dt}\right)_{max}$ is the maximum rate of weight loss (%/s). Reactivity indices were calculated based on the incineration rate and listed in Table 7.3. It should be highlighted that a greater R represents a higher reactivity describing that constituents of biomass or char volatises easier by the gasifying agent (Gil et al., 2012; Gomes et al., 2006). As can be seen, KL and LPHL had the highest reactivity indices of 51,758 and 22,222 % $kg^{-1}.s^{-1}$, respectively; while other samples had the reactivity index of 5,000-7,000 % $kg^{-1}.s^{-1}$. In the literature, it was stated that olive waste had a reactivity index of 23,807 % $kg^{-1}.s^{-1}$ (Gil et al., 2012). In other words, KL and LPHL reacts faster with the gasifying agent (air) than other samples. It can be concluded that KL and LPHL incinerated more efficiently than other lignin samples.

Table 7.3. Characteristic parameters of combustion of lignin samples in air

Lignin	T_P (°C)				DTG_{max} (%/°C)	W_R (%)	R (% $kg^{-1}.s^{-1}$)
	T_{P1}	T_{P2}	T_{P3}	T_{P4}			
LPHL	-	374.7	-	-	1.200	0.00	22222
LSL	214.2	382.9	467.9	-	0.357	14.95	7256
LS1	-	296.8	439.1	-	0.225	51.03	5000
LS2	-	299.2	478.6	665.6	0.259	26.70	6167
KL	-	469.1	-	-	2.267	0.00	51758

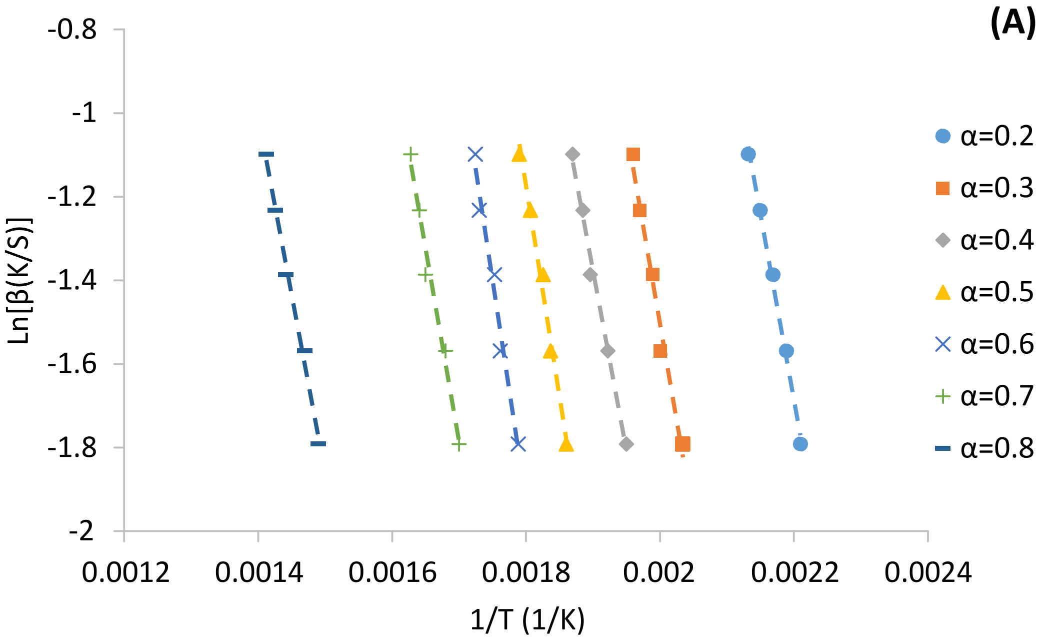
T_P: peak temperature
DTG_{max}: maximum rate of weight loss
W_R: residual mass

7.4.5 Kinetic analysis

To comprehend a detailed understanding of combustion behaviour of lignin samples, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) non-isothermal methods were applied on thermogravimetric data obtained in Figure 7.2. The apparent activation energy (E) was calculated by plotting ln(β) vs. 1/T (FWO method) and $\ln(\beta/T^2)$ vs. 1/T (KAS method) at various sample conversions (α) based on equations 7.12 and 7.13. As was stated earlier, the heating rates (β) of 10, 12.5, 15, 17.5 and 20 °C/min were used to evaluate the activation energy of samples under air (35 ml/min). Figures 7.3 and 7.4 correspond to FWO and KAS analyses, respectively. It is evident that the slopes of fitted lines were similar in each sample, but were not the same at all conversions (α). Variation in slopes at conversion ratios may be due to the complexity and multi-step reactions of lignin to char during the combustion.(Slopiecka et al., 2012).

Table 7.4 lists the calculated activation energy (the energy required for rapturing lignin molecules to start incinerating) at all α (conversion of lignin to char and volatiles) values via FWO and KAS methods. The average value of E was reported for each sample as apparent activation energy. As can be seen, the highest apparent activation energies were achieved for LSL, which were 173.98 (FWO) and 172.89 (KAS) kJ/mol. Also, the apparent activation energies of 126.64 (FWO) and 122.16 (KAS) kJ/mol for KL, 99.14 (FWO) and 94.73 (KAS) kJ/mol for LPHL, 73.49 (FWO) and 68.03 (KAS) kJ/mol for LS1 and 65.17 (FWO) and 58.49 (KAS) kJ/mol for LS2 were obtained, correspondingly. It was previously reported that lignin extracted from spruce sawdust had the activation energy (based on Arrhenius equation without the temperature integral) of 13-19 kcal/mol (≈ 54-79.5 kJ/mol) (Ramiah, 1970). It should be highlighted that the Arrhenius equation (without the temperature integral) is insufficiently accurate for complex condensed phase systems of thermal analysis (Flynn, 1997).

In another study, the apparent activation energy for poplar was reported to be in the range of 107.86–209.49 kJ/mol and 104.95–209.90 kJ/mol for FWO and KAS, respectively (Slopiecka et al., 2012). This comparison implies that the values of activation energies were significantly different among various studies. In other words, the apparent activation energy for combustion of lignin is a function of lignin origin and probably structure. Consequently, LSL needs more energy than other samples in order to start the combustion. It should be highlighted that LPHL required less energy than KL to start burning.



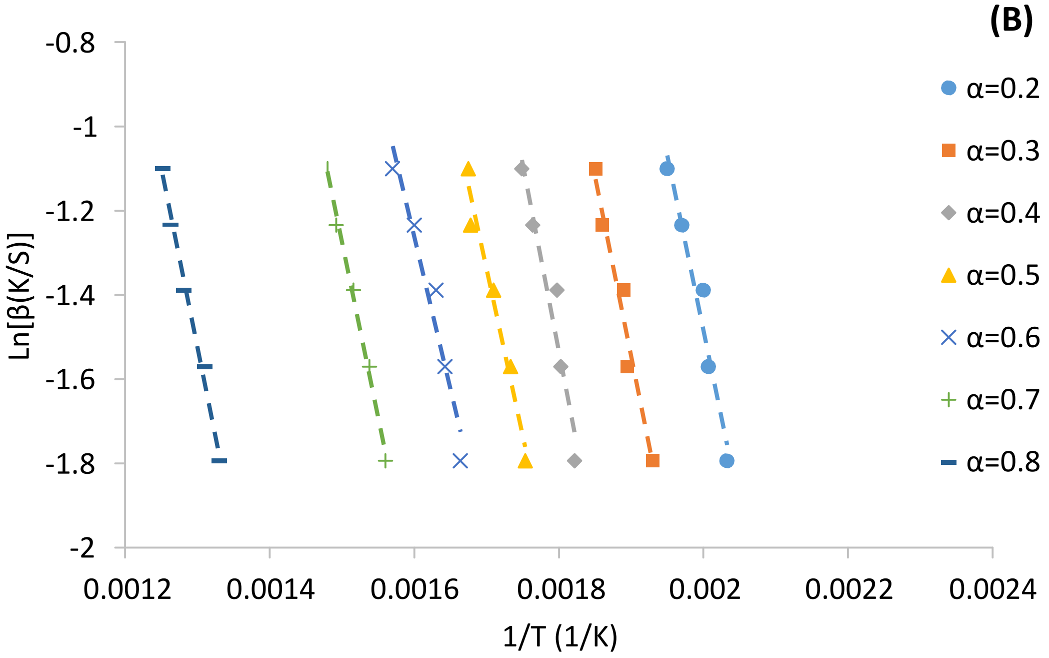


Figure 7.3. Determination of activation energy of (A) LS1 (B) LS2 (C) LSL (D) LPHL and (E) KL at different α values using FWO method

