Application of Biomass-based Fly Ash in the Pressate of a Thermomechanical Pulping Process

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To my parents, sister and husband for all of their love, support, patience and encouragement.

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Abstract

In the thermomechanical pulping (TMP) process wood chips are pretreated with steam prior to refining, and the resultant effluent (TMP pressate) is currently treated in the wastewater treatment facility of the pulp mill. Pulp mills also generate a substantial amount of biomass fly ash as a residue from burning wood and wastewater sludge in boilers and most of the fly ash is landfilled. Strict effluent regulations may require the use of tertiary treatment operations at pulp mills and alternative uses for biomass fly ash are required.

In this study, two biomass fly ash samples (FA1 and FA2) were received from a pulp mill, fractionated and characterized. Definitive screening design (DSD) experiments were conducted to evaluate the impact of process parameters (e.g. time, temperature) on the chemical oxygen demand (COD) and lignin contents in a TMP pressate. Model equations were developed and used to optimize the COD and lignin removals from a TMP pressate on the fly ash samples. It was determined that the main factor that impacted the lignocelluloses removal from a TMP pressate was dosage, and FA1 was more effective than FA2. A maximum COD removal by FA1 of 91.3 % was observed under the conditions of a weight-based average particle size of 0.43 mm, a dosage of 70.0 mg/g FA1/TMP pressate and a treatment time of 2 h. The maximum lignin removal from the TMP pressate by FA1 was 95.0 % under the conditions of a weight-based average particle size of 0.11 mm, a dosage of 46.5 mg/g FA1/TMP pressate and a pH of 6.

In this study, a biomass fly ash was fractionated and ground to generate five fly ash samples with different compositions of similar particle size, and four fly ash fractions of different sizes of similar composition. Isotherm analysis with respect to the COD and lignin removals from a TMP pressate by the biomass fly ash samples were done and it was determined that the Freundlich model fit the adsorption data best. The Freundlich maximum adsorption capacities for the COD and lignin from a TMP pressate by the biomass fly ash were estimated. Furthermore, the potential impact of various physicochemical properties on the experimentally determined Freundlich parameters were evaluated.

In this study, a biomass fly ash was fractionated and ground to produce two fly ash samples (S1 and S2) with a similar particle size. Leaching tests of the biomass fly ash samples were conducted under various conditions in water and in a TMP pressate. It was determined that the leaching characteristics of the biomass fly ash in a TMP pressate differed from that in water and overall it was observed that the total metal content leached from the biomass fly ash was greater in water when compared with that in a TMP pressate under the conditions studied. The potential use of a biomass-based fly ash adsorbent on a TMP pressate was then assessed against the wastewater effluent guidelines of the metal mining sector.

In this study, the coagulation performance of various commercial coagulants and a biomass fly ash leachate (FLC) on a TMP pressate was also assessed. The effect of coagulant dosage, pH, agitation speed and treatment time on the chord length distribution of the resultant coagulant/TMP pressate solutions was monitored using focused beam reflectance measurement (FBRM) analysis. The COD and lignin removals of the coagulant treatments on a TMP pressate were also determined. A FLC-based treatment of a TMP pressate removed 18.4 % of the COD and 26.9 % of the lignin under the conditions of 5060 mg/kg FLC/TMP pressate, 200 rpm, pH 12.5 and 298 K for 30 min. Coagulation of a TMP pressate using alum removed 41.2 % of the COD and 40.6 % of the lignin under the conditions of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate, 200 rpm, pH 6 and 298 K for 30 min.

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1 Chapter 1: Introduction

1.1 Overview

The pulp and paper industry is the third largest consumer of fresh water in the world (Savant et al., 2006). Subsequently, pulp and paper mills require extensive wastewater treatment operations. The wastewater treatment operations employed on pulp and paper mill effluents usually consists of primary clarification followed by an activated sludge process system (Pokhrel & Viraraghavan, 2004; Thompson et al., 2001). However, an activated sludge process has a limited ability to remove recalcitrant compounds and produces an effluent with a considerable amount of chemical oxygen demand (COD). As a result, the use of tertiary wastewater treatments may be required (Thompson et al., 2001; Pokhrel & Viraraghavan, 2004). Pulp and paper mills also produce a significant amount of solid wastes, such as sludge from the wastewater treatment and biomass fly ash as residues of boilers. The solid wastes generated are usually landfilled (Bajpai, 2015; Elliot & Mahmood, 2006; Mahmood & Elliot, 2006).

Wastewater treatment operations and the disposal of solid wastes requires land space. However, the availability of land space may be limited in some areas or costs related to landfilling may become economically unfeasible for the pulp and paper industry. Pulp and paper mills are thus interested in reducing the overall load on wastewater treatment operations as well as diverting solid wastes from landfills. Thus, more research on alternative approaches related to wastewater treatment and biomass fly ash utilization is attractive for pulp and paper mills.

Recently, Oveissi & Fatehi (2015) proposed to use a biomass fly ash generated at a thermomechanical pulping (TMP) mill as an adsorbent for a TMP pressate, which is a wastewater generated in the TMP process. The TMP pressate has a high COD and biochemical oxygen demand (BOD) load (Andersson et al., 2008; Sumathi & Hung, 2006; Zheng & Liao, 2014), and thus tertiary treatment of a TMP pressate may reduce the overall load on the subsequent wastewater treatment plant at a TMP mill. In the previous work by Oveissi & Fatehi (2015), lignin adsorption from a TMP pressate onto a biomass fly ash was partially studied. The researchers determined that for a one-stage and two stage-adsorption process, 53 % and 68 % of the lignin was adsorbed, respectively. Many factors such as the particle size of an adsorbent, the agitation speed, the temperature of the adsorption treatment process and the characteristics of the adsorbent, may affect the performance of an adsorption process (Cheng et al., 2005; Faust & Aly, 1998; Evans et al., 2002; Kusmierek & Swiatkowski, 2015; Li et al., 2002). However, the impact of the particle size of a biomass fly ash and the agitation speed and temperature of a biomass fly ash/TMP pressate system were not previously studied, and thus further research was required in order to optimize a biomass-based fly ash adsorption treatment of a TMP pressate.

The use of a biomass fly ash in an aqueous system may also present a concern for the environment due to the potential leaching of heavy metals (Reijinder, 2005). Leaching studies of wood fly ash in water have been previously conducted (Consigli et al., 2016; Laohaprapanon et al., 2010; Saqib & Backstrom, 2016). Standard leaching tests may underestimate or overestimate leaching characteristics of an actual process and leaching tests should be conducted for the system under consideration (Reijinder, 2005; Wang & Wu, 2006). The leaching characteristics of a biomass fly ash in a TMP pressate are unknown. Thus, the development of a biomass fly ash adsorbent for a TMP pressate requires an evaluation of the leaching characteristics of a biomass fly ash under representative conditions of a real process.

In this MSc thesis, the potential use of a biomass fly ash on a TMP pressate was studied with respect to the impact of various physicochemical properties and optimization. The environmental feasibility of biomass-based fly ash adsorption treatment of a TMP pressate was evaluated with respect to the leaching characteristics of a biomass fly ash into a TMP pressate under various conditions. Furthermore, the coagulating effect of the metals leached from a biomass fly ash on a TMP pressate was investigated and compared with alum and calcium chloride. In this chapter, a brief summary of the subsequent chapters in this thesis is provided. Furthermore, the objectives and novelty of this work are also presented in this chapter.

Chapter two provides a brief introduction to the TMP process and the production of a TMP pressate, as well as a brief introduction to the constituents of a TMP pressate such as lignin. In chapter two, a literature review is summarized for the research related to treating a TMP pressate by various tertiary treatment technologies and presents some of the previous research related to alternative uses of biomass fly ash wastes.

In chapter three, two biomass fly ash samples were fractionated and characterized, and the potential impact of various factors, such as, fly ash particle size and dosage, on the COD and lignin removals from a TMP pressate were evaluated using definitive screening design (DSD) analysis. Model equations for the COD and lignin removals from a TMP pressate onto the biomass fly ash samples were then developed using forward stepwise regression analysis of the results of the DSD experiments and validated. Furthermore, the COD and lignin removals from a TMP pressate were then optimized using the resultant model equations.

In chapter four, a biomass fly ash was fractionated and ground to produce five samples with differing compositions of a similar particle size, and four fly ash fractions of different sizes but with a similar composition. The isotherm analysis of lignin adsorption and COD removal from a TMP pressate was then conducted on the fly ash samples at pH 6 or without pH adjustment. The potential impact of various physicochemical properties, such as pH, ionic strength, particle size and the metal content on the adsorption capacity for lignin and COD were then evaluated.

In chapter five, the biomass fly ash was fractionated and ground to produce two fly ash samples with a similar particle size. Leaching experiments of the biomass fly ash samples were conducted in water and a TMP pressate to determine the leaching characteristics of metals under various conditions developed for the potential use of biomass fly ash in a TMP pressate. The results were then evaluated against the wastewater effluent guidelines of the metal mining sector.

In chapter six, the potential use of aluminium sulphate (alum) as a coagulant on a TMP pressate as well as the use of alternative coagulants, potassium chloride, calcium chloride and a biomass fly ash leachate, was assessed and compared. In this, focused beam reflectance measurement (FBRM) analysis was used to study the effect of dosage, pH, and agitation speed on the mean chord length and cord length distribution of the coagulant/TMP pressate solution. Furthermore, the impact of dosage, pH, and agitation speed on the COD and lignin removals were determined.

In chapter seven, the overall conclusions are stated and recommendations for future work are provided.

1.2 Objectives

The objectives in this thesis were to:

1. study characteristics of biomass fly ash and TMP pressate;
2. determine the main factors that impact the removal of COD and lignin from a TMP pressate by a biomass fly ash;
3. determine the optimized conditions for a biomass-based fly ash adsorbent treatment of a TMP pressate;
4. evaluate the use of different biomass fly ash samples on a TMP pressate:
5. determine the isotherm model that adequately describes lignin adsorption and COD removal from a TMP pressate on a biomass fly ash under different conditions;
6. determine the leaching characteristics of biomass fly ash in a TMP pressate under such conditions that fly ash would be used as an adsorbent for the TMP pressate;
7. determine the potential environmental impact of the metals leached from biomass fly ash when used as an adsorbent on a TMP pressate; and

8. study and compare the coagulation efficiency of commercial coagulants and a biomass fly ash leachate on a TMP pressate.

1.3 Novelty of this study

To the best of our knowledge, the following aspects have not been previously studied:

1. The impact of particle size, agitation speed, and temperature on the adsorption of lignin and COD removal from a TMP pressate by a biomass fly ash have not been conducted prior to this study.

2. The adsorption of lignin and removal of COD from a TMP pressate on a biomass fly ash have not been modeled nor has DSD been used to optimize the biomass-based fly ash adsorption treatment of a TMP pressate prior to this study.

3. The extent of metals leached into the TMP pressate upon the application of a biomass-based fly ash has been studied under different conditions for the first time.

4. The coagulation efficiency of potassium chloride, calcium chloride, a biomass fly ash leachate and alum on a TMP pressate have been studied for the first time in this work.

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2 Chapter 2: Literature review

2.1 Introduction

Pulp and paper mills have large water requirements, and the subsequent effluents are often treated in a secondary wastewater treatment plant on site. This requires a large capital cost, a large area of land for the operation of a wastewater treatment plant and landfilling the sludge produced. Furthermore, solid wastes, such as fly ash, are produced as residues in boilers from burning hog fuel, sawdust and wastewater treatment sludge; and subsequently, they must be landfilled. Pulp and paper mills are interested in reducing their water consumption, decreasing the load on the wastewater treatment systems, and reducing solid wastes from landfills.

The treatment process for reusing water in the pulp and paper mill would reduce the use of fresh water, thereby decreasing the effluent volume. Depending on the treatment process employed, it may also decrease the sludge produced at the mills. The incorporation of a tertiary wastewater treatment option, such as membrane filtration, may also allow for the recovery of fibres and chemicals and thus provide an added benefit. However, water recycling and reusing would also increase the capital costs and operating costs of the plants. Furthermore, some constituents may accumulate in the process, which may adversely affect the process operation (Smook, 2002). Thus, research on alternative strategies related to wastewater treatment and biomass fly ash utilization is attractive for the mills.

2.2 Thermomechanical pulping (TMP)

TMP is a mechanical pulping process, in which wood chips are first washed and then treated with steam (i.e. thermo) prior to refining (i.e. mechanical). The TMP pulp is then screened, cleaned, and thickened, and then may be bleached prior to paper production. A flowchart of the TMP process is given in Figure 2.1 TMP pulp can be used to manufacture paper products such as newsprint, magazines and paperboard. The raw materials used in the production of TMP pulp are mostly woodchips from softwood since softwood TMP pulps impart higher strength properties than hardwood TMP pulps (Sixta, 2006).

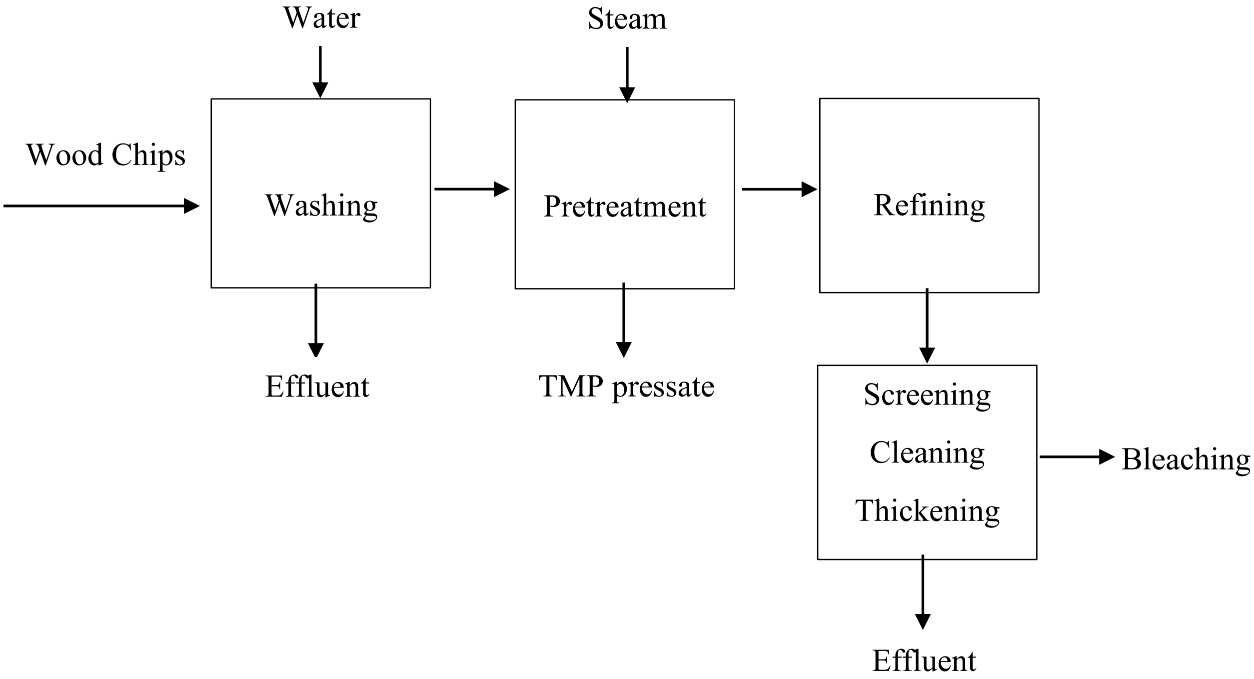

Figure 2.1 The process flow diagram of a TMP process

2.3 TMP pressate

The TMP process requires a substantial amount of water and subsequently produces numerous wastewater streams. The effluent produced prior to the refining stage in a TMP process is referred as a TMP pressate. In the pretreatment stage of wood chips with water, lignin, hemicelluloses and some extractives may be dissolved in water, and thus the TMP process water consists of lignin, hemicelluloses and wood extractives (Zasadowski et al., 2014). The TMP pressate is the strongest wastewater in the TMP process; it has a high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) load (Sumathi & Hung, 2006; Andersson et al., 2008; Zheng & Liao, 2014). Therefore, it must be treated prior to its release into a receiving water reservoir.

2.4 Softwood lignin

Lignin is a complex phenolic polymer that provides structural support for the cell walls of plants and acts as a glue to bond cells of fibers together. Lignin is resistant to degradation by microorganisms and thus is considered a recalcitrant polymer (Himmel et al., 2007). Lignin is constructed from three monolignols of p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; which are incorporated into lignin in the form of p-hydroxyphenyl (H), guaicyl (G), and syringyl (S) units, respectively; and softwood lignin consists mostly of guaicyl units (Sixta, 2006). The most frequent dimers formed by softwood lignin, have β–β, β-O-4 or β-5 linkages (Vanholme et al., 2010). Furthermore, lignin present in the TMP pressate may resemble a fragmented native softwood lignin, when compared with modified lignin such as Kraft lignin or bleached lignin, as it has not been subjected to any significant chemical modification. The main source of colour in wastewater effluents from the pulp and paper industry is attributed to lignin. Thus, the removal of lignin from effluents is essential for aesthetic reasons and would also reduce the residual BOD.

2.5 Hemicelluloses

Hemicelluloses are heteropolysaccharides and their monomers consist of D-xylose, L-arabinose, D-glucose, D-mannose, D-galactose, D-rhamnose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid (Sixta, 2006; Sjostrom, 1993). The main hemicelluloses in softwoods are 1) galactoglucomannans, which are linear and consist of (1→4)-linked β-D-glucopyranose and β-D-mannopyranose subunits, and 2) arabinoglucuronoxylans, which consist of (1→4)-linked β-D-xylopyranose subunits that are partially substituted with approximately two 4-O-methyl-α-D-glucuronic acid groups for every ten xylose units (Sjostrom, 1993). Analysis of spruce TMP process waters has indicated that the hemicelluloses most commonly present are galactoclucomannans (Zasadowski et al., 2014).

2.6 Wood extractives

Wood extractives are non-structural constituents of wood and their presence imparts resistance to decay and termite attack (Kiker et al., 2013). Wood extractives consist of numerous lipophilic and hydrophilic components such as terpenoids, steroids, waxes, fats and phenolics, and the composition varies between trees species (Sjostrom, 1993). Wood extractives can be extracted to produce various products such as fragrances, flavours, adhesives, medicines and fuels (Beatson, 2011). The wood extractives that have been detected in TMP process water include fatty acids, resin acids, lignans, sterols, steryl esters and triglycerides (Zasadowski et al., 2014).

2.7 Solid wastes

The largest volume of solid wastes generated in pulp and paper mills is the residual from the wastewater treatment plant, and the sludge is mostly landfilled or incinerated (Mahmood & Elliot, 2006; Bajpai, 2015). Pulp mills also produce a substantial amount of biomass fly ash by burning hog fuel, wood residuals, and wastewater treatment sludge in their boilers. In 2002, 775,000 tons of ash was produced in Canadian mills, and most of the ash (78 %) was landfilled, and the remainder was used for beneficial purposes such as composting, road construction and soil conditioning (Elliot & Mahmood, 2006). There is interest in an increased application of non-coal ashes for beneficial purposes (Insam & Knapp, 2011; Monte et al., 2009; Ribbing, 2007). For example, biomass fly ash may potentially be used as a low-cost adsorbent for treating wastewater effluents (Gupta et al., 2009; Wang & Wu, 2006).

2.8 Treatment options for pulp and paper wastewaters

Most of the pulp and paper wastewaters are treated by a clarification step followed by biological treatments. When an activated sludge process is used as the biological treatment step, which is often the case, the treatment is sensitive to toxicity and shock loading, and substances that are difficult to biodegrade can remain in the effluent (Thompson et al., 2001). Pulp and paper mills are interested in improving their wastewater treatment processes as governments may enforce more stringent regulations. Various treatment options for pulp mill effluents were reviewed by Pokhrel & Viraraghavan (2004), Sumathi & Hung (2006), and more recently by Kamali & Khodaparast (2015). The reviews indicated that recalcitrant compounds such as lignin can be efficiently removed by membrane filtration, adsorption, coagulation, or degraded by oxidation treatment. These methods were considered to be more expensive when compared with conventional biological treatment. However, a combination of physicochemical and biological treatments would offer a long-term solution for wastewater treatment operations for treating pulp and paper effluents (Pokhrel & Viraraghavan, 2004).

2.9 Alternatives for treating TMP pressates

2.9.1 Membrane filtration

Ultrafiltration and nanofiltration are pressure driven membrane processes that separate a wastewater stream into two streams of the permeate and the concentrate. The permeate passes through a membrane and the concentrate is rejected by the membrane. Particles can be removed in ultrafiltration and dissolved particles can be removed in nanofiltration (Edzwald, 2011). A potential limitation in the use of membrane filtration is that the concentrate requires disposal and membrane filtration is subject to fouling (Pokhrel & Viraraghavan, 2004). However, membrane fouling may be minimized by adjusting various operation conditions, such as pH and temperature (Kamali & Khodaparast, 2015). Singh et al. (2012) studied the impact of a pretreatment step on membrane fouling in the ultrafiltration treatment of a TMP process water. The researchers concluded that a pretreatment step consisting of a combination of sodium hydroxide and sodium dodecyl sulfate (SDS) minimized the “irreversible fouling” and increased the solubility of lipophilic extractives, respectively. The pretreatment step consisted of a pH adjustment to 8 (i.e. sodium hydroxide addition) and treatment of 0.04 mol/L SDS, followed by 30 min of mixing and particle settlement. The researchers also determined that ultrafiltration treatment of the subsequent supernatant, yielded a permeate with a COD of less than 250 mg/L and thus, the method was deemed suitable for reuse as a process fluid.

In a case study (New Logic International, Inc.), a TMP wastewater from the screw press filtrate after the refining stage was treated by nanofiltration membranes. The material of the membrane was not disclosed and the entire assembly was vibrated yielding a shear of 150,000 s^{-1} for fouling control. It was determined that 98 % of the COD was removed under operating conditions of 353 K, a permeate flux range of 22-40 gal/ft^2 and a feed pressure of 500 psig when using a 16.8 ft^2 pilot unit. The nanofiltration membrane module was installed at a medium density fiberboard manufacturing facility for commercial operation and the maximum flow rate that was achieved was 100 gallons per min. The authors also reported that almost 85 % of the TMP pressate could be recovered as water suitable for discharge or for reuse as a process water.

2.9.2 Biological treatment

In an aerobic biological treatment process, microorganisms convert organic matter in the presence of oxygen to carbon dioxide and water, and in anaerobic process, microorganisms convert organic matter in the absence of oxygen to methane and carbon dioxide (i.e. biogas). Bioprocesses that use a membrane as a solids-separation device are called membrane bioreactors. Membrane bioreactors allow for the retention of bacteria and suspended solids within the bioreactor. The use of a membrane bioreactor is beneficial since it requires a smaller footprint, can accommodate a higher volumetric loading, and produces less sludge than conventional wastewater treatment processes (Le-Clech et al., 2006).

Langevin & Liao (2010) did a comparative study on the treatment of a TMP pressate using thermophilic (328 K) and mesophilic (308 K) sequencing batch reactors. It was determined that the soluble COD removals for the thermophilic and mesophilic sequencing batch reactors were 77-91 % for an organic loading rate of 0.7-1.3 kg/m^3d, and the settleability of the sludge produced from the mesophilic batch reactor was slightly better. Zheng & Liao (2014) also performed a comparative study on the treatment of a TMP pressate by sequencing batch reactors operated at mesophilic (303 K) or thermophilic conditions (328 K). The COD removals for the mesophilic and thermophilic sequencing batch reactors were 80-90 % and 75-85 % for the hydraulic retention times of 12 and 24 h, respectively. Furthermore, the optimal hydraulic retention time was determined to be 12 h on the basis of COD removal and overall membrane performance.

In a study on the treatment of a TMP pressate, Gao et al., (2011) examined the impact of temperature shock on the performance of a submerged anaerobic membrane bioreactor. The submerged anaerobic membrane bioreactor removed 76-83 % of the COD from a TMP pressate while operating at a temperature range of 310 K and 328 K. In the study by Qu et al. (2012), a TMP pressate was treated in a thermophilic (324 K) submerged aerobic membrane bioreactor, and subsequently treated by electrochemical oxidation. The thermophilic submerged aerobic membrane bioreactor removed 89-92 % of the COD from a TMP pressate, and the optimal hydraulic retention time was determined to be 1.1 days on the basis of COD removal and overall membrane performance. The subsequent treatment of the filtrate from the thermophilic submerged aerobic membrane bioreactor by electrochemical oxidation using a Ti/SnO_2-Sb_2O_5-IrO_2 electrode for 6 h yielded an overall COD removal of 96-98 %.

Membrane bioreactors appear to be an efficient and effective technology with respect to their use in treating a TMP pressate. However, membrane fouling leads to a decrease in membrane performance, consequently requiring frequent cleaning or replacement (Gao et al., 2013; Le-Clech, et al., 2006). Therefore, membrane fouling imparts practical and economical limitations on the use of membrane bioreactors for wastewater treatment. Further studies related to the mitigation of fouling issue is required to make this process more industrially attractive.

2.9.3 Coagulation and flocculation

In wastewaters that contain dissolved molecules and colloids with the same charge, repulsive forces prevent collisions of the substituents and the suspension is stabilized. Coagulation involves the addition of a chemical (i.e. coagulant) to an aqueous system to destabilize the suspension. Mechanisms of destabilization include compression of the diffuse double layer, adsorption and charge neutralization, adsorption and interparticle bridging and precipitate enmeshment (Benjamin & Lawler, 2013; Bratby, 2016). Flocculation is the aggregation of destabilized particles into larger sizes (i.e. forming flocs) that can then be removed by gravity sedimentation or filtration.

A United States patent describes a method for removing fatty acids and resin acids from a TMP pressate (Roberts, 1994). In this patent, an anionic material, such as gelatin, albumin and alginate is first added to the wastewater and then the complexed fatty acids and resin acids are removed by coagulation and flocculation after the addition of the cationic polyamide and polyacrylamide. This invention demonstrated that up to 97 % of the fatty acids and 98 % of the resin acids were removed from a TMP pressate when the dosages of alginate, polyamide and polyacrylamide were 50 ppm, 100 ppm, and 75 ppm, respectively.