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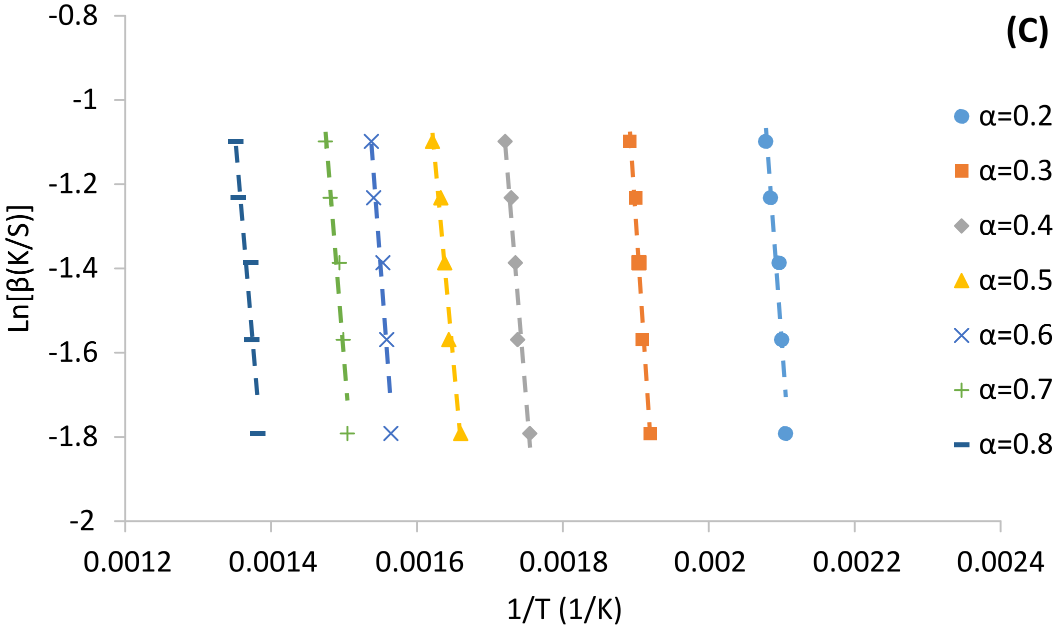

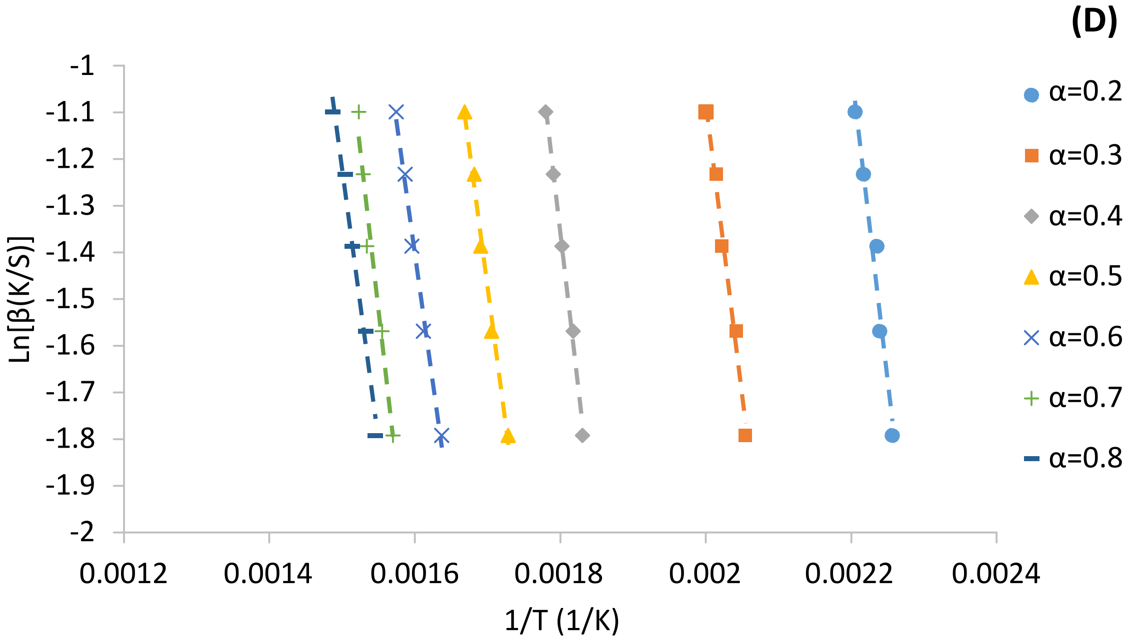

Figure 7.3 continued

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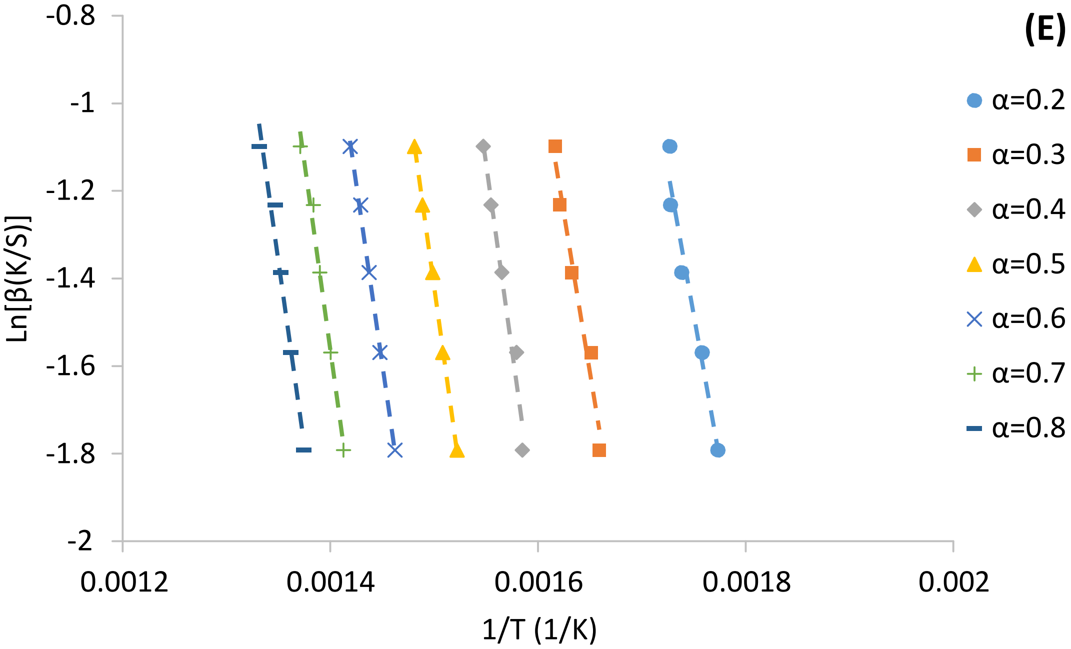

Figure 7.3 continued

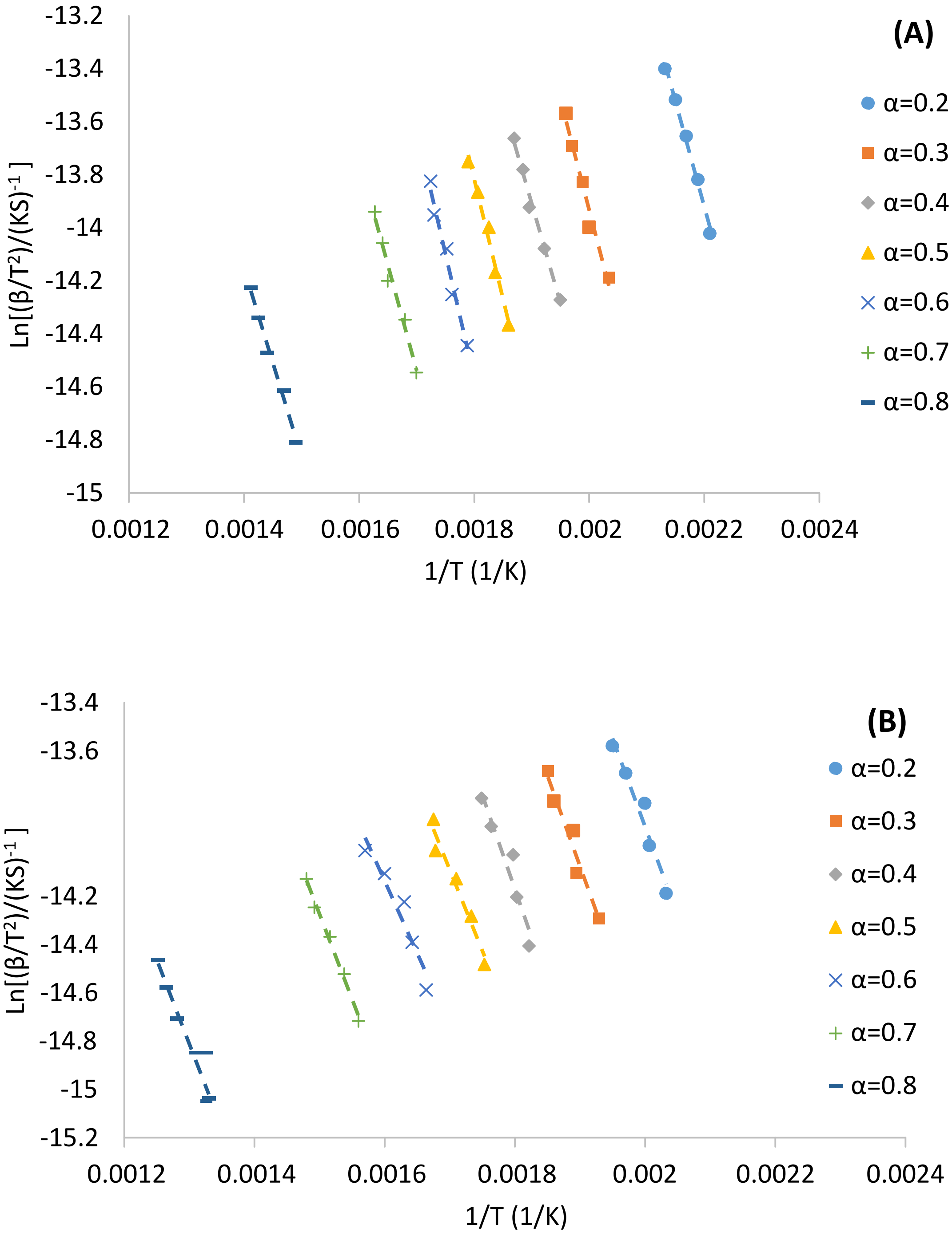

Figure 7.4. Determination of activation energy of (A) LS1 (B) LS2 (C) LSL (D) LPHL and (E) KL at different α values using KAS method

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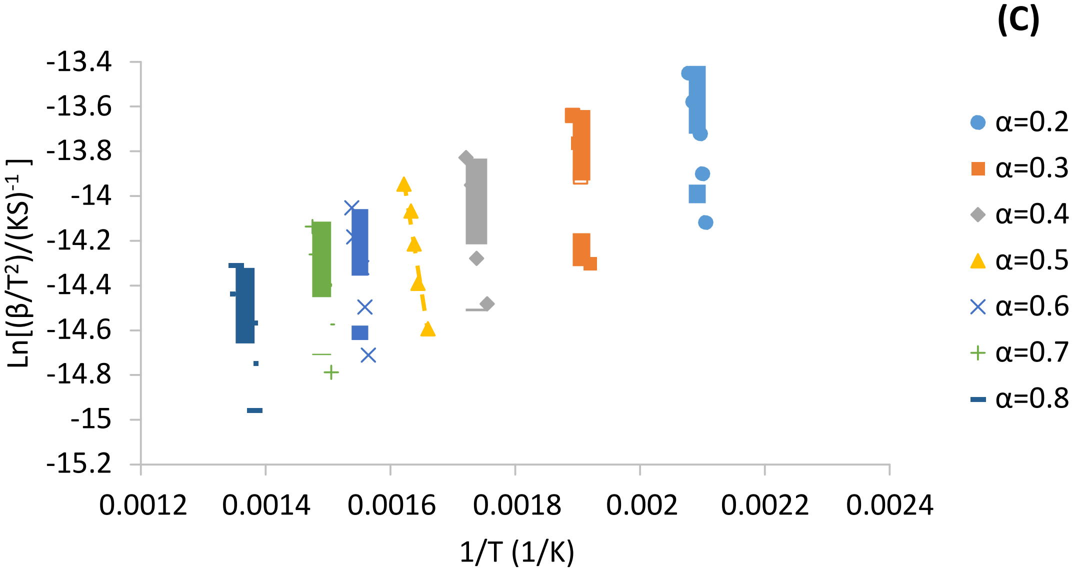