A coagulation study has also been conducted recently on a prehydrolysis liquor (PHL). PHL is the resultant filtrate produced by a hot water or steam treatment of wood chips, and thus may be similar to a TMP pressate. Wu et al. (2016) studied the effect of alum, polyaluminum chloride (PAC) and polydiallydimethyl ammonium chloride (PDADMAC) on the coagulation of a PHL with the objective to selectively remove lignin and maximize the retention of oligomeric xylose. The researchers determined that under the conditions of an alum dose of 120 mg/L, a temperature of 301 K, no pH adjustment (i.e. pH 4.64 due to the addition of alum) and at a stirring rate of 500 rpm for 60 min, 44 % of the lignin was removed and 98 % of the oligomeric xylose was retained. In another study on the flocculation of a PHL by Saeed et al. (2012), the effectiveness of chitosan and PDADMAC was determined after a pretreatment step with acid and lime. Initially a PHL was treated with acid to pH 3.5 and then with lime to pH 7, and then the solution was filtered. The subsequent treatment of 0.5 mg/g chitosan or 0.4 mg/g PDADMAC on the acid-lime treated PHL filtrate (i.e. mg/g coagulant/PHL filtrate) yielded the maximal removals of 5 and 6 % monomeric sugars, 25 % oligomeric sugars, 13 and 14 % acetic acid and 50 and 40 % furfural, respectively.

Overall, the studies by Roberts (1994) and Wu et al. (2016) were aimed at the selective removals of wood extractives from a TMP pressate and lignin from a PHL, respectively, and thus further treatment of the resultant filtrates may be required. Furthermore, the results on the coagulation treatment on the PHL samples may not predict the effectiveness of coagulation of a TMP pressate. Therefore, to determine the potential effectiveness of coagulation on a TMP pressate, further studies would be required.

2.9.4 Flotation

Flotation is a gravity separation process whereby constituents of a solution attach to air bubbles that are introduced to a flotation unit, thereby decreasing their apparent density and float to the surface for subsequent removal. Different methods of air bubble production yields different types of flotation. In dissolved air floatation, air bubbles are introduced as a result of the reduction in pressure of a water stream saturated with air; and in froth flotation, air is dispersed by mechanical means. In dissolved air flotation, a flocculation pretreatment step is required and an optimum flotation efficiently is associated when the air bubbles are similar in size with the particles that are to be removed (Edzwald, 2011; Opedal et al., 2011a). In froth flotation the selective affinity of the desired constituents to adhere to the gas bubbles is induced with the addition of surfactants called collectors.

In a pilot trial study, Opedal et al. (2011b) investigated the efficiency of a dissolved air flotation unit in the removal of dissolved and colloidal substances in water from a TMP pressate. It was determined that 76 % of the lipophilic extractives were removed from the TMP pressate under the conditions of a 1:1 mass ratio of Poly-(trimethyl(3-methacrylamidopropyl)-ammonium)chloride and poly-(N-N-dimethyldiallyl-3-4-ethylenpyrrolidonium)chloride and polymer dosage of 50 mg/L, 343 K, pH between 6.6 and 7.1, and a 2 L/min flow rate of air-saturated water at 6 bar. In the study by Strand et al. (2012) dissolved and colloidal pitch constituents (which includes fatty and resin acids) of a TMP pressate were selectively removed by froth flotation using dodecyltrimethylammonium chloride as a cationic foaming agent. The researchers observed that 86 % of the pitch was removed under the conditions of pH 3.5, 293 K and 80 mg/L dodecythrimethylammonium chloride. The researchers also reported that extensive foaming occurred at neutral and alkaline conditions and that a decrease pitch removal was observed when the calcium concentration was increased to 3 mM. Singh et al. (2016) also studied the removal of wood extractives from a TMP process water by froth flotation. The researchers determined that 95 % of the wood extractive were removed under the conditions of 80 mg/L dodecythrimethylammonium bromide, pH 5, 333K, 20 min, 4.5 L/min airflow and an impeller speed of 1300 rpm. Singh et al. (2016) also noted that the presence of calcium diminished the removal of the extractives.

These studies indicated that dissolved air flotation and froth flotation were selective in removing wood extractives, but further treatment of the TMP pressate stream would be required. Furthermore, dodecyltrimethylammonium chloride and dodecyltrimethylammonium bromide are toxic to fish and other aquatic organisms (Zhang et al., 2015), and thus their use in pre-treating a TMP pressate would negate any reduction in the toxicity imparted by the removal of the wood extractives. Furthermore, the use of polymers or cationic foaming agents would increase operational costs, and thus their use may not be suitable as a pretreatment of a TMP pressate from an economic standpoint.

2.9.5 Adsorption

Adsorption is the process in which a chemical species (adsorbate) accumulates on the surface of a material (adsorbent). The accumulation of adsorbates on the surface of an adsorbent can occur by physical attraction (physical adsorption) through van der Waals forces or hydrogen bonding or by chemical reaction (chemisorption). Physical adsorption involves electrostatic interactions and the formation of relatively weak bonds, whereas chemisorption involves a specific exchange of electrons (donation or receiving), or sharing of electrons, which are stronger bonds. In general, physical adsorption is a reversible process and chemisorption is an irreversible process.

Adsorption is a tertiary treatment, the use of an adsorption stage is easily integrated, and the operation is relatively simple. The cost of implementing an adsorption step into a process may be inexpensive depending on the type of adsorbent used. The most commonly used adsorbents in water and wastewater treatment are granular and powdered activated carbon (Benjamin & Lawler, 2013; Edzwald, 2011). Activated carbon is expensive, ranging in price from $1650-9,900 in US dollars (Zhi et al., 2014) and a regeneration process that is cost-effective is then required for commercial use (Gutsch & Sixta, 2012). Regeneration of activated carbon onsite requires a greater investment in capital cost and increases the complexity of the overall process. However, the use of alternatives, as suggested by Gupta et al., 2009 and Wang & Wu, 2006, would reduce the cost and subsequent regeneration would not be necessary.

Limited studies currently exist on the removal of constituents from a TMP pressate by adsorption. Oveissi & Fatehi (2014) treated a TMP pressate via adsorption on activated carbon, and determined that under the optimum conditions of pH 5.2, 303 K, and 3 h, 22 % of the COD and 45 % of the lignin were removed. When a two-stage adsorption process was applied, 32 % of the COD and 60 % of the lignin were removed. In another study by Oveissi & Fatehi (2015), the removal of COD and lignin from a TMP pressate on a biomass fly ash was partly studied. It was observed that under the conditions of a biomass fly ash dosage of 55 mg/L in TMP pressate, 303 K and 3 hours; 70 % of the COD and 68 % of the lignin was removed in a two-stage adsorption process.

Adsorption studies have also been performed on PHL. Various studies were conducted on the removal of lignocelluloses using calcium carbonate. Shen et al. (2011) studied the recovery of lignocelluloses on two samples of prehydrolysis liquor and it was determined that 9.8-15 % lignin and 0-5.4 % hemicelluloses was removed under the conditions of a lime dosage of 5 wt. %, 1 h, 150 rpm and 299 K. In another study, Saeed et al. (2012) determined that 16 % of lignin and an insignificant amount of hemicelluloses were removed when the conditions were pH 7, 30 min and at room temperature. In the study by Fatehi et al. (2013), adsorption studies were carried out on two precipitated calcium carbonate (PCC) samples, one porous and the other nano-sized. It was determined that 31 mg/g and 54 mg/g lignin, and 67 mg/g and 137 mg/g hemicelluloses were removed on porous and nano-sized PCC, respectively at a pH of 7, a PHL/PCC weight ratio of 40, 313 K, 120 rpm and 24 h. Liu et al. (2011) also studied the adsorption of lignocelluloses from PHL on activated carbon that was pretreated by hydrogen peroxide or sulfuric acid. It was determined that the adsorption capacities for lignin was 300 mg/g for both activated carbons, and the adsorption capacity for hemicelluloses was 760 mg/g and 600 mg/g for the hydrogen peroxide and acid treated activated carbons, respectively.

Overall, adsorption appears to be an effective method for removing COD and lignin from TMP pressates and related wastewaters. Furthermore, the use of biomass fly ash as an adsorbent for a TMP wastewater would be convenient and it may be cost effective since biomass fly ash is available on-site at no cost. However, further analysis is required for the optimization of a wood ash-based adsorption treatment of a TMP pressate, since the impact of factors such as their particle size, the agitation speed, and the temperature on a TMP pressate adsorption system were not studied earlier. The decrease in particle size of an adsorbent might increase the surface area that is accessible to an adsorbate (Faust & Aly, 1998). The agitation speed may affect the adsorption process by reducing the boundary layer resistance, thereby increasing the rate of external diffusion (Evans et al., 2002; Kusmierek & Swiatkowski, 2015). Although adsorption is usually considered to be an exothermic process, endothermic adsorption processes have been previously reported (Chen et al., 2015; Rytwo et al., 2006; Sharma et al., 2007), and thus the impact of temperature should be studied for each adsorption system studied.

2.9.6 Chemical oxidation

Organic compounds in wastewaters can be chemically oxidized through the addition of chemicals such as potassium permanganate, chlorine, ozone and hydrogen peroxide to produce smaller biodegradable molecules, carbon dioxide, and water (Gupta et al., 2012). If ozone is selected, organic compounds may also be indirectly oxidized by hydroxyl radicals, which are generated via ozone decomposition as is indicated by equation 1.

$$\mathrm{O_3 + H_2O \rightarrow O_2 + 2\,OH\bullet} \qquad (1)$$

Hydroxyl radicals are reactive electrophiles that readily react with most organic compounds through hydroxyl addition reactions (equation 2) or extraction of hydrogen atoms (equation 3), producing organic radicals, which then undergo radical chain reactions, and ultimately yielding carbon dioxide and mineral acids (Crittenden et al., 2012). An advanced oxidation process consists of any oxidation process that produces hydroxyl radicals (OH•) at ambient temperature and pressure (Crittenden et al. 2012). Thus, ozonation may also be considered to be an advanced oxidation process.

$$\mathrm{R} + \mathrm{OH} \bullet \rightarrow + \mathrm{ROH} \bullet \qquad (2)$$

$$\mathrm{RH} + \mathrm{OH} \bullet \rightarrow + \mathrm{R} \bullet + \mathrm{H_2O} \qquad (3)$$

Ozone does not produce toxic residuals and hydrogen peroxide produces few toxic residuals (Cheremisinoff, 1995), and thus may be environmentally friendly options. However, ozone must be generated on site due to its instability, and hydrogen peroxide is expensive. Furthermore, the use of ozone also requires trained personnel as fugitive ozone emissions poses a serious health risk to humans. Currently, it does not appear that any chemical oxidation studies have been carried out on TMP pressates, and thus studies are required. However, ozonation was conducted on the removal of lipophilic wood extractives from TMP circulation water by Laari et al. (2000), and it was reported that a high dose of 100-300 mg was required to remove 50 % of the extractives. The authors concluded that the low removals despite the high selectivity of the reaction, were attributed to the high organic content in the wastewater. Thus, ozonation may be more suitable as a polishing step.

2.10 Alternatives for processing solid wastes

2.10.1 Forest fertilizer and soil conditioning

Several reviews on the application of wood fly ash in forestry have been performed (Demeyer et al., 2001; Pitman, 2006; Marron, 2015). Overall, the application of wood fly ash had a positive effect on tree growth if the dose rates were less than 10 t/ha and in some cases less than 2 t/ha. Potential environmental problems associated with the use of wood fly ash were more likely to be related to its high calcium content rather than its heavy metal content. However, the use of ashes with a diameter smaller than 0.2 mm should not be used as a fertilizer due to the potential accumulation of toxic metals.

In 2011, Finland set a new nutrient concentration minimum of 6 % (dry wt.) calcium and 2 % (dry wt.) for phosphorous and potassium combined, and heavy metal concentrations maximum values that range from 1 mg/kg (dry wt.) for mercury and 4500 mg/kg (dry wt.) for zinc. Nurmesniemi et al. (2012) studied the forest fertilizer properties of fly ash samples generated from two pulp and paper mills located in Finland. In this study, it was determined that all samples were suitable for use with respect to their low heavy metal contents, but most of the samples studied would require the addition of phosphorous or potassium.

Cabral et al. (2008) studied the use of pulp mill fly ash (sieved to less than 2 mm) as an alternative liming material and compared the results with that of a commercial agricultural limestone. It was determined that a dose of 2.5 g/kg ash/soil was required to reach a soil pH of 6.5, improved the soil fertility by providing potassium and phosphorous, and the resulting heavy metal content was below the limit values. Overall, the researchers concluded that the pulp and paper fly ash would be a suitable low-cost alternative to the commercial liming agent.

2.10.2 Composting

Wood fly ash has been used as an additive in composting to enhance the microbial activity, increase the pH and reduce odours (Bougnom & Insam, 2009; Kurola et al., 2011; Koivaula et al., 2004). These studies were in part motivated to increase the use of wood fly ash and to determine the optimum dose required to improve the compost quality, while limiting the application of heavy metals. In the study by Bougnom & Insam (2009), the impact of wood fly ash additives of 8 % and 16 % on the resulting microbial communities and their activity were examined. It was determined that composts with an additive of 8 % wood fly ash to led to an improved utilization of all carbon sources by the altered bacterial community, but the addition of 16 % was deemed beyond optimum. Furthermore, it was determined that the addition of 8 %

wood fly ash was not toxic and in fact improved root growth of apple seeds. Kurola et al. (2011) studied the use of wood fly ash in a biowaste composting plant that was experiencing issues with process efficiency. The study determined that low doses of 4-8 % wood fly ash increased the pH from approximately 5 to 7 and the temperature from 313-323 K to 338-343 K after one day and the microbial activity was improved. However, the study reported that the treatment was not effective in odor reduction. In the study by Koivaula et al. (2004), it was determined that compost mixes with 20 % ash increased the mineralization of the organic matter from 39 to 137 mg/g humic acid/organic matter in 12 months and reduced the formation of malodorous gases.

2.10.3 Road construction

In a review study by Russell (2015), it was determined that pulp and paper mill fly ash appeared to have suitable chemical and mechanical properties for its use as a road stabilizer. Bajpai (2015) recently reported that various paper mills have utilized mill fly ash in road construction, and that Stora Enso used all of their boiler ash from the Anjalankoski mill in road construction. In a case study, Nordmark et al. (2014) studied the geochemical behaviour of a gravel road in Sweden that was mechanically stabilized by mixing 30 % wood fly ash into the road-based material. It was determined that potassium, calcium, chloride and sulphate levels in the runoff from the gravel road that had wood fly ash applied were elevated after one year, but that the concentrations returned to background levels after two years. Furthermore, the researchers observed that the leaching of heavy metals was minimal. However, it was observed that the wood fly ash stabilization impacted the infiltration capacity by reducing it by a factor of four (i.e. the rate at which water can enter the road decreased), and thus the authors recommended more long-term studies related to potential new leaching channels to the surroundings.

2.10.4 Cement and concrete

The use of wood fly ash or mill sludge ash as a partial replacement in cement for the production of concrete was studied in the past. Currently, the use of wood fly ash as a partial cement replacement is not allowed by ASTM standards and characterization tests of wood fly ash samples indicated that fly ash was too large (i.e. the amount retained on a 45 µm sieve was greater than 40 wt. %) and fly ash did not have sufficient pozzolanic oxides (Berra et al., 2015). Further studies by Berra et al. (2015) indicated that wood fly ash would be suitable as a filler/partial sand replacement for the production of low-quality concrete (i.e. concrete that does not need to meet code). However, in the review by Ban and Ramli (2011) it was reported that the addition of wood fly ash to cement might produce structural grade concrete that would meet acceptable levels of strength and durability if the incorporation of the wood fly ash were limited up to 10 wt. % of the cement. In another study by Fava et al. (2011), the use of a mill sludge ash as a partial replacement in cement for mortar production was studied. The researchers observed that a 5 wt. % addition of sludge ash produced mortars that exhibited compressive strengths higher than that made of cement. Furthermore, it was determined that a sludge ash replacement up to 10 wt. % of cement had a positive effect on the mechanical properties of the mortar produced, but that a higher amount of water was required.

2.11 Alternative options for solid wastes as an adsorbent

2.11.1 Metals

Several studies were previously conducted on the removal of metals in model solutions using wood fly ash as an adsorbent. Hasan et al. (2000) studied the removal of nickel from a dilute model solution using a rubber wood fly ash that was ground, sieved to a particle size of less than 0.055 mm and treated with nitric acid prior to adsorption studies. The researchers determined that the maximum adsorption capacity of wood fly ash for nickel was 0.492 mm/g at a pH of 5 and at 303 K, but the removals on untreated wood fly ash were not studied. Rahman et al. (2004) conducted experimental and numerical modeling studies of arsenic removal from model solutions using wood fly ash that was sieved to a particle diameter of less than 0.425 mm. The researchers determined that at the pH between 11.5-11.9 wood fly ash could adsorb trivalent and pentavalent arsenic to a concentration that was below the maximum allowable concentration limit of arsenic, but that a 5 ppm arsenic solution took 20 days to reach equilibrium. Malakootian et al., (2008) examined Pb and Co removals from the effluent of a paint industry using a wood fly ash. It was determined that the maximum removals of Pb and Co were 96.1 % and 99 % respectively under the conditions of pH 2, 3 h, 100 g/L and the adsorption process followed the Langmuir isotherm. Furthermore, the researchers noted that the wood fly ash dose had a major impact on the metal removals. Seco-Reigosa et al. (2013) studied the removal of arsenic, chromium, and mercury removal from model solutions using an ash mixture from mussel shell, sewage sludge, and wood waste. The researchers determined that the removals were 98 % mercury (II) and 88 % arsenic (V) when the dosage of ash mixture was 0.1 mg/L ash and the adsorption time was 24 h, and 30-88 % chromium when the dosage of ash mixture was 0.2 mg/L and an adsorption time of 24 h.

Studies were also done on the removal of metals in industrial wastes using wood fly ash as an adsorbent. Orescanin et al. (2004) studied the purification of electroplating wastewaters using waste by-products of ferrous sulfate and wood fly ash. The researchers used the ferrous sulfate to reduce the chromium (VI) to chromium (III) and the fly ash was used to raise the pH and remove heavy metals to less than the maximum allowable value. The researchers determined that the removal of heavy metals ranged from 97.5 % for zinc to 99.97 % for copper when the pH was 11, and the agitation speed was set to 200 rpm; but the impact of agitation was not studied. Chirenje et al. (2006) studied removal of the heavy metals Pb, Cd, Cu and Zn from model solutions using wood fly ash. It was determined that 100 % of Cu and Pb, 97 % of Cd and 94 % of Zn were removed under the conditions of a wood fly ash dose of 20 g/L and a treatment time of 2 h. The researchers noted that the dose was the most important factor in metal adsorption. Heviankova et al. (2014) studied the application of wood fly ash in the removal of metals from an acid mine drainage open pit. It was determined that approximately 100 % of iron, arsenic, cobalt, aluminum and zinc were removed, and 57 % and 33 % of the manganese and nickel were removed respectively, at a dosage of 0.5 g/L in order to adjust the pH to 8.3. Furthermore, the researchers determined that the sludge volume was 10 mL/L a after a 30 min sedimentation period.

2.11.2 Dye or organic matter

Leechart et al. (2009) studied the adsorption of azo reactive dye on a wood fly ash that was either washed with water or treated with sulphuric acid in a pretreatment step. The adsorption capacity at 303 K for the dye on the washed and acid-treated wood fly ash was 24.3 mg/g and 29.9 mg/g, respectively. Furthermore, both ashes were used to treat two textile wastewaters. It was determined that the washed and acid-treated wood fly ash reduced the COD in one factory from 129,300 mg/L to 77,600 mg/L and 51,700 mg/L, respectively, and the other factory from 25,500 mg/L to 7,600 mg/L and 5,600 mg/L, respectively. Bazrafshan et al. (2012) studied the adsorption of the cationic dye, methylene blue, using a wood fly ash. It was determined that when the initial dye concentration was 80 mg/L, the wood ash removed 97 % methylene blue under the conditions of 5 g/L wood fly ash dose, 1 h, 293 K, and pH 13. Azizi et al. (2012) studied the removal of reactive blue 19 dye from model solutions and a textile wastewater using a pulp and paper sludge ash. The researchers determined that 90 % of the dye was removed under the optimum conditions of 30 min, initial pH 11, 4 g/L sludge ash dose, and an initial dye concentration of 100 mg/L. Furthermore, it was determined that 59 % dye removal was achieved for a textile wastewater. The researchers noted that the lower removals were attributed to the higher initial dye concentration of 500 mg/L and determined that 68 % dye removal was obtained for a synthetic wastewater under similar conditions as the textile wastewater.

Andersson et al. (2011) studied the adsorption of a TMP lignin in a model solution using activated carbon and wood fly ash that was produced in a mill's boiler. The wood fly ash was sieved and the particles that were smaller than 0.053 mm were retained for the adsorption studies. The adsorption capacity of the activated carbon and wood fly ash were 270 mg/g and 13 mg/g at 293 k, respectively. Leaching tests of the wood fly ash were also conducted and revealed that the dominant elements in filtrates were K, Ca, Na and S. However, the leaching tests were only performed in deionized water and the leaching effects in the complex mixture are unknown.

Laohaprapanon et al. (2010) studied the COD removal of wastewater from a wood-laminate floor industry by a wood fly ash. The wood fly ash was sieved to three different size fractions of 1-2 mm, less than 1 mm, and less than 0.5 mm for the adsorption studies. The COD removal increased with a decrease in the particle size, even though there was no significant difference between those with the sizes of the less than 1 mm and less than 0.5 mm fractions. Rapid COD removal occurred within the first 5 min and equilibrium was reached after 20 min. A COD removal of 37 % was achieved when the adsorbent dose was 160 g/L and the particle size was less than 1 mm, and the COD removal increased to 42 % when the wood fly ash was pretreated with hot water. The researchers also investigated the amount of twelve trace elements that are leached when wood fly ash was added to distilled water at 293 K for 24 h at two different liquid to ratios (L/S) (5 and 10). The trace metals that the researchers detected to a significant extent in the leachate for the L/S, 5 and 10, were 3.2 and 1.7 mg/L Cr, 0.4 and 0.3 mg/L Zn, 0.3 and 0.4 mg/L Ba, and 0.1 mg/L Pb, respectively. However, leaching effects in the complex mixture were not conducted, and thus are not known.

2.12 Potential negative impacts of wood fly ash use

The use of wood fly ash on soils and roads, and in aqueous solutions for adsorption treatments may be limited. The dominant metals in wood are Ca, K, Mg, Si, Al, Na, Mg and Mn and trace metals include Fe, Zn, As, Ni, Cr, Pb, Cu and Cd (Demeyer et al., 2001; Steenari & Linqvist, 1997). The use of a wood fly ash in an aqueous system may lead to potential leaching of heavy metals and thus its use may be a concern for the environment (Reijnder, 2005). Biomass fly ash is considered non-hazardous in Ontario (EPA, 1990). However, the composition of biomass fly ash is highly variable (Vassilev et al., 2013; Demeyer et al., 2001) and stricter regulations may consider some biomass fly ash as hazardous (Ribbing, 2007). Furthermore, the leachate results presented in the previous section (section 2.11.2) by Laohaprapanon et al. (2010), suggests that some wood fly ash may not be suitable for adsorption in aqueous systems as the resultant Cr concentration may be too high (Consigli et al., 2016). A standard test, US EPA Toxicity characteristic leaching procedure (TCLP) Method 1131, can be used to determine whether a solid waste is hazardous or non-hazardous, and it is conducted with a liquid/solid ratio (L/S) of 20 and an acidic (pH 2.9) leaching solution for 18 h. A TCLP result of greater than 0.6 mg/L Cr would currently deem a solid waste as not fit for landfill disposal in Ontario (EPA, 1990). However, standard leaching tests may under or overestimate real life leaching conditions and leaching behaviour tests should also be conducted for the particular water system under investigation (Wang & Wu, 2006; Reijnder, 2005). A review of the literature did not reveal any quality criteria or regulations regarding the use of biomass fly ash as an adsorbent for wastewater treatment in Canada. Thus, it is currently unknown what leaching method is suitable nor what acceptability criteria should be met.

2.13 Summary

The potential limitation of available land space for to disposal of solid wastes has led to an interest in using biomass fly ash wastes for other beneficial purposes. Furthermore, stricter limitations on effluent guidelines may require the use of tertiary wastewater treatments in the pulp and paper industry. Many tertiary treatment options, such as membrane filtration, adsorption, coagulation, and ozonation may be expensive to incorporate into existing infrastructure and or costly to operate. However, adsorption process may be an inexpensive process depending on the complexity of the process and the adsorbent type. For example, the use of activated carbon may be cost prohibitive and requires an additional stage for regeneration. The use of biomass fly ash, which is abundant and available on-site, may be suitable as a low-cost adsorbent for COD removal in a TMP pressate according to the literature review. However, further research is required, since the impact of factors such as the particle size of fly ash, the agitation speed, and the temperature on an adsorption system have not been studied on a TMP pressate, and are crucial in the development of a biomass-based fly ash wastewater treatment system. Furthermore, studies are required to determine: 1) the main factors that impact the removal of COD from a TMP pressate by a biomass fly ash; 2) the characteristics of the adsorbent and adsorbate; 3) the isotherm model that the adsorption follows; 4) the optimized conditions; and 5) the impact of leaching of biomass addition to a TMP pressate. In addition, there is a lack of research on the treatment of TMP pressate by coagulation, and further studies should be conducted to evaluate its potential use as a treatment option.

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3 Chapter 3: Optimization of a biomass-based fly ash adsorption treatment of a TMP pressate using definitive screening design (DSD)

3.1 Abstract

Wood chips are pretreated with steam prior to refining in thermomechanical pulping (TMP) process. Currently, the resultant effluent (TMP pressate) must be treated in the wastewater treatment facility of the mill. Biomass fly ash is also generated in pulp mills as a residue from burning wood and other biomass in boilers. Fly ash utilization is currently limited and most of the fly ash is landfilled worldwide. In this study, biomass fly ash is used as an adsorbent for removing lignocelluloses from a TMP pressate. Biomass fly ash samples were fractionated, and the results showed that the carbon content and the surface area of the fly ash decreased, and the metal content increased, as the particle size of the fly ash decreased. The main factors that impacted the reductions in chemical oxygen demand (COD) level and the lignin concentration of a TMP pressate by biomass fly ash samples (FA1 and FA2) were determined, and model equations and optimum conditions for these reductions were developed using definitive screening design (DSD). Generally, FA1 was considered a more effective adsorbent than FA2. The maximum COD removal from a TMP pressate (91.3 %) was by FA1 with the particle size of 0.43 mm at a dosage of 70.0 mg/g FA1/TMP pressate and a treatment time of 2 h. The maximum lignin removal from the TMP pressate (95 %) was by FA1 with the particle size of 0.11 mm at a dosage of 46.5 mg/g FA1/TMP pressate and a pH of 6.