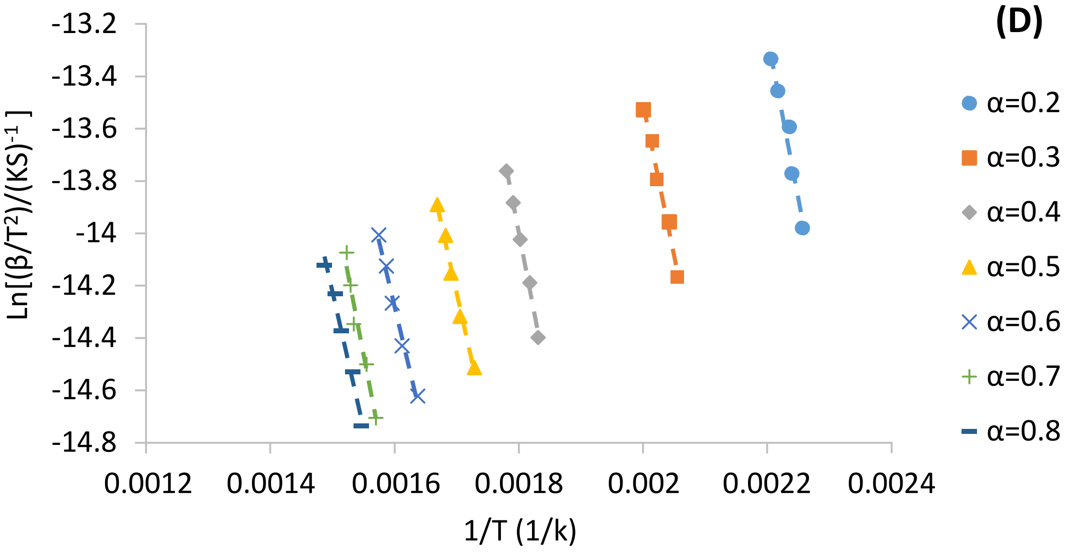

Figure 7.4 continued

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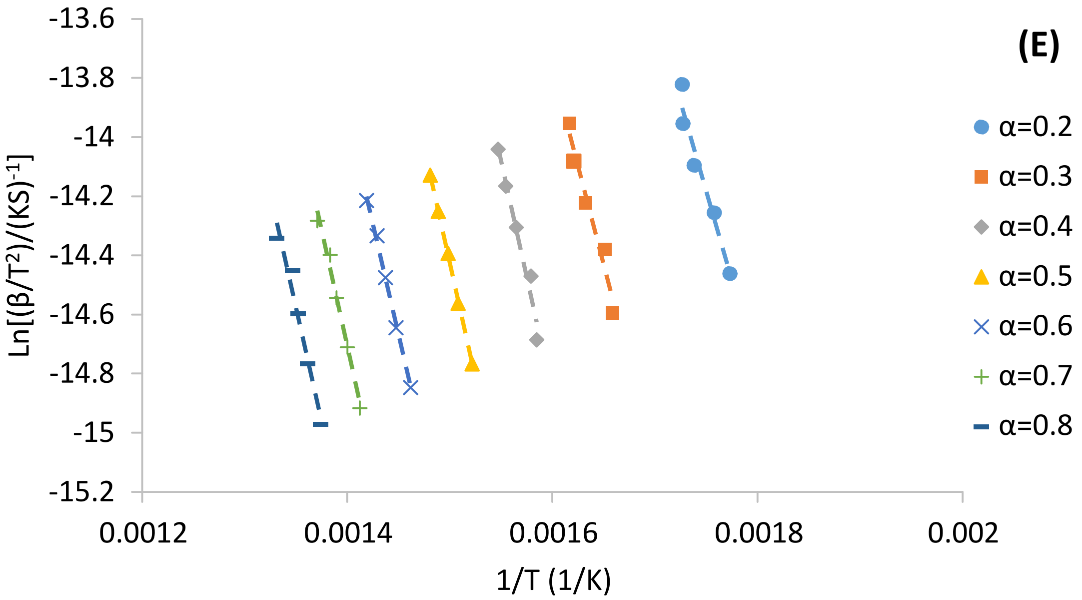

Figure 7.4 continued

Table 7.4. Activation energy calculated based on FWO and KAS methods for the combustion of various lignin samples in air.

sample ID	α	FOW method E (kJ/mol)	FOW method R^2	KAS method E (kJ/mol)	KAS method R^2
LPHL	0.2	105.90	0.962	103.91	0.956
	0.3	99.33	0.987	96.25	0.984
	0.4	106.20	0.996	102.47	0.995
	0.5	93.69	0.991	88.74	0.989
	0.6	88.55	0.989	82.76	0.986
	0.7	108.14	0.966	102.97	0.959
	0.8	92.19	0.984	85.98	0.980
	Average	**99.14**		**94.73**	
LSL	0.2	185.80	0.927	187.43	0.921
	0.3	204.69	0.980	206.53	0.978
	0.4	167.71	0.950	166.80	0.945
	0.5	149.41	0.972	146.98	0.968
	0.6	183.34	0.947	182.08	0.941
	0.7	167.13	0.941	164.59	0.933
	0.8	159.76	0.904	155.84	0.890
	Average	**173.98**		**172.89**	

Continued on next page

Table 7.4 continued

sample ID	α	FOW method			
		E (kJ/mol)	R^2	E (kJ/mol)	R^2
LS1	0.2	70.01	0.995	65.96	0.994
	0.3	73.78	0.978	69.26	0.973
	0.4	67.94	0.991	62.75	0.988
	0.5	79.60	0.987	74.59	0.983
	0.6	83.20	0.977	78.02	0.971
	0.7	72.67	0.982	66.43	0.976
	0.8	67.21	0.991	59.22	0.988
	Average	**73.49**		**68.03**	
LS2	0.2	65.71	0.959	60.75	0.947
	0.3	67.75	0.961	62.44	0.950
	0.4	70.20	0.933	64.50	0.913
	0.5	62.33	0.969	55.83	0.958
	0.6	57.05	0.944	49.70	0.919
	0.7	65.94	0.994	58.39	0.991
	0.8	67.21	0.991	57.80	0.987
	Average	**65.17**		**58.49**	
KL	0.2	104.52	0.961	100.41	0.953
	0.3	114.86	0.966	110.63	0.959
	0.4	134.03	0.971	130.33	0.966
	0.5	134.42	0.999	130.28	0.999
	0.6	129.90	0.997	125.05	0.997
	0.7	135.48	0.987	130.52	0.985
	0.8	133.31	0.968	127.89	0.962
	Average	**126.64**		**122.16**	

7.5 CONCLUSIONS

KL, LPHL, LSL, LS1 and LS2 had 0.67, 0.25, 0.90 and 1.25-1.52 meq/g anionic charge densities; 0.54, 0.22, 0.14 and 0.11-0.23 meq/g carboxylic group and 0, 0.01, 0.70 and 1.33-1.92 meq/g sulfonated group, respectively. The results also indicated that LSL and LS1 had the same hydrodynamic diameter (10.1 nm), which was higher than that of KL, LPHL and LS2. The hydrodynamic diameter and charge density analyses confirmed that lignosulfonates (LSL, LS1 and

LS2) were more appropriate to be used as a filler modifier, flocculants and dispersants. The TGA analysis confirmed low thermal resistance and ash content of LHPL and KL. The results also indicated that LPHL had better incineration efficiency than other samples with HHV of 27.02 and 19.2 MJ/kg, and reactivity indices of 51758 and 22222 %.kg^{-1}.s^{-1}, respectively. In addition, the apparent activation energy of 126.64, 99.14, 173.98, 73.49 and 65.17 kJ/mol through FWO method and 122.16, 94.73, 172.89, 68.03 and 58.49 kJ/mol via KAS method were obtained for KL, LPHL, LSL, LS1 and LS2, respectively. These results suggest that LPHL would be a suitable fuel source after KL.

7.6 ACKNOWLEDGMENT

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8 CHAPTER EIGHT: OVERALL CONCLUSIONS AND RECOMMENDATIONS

8.1 OVERALL CONCLUSIONS

Adsorption can be used as an economical, fast and feasible alternative to extract lignin and hemicelluloses from spent liquor (SL) of neutral sulfite semichemical (NSSC) pulping and spent liquor (pressate) of thermomechanical pulping (TMP), which can be readily integrated into existing facilities of these two pulping processes. The adsorption of lignocelluloses from SL of TMP on activated carbon (AC) was optimized under the conditions of 5.2 pH, 30 ºC for 3h adsorption treatment, which resulted in 45% lignin removal (166 mg/g of lignin was adsorbed on AC). Interestingly, the acidification (to pH 2) and a subsequent adsorption treatment (using AC) resulted in an overall lignin removal of 89 %. Additionally, 60 % of lignin, 19 % of hemicelluloses, 32 % of COD and 39 % of turbidity were removed in the two-stage process at pH 5.2. Also, the adsorption of lignin from SL of TMP process via fly ash was successful. The results suggested that, with using fly ash in the TMP spent liquor, the adsorption of lignin on fly ash was insensitive to pH, but the coagulation of other constituents of SL with fly ash components was pH sensitive and the coagulation was faster than the adsorption. It was observed that under the optimal conditions (fly ash/SL ratio of 55 mg/g and pH 5.3 for 3h), 53% of lignin, 49 % of COD and 89 % of turbidity was removed from the SL of TMP process. The process was modified by adding another stage of adsorption and neutralizing the pH. The two stage adsorption process had 68 %, 70 % and 94 % lignin, COD and turbidity removals, respectively. These results show that the adsorption process with fly ash can be applied to decrease the load of wastewater system of pulping TMP process.

It was generally observed that lignin was adsorbed more than hemicellulose from the SL of NSSC process on bentonite. By adding PDADMAC to the SL of this system, the maximum of 1.8 g lignin and 0.5 g/g hemicellulose were adsorbed on bentonite. These adsorption levels corresponded to 57% lignin and 67 % hemicellulose, 93% turbidity and 38% COD removals from the SL. The high heating value of bentonite was increased from 0 to 15.4 MJ/kg for the precipitates made from SL/bentonite/PDADMAC (low molecular weight) treatment. The final product of this process can be used as filler in the production of corrugated medium papers or as fuel.

In another attempt, aluminium silicate, calcium carbonates (PCC1 and PCC2), kaolin, talc and kaolinite were added to the spent liquors of TMP and NSSC pulping at 30 °C, 90 g/g SL/adsorbent ratio and 100 rpm for 24 h. It was observed that PCC1 adsorbed 331 and 837 mg/g of lignin and 0 and 161 mg/g of hemicelluloses from SLs of TMP and NSSC, respectively. Also, COD and turbidity removals via adding PCC1 were 30 and 63 % from SL of TMP and 5 and 27 % from SL of NSSC, correspondingly. The study on the impact of fly ash (FA) on lignocelluloses of SL of TMP process revealed that, under the conditions of 30 °C, 90 g/g SL/FA ratio and 100 rpm for 24 h, FA4 were the most effective one with lignin and hemicellulose adsorptions of 129 and 194 mg/g, respectively. The turbidity and COD removals via FA4 treatment were 69 and 24 %, correspondingly. Consequently, this analysis showed that adsorption of lignocellulose on kaolinite and PCC1 and FA could decrease the load of wastewater treatment.

In another study, lignin samples isolated from the pre-hydrolysis liquor (PHL), LPHL, and from SL of NSSC, LSL, were compared with two commercial lignosulfonastes (LS1 and LS2) and kraft lignin (KL). The results indicated that LSL and LS1 had the same hydrodynamic diameter (10.1 nm), which was higher than that of KL, LPHL and LS2. The hydrodynamic diameter and charge density analyses confirmed that lignosulfonates (LSL, LS1 and LS2) were more appropriate to be used as a filler modifier, flocculants and dispersants. The results also indicated that LPHL had better incineration efficiency than other samples with HHV of 27.02 and 19.2 MJ/kg. The results suggest that LPHL would be a suitable fuel source after KL.

8.2 FUTURE WORK:

NMR analysis is suggested for further understanding and characterization of all lignin samples investigated in this work. In this thesis, the charge density and surface area of adsorbents presented as the dominant factors of adsorptions. However, in some cases, it seems that other parameters (i.e. chemical structure of adsorbents) have more important roles than the aforementioned factors. Therefore, more analyses on surface morphology of all tested adsorbents are suggested. Also, more studies are suggested for thermodynamics and mass transfer of lignin adsorption on all tested adsorbents. The lignocellulosic compounds produced in this study have the potentiality to be used in various polymer industries such as composites. Thus, the application of lignin in composites should be studied. In order to utilize the obtained data of this study at industrial scales, cost analysis must be conducted and compared with other separating alternatives such as ultrafiltration and solvent extraction. Also, BOD and elemental analysis on the SLs should be investigated to further understand the impact of adsorbents, e.g. fly ash, on SL properties.

Appendix A

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A process for producing lignocellulosic flocs from NSSC spent liquor

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abstract

Presently, the spent liquor (SL) of neutral sulfite semi chemical (NSSC) pulping process is treated in the waste water system. In this work, a new process for isolating lignocelluloses from the SL of an NSSC process is proposed and the effectiveness of this process is evaluated on industrially produced SL. The results showed that under the optimal conditions of pH 6, 30 °C and 15 mg/g poly ethylene imine (PEI) concentration in the SL, a maximum of 37% lignin and 37% hemicelluloses could be removed from SL. Alternatively, the dual system of poly diallyldimethyl ammonium chloride (PDADMAC) and PEI (7.5 mg/g each) was evaluated in removing lignocelluloses from the SL; and the results showed that lignin and hemicellulose removals were improved to 47% and 50%, respectively. The turbidity and chemical oxygen demand (COD) of SL, as well as the elemental analysis of generated flocs were also assessed in this work.

1. Introduction

Neutral sulfite semi chemical (NSSC) is a semichemical pulping process that produces pulp with a yield of 60–80%, which is 10–40% higher than conventional chemical pulping processes (Malo, 1967). In this process, wood chips are treated with sodium sulfite and sodium bicarbonate and subsequently, the treated wood chips are mechanically disintegrated to produce pulp (Benjamin et al., 1969).

However, the disposal or recovery of the spent liquor (SL) generated in the pretreatment stage is a major environmental issue of this process. Due to the presence of lignocelluloses in the SL, it has a high oxygen demand (COD) and in some cases an odor (Malo, 1967). Current practices are to either recover the spent chemicals through ponding for example or treating it in a waste water treatment system (Benjamin et al., 1969). Recovery process of SL can be very expensive because SL is very dilute and thus an extensive evaporation is needed.

However, the lignocelluloses can be separated from the SL via flocculation (Duarte et al., 2010; Fatehi and Ni, 2011; Graham et al., 2008; Saeed et al., 2011, 2012a,b; Li and Pelton, 1992; Strom and Stenius, 1981; Tian et al., 2010). In fact, flocculation has been applied worldwide to isolate lignocelluloses from various spent liquors, and was proven to be an efficient method to recover the lignocelluloses from the pre-hydrolysis liquor (PHL) of kraft-based dissolving pulp process (Duarte et al., 2010; Saeed et al., 2011, 2012a,b; Negro et al., 2005). A previous study showed that the addition of 0.5 mg/g poly diallyldimethyl ammonium chloride (PDADMAC) to PHL caused 35 wt.% removal of lignin from PHL (Saeed et al., 2012a,b). As the SL and PHL have different compositions and their lignocelluloses have different properties, the results of PHL analysis cannot be applicable to the SL. One objective of this study was to investigate the application of flocculation as a means to isolate the lignocelluloses from the SL of an NSSC process.

To remove lignin and hemicelluloses from PHL, different dosages of cationic polymer were required in one study, which was attributed to the altered properties of lignocelluloses in the PHL (Liu et al., 2011a,b; Saeed et al., 2012a). Chitosan and PDADMAC have been used as flocculants for various spent liquors of pulping processes (Fredheim and Christensen, 2003; Guibal and Roussy, 2007; Kekkonen et al., 2002), but the performance of chitosan depends on the pH of the process. Another objective of this research was to investigate how poly ethylenemine, PEI will affect the selectivity in removing lignocelluloses from SL. In fact, PEI was used for the first time to isolate the lignocelluloses from SL.

In this paper, a process was proposed for isolating lignocelluloses from SL and utilizing isolated lignocelluloses. At first, the application of PEI in SL was optimized under different process conditions. The formed flocs could be used as an alternate energy source in heat recovery or as organic filler in composites or old corrugated container board production. Subsequently, the ultimate analysis was conducted on the flocs in order to investigate the properties of flocs. In the proposed process, the wasted lignocelluloses

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of an NSSC process will be isolated and used as value-added chemicals, which implies that the proposed process will convert the NSSC process to an NSSC-based biorefinery.