3.2 Introduction

Thermomechanical pulping (TMP) is a process that uses steam pretreatment to soften softwood chips prior to mechanical refining. The TMP pressate (i.e. the filtrate from the pretreatment stage) is an effluent that requires wastewater treatment prior to its release into the environment. This effluent mostly consists of lignin, hemicelluloses and some wood extractives (Zasadowski et al., 2014). A secondary biological treatment is usually applied to treat this effluent, as this wastewater contains high chemical oxygen demand (COD) load (Sumathi & Hung, 2006; Andersson et al., 2008).

Various treatment options for effluents of pulp mills were reviewed by Pokhrel & Viraraghavan (2004), Sumathi & Hung (2006) and more recently by Kamali & Khodaparast (2015). It was indicated that recalcitrant compounds, such as lignin could be removed by membrane filtration, adsorption and oxidation treatment. Nevertheless, membrane filtration is subjected to fouling leading to increased maintenance and operational costs, and oxidation may be expensive. Adsorption was considered an appropriate treatment option for the removal of high molecular weight organic constituents from effluents (Kamali & Khodaparast, 2015). It was alternatively suggested that a combination of physicochemical and biological treatments would offer a long-term solution for wastewater treatment operations for treating pulp and paper effluents (Pokhrel & Viraraghavan, 2004).

Canadian pulp mills produce a substantial amount of biomass fly ash by burning wood residuals and sludge in their boilers. Approximately, 22 % of the produced fly ash is used for beneficial purposes, such as composting, road construction and soil conditioning; however, as mentioned earlier most of the fly ash is landfilled (Elliot & Mahmood, 2006). There is an increasing interest in diversifying the application of non-coal ashes for beneficial purposes (Ribbing, 2007). Fly ash was proposed to be used as an additive to cement admixtures (Ban & Ramli, 2011) as well as a filler in concrete (Berra et al., 2015).

Meanwhile, adsorption may be an inexpensive and industrially attractive process. Granular and powdered activated carbon are common adsorbents for water and wastewater treatment (Benjamin & Lawler, 2013; Edzwald, 2011). In the past, some studies examined the use of a wood fly ash as an adsorbent for the effluents made from various wood related industries. One study on the wastewater effluent made from a wood-laminate floor industry suggested that the particle size of fly ash might impact its performance on the COD removal (Laohaprapanon et al., 2010). In another study using a mixed wastewater effluent of an integrated TMP mill, it was claimed that activated carbon had a higher adsorption capacity than did fly ash; whereas, that activated carbon would be more expensive (Andersson et al. 2011). Low cost adsorbents, such as biomass fly ash could be an alternative resource for treating wastewater effluents (Gupta et al., 2009; Wang & Wu, 2006). In our previous work (Oveissi & Fatehi, 2015), the removal of lignin from a TMP pressate was partly studied. It was observed that under the conditions of a biomass fly ash dosage of 55 mg/L in TMP pressate, 303 K, and 3 h treatment; 53 % and 68 % of lignin was removed through one-stage and two-stage adsorption processes, respectively.

Various factors such as the characteristics of the adsorbent (Cheng et al., 2005; Faust & Aly, 1998; Li et al., 2002), the agitation speed (Evans et al., 2002; Kusmierek & Swiatkowski, 2015), and the temperature of the adsorption treatment process may affect the performance of an adsorption process. To the best of our knowledge, the impact of these factors on the adsorption of lignin of TMP pressates on biomass fly ash was not studied previously. The decrease in particle size of an adsorbent might increase its surface area that is accessible to an adsorbate (Faust & Aly, 1998). The agitation speed may also affect the adsorption process (Evans et al., 2002; Kusmierek & Swiatkowski, 2015). Adsorption could be either an exothermic or endothermic process (Chen et al., 2015; Rytwo et al., 2006; Sharma et al., 2007). Therefore, the impact of particle size, agitation speed, and temperature on an adsorption system requires analysis and are the objectives of this study.

In order to optimize a biomass-based fly ash adsorption process to treat a TMP pressate, a design of experiment can be used to determine the influential factors in the adsorption process. Definitive screening design (DSD) is a three-level design that can identify the main factors that impact a process; moreover, this model is able to characterize the full quadratic model of a process (Jones & Nachtsheim, 2011). Thus, DSD can assess the impact of the adsorption parameters of fly ash in the TMP pressate. To the best of our knowledge, DSD analysis has not been used to model and optimize the adsorption of lignocelluloses of a pulp and paper effluent on biomass fly ash.

In this study, two biomass fly ash samples were fractionated and characterized. The significance of the impacts of fly ash particle size and dosage, adsorption time, temperature, agitation speed, and the pH of the adsorption system on COD and lignin removals from a TMP pressate were evaluated by DSD analysis. Model equations for the COD and lignin removals were then developed and validated. Based on the models, the conditions required for optimizing the COD and lignin removals within the boundary conditions were subsequently assessed.

3.3 Materials and methods

3.3.1 Materials

A TMP pressate and two biomass fly ash samples (FA1 and FA2) were obtained from a pulp mill that is located in central Canada. The fly ash samples were generated by two different boilers, both of which use a mixture of wood and wastewater sludge as fuel. These two boilers have different combustion performances. FA1 and FA2 were dried in an oven at 378 K prior to use and then sieved to various fractions as described in section 3.3.2. The TMP pressate was stored in a refrigerator at 277 K and the fly ash samples were stored in plastic bags at room temperature prior to use. Sodium hydroxide (98 wt. %), hydrochloric acid (37 wt. %), potassium hydroxide, and sodium nitrate were purchased from Sigma Aldrich Company. The Chemical oxygen demand (COD) kit (K-7365) was obtained from CHEMetrics Inc., USA.

3.3.2 Characterization of biomass fly ash

The particle size distributions of FA1 and FA2 were determined based on a method described previously (Zhu et al., 2013). The fly ash samples were mechanically sieved using ASTM E11 sieves with mesh numbers of 10, 20, 60, 200, and 400. In this method, 200 g of fly ash samples were placed on a mechanical sieve shaker (CSC Scientific, Meinzer II Sieve Shaker) and shaken for 10 min for fractionation and the retained fly ash on each sieve was weighed. The density of the fly ash fractions was determined by the kerosene displacement method (ASTM C188-15). This method was previously used to measure the density of fly ash (Yeboah et al., 2014). The crystalline phases of 0.2-0.4 g samples of FA1 and FA2 were determined by a powder X-ray diffraction crystallography (XRD) using an X-ray diffractometer (Pananalytical Xpert Pro with copper Kα radiation; λ = 1.5406 A; 40 mA and 45 kV). Data was collected in the range of 6.0-96.9 ° with a step width of 0.026 °/2ϴ. The minerals were identified using HighScorePlus 2.2d software and the reference database was provided by PANalytical. All fly ash samples were ground to powder using a grinder (Bel-Art SP Scienceware micro-mill) prior to XRD analysis.

The organic elements of 0.02 g fly ash samples were determined using an elemental analyser (Vario EL cube) as described previously (Fadeeva et al., 2008). The metal contents of the FA1 and FA2 fractions were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro with CETAC ASX-510 Auto Sampler. In this modified EPA method 3051A, 0.2 g samples of fly ash were digested with aqua regia (i.e. nitric acid and hydrochloric acid in a 1:3 molar ratio) in a microwave (CEM Mars Xpress microwave) using an Xpress closed vessel. The digestion conditions consisted of a 20 min ramp time to a temperature of 448 K and 25 min digestion at 448 K. After digestion, the samples were cooled and then diluted with 40 mL deionized water prior to ICP-OES analysis.

The surface area of the fly ash samples was determined by measuring the nitrogen gas adsorption-desorption isotherms with a surface area analyzer (Quantachrome NOVA-2200e) based on the method previously described by Wang et al. (2016) considering Brunauer-Emmett-Teller (BET) theory. In this method, the fly ash samples were dried overnight at 403 K, and then 0.05 g of the fly ash samples were degassed at 523 K for 4 h before analysis. The isotherms were determined at 77 K between the relative pressure range of 0.01 and 0.99 and the multipoint-BET surface area was determined by fitting the data of the nitrogen adsorption isotherms at a relative pressure ranging between 0.05 and 0.3. The total pore volumes were calculated by NovaWin software, version 11.0. The micropore volume of the fly ash samples was determined by fitting the data of the nitrogen adsorption isotherms at a relative pressure ranging between 0.06 to 0.2 to Dubinin-Radushkevich (DR) equation (Scherdel et al., 2010; Hsieh and Teng, 2000). The mesopore volume was approximated by subtracting the micropore volume from the total pore volume (Hsieh & Teng, 2000; Yang et al., 2010).

3.3.3 Adsorption experiments

Fractionated FA1 or FA2 samples were added to 50 g of TMP pressate in 250 mL Erlenmeyer flasks at various dosages ranging from 10 to 70 mg/g FA/TMP pressate, the pH of the mixture was then adjusted to 6, 9, or 12.5, and the flasks were sealed. The samples were then shaken at 100, 150, or 200 rpm in a Boekel water bath shaker at 298 K, 318 K, or 338 K for various time intervals of 0.5 h, 1.25 h, or 2 h. After the adsorption treatments, the samples were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1), and the filtrates were collected for COD, lignin, and pH analyses. Separate control experiments (i.e. TMP samples with no fly ash) were carried out to determine the COD, lignin, and turbidity removals from the TMP pressate samples via only filtration. These control tests were also used to validate if pH has any effect on the COD and lignin removals (i.e. in the absence of adsorption treatments). The filtrates of the adsorption and control tests were collected for COD, lignin, and turbidity analyses. All tests were carried out in duplicate. The COD and lignin removals were determined using equation 1:

$$y_{\mathrm{COD}}\ \%\ \text{or}\ y_{\mathrm{Lignin}}\ \% = \frac{C_F - C_A}{C_F} \times 100 \tag{1}$$

where C_F refers to the COD or lignin concentrations in the filtrates of the control experiments, which were determined to be 2138 mg/L and 1.95 mg/L, respectively, and C_A refers to the COD or lignin concentrations in the filtrates after the fly ash adsorption treatments.

3.3.4 Design of experiment with definitive screening design (DSD)

A definitive screening design was used for determining the impacts of fly ash particle size and dosage, adsorption time, temperature, and agitation speed, and the effect of pH adjustment after adding fly ash on the COD and lignin removals from a TMP pressate. The parameters and levels for the DSD experiments are given in Table 3.1. It is to be mentioned that the DSD of the six parameters used in this set of experiments was based on the work carried out by Jones & Nachtsheim (2011). The experiments were done in duplicate and all runs including duplicates were conducted in a randomized order, but identical for FA1 and FA2.

Table 3.1 Parameters and levels of DSD of the adsorption experiments for COD and lignin removals from a TMP pressate by FA1 and FA2

	Parameter	**Levels**		
		-1	**0**	**1**
X_1	Weight-based average fly ash particle size, mm	0.11 (0.11)	0.43 (0.53)	1.01 (1.30)
X_2	Fly ash dosage, mg/g TMP	10	40	70
X_3	Adsorption time, h	0.50	1.25	2.00
X_4	Temperature, °K	298	318	338
X_5	pH adjustment (by acid or base)	6.0	9.0	12.5
X_6	Agitation speed, rpm	100	150	200

Brackets indicate the weight-based average particle size for FA2

3.3.5 Model analysis with definitive screening design

A forward stepwise regression analysis using MATLAB software (R2011b) was used for estimating the coefficients of a predictive model for COD and lignin removals by FA1 and FA2. In this method, a p-value of 0.05 or less was used. In addition to the principle of heredity, the principles of hierarchy and sparsity were considered for analyzing the data (Goos & Jones, 2011), which implied that the forward stepwise regression was conducted in stages. In the first stage, only lower order terms (i.e. particle size, dosage, time, temperature, pH adjustment, and agitation speed) were evaluated to determine which factors had the most significant impact on COD and lignin removals. Subsequent stages evaluated the significant lower order terms and the significant interaction terms or quadratic terms with respect to COD and lignin removals. The final stage evaluated the significant lower order terms and quadratic terms, and all interactions of the significant quadratic terms with respect to COD and lignin removals. Therefore, a maximum of four potential models for each dependent variable for fly ash samples were possible. The residuals of the predicted values of the potential models were then determined using ‘Analysis ToolPak’ in Excel, and then all models were evaluated by residual analysis. All models that exhibited residuals with normal distributions were then evaluated based on their ability to predict COD and lignin removals of the validation runs. The models were also evaluated for overfitting based on the procedure described by Hawkins (2004).

3.3.6 Validation and optimization of the models

The validation runs of the models (i.e. equations) consisted of 15 additional adsorption tests that were performed after the DSD analysis. In one set of experiments, 9 validation runs were performed on each of the FA1 and FA2 fractionated samples, where three runs were carried out on each of the small, medium, and large particle size fractions (i.e. 0.037-0.250 mm, 0.250-0.841 mm, and 0.841-2.00 mm, respectively). In another set of experiments, 6 validation runs were performed on each of the unfractionated FA1 and FA2 samples with a particle size range of 0.037-2.00 mm, where the weight-based average particle size for FA1 and FA2 were 0.18 mm and 0.71 mm, respectively (Figure 3.1).

The validation tests were conducted in a similar manner as stated in section 3.3.3, but consisted of different parameter levels that were within the boundary conditions given in Table 3.1. The design of the 15 validation runs were randomly chosen and they are given in Tables 8.1 and 8.2 in the Appendix. The validation runs were identical for FA1 and FA2 and they were done in duplicate. After the validation of the models, excel solver was used to determine the optimum conditions (i.e. the levels of the significant factors) and the maximum removal possible was set to 102 % (based on the model prediction, but 102 % only physically removal means a complete removal). Then, adsorption tests were performed at the optimum conditions for COD and lignin removals on a TMP pressate by FA1 and FA2 in order to obtain experimental results for comparing with theoretical ones. The adsorption tests at the optimum conditions were carried out in duplicate.

3.3.7 Molecular weight analysis

The weight average (M_w) and number average (M_n) molecular weight of the lignin present in the TMP pressate were determined by a gel permeation chromatography (GPC) (GPC Max VE 2001 separation module and a Viscotek TDA 305, Malvern). The TMP pressate was filtered with a 13 mm diameter nylon filter (0.2 μm pore size), prior to the molecular weight analysis. A solution of 0.1 mol/L $NaNO_3$ was used as the eluent and the flow rate was set to 0.7 mL/min. The columns used were PolyAnalytic PAA206 and PAA203 and they were operated at 308 K. The standard used for the GPC calibration was polyethylene oxide.

3.3.8 COD and Lignin analysis

The COD analysis was carried out by adding 2 mL samples to COD vials obtained from CHEMetrics, incubating them in a reactor (CR 2200 WTW thermoreactor) for 2 h at 423 K and measuring the COD by the spectrophotometric method at 620 nm using a spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific) as described by the COD kit. The lignin analysis was performed based on a spectrophotometric method described previously (Liu et al., 2011). The pH of the samples was adjusted to 7 (± 0.25) with 0.1 M NaOH or 0.1 M HCl prior to analysis at 205 nm (Saeed et al., 2012a) using a UV-Vis spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific).

3.3.9 Hemicellulose and turbidity analysis

The hemicellulose concentration in the TMP pressate was determined by ion chromatography (Dionex ICS 5000, Thermo Scientific, equipped with an electrochemical detector (ED) and a CarboPac™ SA10 column), at a column operating temperature of 303 K. The eluent flow rate was 1.2 mL/min and the concentration was 1.00 mM KOH using an eluent generator (EGC 500 KOH, Thermo Scientific). The turbidity analysis was conducted at room temperature using a turbidity meter (2100AN Turbidimeter, HACH).

3.4 Results and discussion

3.4.1 Characterization of TMP pressate and biomass fly ash samples

Table 3.2 presents the characteristics of a TMP pressate at different pH conditions. The original TMP pressate had 2.2 g/L lignin, 0.7 g/L hemicelluloses, 2912 mg/L COD, a turbidity of 637 NTU, and a pH of 6.1 (Table 3.2). In one study, a TMP pressate was reported to have 1.3 g/L of lignin, 0.5 g/L of other extractives, 2.6 g/L of hemicelluloses, a turbidity of 3350 NTU and a pH of 3.5 (Zasadowski et al., 2014). In another study, a TMP pressate was reported to have 4.5 g/L of lignin, 0.7 g/L of hemicelluloses, 5311 mg/L of COD, a turbidity of 486 NTU and a pH of 5.3 (Oveissi & Fatehi, 2015). The M_w and the M_n of the lignin present in the TMP pressate studied in the present paper were 2,562 g/mol and 1,088 g/mol, respectively. In a study on a TMP pressate collected after the second stage refiner, the M_w of lignin was 1,470 g/mol (Pranovich et al., 2005).

Table 3.2 Characteristics of the original TMP pressate and after pH adjustment and filtration

Parameter	Original TMP	TMP after pH adjustment and filtration		
pH	6.1 ± 0.1	6.1 ± 0.1	8.9 ± 0.1	12.5 ± 0.1
COD, mg/L	2912 ± 63	2140 ± 50	2122 ± 35	2151 ± 64
Lignin, g/L	2.17 ± 0.04	1.96 ± 0.03	1.95 ± 0.02	1.95 ± 0.03
Hemicellulose, g/L	0.66 ± 0.02	ND	ND	ND
Turbidity, NTU	637 ± 5	275 ± 3	169 ± 34	135 ± 18

ND = not determined

Table 3.2 also indicates that pH adjustment in the control experiments did not appear to have a significant effect on the removals of COD and lignin by filtration (i.e. without an adsorption step). However, the results suggested that the pH adjustment had some effects on the turbidity. The particle size distribution of FA1 and FA2 samples are shown in Figure 3.1. The d_{10}, d_{50}, and

d_{90} (i.e. the particle size diameter indicates that 10 wt. %, 50 wt. %, and 90 wt. % of the particles is lower than this value, respectively) of FA1 were 0.048 mm, 0.19 mm, and 1.75 mm; and of FA2 were 0.07 mm, 1.10 mm and 5.30 mm, respectively. In a study by Yeboah et al. (2014), it was reported that the median particle sizes of three different wood-based fly ash samples were 0.17 mm, 0.64 mm and 1.4 mm.

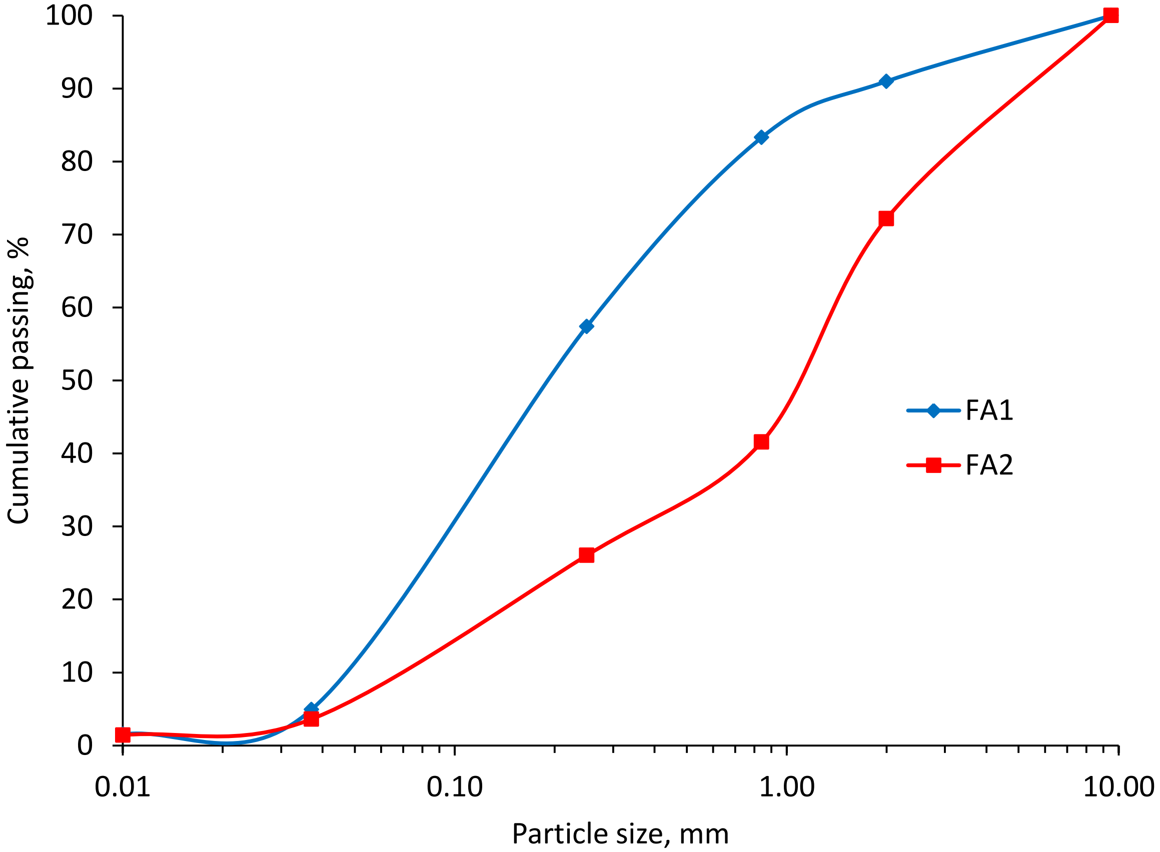

Figure 3.1 Particle size distribution of FA1 and FA2

Three size fractions of 0.037-0.250 mm, 0.250-0.841 mm and 0.841-2 mm were chosen for adsorption studies, and they are identified as small, medium, and large, respectively. The corresponding weight-based average particle sizes for each fraction of FA1 and FA2 were 0.11 mm, 0.43 mm, and 1.01 mm, and 0.11 mm, 0.53 mm, and 1.30 mm, respectively (Figure 3.1). Particle sizes greater than 2 mm were considered to be unacceptable (i.e. too large) and were subsequently omitted from this study. Granular activated carbon and powdered activated carbon, two common adsorbents for wastewater treatment, have particle sizes between 0.42 and 2.38 mm or less than 0.044 mm, respectively (Edzwald, 2011).

Table 3.3 lists various elements present in the biomass fly ash fractions of FA1 and FA2. The results indicate that, as the particle size of the fly ash decreased, the carbon content decreased and the metal content increased. Similar results were reported for eucalyptus bark fly ash (Giron et al., 2013). Table 3.3 also indicates that the predominant metals present in the wood fly ash samples were calcium, sulfur, potassium and magnesium. Furthermore, the calcium, sulfur, potassium and magnesium contents of FA1 were also significantly higher than those of FA2. Andersson et al. (2012) reported that the predominant metals in a wood fly ash consisted mainly of calcium, potassium, manganese and magnesium. In another study, fly ash from wood combustion had a significantly higher sodium, potassium, calcium, magnesium and phosphorous contents than did coal fly ash (Elliot & Mahmood, 2006). The compositions of wood fly ash depend on the raw materials used to generate the fly ash (Reimann et al., 2008).

Table 3.3 Elemental analysis of FA1 and FA2

Element	**FA1**			**FA2**		
	Particle size range, mm					
	0.037-0.250	**0.250-0.841**	**0.841-2.00**	**0.037-0.250**	**0.250-0.841**	**0.841-2.00**
	Wt. %					
Carbon	21.35	23.85	85.01	41.35	61.72	79.63
Aluminum	0.938	0.707	0.084	0.609	0.279	0.022
Barium	0.139	0.097	0.034	0.091	0.044	0.030
Calcium	19.159	17.627	3.089	7.328	4.105	2.208
Iron	0.585	0.458	0.046	0.669	0.254	0.013
Potassium	3.818	3.520	0.772	1.811	1.505	1.415
Magnesium	1.484	1.273	0.172	1.051	0.437	0.196
Manganese	0.786	0.703	0.118	0.297	0.133	0.072
Sodium	0.703	0.647	0.121	0.174	0.106	0.079
Phosphorous	0.758	0.616	0.073	0.451	0.136	<DL
Sulfur	4.867	4.836	0.342	0.058	0.044	0.028
Zinc	0.189	0.166	0.010	0.018	0.008	0.003
Other[a]	45.225	45.501	10.129	46.094	31.228	16.305

DL = detection limit

[a] consists of oxygen, hydrogen, nitrogen, and other metals

The density of FA1 and FA2 fractions are given in Table 3.4. The results indicate that the density increased as the particle size of the fly ash decreased. The variation in the density of the fly ash fractions of FA1 and FA2 was due to the variations in their compositions (Table 3.3). The density analysis also indicates that FA1 was denser than FA2.

Table 3.4 Density, surface area; and the total pore, micropore, and mesopore volumes of FA1 and FA2

Parameter	**FA1**			**FA2**		
	Particle size range, mm					
	0.037-0.250	**0.250-0.841**	**0.841-2.00**	**0.037-0.250**	**0.250-0.841**	**0.841-2.00**
Density, g/mL	2.27	2.12	1.44	1.67	1.49	1.39
Surface area, m^2/g	108.2	187.5	409.8	128.2	245.0	328.7
V_{total}, cm^3/g	0.085	0.126	0.247	0.094	0.157	0.202
DR V_{micro}, cm^3/g	0.054	0.095	0.213	0.065	0.122	0.170
V_{meso}, cm^3/g	0.031	0.031	0.034	0.029	0.035	0.032

V_{total} = total pore volume

DR V_{micro} = micropore volume determined by Dubinin-Radsukevich analysis

V_{meso} = mesopore volume (total pore volume - micropore volume)

The surface area of FA1 and FA2 fractions were determined to be in the range of 110 m^2/g and 409.8 m^2/g (Table 3.4). In the literature, the surface area of different biomass fly ash samples were 28.6 m^2/g for a wood fly ash (Andersson et al., 2011); 63.7 m^2/g for a sludge/wood fly ash (Oveissi & Fatehi, 2015),116 m^2/g, 180 m^2/g and 687 m^2/g for three different wood fly ash samples (Yeboah et al., 2014). On the other hand, the surface area of different activated carbons ranged between 378 m^2/g and 2,451 m^2/g (Yang et al., 2010). Therefore, the surface area of the fly ash studied in this work is relatively high for a wood fly ash and is comparable with that of activated carbon with a small surface area.

The results in Table 3.4 also indicate that the surface area, along with the total pore volume decreased as the particle size of the fly ash decreased. In another study, a decrease in surface area, as well as the total pore volume was observed when the particle size of bagasse fly ash decreased (Deokar et al., 2016). In other studies, larger particles were associated with a higher surface area for coal-based fly ash, and they also suggested that the increase in surface area may be related to the increase in the carbon content of the fly ash (Kao et al., 2000; Wang et al., 2005). In the present study, the increase in surface area of both FA1 and FA2 appears to be related to the increase in their carbon contents (Tables 3.3 and 3.4). The results in Table 3.4 also indicate that the micropore volumes increased, as the particle size of the fly ash increased, while the mesopore volume remained relatively constant. The results also suggest that the increase in surface area of both FA1 and FA2 was attributed to the increase in micropore volume and that the latter may be attributed to the carbonaceous matter.

XRD analysis was performed to determine the crystalline phases present in the different biomass fly ash samples. The XRD spectra of the fly ash samples are given in Figure 3.2. Table 3.5, provides the crystalline phases that were identified by their main characteristic peaks at 2Θ in Figure 3.2. The XRD analysis indicates that lime (CaO), anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$) were present in the small fraction of FA1. The crystalline phases present in the medium fraction of FA1 were identified as anhydrite, calcite and portlandite. Calcite was the only crystalline phase detected in the large fraction of FA1. The crystalline phases present in the small and medium fractions of FA2 were identified as calcite and quartz (SiO_2), and only calcite was detected in a large fraction of FA2. The results in Figure 3.2 and Table 3.5 indicate that 1) FA1 contains various minerals composed of calcium, 2) all fly ash fractions for FA1 and FA2 contain calcite, and 3) quartz was only detected in small and medium fly ash fractions of FA2. Demeyer et al. (2001) suggested that the major mineral present in wood ash is calcite even though other minerals such as lime, portlandite, and calcium silicate were also identified. Vassilev et al. (2013) also suggested that the characteristics of biomass were highly variable and numerous crystalline phases could be found in fly ash samples.

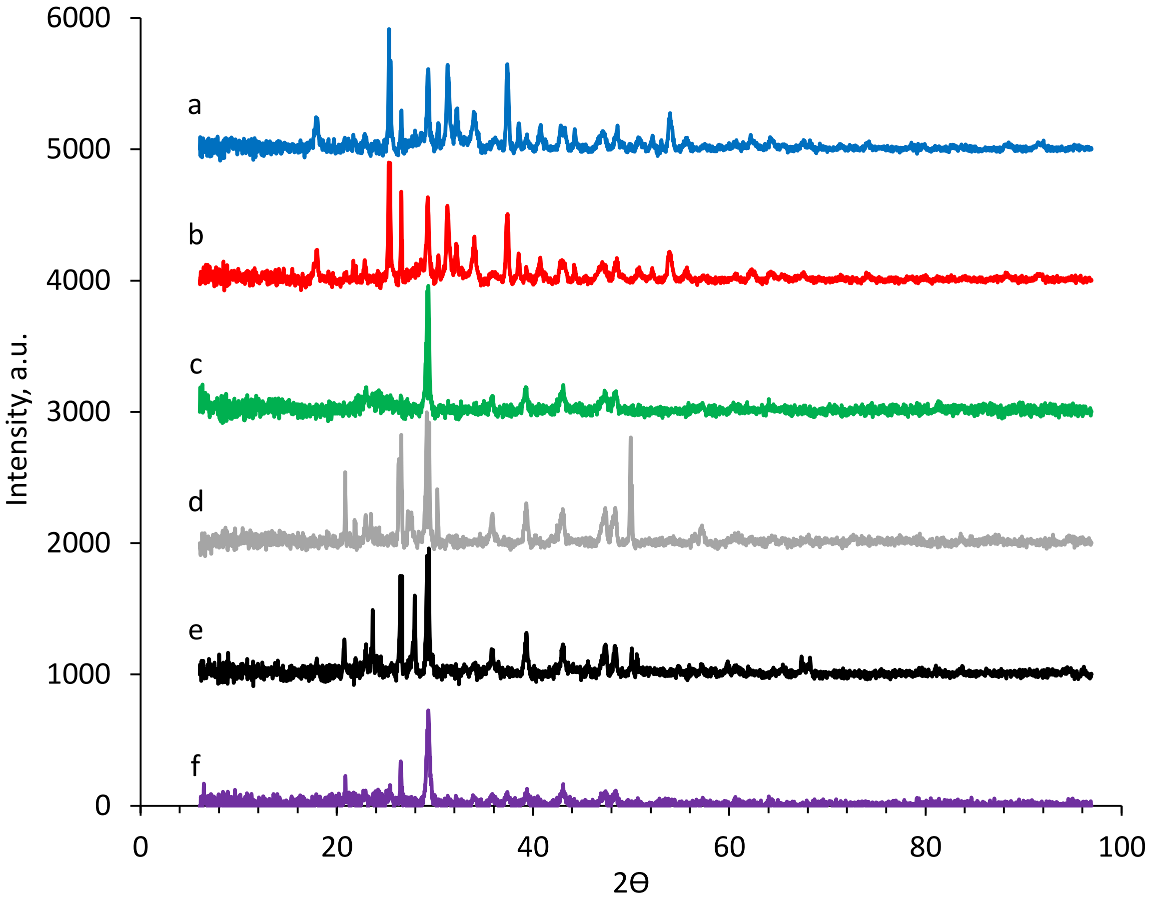

Figure 3.2 The XRD analysis of FA1 and FA2. a) small-, b) medium-, and c) large-sized fraction of FA1; d) small-, e) medium-, and f) large-sized fraction of FA2. The small, medium and large fractions have particle sizes in the ranges of 0.037-0.250 mm, 0.250-0.841 mm, and 0.841-2.00 mm, respectively.

Table 3.5 Crystalline phases and corresponding peaks detected by XRD analysis for FA1 and FA2

Crystalline phase	**pH_{PZC}**	**FA1**			**References**
		Particle size range, mm			
		0.037-0.250	**0.250-0.841**	**0.841-2.00**	
		Peaks at °2Θ			
CaO	11.6	37.5, 54.0, 32.4	ND	ND	(Oladoja & Ahmad, 2013)
$CaSO_4$	12	2 at 25.4, 31.3, 40.8	2 at 25.4, 31.3, 40.8	ND	(Kosmulski, 2009)
$Ca(OH)_2$	12.9	34.1, 18.0, 47.1	34.1, 18.0, 47.2	ND	(Zhang, 2014)
$CaCO_3$	8.5-9.5	29.2, 48.3, 43.2	29.2, 48.3, 43.3	29.3, 48.5, 47.6	(Farooq et al., 2011; Churchill et al., 2004; Somasundaran & Agar, 1967)
		FA2			
$CaCO_3$	8.5-9.5	29.3, 48.5, 47.5	29.3, 48.5, 47.5	29.3, 48.5, 47.5	(Farooq et al., 2011; Churchill et al., 2004; Somasundaran & Agar, 1968)
SiO_2	2	26.6, 20.8, 50.0	26.6, 20.8, 50.1	ND	(Alvarez-Silva et al., 2010)

pH_{PZC} = point of zero charge

ND = not detected

3.4.2 DSD analysis

The removals of lignin and COD from a TMP pressate under different experimental conditions were determined using equation 1 and the results are listed in Table 3.6. The results indicate that lignin removal was greater than COD removal for most of the conditions studied.

Table 3.6 COD and lignin removals by FA1 and FA2 treatment in the DSD experiments

Run #	X_1 Weight-based average particle size, mm		X_2 Dosage, mg/g	X_3 Time, h	X_4 Temp., K	X_5 pH	X_6 Agitation speed, rpm	COD removal, %	Lignin removal, %	COD removal, %	Lignin removal, %
	FA1	FA2						FA1	FA1	FA2	FA2
1	0.43	0.53	70	0.50	298	6.0	100	75.0	97.5	51.8	86.8
2	0.43	0.53	10	2.00	338	12.5	200	49.0	47.0	6.1	11.3
3	1.01	1.30	40	0.50	338	12.5	100	41.8	61.4	11.8	16.1
4	0.11	0.11	40	2.00	298	6.0	200	62.6	96.3	49.0	84.7
5	0.11	0.11	10	1.25	338	6.0	100	30.8	62.3	20.7	43.5
6	1.01	1.30	70	1.25	298	12.5	200	67.9	81.3	32.5	35.3
7	0.11	0.11	70	2.00	318	12.5	100	89.3	94.5	39.4	46.8
8	1.01	1.30	10	0.50	318	6.0	200	17.9	43.6	11.1	26.2
9	1.01	1.30	10	2.00	298	9.0	100	30.2	39.1	28.1	24.0
10	0.11	0.11	70	0.50	338	9.0	200	77.2	96.5	54.1	81.6
11	1.01	1.30	70	2.00	338	6.0	150	76.6	97.5	53.6	87.1
12	0.11	0.11	10	0.50	298	12.5	150	44.3	42.6	8.6	11.6
13	0.43	0.53	40	1.25	318	9.0	150	77.4	94.1	34.0	62.5

3.4.3 Modelling analysis

Forward stepwise regression analysis using Matlab was performed as described in section 3.3.5 on the results listed in Table 3.6 to develop equations 2 to 5 for predicting the COD and lignin removals from the TMP pressate.

$$y_{COD,FA1}\ (\%) = 18.7175 + 51.9131X_1 + 0.7132X_2 + 6.7927X_3 - 60.1132X_1^2 \qquad (2)$$

$$y_{COD,FA2}\ (\%) = 33.9731 - 5.8239X_1 + 0.5247X_2 + 5.0040X_3 - 2.8735X_5 \qquad (3)$$

$$y_{Lig,FA1}\ (\%) = 57.583 - 15.941X_1 + 1.9780X_2 - 2.2327X_5 - 0.0150X_2^2 \qquad (4)$$

$$y_{Lig,FA2}\ (\%) = 59.7914 - 13.5597X_1 + 2.0029X_2 - 4.5242X_5 - 0.0097X_2^2 - 0.0524X_2X_5 \qquad (5)$$

In these models, X_1 is the weight-based average particle size of the fly ash (mm), X_2 is the fly ash dosage on TMP pressate (mg/g), X_3 is the adsorption time (h), and X_5 is the pH of the adsorption treatment. The coefficients of the significant factors of the models and their p-values are listed in Table 3.7. Factors that were not considered significant based on the analysis described in section 3.3.5 were not included in Table 3.7.

Table 3.7 Coefficients and parameters of the models for removing COD and lignin from a TMP pressate by FA1 and FA2

	$y_{COD,FA1}$			$y_{COD,FA2}$	
factor	**coefficient**	**p-value**	**factor**	**coefficient**	**p-value**
β_o	18.7150	4.0E-04	β_o	33.9731	1.1E-06
X_1	51.9131	1.0E-02	X_1	-5.8239	1.3E-02
X_2	0.7132	7.6E-13	X_2	0.5247	5.2E-11
X_3	6.7927	1.5E-03	X_3	5.0040	8.5E-03
X_1^2	-60.1132	1.1E-03	X_5	-2.8735	5.9E-07
R^2_{adj}	0.92		R^2_{adj}	0.89	
RMSE	6.27		**RMSE**	5.78	
	$y_{Lig,FA1}$			$y_{Lig,FA2}$	
β_o	57.5830	3.9E-11	β_o	59.7914	4.8E-08
X_1	-15.9410	2.4E-06	X_1	-13.5597	1.0E-07
X_2	1.9780	7.2E-09	X_2	2.0029	1.4E-07
X_5	-2.2327	3.0E-06	X_5	-4.5242	1.3E-06
X_2^2	-0.0150	1.1E-05	X_2^2	-0.0097	1.8E-03
			X_2X_5	-0.0524	1.1E-03
R^2_{adj}	0.96		R^2_{adj}	0.97	
RMSE	5.06		**RMSE**	5.24	

β_o = constant term
X_1= weight-based average particle size of the fly ash in mm
X_2= fly ash dosage in mg/g TMP
X_3= adsorption time in h
X_5= pH of the adsorption treatment
R^2_{adj} = adjusted R^2
RMSE = root mean square error

3.4.4 Impact of dosage

The DSD analysis indicates that the dosage was a significant factor with respect to the COD and lignin removals by both FA1 and FA2 (Table 3.7). When the dosage was increased, it was observed that the COD and lignin removals increased, which was likely due to an increase in the total effective adsorption sites that are available. Furthermore, analysis of the models (equations 2-5) indicates that the dosage had the largest impact on the COD and lignin removals by the biomass fly ash studied here. In a previous study by Rathinam et al. (2011), it was determined that dosage was the main factor that affected the adsorption of phenol onto an activated carbon.

3.4.5 Impact of size

The DSD results indicated that a decrease in the fly ash particle size had increased the COD and lignin removals. However, the COD and lignin removals do not appear to be attributed to the micropore volume and its associated surface area, since the surface area and the micropore volume both decreased as the particle size decreased (Table 3.4). Lignin molecules in the TMP pressate may be spherical (Sjostrom, 1993) with an estimated diameter of 1.8 nm or may be cylindrical (Petridis & Smith, 2016) with an estimated diameter and length of 1.7 nm and 2.1 nm, respectively (section 8.6 in the Appendix). Therefore, lignin molecules may not diffuse into the micropores but adsorb in mesopores (Radovic, 2001) since micropores have a diameter of less than 2 nm.

In addition, the composition change in fly ash may have also contributed to the adsorption (Table 3.3). The decrease in particle size was associated with an increase in calcium minerals and a decrease in carbon (Tables 3.3 and 3.5); lignin in the TMP pressate may have been preferably adsorbed onto calcium minerals present in the fly ash. It was reported previously that lignocelluloses from prehydrolysis liquor were adsorbed onto lime (Saeed et al., 2012b) and precipitated calcium carbonate (Fatehi et al., 2013).

3.4.6 Impact of pH

The significant effect of pH adjustment on the lignin removal in a TMP pressate by fly ash adsorption may be due to electrostatic interactions of molecules in the TMP. The pKa of the phenolic hydroxyls present in TMP lignin macromolecules may be between 6.2-11.3 (Ragnar et al., 2000). Thus, phenolic hydroxyl groups on TMP lignin would have been deprotonated at pH 12.5, and protonated at acidic pH. The point of zero charge (pH_{PZC}) of calcite is 8.5-9.5 (Churchill et al., 2004; Farooq et al., 2011; Somasundaran & Agar, 1967). Calcite present on the surface of fly ash would be expected to have a net negative charge at a $pH > pH_{PZC}$ and a net positive charge at a $pH < pH_{PZC}$, and thus the number of positive charges on the surface of fly ash may have increased as the pH decreased from 12.5 to 6. Electrostatic repulsion at a $pH > pH_{PZC}$ and electrostatic attraction at a $pH < pH_{PZC}$ between lignin's hydroxyl groups and calcite would be expected. The ion-dipole interactions may have also occurred between positively charged calcite and lignin's protonated hydroxyl groups at a pH below the pH_{PZC}. As stated earlier, the biomass fly ash samples contained other crystalline structures and their corresponding pH_{PZC} are given in Table 3.5. Positive charges would be expected on the lime and anhydrite for most of the pH range, and on portlandite for the entire pH range studied in this work. Therefore, electrostatic interactions between lignin's hydroxyl groups and calcite, lime, anhydrite and portlandite present on the surface of fly ash may have aided the removal of lignin in the TMP pressate at acidic pH.

3.4.7 Impact of time

The COD in the TMP pressate represents a broad range of constituents including lignin, monomeric and oligomeric sugars and wood extractives (Zasadowski et al., 2014). These constituents have different molecular weights. Although lignin may not be able to diffuse into the micropores, other smaller compounds may diffuse into the small pores. It is well known that the diffusion of molecules into micropores is kinetic dependent, and thus time is expected to have an impact when molecules are adsorbed into micropores. Therefore, it is hypothesized that the dependence of COD to time might be due to the diffusion and adsorption of small organic materials present in a TMP pressate into the micropores of fly ash (Li et al., 2003; Pelekani & Snoeyink, 2000).

3.4.8 Impact of temperature and agitation speed

The DSD analysis in this study indicates that the temperature did not have a significant effect on the COD and lignin removals from a TMP pressate by biomass fly ash within the boundary conditions tested. In the previous study on a lignin-model adsorption process, the impact of temperature was considered negligible under similar boundary conditions (Andersson et al., 2012). Thus, the results suggest that the use of either FA1 or FA2 as an adsorbent on a TMP pressate could be carried out at any temperature between 298 K and 338 K without a significant effect on the COD or lignin removals. The DSD analysis also indicated that the agitation speed did not have a significant impact on the COD and lignin removals within the boundary conditions tested. Since, agitation is required to ensure adequate interaction of an adsorbate with the adsorbent; the results indicate that 100 rpm was sufficient for the adsorption system studied.

3.4.9 Validation of the DSD experiments

To confirm that the models can adequately predict the COD and lignin removals by biomass fly ash treatment, validation runs were conducted as described in section 3.3.6. The results of the predicted and experimental removals of COD and lignin by FA1 and FA2 are shown in Figure 3.3. The close proximity of the DSD results to ratio of one in this figure indicates that the generated models were fitted well with the results in Table 3.6. The close proximity of all of the validation results to this ratio also indicates that the generated models were able to successfully predict the COD and lignin removals on a TMP pressate by fractionated and unfractionated fly ash samples. Therefore, the models adequately predict the impact of the significant factors on the COD and lignin removals of a TMP pressate by FA1 and FA2, and hence can be used to determine the optimum conditions (section 3.3.6) within the boundary conditions studied (Table 3.1).

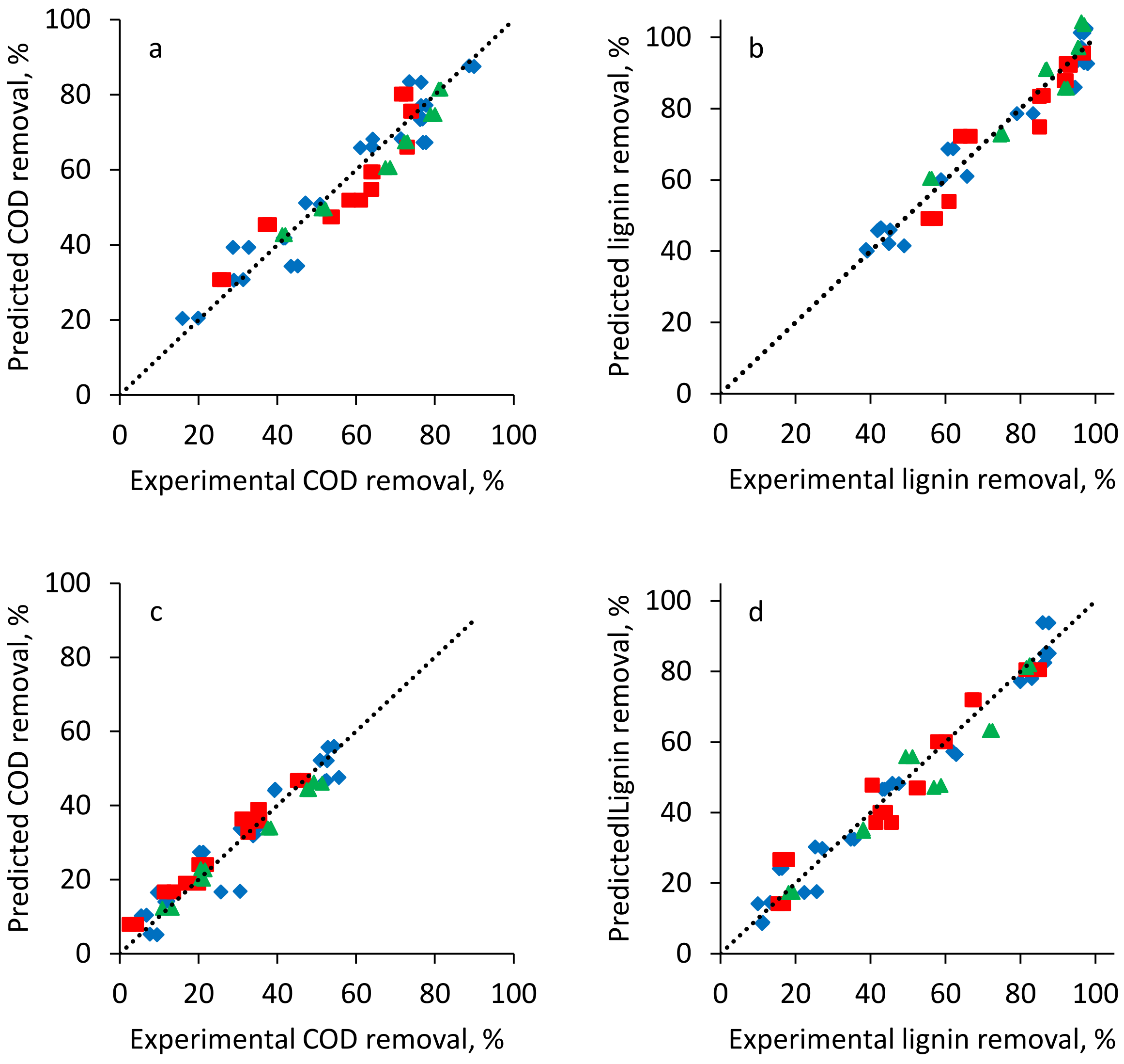

Figure 3.3 Predicted values versus experimental values for the removals of COD and lignin by FA1 and FA2. a) COD removal by FA1 b) lignin removal by FA1 c) COD removal by FA2 and d) lignin removal by FA2. The results of the DSD experiments are indicated by (◊), the validation tests for the fly ash fractions are indicated by (□), the validation tests for the unfractionated fly ash (with a particle size range of 0.037-2.00 mm) are indicated by (Δ), and 1 to 1 ratio is indicated by (…).

3.4.10 Optimal conditions for COD and lignin removals

The optimal conditions for the maximum removals of COD and lignin from a TMP pressate by FA1 and FA2 were determined under the boundary conditions tested and the results are listed in Table 3.8. The optimal conditions for COD removal by FA1 were a weight-based average particle size of 0.43 mm, a dosage of 70.0 mg/g FA/TMP pressate, and a treatment time of 2 h. The optimal conditions for COD removal by FA2 were a weight-based average particle size of 0.11 mm, a dosage of 70.0 mg/g FA/TMP pressate, a treatment time of 2 h, and an adsorption pH of 6. The predicted and experimental COD removals for FA1 were 93.4 % and 91.3 %, respectively, and for FA2 were 62.8 % and 55.3 % respectively. The optimal conditions for lignin removal by FA1 and FA2 were similar, both of which were a weight-based average particle size of 0.11 mm and an adsorption pH of 6, but FA1 required a dosage of 46.5 mg/g FA/TMP pressate, whereas FA2 required a dosage of 70.0 mg/g FA/TMP pressate. The predicted and experimental lignin removals for FA1 were 102.0 % (full removal) and 95.0 %, respectively, and for FA2 were 101.8 % (full removal) and 90.3 %, respectively.

The results in Table 3.8 indicate that 1) FA1 was able to remove significantly more COD than was FA2 and thus was a more effective adsorbent for the TMP pressate, and 2) the lignin removals by FA1 and FA2 were comparable under their respective optimal conditions. The different behavior of FA1 and FA2 may be related to the differences in their chemical compositions and structures, as explained earlier.

Table 3.8 Optimum conditions to obtain the maximum COD and lignin removals from a TMP pressate with FA1 and FA2

FA1			
Parameters for optimum COD removal	**Value**	**Parameters for optimum lignin removal**	**Value**
Weight-based average particle size	0.43 mm	Weight-based average particle size	0.11 mm
Dosage	70.0 mg/g TMP	Dosage	46.5 mg/g TMP
Time	2 hours	pH	6
Pred. COD removal	93.4 %	Pred. lignin removal	102.0 %
Exp. COD removal	91.3 %	Exp. lignin removal	95.0 %
Pred. lignin removal	87.8 %	Pred. COD removal	63.7 %
Exp. lignin removal	88.1 %	Exp. COD removal	60.2 %
FA2			
Weight-based average particle size	0.11 mm	Weight-based average particle size	0.11 mm
Dosage	70.0 mg/g TMP	Dosage	70.0 mg/g TMP
Time	2 hours	pH	6
pH	6		
Pred. COD removal	62.8 %	Pred. lignin removal	101.8 %
Exp. COD removal	55.3 %	Exp. lignin removal	90.3 %
Pred. lignin removal	101.8 %	Pred. COD removal	57.8 %
Exp. lignin removal	90.1 %	Exp. COD removal	53.6 %

Conditions not specified above were: 298 K, 100 rpm, 1 h, and the pH as influenced by the addition of the fly ash

3.5 Conclusions

The fractionation of biomass fly ash samples indicated that the carbon content, total pore volume, micropore volume, and the surface area decreased; while, the metal content, and the density increased as the particle size of the fly ash decreased. The mesopore volume was the same in all fly ash fractions. The predominant metals present in the biomass fly ash samples were calcium, sulfur, potassium, and magnesium, and the concentration of these metals was significantly higher in FA1 than in FA2. Dosage of the biomass fly ash was determined to be the most significant factor for the COD and lignin removals by FA1 and FA2micropores did not appear to contribute to the lignin removal. The lignin removal increased when the pH of the adsorption treatment was decreased, and the COD removal increased when the adsorption treatment time extended. Overall, FA1 was considered a more effective adsorbent than FA2. The optimum COD removal for FA1 was 91.3 % under the conditions of fly ash particle size of 0.43 mm, dosage of 70.0 mg/g FA/TMP pressate, and 2 h treatment. The optimal lignin removal for FA1 was 95.0 %, which was achieved with a dosage of 46.5 mg/g FA/TMP pressate, a fly ash particle size of 0.11 mm, and pH 6.

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4 Chapter 4: Isotherm analysis and the impact of various physicochemical properties of biomass fly ash

4.1 Abstract

In this study, a biomass fly ash was fractionated and ground to produce fly ash adsorbents with varying compositions, and it was determined that grinding had no significant impact on the surface area and micropore volume but a 5-65 % increase in the mesopore volume was observed. Isotherm analysis was then conducted on the lignin and COD removals from a TMP pressate by the biomass fly ash samples. It was determined that the adsorption data followed the Freundlich model, and the estimated Freundlich maximum adsorption capacities for lignin and COD were determined. The highest adsorption capacity for COD was 212 mg/g fly ash/TMP pressate under the conditions of 298 K, no pH adjustment, 100 rpm, and 24 h. Under the conditions of 298 K, pH 6, 100 rpm, and 24 h, the highest estimated Freundlich adsorption capacity for lignin was 149 mg/g fly ash/TMP pressate. The potential impact of various physicochemical properties such as the ionic strength, pH and the metal content on the adsorption capacity for lignin and COD were then evaluated.