2. Materials and methods

2.1. Materials

Polyethyleneimine with the molecular weight (MW) of 60–75 kDa (P3143) and poly diallyldimethyl ammonium chloride with a MW of 100–200 kDa, 20 wt.% in water, were purchased from Aldrich Co. and dissolved in deionized water to 10 wt.% prior to use. Sulphuric acid (98%) and sodium hydroxide pellets (analytical grade) were purchased from Fisher Scientific Co. The spent liquor (SL) was received from an NSSC process mill located in Eastern Canada, in June 2013 and centrifuged at 1000 rpm (9 G) for 10 min prior to analysis. The centrifuged samples were considered as original samples throughout analysis in this process.

2.2. Singular polymer system

In one set of experiments, different dosages of PEI were applied to the original SL at 30 °C and the solution was shaken at 100 rpm in a Boekel water bath shaker for 10 min. In a previous work, flocculation occurred within the first 10 min of treating PHL with PDADMAC (Duarte et al., 2010; Saeed et al., 2011, 2012a). After mixing, the treated SLs were centrifuged at 1000 rpm (9 G) for 10 min. In this process, the flocs were precipitated and adhered to the centrifugal tubes. The supernatants were separated from precipitates by carefully pouring the top part of solutions contained in centrifugal tubes in other containers, which were considered as the SLs after treating with polymers. Lignin, hemicelluloses, turbidity and chemical oxygen demand (COD) of the samples were measured for each sample, and the dosage (15 mg/g) that generated the maximum removals was selected for further analysis. In another set of experiments, the pH of SL was varied between 3 and 11 by adding sulfuric acid or sodium hydroxide solution (10 wt.%), and subsequently 15 mg/g PEI was added to the SLs having different pHs at 30 °C in order to identify the optimal pH that PEI was the most effective flocculants. In another set of experiments, the SL and PEI solutions were preheated to different temperatures in the water bath shaker, and then 15 mg/g of PEI was added to the SL at pH 6 (optimal pH) in order to investigate the impact of temperature on the effectiveness of PEI. Control samples were prepared via treating SL under the same conditions as the actual samples, but with water instead of PEI; and lignin, hemicelluloses (sugar), and COD of the filtrates and the original samples were then assessed. Alternatively, 15 mg/g of PDADMAC was added to the SL under the optimal conditions of pH 6, 30 °C for 10 min and the supernatants and precipitates were collected for analysis.

2.3. Dual polymer system

In the past, the dual polymer system of PDADMAC and CPAM showed greater results than the singular system of PDADMAC or CPAM in removing the lignocelluloses from PHL (Fatehi et al., 2013). In this work, the dual polymers of PEI and PDADMAC were applied subsequently (first 7.5 mg/g PEI and after 30 s, 7.5 mg/g PDADMAC) to the SL under the optimal conditions (pH 6, 30 °C for 10 min). The samples were shaken for 10 min and then centrifuged. The turbidity, COD, lignin and hemicelluloses of SL before and after the treatment were determined.

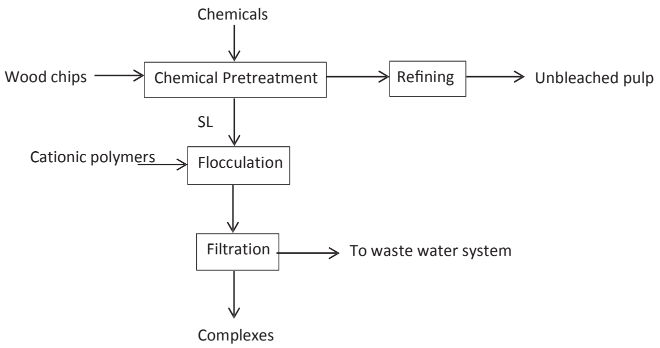

Fig. 1. An integrated process for producing lignocellulosic flocs from SL of an NSSC pulping process.

2.4. Hemicellulose analysis

The concentration of hemicelluloses in the SL (i.e. before and after mixing with PEI) was determined via using a previously described microplate-based method with using 3,5-dinitrosalicylic acid chemical (DNS reagent) (Dashtban et al., 2011). To measure the total sugars of SL, the SL was first treated with 4 wt.% sulfuric acid and then incubated at 121 °C for 1 h in an oil bath (acid hydrolysis). This treatment will convert oligomeric sugars to monomeric sugars, which can ultimately be determined by the DNS method. Thus, the total sugars of SLs before and after the adsorption experiments was determined, which could reflect the adsorbed amount of hemicelluloses on ACs (i.e. removal of hemicelluloses from SLs).

2.5. Lignin, ash and ultimate analyses

The ash content of the SLs was determined according to TAPPI T412, and the lignin content of SLs was determined according to TAPPI UM 250 using a UV spectrophotometry at 205 nm (GENESYS 10S UV-Vis, Thermo Scientific) (Liu et al., 2011a,b). The ultimate (elemental) analysis of flocs was conducted using a Vario EL cube instrument (Germany) according to the previously established method (Fadeeva et al., 2008).

2.6. Turbidity, COD and zeta ponetial analyses

The turbidity of SL samples after centrifugation was determined using a HACH 2100AN turbidity meter (Colo, USA) at room temperature. The chemical oxygen demand (COD) of the SL samples after centrifugation was measured using the Thermoreaktor CR2200 incubator according to PAPTAC standard procedure. The zeta potential of the SL sample prior to analysis was measured using a zeta phoremeter, CAD instrument, Paris, France.

3. Results and discussion

3.1. Proposed process for isolating lignocelluloses from SL using a flocculation system

As described earlier, part of lignin and hemicelluloses are removed from wood chips and dissolved in the SL of an NSSC process. This spent liquor is currently sent to the waste water system of the mill, and thus its lignocelluloses are under-utilized. Fig. 1 shows a process for isolating lignocelluloses from the SL of an NSSC pulping process. Lignocelluloses have generally anionic charges due to the carboxylic, carbonyl and sulphonated groups associated with their structures (Liu et al., 2011b, 2012). In the proposed process, a cationic polymer is added to the SL, which forms complexes (flocs) via charge interaction with lignocelluloses of SL (Saeed et al., 2011,

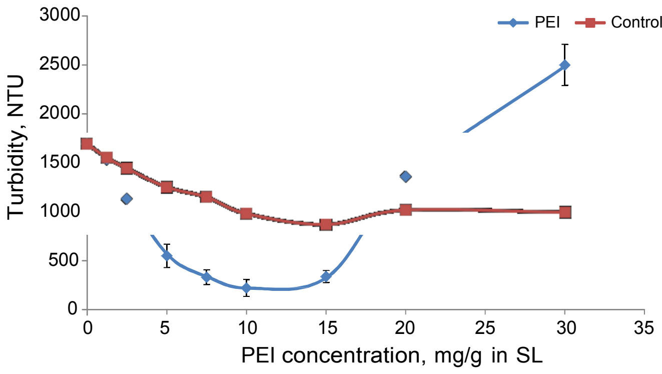

Fig. 2. Effect of PEI addition on the turbidity of the SL (after centrifugation) (30 °C and pH 6).

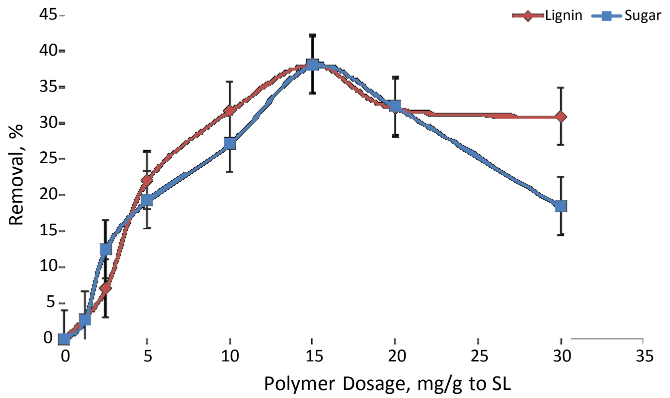

Fig. 3. Influence of PEI addition in removing lignin and hemicelluloses from SL (30 °C and pH 6).