4.2 Introduction

In the thermomechanical pulping (TMP), wood chips are first washed and then treated with steam prior to refining (Sixta, 2006). The TMP process requires a substantial amount of water and an activated sludge process is often used to treat the produced effluents, but this treatment is sensitive to toxicity and shock loading, and substances that are difficult to biodegrade can remain in the effluent (Thompson et al., 2001). Secondary treatment also requires a large area of land for operation and for landfilling the sludge that is produced in the process. Furthermore, other solid wastes, such as biomass fly ash, are produced as a residue in recovery boilers from wood residues and sludge. Canadian mills only use approximately 22 % of the fly ash for beneficial purposes such as composting, road construction, and soil conditioning, and the remainder of the ash is landfilled (Elliot & Mahmood, 2006). TMP mills are interested in reducing the load on their wastewater treatment systems and diverting solid wastes from landfills.

The most concentrated wastewater in the TMP process is the TMP pressate, which is the filtrate from the primary refiner stage (Zheng & Liao, 2014). This process water consists mostly of lignin, hemicelluloses, and some wood extractives (Zasadowski et al., 2014), and has a high chemical oxygen demand (COD) load (Sumathi & Hung, 2006; Andersson et al., 2008). It was stated previously that a combination of physicochemical and biological treatments would potentially offer a long-term solution for pulp and paper wastewater treatment operations (Pokhrel & Viraraghavan, 2004). Furthermore, the use of an adsorption treatment step was considered a suitable method for the removal of recalcitrant compounds such as lignin in pulp mill effluents (Pokhrel & Viraraghavan, 2004; Sumathi & Hung, 2006; Kamali & Khodaparast, 2015). Biomass fly ash may potentially be used as a low-cost adsorbent for treating wastewater effluents (Gupta et al., 2009; Wang & Wu, 2006), but limited research has been conducted on treating a TMP pressate with biomass fly ash.

In our previous work, lignin removal from a TMP pressate on a biomass fly ash was studied in part (Oveissi & Fatehi, 2015a). It was observed that 53 % and 68 % of the lignin was removed in a one-stage and two-stage adsorption process, respectively, under the conditions of a biomass fly ash dosage of 55 mg/g in TMP pressate, 303 K, and 3 h. In a series of studies, the adsorption of lignin in a model solution (Andersson et al., 2011) and the adsorption of lignin from a bleaching effluent from a TMP plant (Andersson et al., 2112) were studied on a biomass fly ash. In the former study, the adsorption capacity was determined to be 13-17 mg/g when the initial lignin concentration was 0.5 g/L and in the later study, the maximum adsorption capacity was estimated to be 28 mg/g. However, it is unknown whether the results in these studies could predict the adsorption capacity of a biomass fly ash on a TMP pressate. The compositions of the effluents are expected to differ in model and industrially produced samples, and lignocelluloses are modified in the bleaching process. Therefore, the results available in literature may not be reliable sources for predicting the adsorption of components of a TMP pressate on a biomass fly ash.

It is well known that the characteristics of the adsorbate may affect the performance of an adsorption process (Faust & Aly, 1998). It was reported previously that particle size reduction increased the adsorption capacity for a sorbate, which was attributed to the possible exposure to more accessible sites for adsorption, but in another study, a particle size reduction of an adsorbent had no impact on its surface area or adsorption capacity (Faust & Aly, 1998). Thus, particle size reduction may have an impact on adsorption process. In the previous chapter (Chapter 3), the particle size reduction by sieving was determined to have a significant impact on the COD and lignin removals from a TMP pressate. However, the fractionation of the fly ash yielded fly ash samples with different compositions and it is unknown what impact the fly ash composition can have on the COD and lignin removals from the TMP pressate.

The purpose of this study was to characterize the biomass fly ash and relate its properties to its adsorption performance of the components of a TMP pressate. In a series of experiments, the particle size and chemical compositions of fly ash was varied and the impact of these parameters on the adsorption capacity of fly ash was studied. Such knowledge may be helpful in optimizing a potential biomass-based fly ash adsorption treatment process on a TMP pressate. In this study, a biomass fly ash was fractionated to create five samples with differing compositions. The fly ash samples were ground and sieved to a narrow particle size range in order to improve the homogeneity of each sample as well as to eliminate any particle size variations. Furthermore, one of the fly ash fractions was also ground and sieved to yield different sized fly ash fractions of similar composition. The impact of particle size reduction on surface area and pore volume was determined by comparison of the initial and final characteristics. Isotherm analysis was then conducted on the fly ash samples using the linearized forms of the Freundlich and Langmuir models to describe the adsorption mechanism of COD and lignin in a TMP pressate on the fly ash samples under the conditions of similar particle size at different pH conditions and different particle size at similar pH conditions. The impact of ionic strength on the removal of lignin and COD by fly ash was evaluated by zeta potential analysis. The relationship of different physicochemical parameters of the fly ash samples on the calculated adsorption parameters was then evaluated.

4.3 Materials and methods

4.3.1 Materials

The biomass fly ash and the TMP pressate used in this study were obtained from a pulp mill, which is located in central Canada. The fly ash was dried overnight in an oven at 378 K prior to use and then sieved to various fractions as described in section 4.3.2. The TMP pressate was stored in a refrigerator at 277 K and the fly ash samples were stored in plastic bags at room temperature prior to use. Sodium hydroxide (98 wt. %), hydrochloric acid (37 wt. %), sulfuric acid (95 wt. %), sodium chloride and potassium chloride were purchased from Sigma Aldrich Company. The Chemical oxygen demand (COD) kit (K-7365) was obtained from CHEMetrics Inc., USA.

4.3.2 Fractionation of biomass fly ash

The fly ash was mechanically sieved based on a method previously described (Zhu et al., 2013). In this method, ASTM E11 sieves were used in conjunction with a mechanical sieve shaker (CSC Scientific, Meinzer II Sieve Shaker), and the fractionation was performed in 10 min intervals with 200 g of fly ash at a time. An illustration of the fractionation and grinding procedure used on the fly ash samples is given in Figures 4.1 and 4.2. Initially, a sample of the fly ash was prepared by sieving with mesh numbers 10 and 400, and the fly ash retained on the mesh # 400 was mixed well and labelled S_0. The fly ash fraction that was retained on mesh number 10 was discarded. Then, a small portion of the S_0 fly ash was set aside and the remainder was used to prepare fractionated and ground fly ash samples using sieves with mesh numbers of 16, 20, 40, 60, 140, 200, and 400. The fly ash fractions that were retained on the sieves with the mesh numbers of 20 and 200 were discarded. The fly ash retained on the sieves with mesh numbers of 400, 140, 60, 40, and 16, were characterized for surface area and pore volume and labelled as F_01, F_02, F_03, F_04 and F_05, and had a particle size range of 0.037-0.074 mm, 0.105-0.250 mm, 0.250-0.420 mm, 0.420-0.841 mm, and 1.19-2.00 mm, respectively. A portion of the $F_0$4 was set aside. The sieved fly ash samples, $F_0$1, $F_0$2, $F_0$3, $F_0$4, and $F_0$5, were then ground separately for 20-30 seconds using a grinder (Bel-Art SP Scienceware micro-mill). The samples were then sieved again with mesh numbers of 200 and 400, and the fly ash retained on the number 400 mesh were labelled as F1, F2, F3, F4, and F5, respectively, and all samples had a particle size range of 0.037-0.074 mm. The ground fly ash samples were then analysed for surface area, pore volume, and their carbon and metal content. The S_0 fly ash sample that was set aside was also ground and sieved prior to use as described for the fly ash samples above, yielding a fly ash sample (S_0G) with a particle size range of 0.037-0.074 mm.

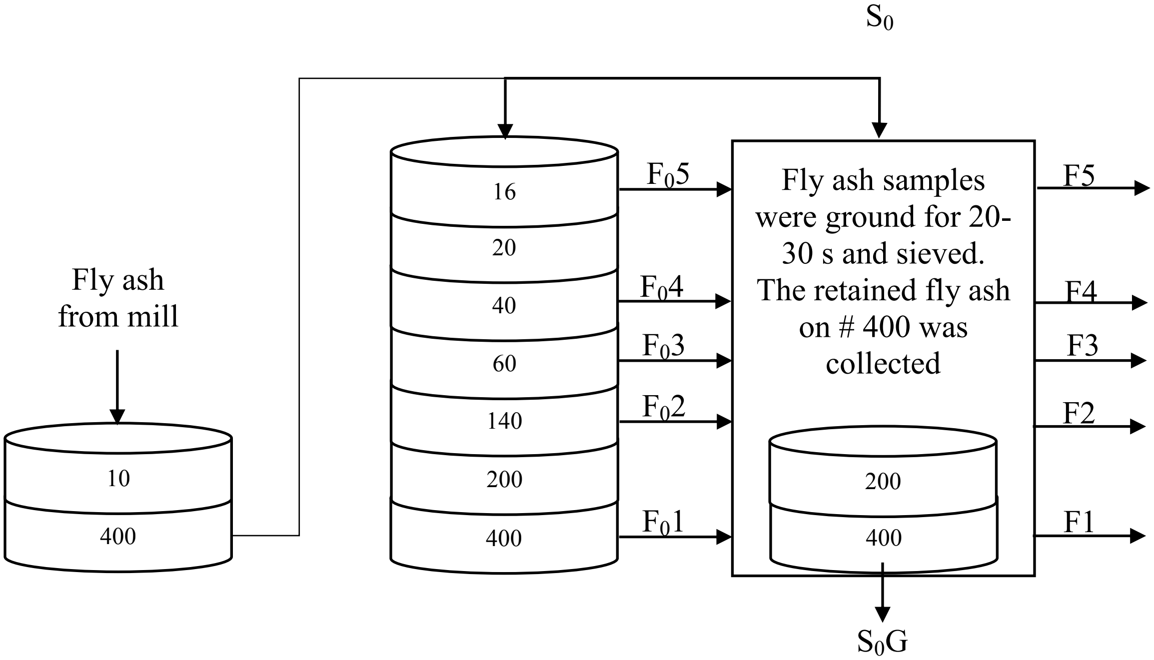


Figure 4.1 Procedure for fly ash particle size fractionation and grinding to produce the fly ash samples F1, F2, F3, F4, and F5

A portion of the $F_0$4 was then ground for 10-15 seconds using a grinder (Bel-Art SP Scienceware micro-mill). The ground $F_0$4 was then fractionated using sieves with mesh numbers of 50, 60, 100, and 140. The fly ash fractions that were retained on the sieves with mesh numbers of 50 and 100 were discarded. The fly ash retained on the sieves with mesh numbers of 140 and 60 were characterized for surface area and pore volume and labelled as F4S and F4M and had a particle size range of 0.105-0.149 mm and 0.250-0.297, respectively.

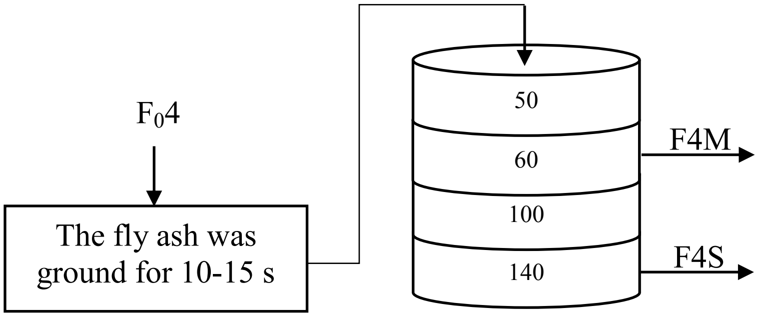


Figure 4.2 Procedure for fly ash grinding and particle size fractionation to produce the fly ash samples F4S and F4M

4.3.3 Characterization of biomass fly ash

In this set of experiments, 0.2 g of fly ash samples were analyzed by an elemental analyser (Elemental, Vario EL cube, Germany) for carbon content determination, as described previously (Fadeeva et al., 2008). The metal content of the fly ash samples was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro with CETAC ASX-510 auto Sampler. The method used was based on the EPA method 3051A. In this method, 0.2 g samples of fly ash were digested with aqua regia (i.e. a 1/3 molar ratio of nitric acid/hydrochloric acid) in a microwave (CEM Mars Xpress microwave) using an Xpress closed vessel. The digestion conditions involved a 20 min ramp time to a temperature of 448 K followed by 25 min at 448 K. After the digestion step was completed, the samples were cooled and diluted with 40 mL deionized water prior to ICP-OES analysis.

The surface area of the fly ash samples was determined with a surface area analyzer (Quantachrome NOVA-2200e) based on the method previously described by Wang et al. (2016a) and by applying Brunauer-Emmett-Teller (BET) theory. The fly ash samples were dried overnight at 403 K, and 0.05 g of the fly ash samples were degassed at 523 K for 4 h prior to analysis. The isotherms were determined between the relative pressure range of 0.01 and 0.99 at a temperature of 77 K. The BET surface area was determined by the multipoint method via fitting the data of the nitrogen adsorption isotherms data between the relative pressure of 0.05 and 0.3. The total pore volumes were determined using the NovaWin software, version 11.0. The micropore volume of the fly ash samples was calculated by fitting the data of the nitrogen adsorption isotherms between the relative pressure range of 0.06 and 0.2 to the Dubinin-Radushkevich (DR) equation (Scherdel et al., 2010; Hsieh & Teng, 2000). The mesopore volume was then estimated by subtracting the micropore volume from the total pore volume (Hsieh & Teng, 2000; Yang et al., 2010).

4.3.4 Kinetic studies

The biomass fly ash sample, S_0G with a particle size range of 0.037-0.074 mm was added to 50 g of TMP pressate in 250 mL Erlenmeyer flasks at a dosage of 15 mg/g fly ash/TMP pressate, the pH of the mixture was then adjusted to 6, and the flasks were sealed. The samples were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for various time intervals of 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 12 h, or 24 h for determining the equilibrium time. The samples were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1) after the adsorption treatment, and the filtrates were collected for COD, lignin, and pH analyses. All adsorptions tests were repeated and the average results were reported.

4.3.5 Isotherm studies

The fly ash samples F1, F2, F3, F4, F5, F4S, F4M, and F_04 were added to 50 g of TMP pressate in 250 mL Erlenmeyer flasks at various dosages ranging from 5 to 100 mg/g fly ash/TMP pressate, the pH of the mixture was adjusted to 6 or left as is, and the flasks were sealed. The samples were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 24 h. The samples were then filtered with a glass filter apparatus (Millipore) and filter paper (Whatman

No. 1), and the filtrates were collected for COD, lignin, and pH analyses. All adsorptions tests were repeated and the average results were reported.

4.3.6 COD and lignin adsorption calculations

The COD and lignin removals were determined using equation 1

$$\text{Removal \%} = \frac{C_0 - C_F}{C_0} \times 100 \tag{1}$$

The amount COD removed and lignin adsorbed per unit of mass of the fly ash at equilibrium conditions was determined using equation 2.

$$q_e = \frac{(C_0 - C_e)}{m} V \tag{2}$$

where m (g) refers to the mass of the fly ash used, V (L) is the volume of TMP pressate used, C_0 is the COD or lignin concentration in the filtrate of the control samples, and C_F and C_e refer to the COD or lignin concentration in the filtrate after the fly ash adsorption treatments. The C_0 was 2138 mg/L and 1.95 g/L for COD and lignin, respectively. The concentration of the filtrates in the control samples was used instead of the original TMP pressate concentration to account for the effect of filtration (i.e. no addition of fly ash). In this method, a portion of the TMP pressate was filtered initially with a glass filter apparatus (Millipore) and filter papers (Whatman No. 1), the filtrates were collected for COD, lignin, and pH analyses, and then randomly chosen replicate adsorption tests for the time and equilibrium studies were performed on the filtrates, and the results were compared.

4.3.7 Model analysis

The data of the isotherm experiments were analysed by regression analysis of the linearized forms of the Freundlich and Langmuir models. The Freundlich equation and the linearized form used in this study are given in equations 3 and 4 respectively,

$$q_e = K_F C_e^{1/n} \tag{3}$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{4}$$

where, K_F is the Freundlich constant ($mg^{1-(1/n)}\, L^{(1/n)}\,/g$), which is the relative adsorption capacity of the adsorbent, and n is a unitless constant that indicates the favourability of adsorption.

The maximum adsorption capacity, q_m (mg/g), was estimated using equation 5 and by performing the isotherm tests with a constant initial concentration and varying the dosage of the adsorbent (Hamdaoui & Naffrechoux, 2007).

$$q_m = K_F C_0^{1/n} \tag{5}$$

The Langmuir equation and the linearized form used in this study are given in equations 6 and 7 respectively,

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{6}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{7}$$

where, b (L/mg), is a constant that is related to the affinity between the adsorbent and the adsorbate.

4.3.8 COD and Lignin analysis

The COD analysis was carried out by the spectrophotometric method at 620 nm using a spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific), as described in the method of CHEMetrics COD kit. In this method, 2 mL samples were added to COD vials (CHEMetrics), and incubated in a reactor (CR 2200 WTW thermoreactor) for 2 h at 423 K prior to measuring the COD in the spectrophotometer. The lignin concentration was determined by the spectrophotometric method described previously (Liu et al., 2011) using a UV-Vis spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific) at 205 nm (Saeed et al., 2012a). The pH of the samples was adjusted to 7 (± 0.25) with 0.1 M NaOH or 0.1 M HCl prior to UV analysis.

4.3.9 Hydrodynamic diameter analysis

In this set of experiments, lignin was separated from the TMP pressate via acidification based on a method previous described (Oveissi & Fatehi, 2015b). Initially, the TMP pressate was centrifuged at 1000 rpm for 10 min using a Thermo Scientific Sorvall ST 16 centrifuge to remove undissolved wood particles. The filtrate was then acidified with sulfuric acid (60 wt. %) to a pH of 1.5 and the solution was then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 1 h. After acidification, the sample was centrifuged at 3000 rpm for 15 min (Thermo Scientific Sorvall ST 16 centrifuge), and the lignin precipitate was collected. The precipitate was suspended in deionized water and neutralized to pH 7. The lignin solution containing the precipitate was then dried to a constant weight in an oven at 333 K. Then, a 1 wt. % lignin solution was prepared in deionized water. The solution was then stirred overnight, and the hydrodynamic diameter of lignin was measured by a dynamic light scattering (DLS) (Brookhaven, BI2000) at a scattering angle of 90° as previously described (Wang et al., 2006).

4.3.10 Zeta potential

The zeta potential of F1 and F4 in a TMP pressate at different concentrations of sodium chloride was determined using a NanoBrook ZetaPALS potential analyzer (Brookhaven Instrument Corporation). In this method, F1 or F4 was added to 50 g of TMP pressate in 250 mL Erlenmeyer flasks at a dosage of 70 mg/g fly ash/TMP pressate and the pH of the mixture was adjusted to 6 or left as is. Then, the mixtures were adjusted to various sodium chloride concentrations ranging from 0.04 to 0.5 mol/L using a 2 mol/L sodium chloride solution, and the flasks were sealed. The samples were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 24 h. Then, 0.5 mL of the unfiltered samples were diluted in 20 mL of 1 mol/L potassium chloride solutions and the electrophoretic mobility was determined in triplicate using a NanoBrook ZetaPALS potential analyzer (Brookhaven Instrument Corporation) at 298 K, and the average results were reported. The zeta potential was then calculated by the software using the Smoluchowski model.

4.4 Results and discussion

4.4.1 Characterization of a TMP pressate

The original TMP pressate had 2.2 g/L lignin, 0.7 g/L hemicelluloses, 2912 mg/L COD, a turbidity of 637 NTU, and a pH of 6.1. Previously, a TMP pressate was reported to have 4.5 g/L of lignin, 0.7 g/L of hemicelluloses, 5311 mg/L of COD, a turbidity of 486 NTU and a pH of 5.3 (Oveissi & Fatehi, 2015a). In another study, a TMP pressate was reported to have 1.3 g/L of lignin, 0.5 g/L of other extractives, 2.6 g/L of hemicelluloses, a turbidity of 3350 NTU and a pH of 3.5 (Zasadowski et al., 2014). The results suggest that the TMP pressate used in this study represents a medium strength TMP wastewater when compared with TMP pressates previously studied. Furthermore, the hydrodynamic diameter of the lignin present in the TMP pressate was determined to be 8.5 nm. In another study, the lignin of a prehydrolysis liquor was determined to have a hydrodynamic diameter of 2.1 nm (Oveissi & Fatehi, 2015b).

Elemental components of the biomass fly ash samples F1, F2, F3, F4, and F5 are given in Table 4.1 and it was assumed that the original samples $F_0$1, $F_0$2, $F_0$3, $F_0$4 and $F_0$5, had the same compositions, respectively. Overall, it was observed that the carbon content decreased and the metal content increased as the particle size of the fly ash decreased. Similar results were reported previously for a biomass fly ash (Giron et al., 2013).

Table 4.1 Elemental components of ground F1, F2, F3, F4, and F5

Element	**F1**	**F2**	**F3**	**F4**	**F5**
			Wt. %		
Carbon	27.14	37.19	42.37	75.04	82.65
Aluminum	0.99	1.43	0.72	0.94	0.11
Barium	0.15	0.15	0.13	0.03	0.05
Calcium	19.68	15.42	16.57	2.76	3.40
Iron	0.63	1.08	0.48	0.76	0.06
Potassium	4.03	3.33	3.70	1.12	0.77
Magnesium	1.54	1.50	1.32	0.40	0.27
Manganese	0.81	0.67	0.74	0.13	0.15
Sodium	0.96	0.65	0.66	0.31	0.15
Zinc	0.20	0.16	0.18	0.02	0.01
Other	43.88	38.43	33.13	18.49	12.38

In Table 4.2, the elemental components of the biomass fly ash samples F4, F4S, F4M, and $F_0$4, are listed. The results confirm that the fly ash samples F4, F4S, F4M, and $F_0$4, all had a similar chemical composition, but they had slightly varied calcium content.

Table 4.2 Elemental components of ground F4, F4S, F4M, and F04

Element	**F4**	**F4S**	**F4M**	**$F_0$4**
	Particle size range, mm			
	0.037-0.074	**0.105-0.149**	**0.250-0.297**	**0.420-0.841**
	Wt. %			
Carbon	75.04	73.11	72.00	73.16
Aluminum	0.94	1.19	0.91	1.09
Barium	0.03	0.03	0.03	0.04
Calcium	2.76	2.53	2.54	3.36

Iron	0.76	0.92	0.68	0.81
Potassium	1.12	1.00	0.93	1.11
Magnesium	0.40	0.50	0.46	0.51
Manganese	0.13	0.11	0.11	0.15
Sodium	0.31	0.45	0.34	0.41
Zinc	0.02	0.02	0.01	0.02
Other	18.49	20.15	20.15	19.35

4.4.2 Characteristics of biomass fly ash

The surface area, and pore volumes of the fractionated biomass fly ash samples of F_01, F_02, F_03, F_04 and F_05, as well as the ground biomass fly ash samples of F1, F2, F3, F4, F5, F4S, and F4M was determined and the results are given in Table 4.3. The surface area ranged from 105.0 m^2/g to 471.9 m^2/g, the total pore volume ranged from 0.077 cm^3/g to 0.287 cm^3/g, the micropore volume ranged from 0.053 cm^3/g to 0.245 cm^3/g, and the mesopore volume ranged from 0.024 cm^3/g to 0.046 cm^3/g for the samples. For the fly ash samples F_01 through F_05 and F1 through F5, the surface area, total pore volume, and micropore volume increased as the particles size increased; the surface areas and micropore volumes of the samples insignificantly changed after grinding. The mesopore volumes of fly ash samples were similar for F_01 through F_05 (~0.031 cm^3/g), and for samples of F1 through F5 (~0.042 cm^3/g). The results indicated that grinding of fly ash samples increased the mesopore volume by approximately 5-65 %, which increased the total pore volume of the ground fly ash samples by 0-22 % (Table 4.2). The results in Tables 4.1 and 4.3 also indicate that, as the carbon content increased, the surface area and the micropore volumes increased. As the carbon content of fly ash originated from unburned biomass, the increase in the carbon content was associated with the increase in the surface area and micropore volume as biomass is a porous material. Similar results were reported previously (Kao et al., 2000; Wang et al., 2005).

It was observable that the surface areas, total pore volumes, and the micropore volumes of F4, F4S, F4M, and F_04 varied. However, no correlation between the morphological properties of these samples was observed and their composition was relatively constant (Table 4.2). The mesopore volumes for of F4, F4S, F4M, and F_04 were similar (~0.039 cm^3/g).

Table 4.3 Surface area, and the total pore, micropore, and mesopore volumes of the fractionated biomass fly ash samples

Parameter	**F_01**	**F_02**	**F_03**	**F_04**	**F_05**
	Particle size range, mm				
	0.037-0.074	**0.105-0.250**	**0.250-0.420**	**0.420-0.841**	**1.19-2.00**
Surface area, m^2/g	105.0	150.0	193.0	387.0	465.6
V_{total}, cm^3/g	0.077	0.106	0.126	0.240	0.269
V_{micro}, cm^3/g	0.053	0.074	0.093	0.203	0.238
V_{meso}, cm^3/g	0.024	0.032	0.033	0.037	0.031
	F1	**F2**	**F3**	**F4**	**F5**
	Particle size range, mm				
	0.037-0.074	**0.037-0.074**	**0.037-0.074**	**0.037-0.074**	**0.037-0.074**
Surface area, m^2/g	109.0	144.9	189.8	393.4	471.9
V_{total}, cm^3/g	0.094	0.118	0.139	0.239	0.287
V_{micro}, cm^3/g	0.054	0.072	0.095	0.200	0.245
V_{meso}, cm^3/g	0.040	0.046	0.044	0.039	0.042
	F4	**F4S**	**F4M**	**F_04**	
	Particle size range, mm				
	0.037-0.074	**0.105-0.149**	**0.250-0.297**	**0.420-0.841**	
Surface area, m^2/g	393.4	318.4	440.9	387.0	
V_{total}, cm^3/g	0.239	0.203	0.268	0.240	
V_{micro}, cm^3/g	0.200	0.164	0.228	0.203	
V_{meso}, cm^3/g	0.039	0.039	0.040	0.037	

V_{total} = total pore volume

V_{micro} = micropore volume determined by Dubinin-Radsukevich analysis

V_{meso} = mesopore volume (total pore volume - micropore volume)

4.4.3 Determination of the equilibrium time

Figure 4.3 shows the equilibrium time for lignin adsorption and COD removal from a TMP pressate by S_0G. The equilibrium time for lignin adsorption was attained at approximately 6 h and the amount of lignin adsorbed from a TMP pressate on S_0G was 89.1 mg/g. In the study by Andersson et al. (2012), the equilibrium time for adsorption of lignin on a biomass fly ash was reported to be 6 h, and thus the results given here are consistent with the literature. The equilibrium time for the COD removal was reached at approximately 2 h and the adsorption of components contributing to COD on S_0G was 74.1 mg/g under the conditions studied. The results also indicate that approximately 89 % of the lignin and COD removals occurred within 1 h of the adsorption treatment.

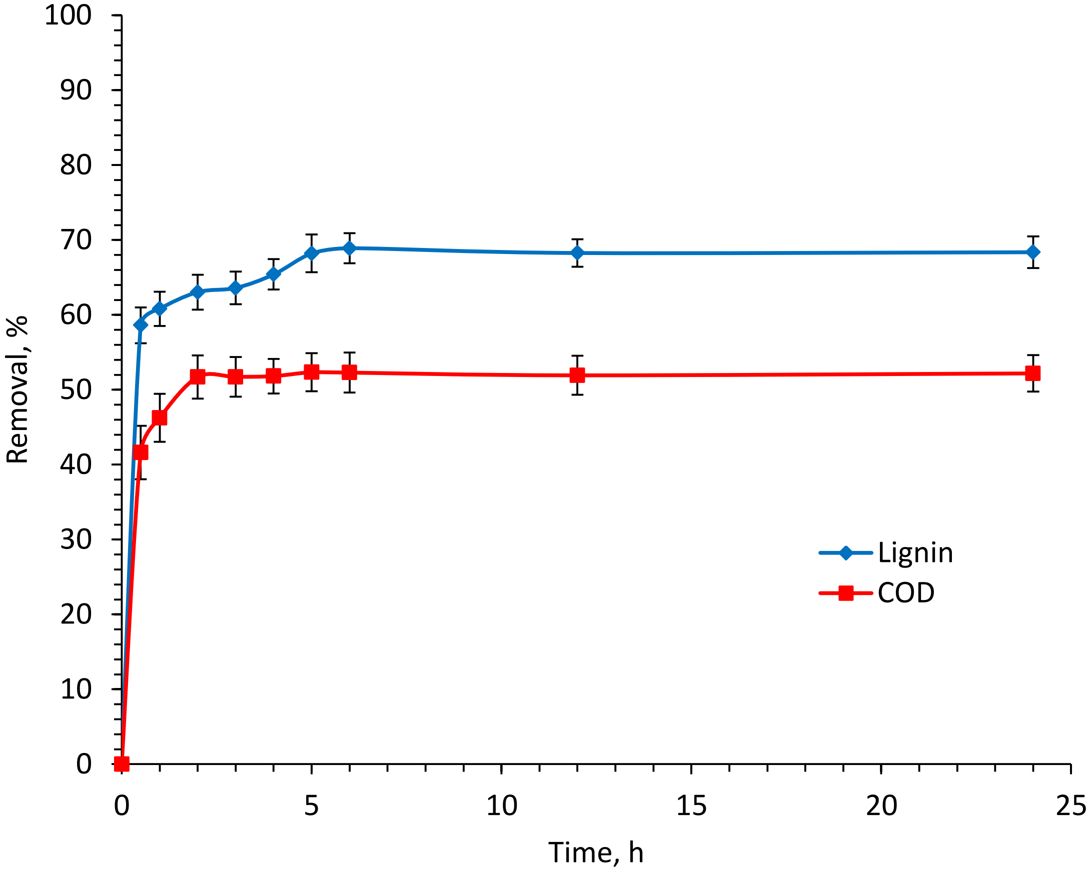


Figure 4.3 Removals of lignin and COD from a TMP pressate by S0G as a function of adsorption time. The adsorption conditions were 15 mg/g fly ash/TMP pressate; pH of 6; 100 rpm agitation speed; and 298 K. The fly ash samples had a particle size range of 0.037-0.074 mm.

It was assumed that the equilibrium time for S_0G would be representative of the individual fly ash samples. All biomass fly ash samples studied here were obtained originally from S_0 and the potential impact of grinding on the equilibrium time may be representative by S_0G. However, the individual fly ash samples may reach equilibrium conditions at different times. To ensure that the isotherm studies were conducted under equilibrium conditions, an equilibrium time of 24 h was used in this study for all isotherm tests. In one study on the removal of phenolic and lignin compounds from a bleached Kraft mill by fly ash, the equilibrium time was observed to occur after 1 h and isotherm studies were conducted for 24 h (Ugurlu et al., 2005). Furthermore, the results in Figure 4.3 indicates that the equilibrium conditions were maintained at 24 h, and thus isotherm tests were assumed to be conducted under equilibrium conditions.

4.4.4 Isotherm analysis

The analysis of the isotherms was conducted using the Freundlich and Langmuir models as they are frequently used and the former is often applied in heterogonous systems (Foo & Hameed, 2010). The data of the lignin and COD removals from a TMP pressate onto eight biomass fly ash samples, F1, F2, F3, F4, F5, F4S, F4M, and F_04, were analyzed by regression analysis to fit the linearized equations of the isotherm models. The results of the experimentally determined Freundlich and Langmuir parameters for F1, F2, F3, F4, and F5 at pH 6 and without pH adjustment are given in Tables 4.4 and 4.5, respectively, and for F4, F4S, F4M, and F_04 without pH adjustment are given in Table 4.6. The linear Freundlich equation yielded R^2 values from 0.868 to 0.993 for lignin adsorption and R^2 values from 0.964 to 0.995 for COD removal. The linear Langmuir equation yielded R^2 values from 0.175 to 0.985 for lignin adsorption and R^2 values from 0.121 to 0.786 for COD removal. Overall, the results indicate that the linear Freundlich equation best described all lignin and COD adsorption systems except lignin adsorption to F4 and F4S without pH adjustment, which were best described by the linear Langmuir equation. However, R^2 values for lignin adsorption by F1, F2, F3, and F5 without pH adjustment were < 0.95, and thus the Freundlich model may not adequately describe the experimental data under the conditions studied.

Table 4.4 Parameters of the Freundlich and Langmuir isotherms for the removals of lignin and COD in a TMP pressate by F1, F2, F3, F4, and F5 at pH 6

Parameter	F1	F2	F3	F4	F5
			Lignin		
Freundlich					
n	2.02	1.92	1.93	1.72	1.67
K_F, $mg^{1-(1/n)}\ L^{(1/n)}/g$	3.49	2.77	2.83	1.31	1.34
q_m , mg/g	149	142	143	106	125
R^2	0.987	0.979	0.993	0.986	0.981
Langmuir					
b, L/mg	2.29E-03	1.92E-03	2.00E-03	1.09E-03	1.69E-03
q_m , mg/g	161	159	157	143	132
R^2	0.918	0.916	0.939	0.922	0.906
			COD		
Freundlich					
n	1.36	1.23	1.23	1.10	1.20
K_F, $mg^{1-(1/n)}\ L^{(1/n)}/g$	0.57	0.33	0.41	0.15	0.12
q_m , mg/g	161	168	204	156	70
R^2	0.990	0.991	0.988	0.995	0.964
Langmuir					
b, L/mg	4.67E-04	3.03E-04	3.25E-04	1.25E-04	1.80E-04
q_m , mg/g	300	399	464	711	248
R^2	0.786	0.768	0.665	0.617	0.318

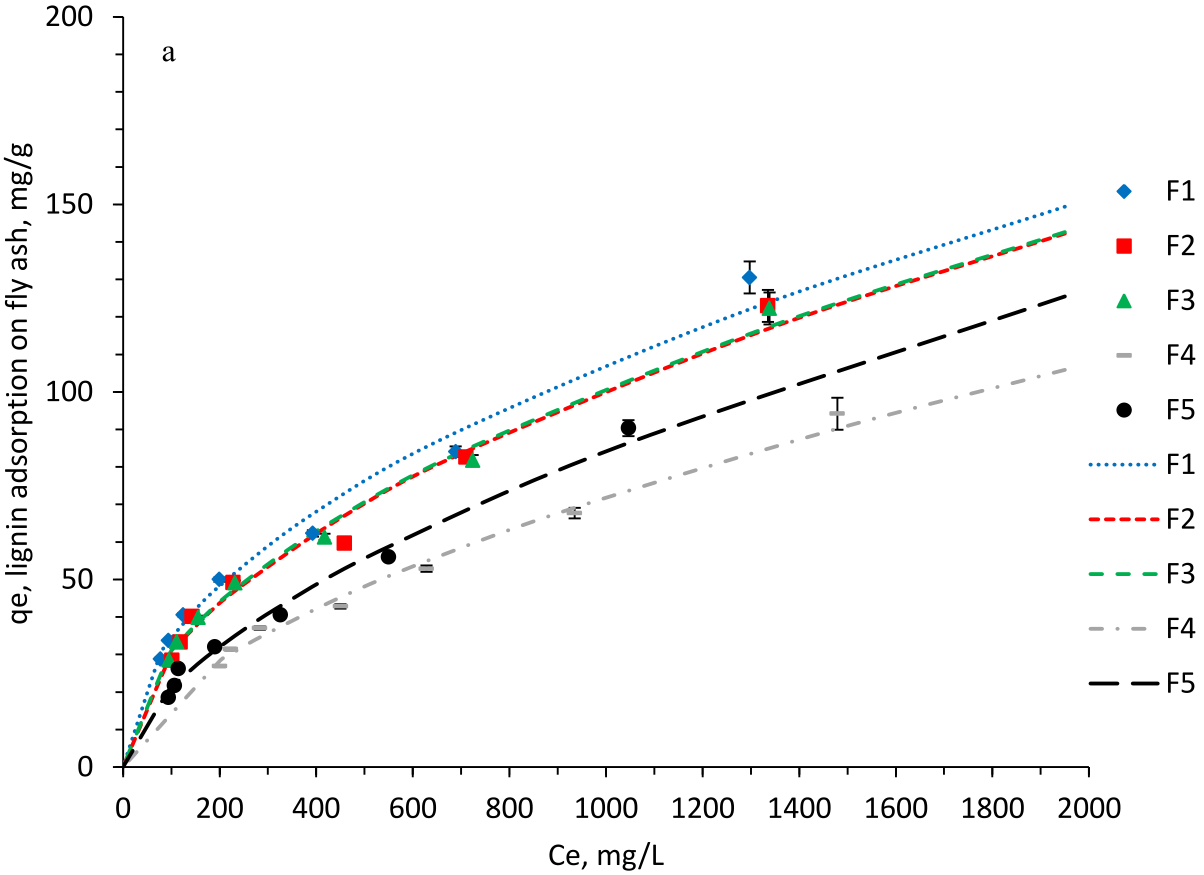
Table 4.5 Parameters of the Freundlich and Langmuir isotherms for the removals of lignin and COD in a TMP pressate by F1, F2, F3, F4, and F5 without pH adjustment

Parameter	F1	F2	F3	F4	F5
			Lignin		
Freundlich					
n	1.35	1.54	1.82	1.66	1.14
K_F, $mg^{1-(1/n)}$ $L^{(1/n)}$/g	0.62	1.18	2.86	2.82	0.53
q_m, mg/g	169	164	185	270	470
R^2	0.868	0.907	0.935	0.951	0.946
Langmuir					
b, L/mg	4.04E-04	7.40E-04	1.74E-03	2.47E-03	7.25E-04
q_m, mg/g	376	266	211	233	492
R^2	0.175	0.418	0.649	0.985	0.372
			COD		
Freundlich					
n	1.31	1.12	1.19	1.04	1.19
K_F, $mg^{1-(1/n)}$ $L^{(1/n)}$/g	0.51	0.21	0.35	0.11	0.13
q_m, mg/g	180	194	212	170	79
R^2	0.983	0.992	0.984	0.986	0.977
Langmuir					
b, L/mg	4.05E-04	1.42E-04	3.00E-04	6.49E-05	2.01E-04
q_m, mg/g	363	806	494	1347	255
R^2	0.634	0.419	0.640	0.170	0.493

In Figures 4.4 and 4.5, the experimental results for F1, F2, F3, F4, and F5 at pH 6 and without pH adjustment, are compared with the predicted isotherm using the calculated parameters given in Tables 4.4 and 4.5, respectively. Figure 4.6 compares the experimental results for F4, F4S, F4M, and $F_0$4 without pH adjustment, with the predicted isotherms using the calculated parameters given in Table 4.6. It is observable that the Freundlich model provided a better fit to the experimental data for COD removal under all conditions studied and for lignin adsorption under most conditions studied. However, when comparing the results in Figures 4.5a and 4.5b it is observable that neither model provided a good fit to the experimental data for F1, F2 and F3 with respect to lignin adsorption without pH adjustment. Furthermore, when comparing the results in Figures 4.5a and 4.5b (also presented in Figures 4.6a and 4.6b), it is observable that the Langmuir model provided a better fit to the experimental data for lignin adsorption onto F4 without pH adjustment. Nevertheless, the Freundlich model does appear to provide a reasonable fit to the experimental data for lignin adsorption onto F4 when the pH was not adjusted.

Table 4.6 Parameters of the Freundlich and Langmuir isotherms for the removals of lignin and COD in a TMP pressate by F4, F4S, F4M, and F04

Parameter	**F4**	**F4S**	**F4M**	**F_04**
	Particle size range, mm			
	0.037-0.074	**0.105-0.149**	**0.250-0.297**	**0.420-0.841**
	Lignin			
Freundlich				
n	1.66	1.98	2.15	1.43
K_F, $mg^{1-(1/n)} L^{(1/n)}/g$	2.82	3.80	3.68	1.15
q_m, mg/g	270	175	124	230
R^2	0.951	0.964	0.974	0.969
Langmuir				
b, L/mg	2.47E-03	2.94E-03	2.37E-03	1.64E-03
q_m, mg/g	233	165	136	204
R^2	0.985	0.975	0.923	0.897
	COD			
Freundlich				
n	1.04	1.04	1.09	1.14
K_F, $mg^{1-(1/n)} L^{(1/n)}/g$	0.11	0.07	0.06	0.12
q_m, mg/g	170	116	64	103
R^2	0.986	0.994	0.969	0.985
Langmuir				
b, L/mg	6.49E-05	4.60E-05	5.80E-05	1.60E-04
q_m, mg/g	1347	1272	580	387
R^2	0.170	0.254	0.121	0.401


a
qe, lignin adsorption on fly ash, mg/g
Ce, mg/L
0
50
100
150
200
0
200
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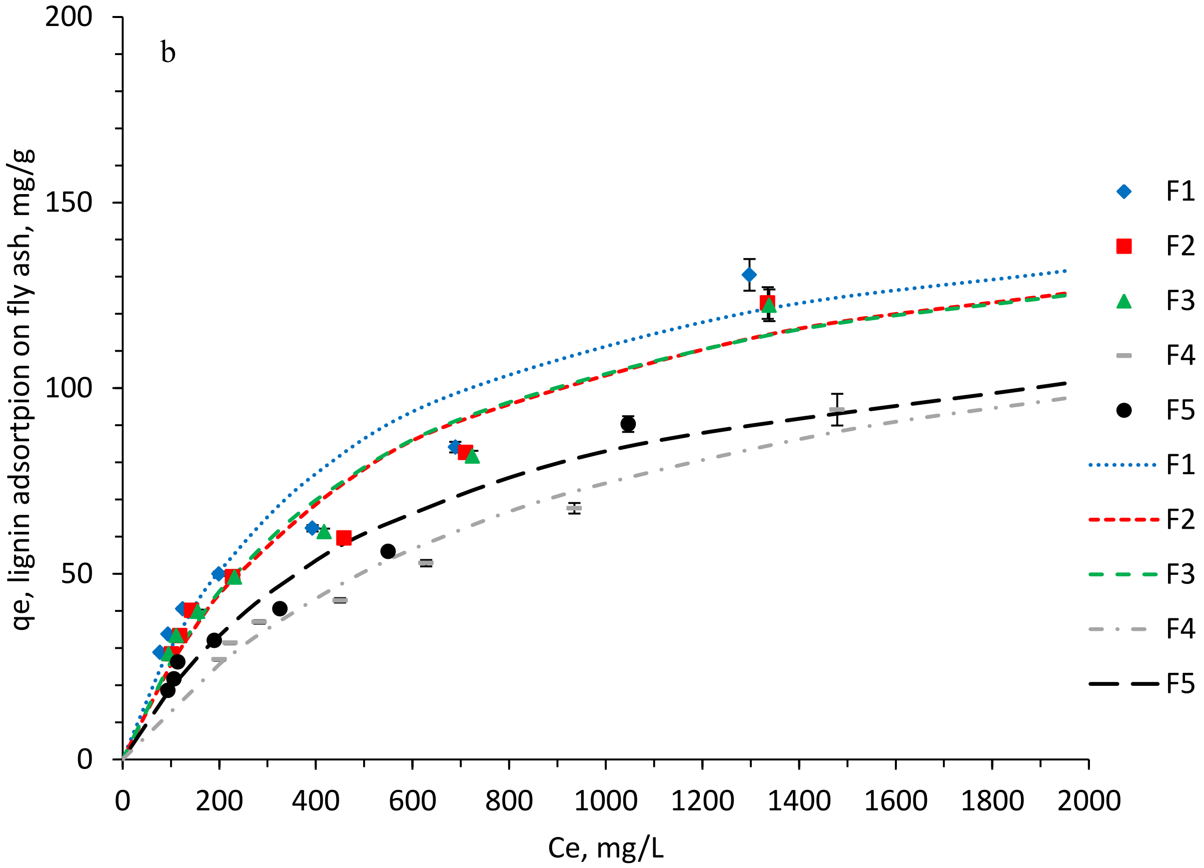
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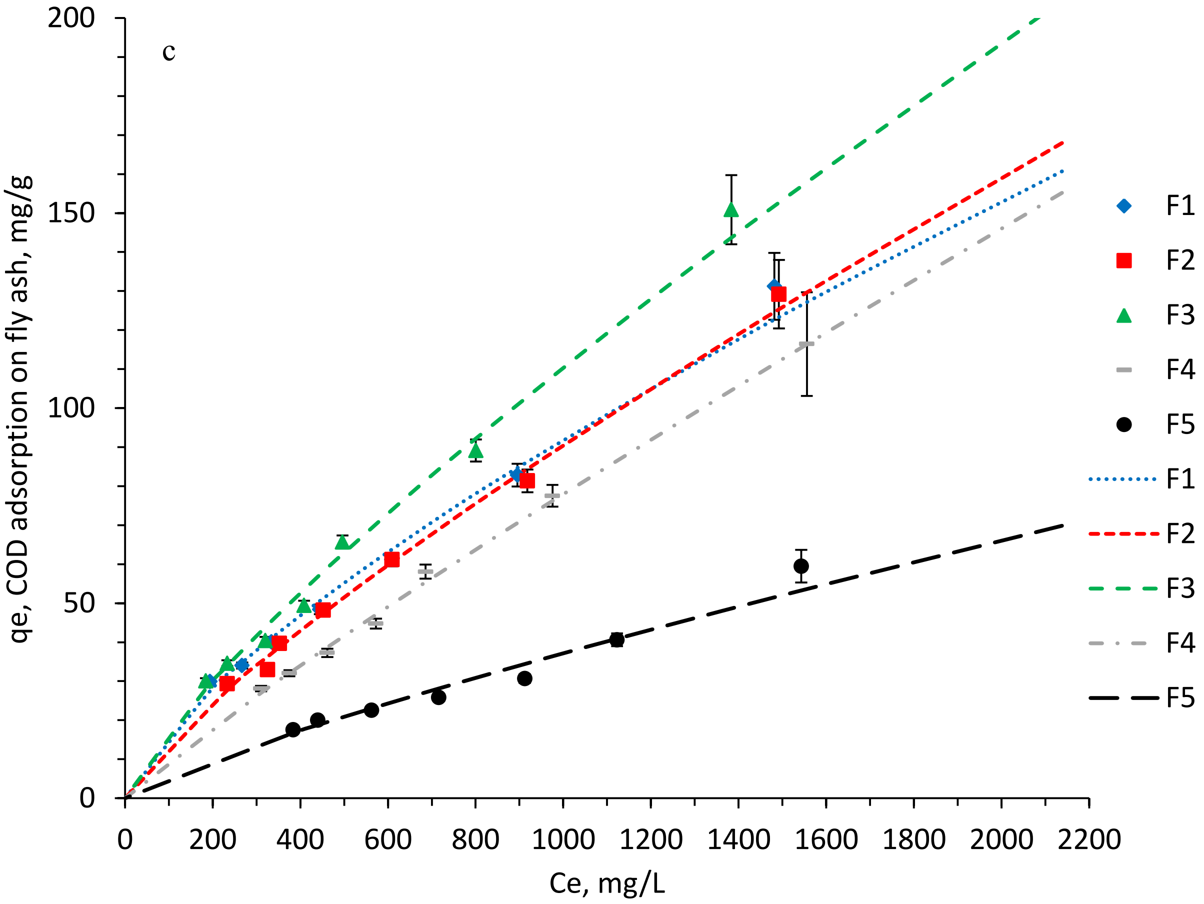
c
qe, COD adsorption on fly ash, mg/g
Ce, mg/L
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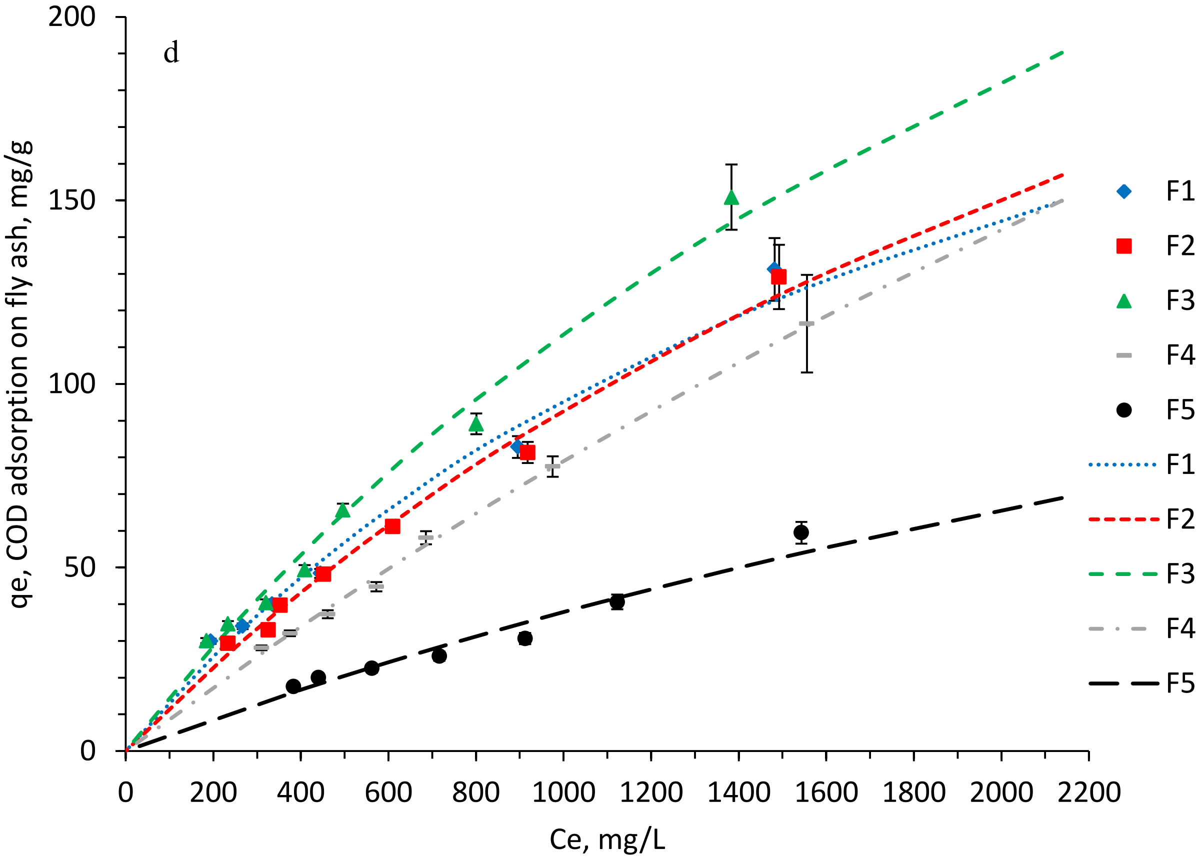
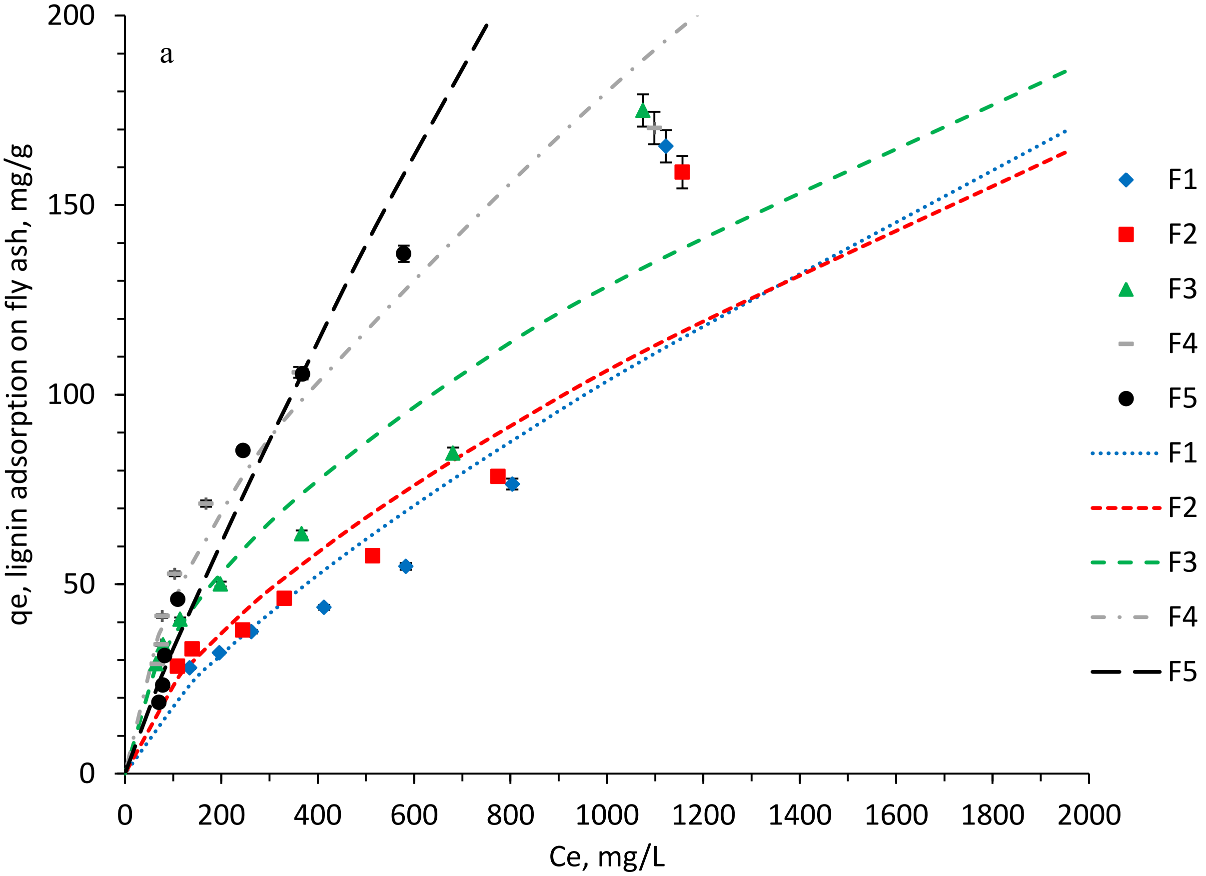


Figure 4.4 Comparison of experimental and model isotherms of lignin adsorption and COD removal by F1, F2, F3, F4, and F5 at pH 6. a) Lignin adsorption, Freundlich model b) lignin adsorption, Langmuir model c) COD removal, Freundlich model d) COD removal, Langmuir model. The markers (◊, □, Δ, −, ○) indicate the experimental data points and the dashed lines indicate the predicted isotherms according to the specified model used.