2012a). The formed flocs will be collected via filtering (e.g. drum filter) in a subsequent stage (Fig. 1). The formed complexes will have high lignin and hemicellulose contents. In this process, the treated SL after floc removals can be handed in the waste water system of the mill, while the separated flocs can be used as fuel in the process or as filler in the production of corrugated medium paper. In other words, the collected flocs can be directly used as value-added products and further purification of flocs may not be needed. If used as fuel, the proposed process will help the NSSC pulping process to be more self-sufficient in terms fuel economy. The main advantages of the proposed process are the reductions in the lignocellulose content of SL, which will reduce the load and cost of waste water treatment systems, or in the use of oil-based fuel as well as in the development of a process for producing value-added chemicals from lignocellulosic wastes. In other words, the mill can benefit from handling less waste water, saving fuel and from the revenues gained via making this value-added product.

3.2. Properties of SL

The properties of SL received from industry are listed in Table 1. The zeta potential of SL sample was −17.5 mV. Evidently, it contained about 60 g/l lignin, 22 g/l hemicelluloses (total mono and oligosugars), 26 g/l acetic acid and 0.5 g/l furfural. These results confirm that the SL indeed contained approximately 10 wt.%. In addition, the SL contained 63 g/l ash, which is originated from chemicals (i.e. sodium sulfite and bicarbonates) used in the pre-treatment step of the NSSC pulping process. It was previously reported that acetic acid minimally interacted with cationic polymers (i.e. PDADMAC or chitosan) to form flocs (Saeed et al., 2011). Consequently, due to the low concentration of furfural, and the weak interaction of acetic acid with cationic polymers, the impact of PEI on acetic acid and furfural removals were excluded from this study.

3.3. Effect of PEI dosage on SL

Fig. 2 shows the turbidity after centrifugation of the SL as a function of PEI dosage. It is observable that, by increasing the concentration of PEI to 10–15 mg/g in the SL, the turbidity of SL was decreased to approximately 220 NTU. With further increase in the concentration of PEI, the turbidity increased to 2500 NTU. The decrease in the turbidity of the control sample was attributed to the dilution of SL with water. As is well-known, PEI has a cationic group, and hence PEI–lignin and PEI–hemicellulose complexes were formed in the SL via adding PEI. The existence of cationic polymer/lignocellulosic complexes in PHL was reported to increase the turbidity of PHL (Saeed et al., 2012a,b; Strom and Stenius, 1981), while the removal of complexes via settlement or centrifugation reduce the turbidity of sample (Duarte et al., 2010; Li and Pelton, 1992).

The lignin and hemicellulose removals as a function of PEI concentration in the SL are shown in Fig. 3. It is observable that the maximum removals of lignin and hemicelluloses (about 37%) occurred at the PEI concentration of 15 mg/g. These results are in agreement with the turbidity results in that, the minimum level of turbidity (Fig. 2) is in harmony with maximum lignocellulose removals (Fig. 3). When PEI is added to the SL, the cationic charge of PEI will interact with the anionic charges of lignin and/or hemicelluloses and form flocs. An increase in the dosage of PEI would presumably increase the turbidity of SL, as more flocs will form. At an optimal dosage, the amount of PEI in the SL is sufficient to make large flocs (via forming more flocs or bridging the already formed flocs) that can be removed from SL via centrifugation. This will explain the lowest turbidity at 15 mg/g in Fig. 2. However, if the concentration of cationic polymer (PEI) is very high (higher than optimum), the formed flocs or the SL will have a net cationic charge (as the concentration of cationic polymer is high in the SL), which generates a repulsion force between the flocs and restabilizes the formed flocs in the SL. In this case, the precipitation and removal of flocs from SL will be reduced and turbidity will increase (Fig. 2) (Duarte et al., 2010).

3.4. Impact of pH on the performance of PEI

Fig. 4 shows the turbidity of the SL after centrifugation as a function pH after treatment with 15 mg/g PEI. Evidently, the turbidity of control sample was increased as pH decreased to 3. The increase in the turbidity is due to the fact that a part of lignin is acid insoluble, and thus by decreasing the pH, the solubility of lignin is reduced. It is also seen that the turbidity of the SL treated with PEI was minimal at neutral pH, and increased to a higher degree at high and low pHs.

Table 1
Properties of SL.

pH	Zeta potential (mV)	Hemicelluloses (g/l)	Lignin (g/l)	Ash (g/l)	Acetic acid (g/l)	Furfural (g/l)
5.7	−17.5 ± 1.1	22.13 ± 0.02	60.22 ± 0.55	63.82 ± 3.3	26.50 ± 1.5	0.52 ± 0.3

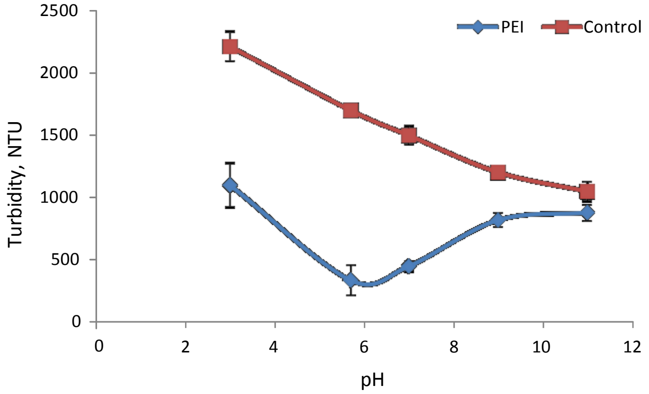

Fig. 4. Effect of pH on turbidity of the SL treated with 15 mg/g PEI at 30 °C.

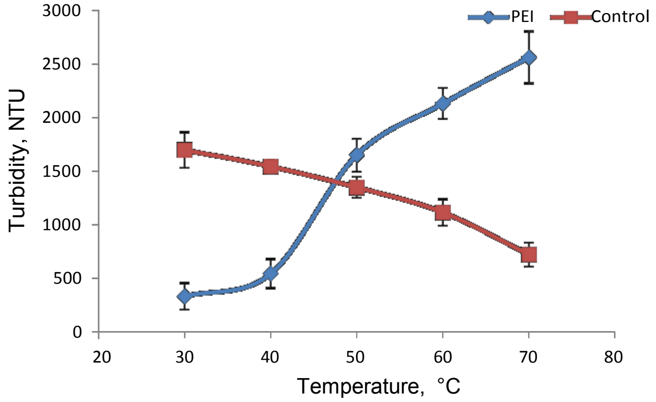

Fig. 6. Effect of temperature on turbidity of SLs treated with 15 mg/g PEI at pH 6.

The removals of lignin and hemicelluloses from SL at different pHs is presented in Fig. 5. It is evident that lignin and hemicellulose removals were the maximum at pH 6. It was reported that at high or low pH, the extra OH^- or H^+ will interact with lignin and hemicellulose via hydrogen bonding development or charge interaction (Liu et al., 2011a,b), and thus the tendency of lignocelluloses to interact with PEI is reduced, and therefore their removal from SL is reduced at a high or low pH. By decreasing pH to 3, 10% of lignin and 12% of hemicelluloses were removed from the SL (not shown in figures). Therefore, the amount of lignin left in SL at pH 3 was less than that at pH 6, thus by adding PEI to the acidified SL, less lignin is removed from the SL. Overall, the lignin and hemicellulose removals were 28% and 42% at pH 3 with 15 mg/g PEI concentration, while they were 37% for lignin and hemicelluloses at pH 6, respectively.