Overall, the lignin adsorption from a TMP pressate by different biomass fly ash fractions appears to follow the Freundlich isotherm, but when the pH was not adjusted, the results suggest there was a negative impact on the fit to the experimental data for F1, F2 and F3. Furthermore, the results clearly indicate that the COD removals from a TMP pressate by all fly ash samples studied follow the Freundlich isotherm under all pH conditions studied. Thus, the removal of COD from a TMP pressate by biomass fly ash does not appear to be limited to monolayer under the conditions studied. Furthermore, since the n values are greater than one, the adsorption of COD from a TMP pressate is favorable (Tables 4.4 to 4.6).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qe, lignin adsorption on fly ash, mg/g
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Ce, mg/L
0
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F1
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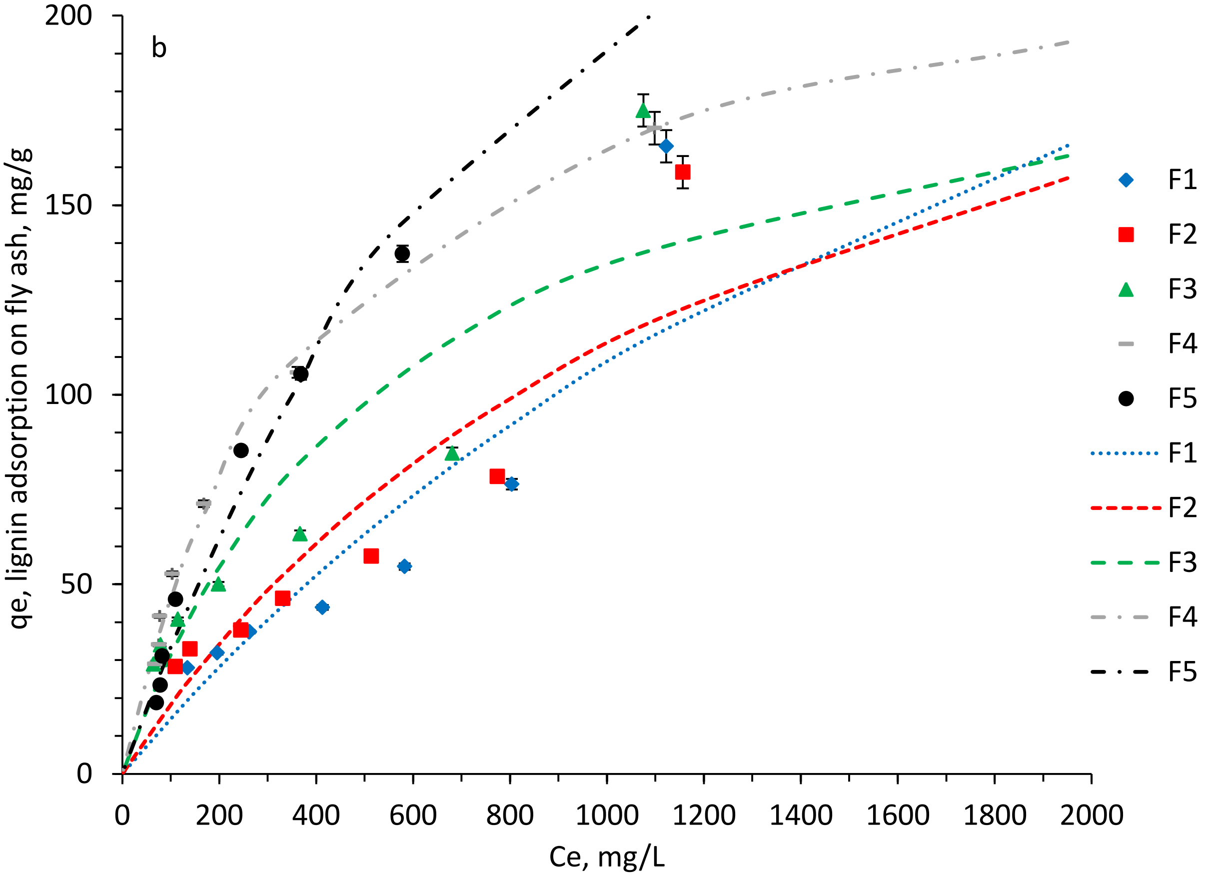
F5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qe, lignin adsorption on fly ash, mg/g
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Ce, mg/L
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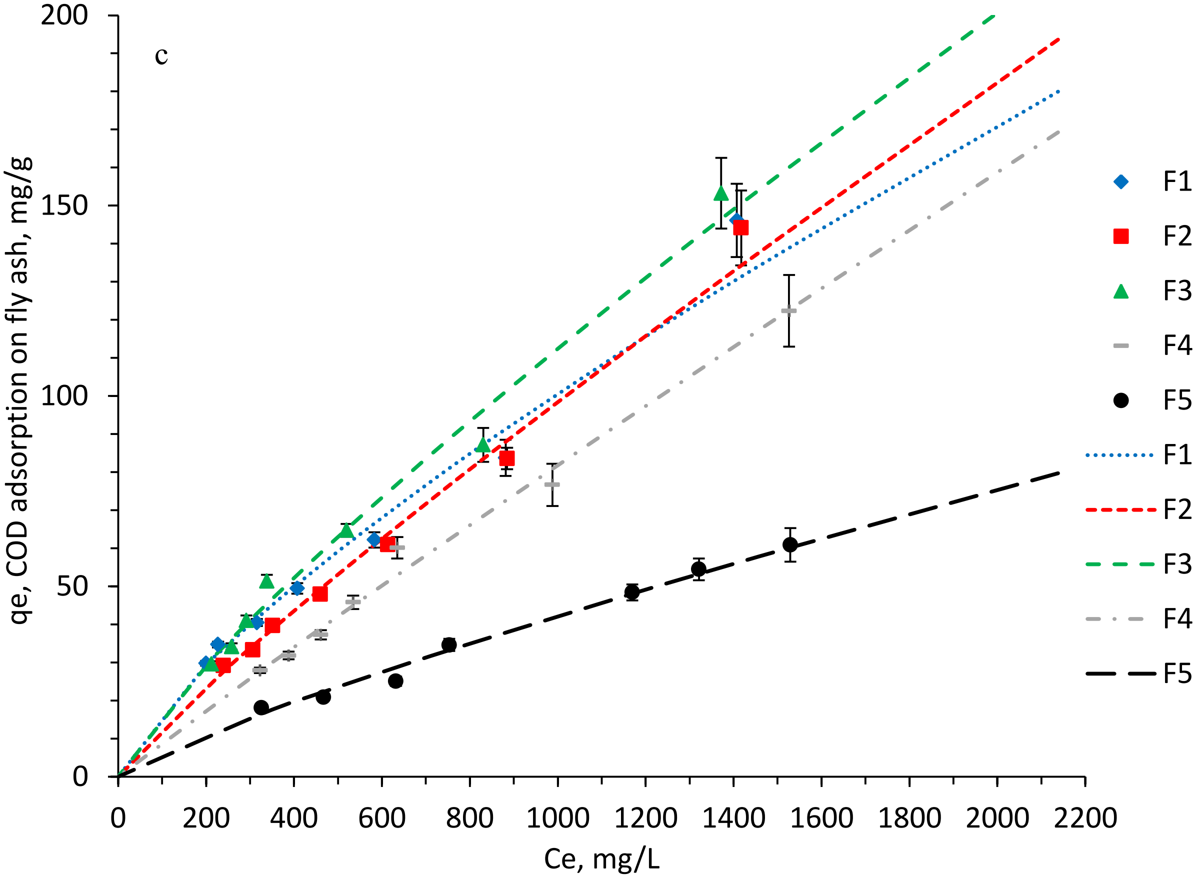
c
qe, COD adsorption on fly ash, mg/g
Ce, mg/L
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0
200
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1000
1200
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1600
1800
2000
2200
F1
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F5
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F4
F5

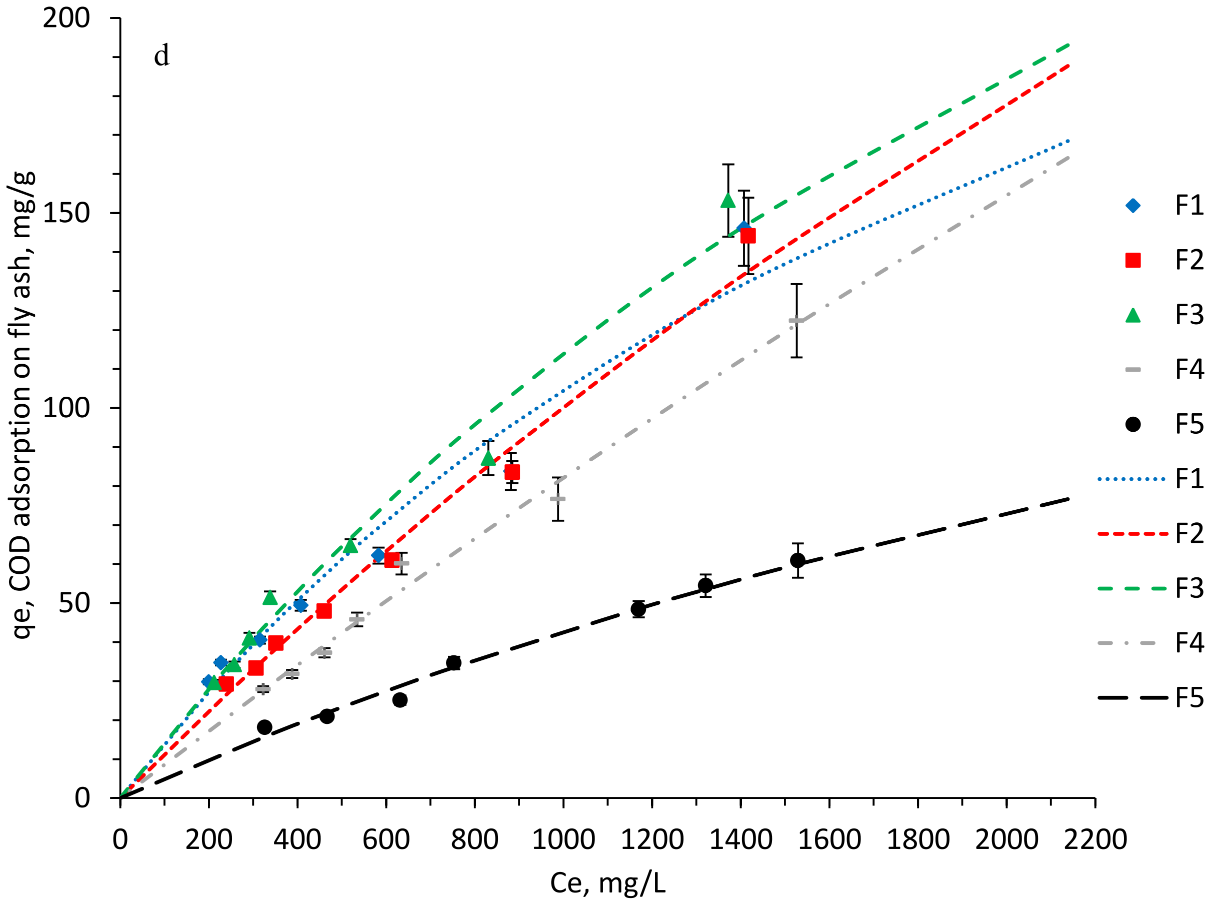
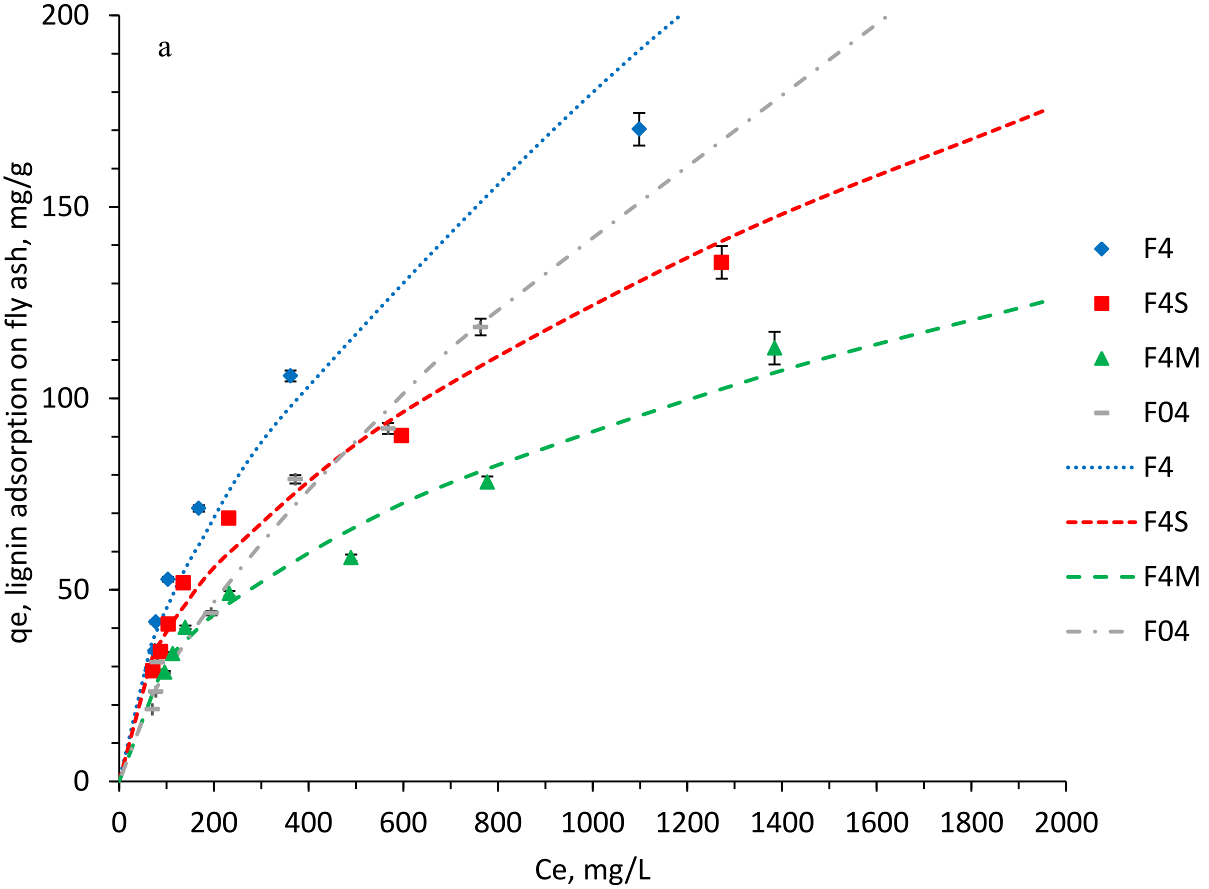


Figure 4.5 Comparison of experimental and model isotherms of lignin adsorption and COD removal by F1, F2, F3, F4, and F5 without pH adjustment. a) Lignin adsorption, Freundlich model b) lignin adsorption, Langmuir model c) COD removal, Freundlich model d) COD removal, Langmuir model. The markers (◊, □, Δ, −, ○) indicate the experimental data points and the dashed lines indicate the predicted isotherms according to the specified model used.

In the study by Andersson et al. (2012), the adsorption of lignin from a TMP bleaching effluent by a biomass fly ash was reported to fit the Freundlich isotherm best and no pH adjustment was reported. Furthermore, in the previous chapter (Chapter 3), the results indicated that pH had a significant effect on the adsorption of lignin, but not on the removal of COD, from a TMP pressate by the same fly ash used to prepare the fractionated samples studied here. The generated results in Tables 4.4 and 4.5 also indicate that the pH should be fixed for lignin removal and that pH adjustment appears to be less important for COD removal.


a
qe, lignin adsorption on fly ash, mg/g
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Ce, mg/L
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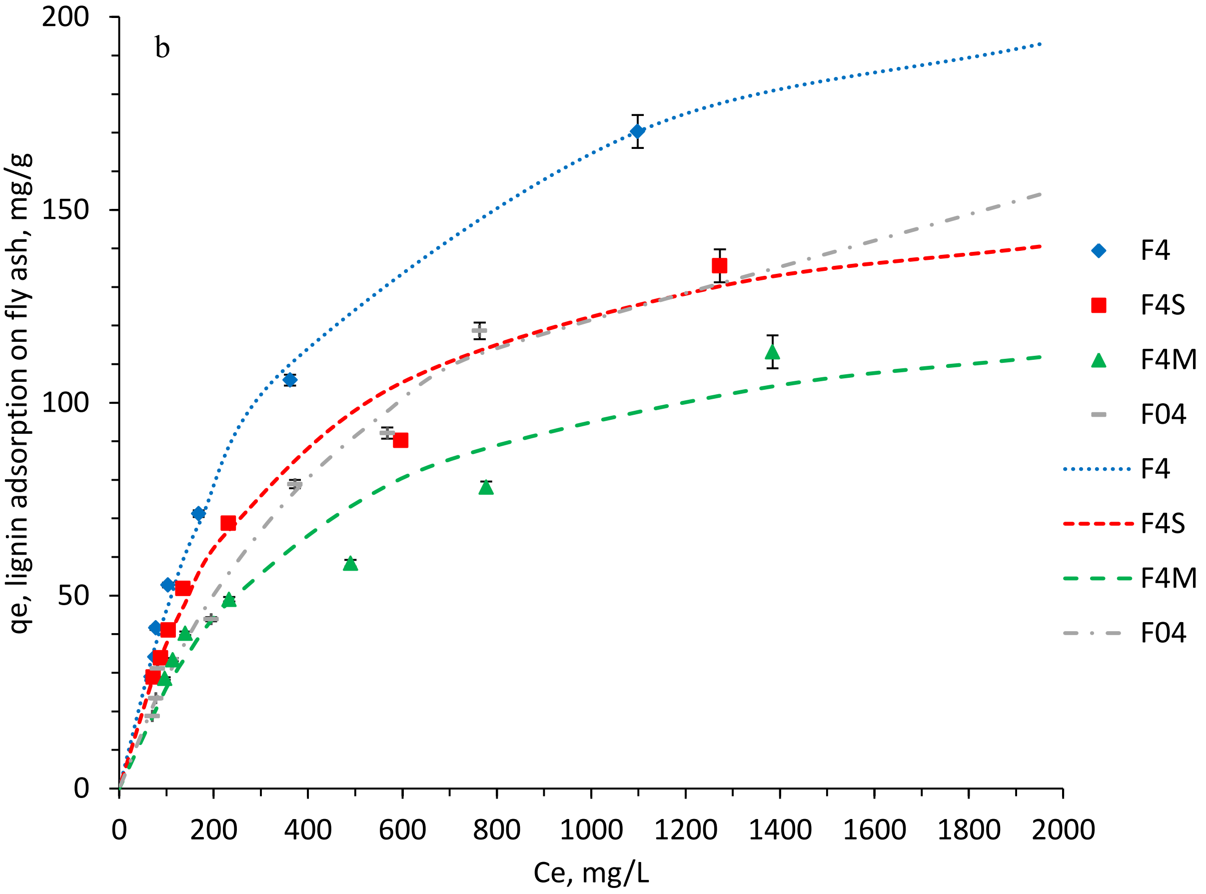
b
qe, lignin adsorption on fly ash, mg/g
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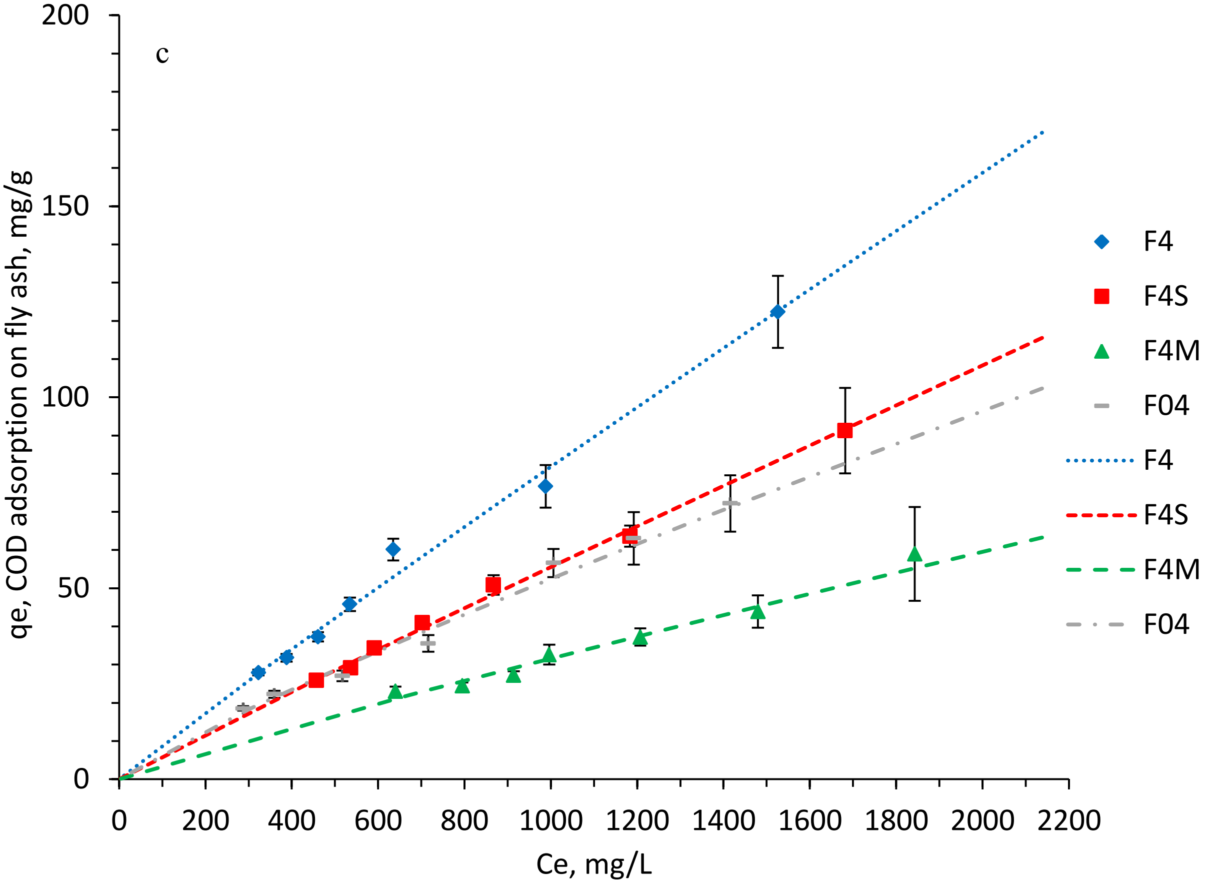
c
qe, COD adsorption on fly ash, mg/g
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Ce, mg/L
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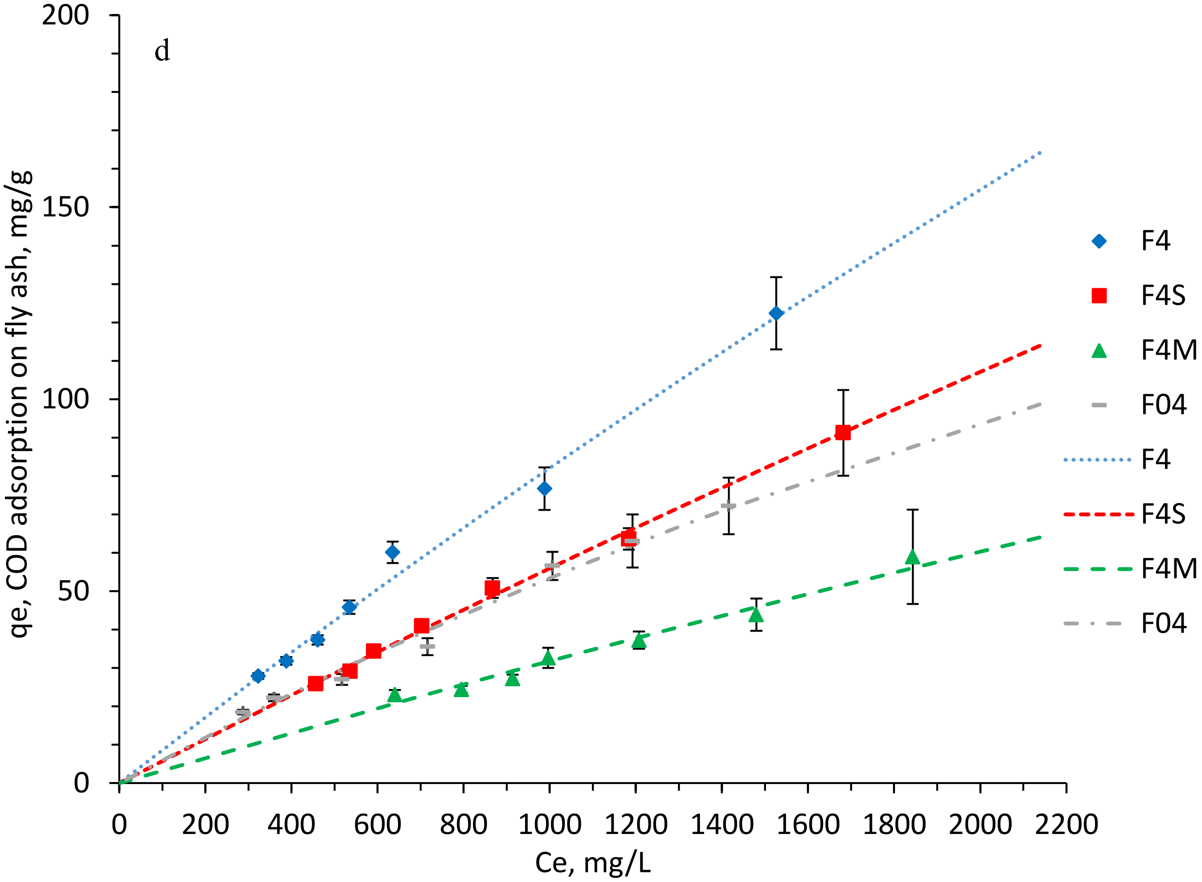

Figure 4.6 Comparison of experimental and model isotherms of lignin adsorption and COD removal by F4, F4S, F4M, and F04 without pH adjustment. a) Lignin adsorption, Freundlich model b) lignin adsorption, Langmuir model c) COD removal, Freundlich model d) COD removal, Langmuir model. The markers (◊, □, Δ, −) indicate the experimental data points and the dashed lines indicate the predicted isotherms according to the specified model used.