3.5. Impact of temperature on lignocellulose removal

Fig. 6 shows the effect of temperature on the turbidity of the SLs treated with 15 mg/g PEI. The results of control samples showed that increasing the temperature reduced the turbidity of SL, which may suggest that increasing temperature might have improved the solubility of lignocelluloses in the SL, as lignocelluloses were not removed from the SL via a temperature increase (Strom and Stenius, 1981; Strom et al., 1985). As can be seen, by increasing the temperature from 30 to 70 °C, the turbidity of SL samples was increased from 220 to 5000 NTU.

Fig. 7 depicts the removal of lignocelluloses from the SL via adding PEI (15 mg/g) as a function of temperature. It is observable that, by increasing the temperature, the lignin and hemicellulose removals decreased to some extent. One reason for such behavior is that the flocs are more soluble in the SL at a higher temperature (Strom and Stenius, 1981). The results also showed that the removal of hemicelluloses was affected slightly more than lignin did by temperature, which would suggest that the solubility of hemicelluloses is more influenced than lignin by the temperature. Additionally, based on the second law of thermodynamics, lignocelluloses will lose their entropy via forming flocs with PEI. Therefore, the enthalpy of the system (SL) should be reduced so that the precipitation is occurred. In other words, flocculation is an exothermic process, and decreasing the temperature will assist the flocculation process (Shi et al., 2012). Fig. 7 also showed that, by increasing temperature, the COD removal was reduced, which is in harmony with the lignin and hemicellulose trends.

3.6. PEI and PDADMAC vs PEI/PDADMAC system

PDADMAC has previously been studied for its effectiveness in forming flocs with the lignocelluloses of PHL (Duarte et al., 2010; Kekkonen et al., 2002; Saeed et al., 2012a). In one study, PDADMAC formed flocs by neutralization, while PEI flocculated the lignocellulose via patch formation (Blanco et al., 2002; Guibal and Roussy, 2007). Therefore, the dual polymer system of PEI and PDADMAC could be an alternative in removing lignocelluloses from SL. Table 2 summarizes the effect of each system on the removal of turbidity, COD, hemicelluloses and lignin. In this dual polymer system, the dosage of each polymer was 7.5 mg/g, while the dosage was

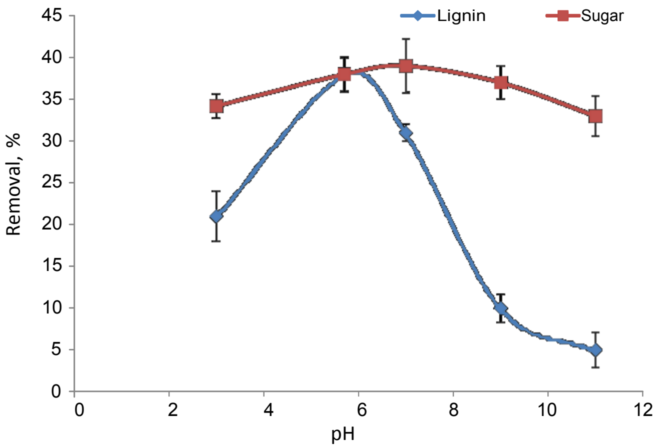

Fig. 5. Effect of pH on lignin and hemicellulose removals from the SL treated by 15 mg/g PEI at 30 °C.

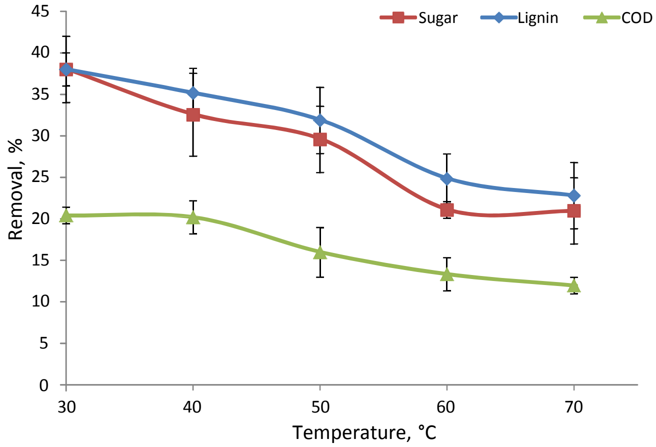

Fig. 7. Lignin, hemicellulose, and COD removals of PHL as a function of the temperature of the SL system (15 mg/g PEI, pH 6).

Table 2
Impact of PEI and PEI/PDADMAC systems on the removal (%) of lignocelluloses from SL.

Polymer	% Removal			
	Turbidity (NTU)	Sugar	COD	Lignin
PEI	220 ± 23	41.3 ± 2.1	20.4 ± 0.6	33.1 ± 0.7
PDADMAC	401 ± 18	35.1 ± 0.8	16.5 ± 0.7	30.2 ± 1.1
PEI/PDADMAC	192 ± 15	50.1 ± 1.5	25.2 ± 2.2	47.6 ± 1.2

Table 3
Ultimate analysis of flocs formed via PEI (15 mg/g) or PEI/PDADMAC (7.5/7.5 mg/g) addition to SL.

Sample	N%	C%	H%	O%	Rest%	Ash%
PEI	4.5	40.99	6.03	46.46	2.02	12.4
PDADMAC	4.3	41.40	6.21	45.21	2.88	14.8
PEI/PDADMAC	2.93	42.12	6.42	37.03	11.51	22.1

15 mg/g in the singular PEI or PDADMAC system. As seen, the dual polymer system had slightly higher lignin, hemicelluloses and COD removals and a turbidity reduction. It is implied from these results that the dual polymer system of PEI/PDADMAC was more effective than the PEI or PDADMAC system in removing lignocelluloses from SL.

3.7. Flocs analysis

The elemental analysis of the complexes generated via PEI, PDADMAC and PEI/PDADMAC systems is shown in Table 3. It is observable that the complexes made from PEI or PDADMAC system had higher nitrogen and oxygen contents, while the complexes made from PEI/PDADMAC system had higher carbon and hydrogen contents. The nitrogen content of complexes is mainly attributed to the presence of PEI, PDADMAC or PEI/PDADMAC in the flocs. The results may suggest that more cationic polymer presented in the flocs via PEI or PDADMAC treatment than PEI/PDADMAC treatment. Also, the ash content (presenting the inorganics) of the flocs made from the PEI/PDADMAC system was higher than that made from the PEI or PDADMAC system. One possible reason could be the fact that inorganic compounds (e.g. ash) could have been trapped inside the PEI/PDADMAC flocs and thus were removed from SL more extensively. The results of Tables 2 and 3 suggest that the PEI or PDADMAC system was less effective in removing lignocelluloses from SL. However, the dual system of PEI/PDADMAC was more effective (than PEI system) in removing both organic and inorganics, which resulted in complexes with more overall impurities.

4. Conclusions

A new process for isolating lignocelluloses from the SL of an NSSC process was proposed. Experimental results on the SL showed that the addition of PEI was effective in removing lignocelluloses, and under the optimal conditions of 30 °C, pH 6 and 15 mg/g PEI concentration in the SL, 37% of lignin and 37% of hemicelluloses could be removed. The turbidity dropped to 220 NTU (from 1700 NTU) and the chemical oxygen demand (COD) dropped by 20% under such conditions. However, the overall removals of lignin and hemicellulose were 28% and 42%, respectively, via applying PEI to the acidified SL (pH 3). Alternatively, a combination of PDADMAC and PEI addition to SL (7.5 mg/g each) under the optimal conditions caused 47%, 50% and 27% removals in lignin, hemicellulose and COD, respectively. The elemental analysis of flocs showed that PEI system produced flocs with lower impurities, but PEI/PDADMAC system was more effective in removing organics and inorganics, which resulted in flocs with higher inorganic contents. This study showed that flocculation can be used as a process to isolate the lignocelluloses from SL and to convert the NSSC process to an NSSC-based biorefinery.

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