4.4.5 Impact of ionic strength

The addition of biomass fly ash to the TMP pressate increased the pH of the solution. For a fly ash dosage of 70 mg/g fly ash/TMP pressate, the pH of the resulting mixture for F1, F2, F3, F4, and F5 was 12.7, 12.6, 12.5, 9.8, and 9.9, respectively. Therefore, significantly different dosages of hydrochloric acid were required to adjust the pH of the systems to 6. For a fly ash dosage of 70 mg/g fly ash/TMP pressate, when 50 g of TMP pressate was used, the final hydrochloride concentration of the mixture to yield a solution pH of 6 was approximately 0.42 mol/L for F1 and 0.04 mol/L for F4. Thus, the pH adjustment step, via the addition of hydrochloric acid, was expected to increase the ionic strength of the solutions to significantly different extents.

The ionic strength of the solution may impact the removal of lignin and COD by fly ash. An increase in the ionic strength screens the surface charge of an adsorbent, thereby reducing electrostatic repulsive or attractive interactions (Moreno-Castilla, 2004). In previous studies, the addition of sodium chloride increased the removal of humic acid on a chitosan modified zeolite (Xie, et al., 2013); phenol on an activated clay (Wang et al., 2016b); calcium lignosulfonate on a coal fly ash (Li et al., 2012); various phenols on activated carbon (Anirudhan et al., 2009). In other study, the addition of sodium chloride decreased the removal of methylene blue on a zeolite (Sun et al., 2010). Comparison of the results in Figures 4.4 and 4.5 depicts that the adsorption of lignin was significantly reduced and that the removal of COD was slightly reduced when the pH was adjusted to 4.6 and under equilibrium conditions (i.e. higher ionic strength).

In Figure 4.7, the zeta potential of the fly ash-TMP pressate mixture was determined at different sodium chloride concentrations, at pH 6 and without pH adjustment, using F1 and F4. This test of experiments was performed to determine the potential impact of the ionic strength on the removals of lignin and COD. As expected, the zeta potential of the samples at pH 6 were higher than the samples without pH adjustment, since the addition of acid is expected to increase the zeta potential due to increased protonation on the surface of the fly ash. The results in Figure 4.7 also indicate that the increase in ionic strength of the solution did not have a remarkable effect on the zeta potential of the fly ash/TMP systems. Therefore, the addition of 0.04-0.5 mol/L sodium chloride did not appear to change the zeta potential. Thus, the significantly different adsorption of lignin on fly ash in Figures 4.4 and 4.5 is not related to the change in the ionic strength of the system. As other parameters were maintained constant for the systems with and without pH adjustment, it can be claimed that the difference in adsorption would be related to the pH of the adsorption systems.

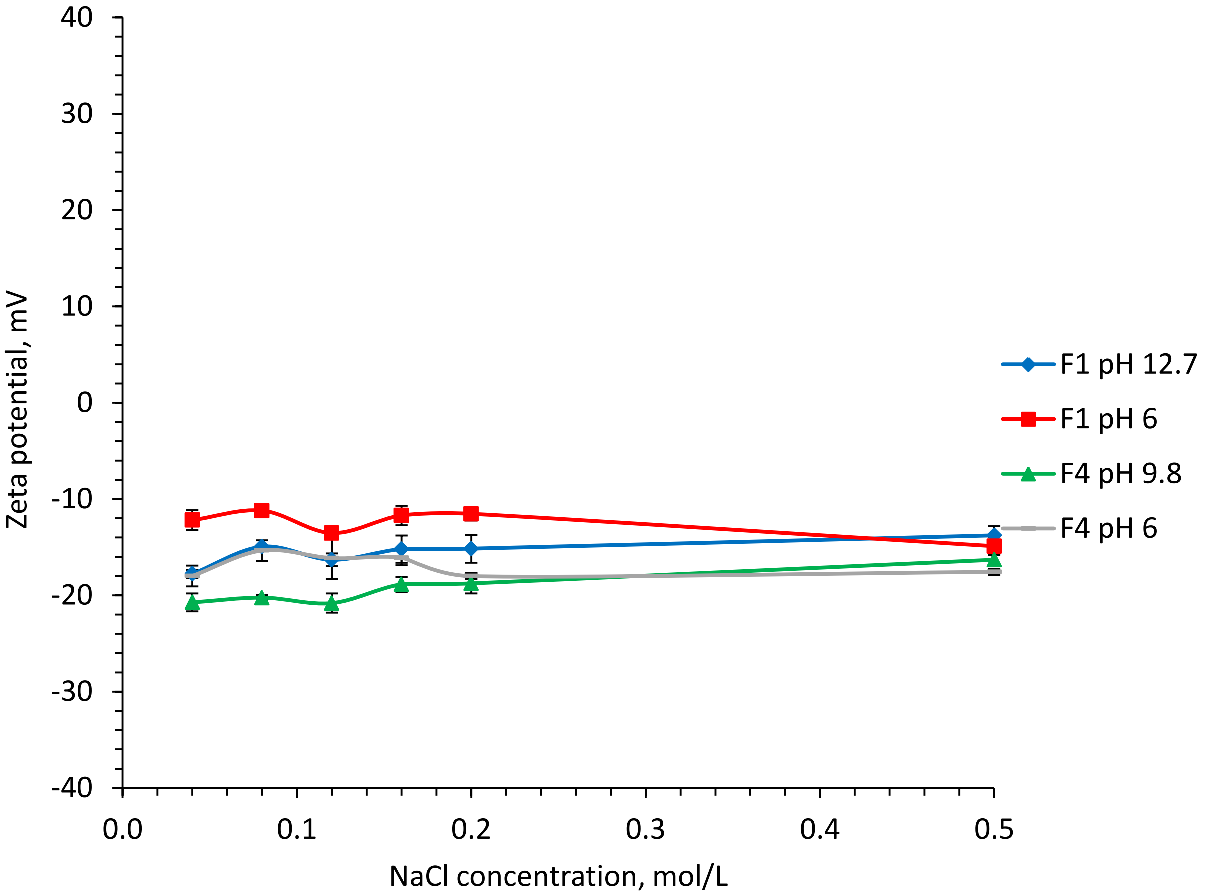

Figure 4.7 Zeta potential of F1 and F4 treated with different dosages of sodium chloride. Fly ash/TMP samples were adjusted to pH 6 or left as is.

4.4.6 Impact of composition on adsorption parameters

The values of the estimated Freundlich maximum adsorption capacity for the lignin adsorption by F1, F2, F3, F4 and F5 were 149 mg/g, 142 mg/g, 143 mg/g, 106 mg/g, and 125 mg/g when the pH was adjusted to 6 (Table 4.3). It was reported previously that the adsorption capacity of a TMP pressate lignin on an activated carbon was 166 mg/g (Oveissi & Fatehi, 2014). The adsorption of lignin was expected to occur mostly in the mesopores of the fly ash (Radovic, 2001) since the hydrodynamic diameter of lignin in the TMP pressate studied here was 8.5 nm and mesopores have a pore width that ranges from 2-50 nm. Furthermore, since the mesopore volumes of F1, F2, F3, F4 and F5 were 0.040 cm^3/g, 0.046 cm^3/g, 0.044 cm^3/g, 0.039 cm^3/g and

0.042 cm^3/g respectively (i.e. similar in all fly ash samples), the pore volumes were assumed to be fixed in this study. The potential impact of particle size was minimized by grinding and sieving the samples to the same size. As indicated earlier, the micropore volume may be related to the surface area and carbon content, and thus the surface area and carbon content were assumed not to have a significant impact on the adsorption of lignin as well. Furthermore, ionic strengths appeared not to have a significant effect on zeta potential and thus adsorption. Thus, it was hypothesized that the metal content was one of the main factors that impacted the adsorption of lignin in the TMP pressate by the biomass fly ash samples.

In Figure 4.8, the relationship between the experimentally determined K_F for lignin adsorption, and the metal, calcium, and potassium content of the fly ash samples F1 through F5 are presented at pH 6. The results suggest that there is a positive correlation with the K_F for lignin adsorption and the metal content of the fly ash samples (R^2 value of 0.981). The metal content of the fly ash consists of various elements, and thus it is not possible to determine the contribution from specific metals on the adsorption of lignin. However, calcium, which represents the largest proportion of the total metal content in the fly ash samples (Table 4.1), exhibited a linear trend with the K_F for lignin adsorption (R^2 value of 0.989). The potassium content also related reasonably well to the K_F for lignin adsorption (R^2 value of 0.965). The slight deviation from linearity at the low concentration may be related to a lower probability of a representative amount of potassium present on the surface of the fly ash. Overall, the increase in calcium and potassium may have improved the adsorption of lignin in the TMP pressate, but further analysis would be required to validate this.

The relationship between the K_F for lignin removal from a TMP pressate, without pH treatment, and the metal, calcium, and potassium contents of the fly ash samples F1 through F5 was also evaluated, and the observed R^2 values were 0.011, 0.021 and 0.001, respectively (results not shown). Thus, the experimentally determined K_F for lignin removal from a TMP pressate does not appear to be related to the metal, calcium, and potassium contents when the pH was not adjusted.

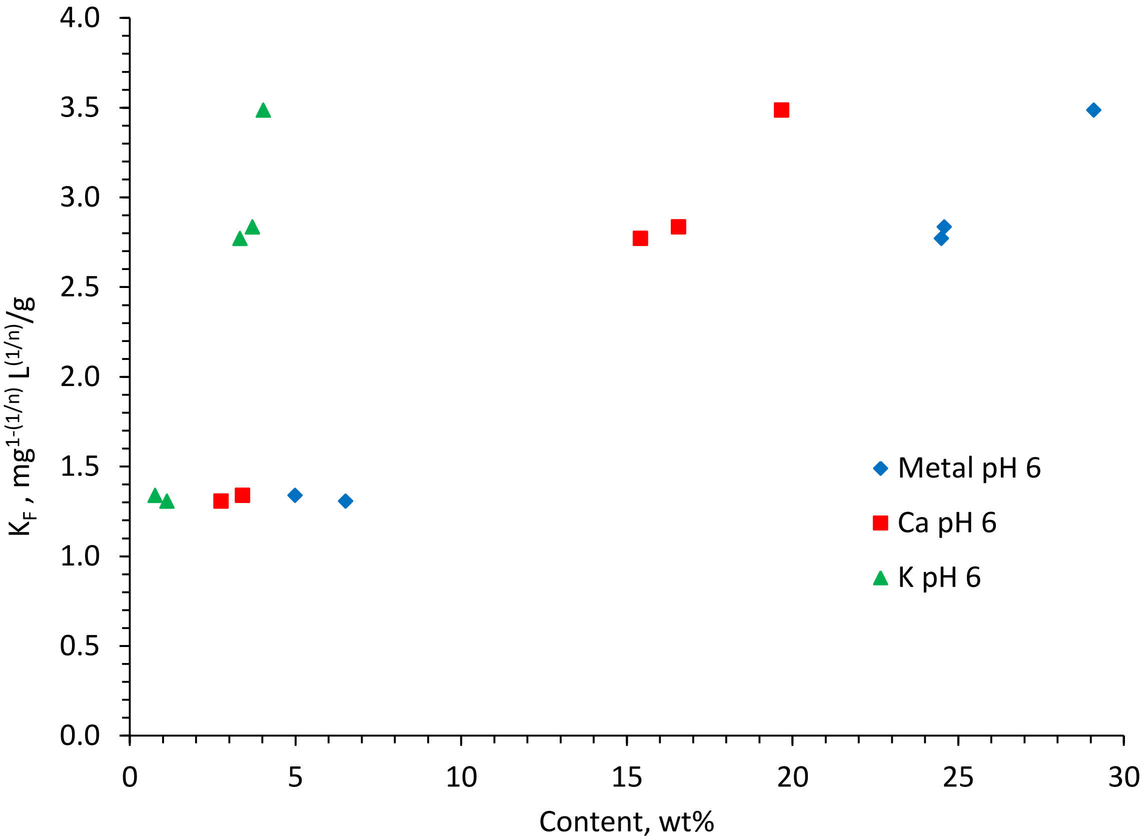

Figure 4.8 The K_F for lignin removal as a function of total metal, calcium, and potassium contents of biomass fly ash. The K_F values for lignin were obtained from isotherm analysis of F1, F2, F3, F4 and F5 at pH 6. The metal, calcium and potassium contents were obtained from ICP-OES analysis of the fly ash samples.

In Figure 4.9, the relationship between K_F for COD removal from a TMP pressate at pH 6 and without pH treatment, and the metal, calcium, and potassium contents of the fly ash samples F1 through F5 is presented. The results indicated that when the pH was adjusted to 6, there appears to be a positive correlation between the K_F for COD removal from a TMP pressate and the metal, calcium, and potassium content in the fly ash (the R^2 values were 0.894, 0.912 and 0.896, respectively). When the pH was not adjusted, the correlation between the K_F for COD removal from a TMP pressate and the metal, calcium, and potassium contents in the fly ash was hampered (the R^2 values were 0.729, 0.776 and 0.741, respectively). It is seen in the figure 4.10 that pH had a significant effect on the results under equilibrium conditions. It was previously stated that pH of the mixture had a pronounced effect on the removal. Furthermore, the results suggest that an increase in the metal content in the fly ash may have improved the COD removal from a TMP pressate at pH 6 and to a lesser extent at a higher pH.

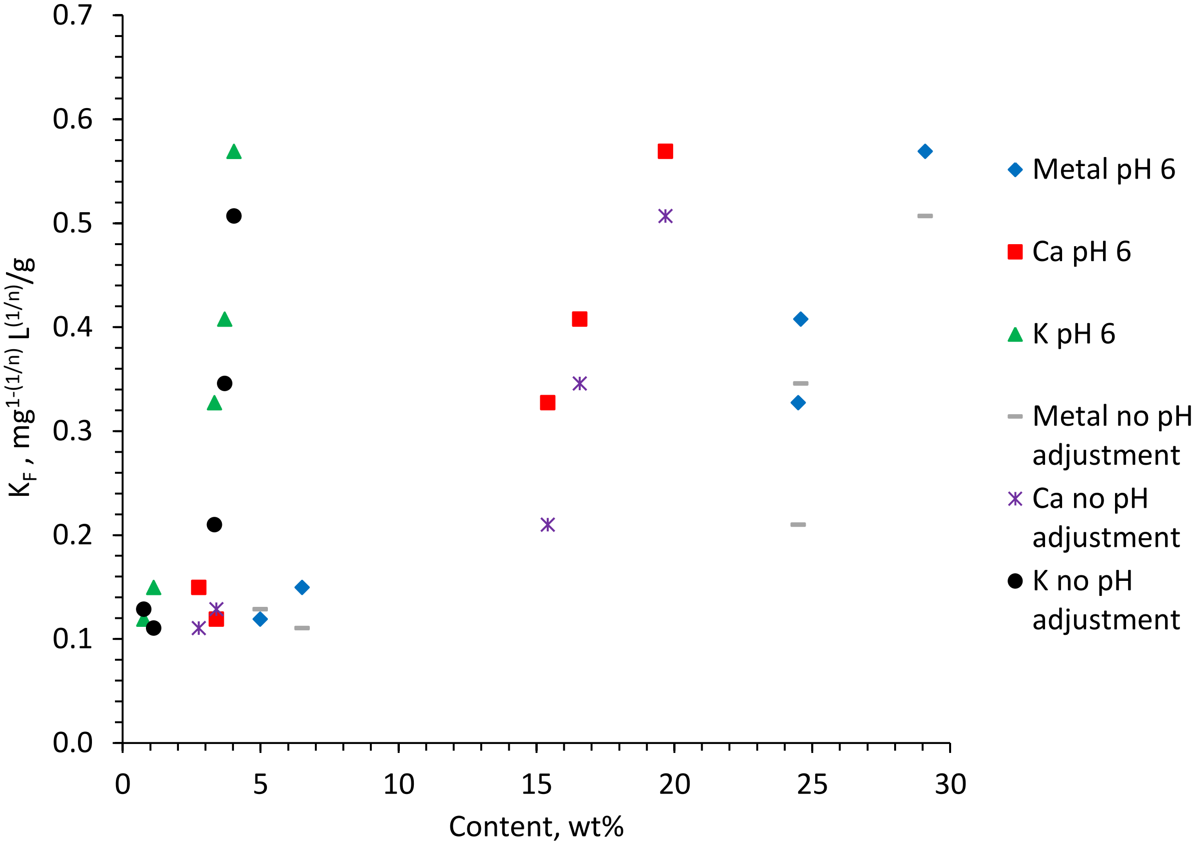

Figure 4.9 The K_F for COD removal as a function of total metal, calcium, and potassium contents of biomass fly ash. The K_F values for COD were obtained from isotherm analysis of F1, F2, F3, F4 and F5 at pH 6 and without pH adjustment. The pH of the fly ash-TMP pressate mixture without pH adjustment varied between 12.0-12.7 for F1, 11.5-12.6 for F2, 11.8-12.5 for F3, 7.9-9.8 for F4 and 8.1-10.1 for F5 as the dosage of fly ash applied increased. The metal, calcium and potassium contents were obtained from ICP-OES analysis of the fly ash samples.

4.4.7 Impact of particle size

In the previous chapter (Chapter 3), it was determined that particle size had a significant effect on the removals of lignin and COD, when one type of biomass fly ash sample was used. However, since the metal content and particle size of the fly ash samples changed in this chapter (Table 4.1), it was unclear if the improved removals were attributed to the decreased particle size, the increased metal content, or a combination of both parameters.

To determine the impact of the particle size on the lignin and COD removals at a constant composition, isotherm analysis was performed on F4, F4S, F4M, and F_04, which had a particle size range of 0.037-0.074 mm, 0.105-0.149 mm, 0.250-0.297, and 0.420-0.841, respectively. In Figure 4.10, the calculated maximum adsorption capacity is compared with the particle size ranges of the fly ash samples studied. The estimated Freundlich adsorption capacity for lignin adsorption by F4, F4S, F4M and F_O4 was 270 mg/g and 175 mg/g, 124 mg/g and 230 mg/g, respectively (Table 4.6). Furthermore, the estimated Freundlich adsorption capacity for COD removal by F4, F4S, F4M, and F_04 was 170 mg/g, 116 mg/g, 64 mg/g, and 103 mg/g (Table 4.6). Except for the largest fraction, the results suggest that as the particle size of the biomass fly ash decreases the lignin and COD removal increases. As stated previously, the chemical compositions of fly ash played an important role on the lignin and COD removals. One possible reason for the deviation of the results for fly ash with largest size may be its slight change in its composition. This sample contained 3.4 % calcium, i.e. more than that of other samples 2.5-2.8 % (Table 4.2). Previous studies on the removal of lignocelluloses from a prehydrolysis liquor reported that lime and precipitated calcium carbonate removed 10-16 % of the lignin present (Saeed et al., 2012b; Fatehi et al., 2013). Therefore, the calcium content of the sample might have contributed to its higher lignin and COD removals. However, further studies need to be conducted to obtain a concrete conclusion.

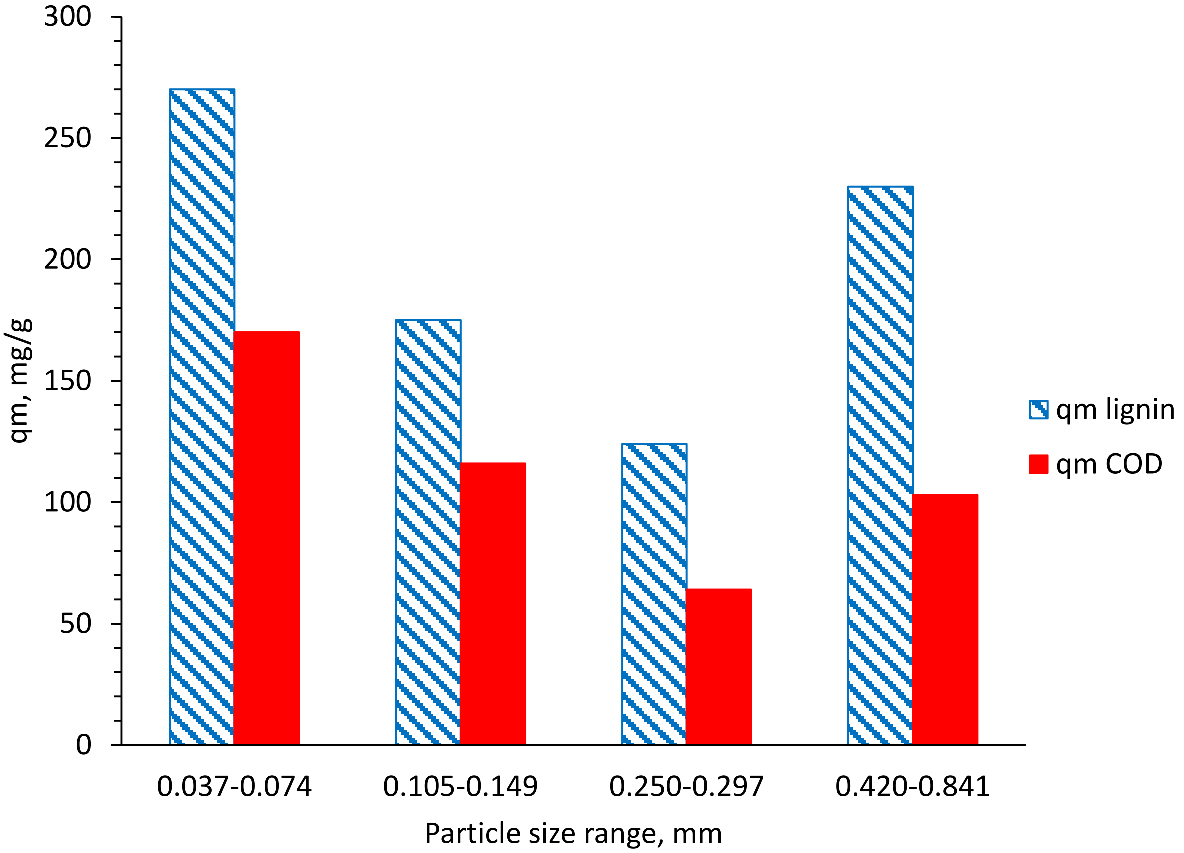

Figure 4.10 Comparison of the maximum adsorption capacity and the particle size ranges of fly ash samples. The fly ash samples were F4, F4S, F4M, and F_04, and corresponded to a particle size range of 0.037-0.074 mm, 0.105-0.149 mm, 0.250-0.297, and 0.420-0.841, respectively.

4.5 Conclusions

Grinding of biomass fly ash had an insignificant impact on its surface area and pore volume, but increased the mesopore volume by 5-65 %. It was determined that the COD and lignin removals from a TMP pressate on biomass fly ash fractions all follow the Freundlich isotherm model when the pH was adjusted to 6. Under the conditions of 298 K, pH 6, 100 rpm, and 24 h, the highest estimated Freundlich adsorption capacity for lignin in a TMP pressate was 149 mg/g fly ash/TMP pressate, and was obtained on a fly ash with the highest metal content (29.1 wt. % metal). The greatest estimated Freundlich adsorption capacity for the COD in a TMP pressate was determined to be 212 mg/g fly ash/TMP pressate under the conditions of 298 K, no pH adjustment, 100 rpm, and 24 h and corresponded with a fly ash with a slightly lower metal content (24.6 wt. %). The results showed that ionic strength of fly ash/TMP system studied did not have a significant effect on the adsorption, but pH had a significant influence. An increase in the pH increased the lignin adsorption significantly under equilibrium conditions. Furthermore, the metal content of biomass fly ash, specifically potassium and calcium, had a significant effect on the K_F for lignin and COD adsorption.

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5 Chapter 5: Leaching characteristics of biomass fly ash in water and a TMP pressate

5.1 Abstract

The feasibility of using a biomass-based fly ash adsorbent on a TMP pressate was assessed with respect to its potential environmental impact. In this study, a biomass fly ash was tested by a standard leaching test (US EPA TCLP Method 1131). Additional leaching tests of biomass fly ash samples were conducted at two liquid to solid ratios (L/S) of 100 and 15 and at neutral (pH 6) and alkaline (pH 12.5) conditions in water and in a TMP pressate at 298 K, 100 rpm, for 2 h. The predominant metals detected in the filtrates were Ca, K, Mg, Mn, Na and Si, the trace metals that were detected to a significant extent were Al, Ba, Sr and Zn. The concentration of the remaining metals such as As, Cd, and Cr were 0.2 mg/L or lower. It was observed that the presence of constituents in a TMP pressate, such as lignin, had a significant impact on the extent of metals that leached into the system studied. The potential use of a biomass-based fly ash adsorbent on a TMP pressate was then evaluated.

5.2 Introduction

In the thermomechanical pulping (TMP) process, wood chips are washed and then steamed prior to refining (Sixta, 2006). The effluent that is generated from the TMP pretreatment stage is known as a TMP pressate and requires wastewater treatment prior to its release into the environment. Adsorption may be a suitable treatment option for pulp and paper mill effluents (Pokhrel & Viraraghavan, 2004; Sumathi & Hung, 2006; Kamali & Khodaparast, 2015). Gupta et al. (2009) and Wang & Wu, (2006) have suggested that biomass fly ash may potentially be used as a low cost adsorbent for treating wastewater effluents. Recently, Oveissi & Fatehi (2015) proposed the use of a biomass fly ash generated at the TMP mill to be used as an adsorbent on a TMP pressate. Furthermore, the results in a previous chapter (Chapter 3) suggested that 91.3 %

of the COD present in the TMP pressate might be removed when a biomass fly ash was used at a dosage of 70 mg/g fly ash/TMP, an average fly ash particle size of 0.43 mm and a 2 h treatment time.

The main metals present in wood fly ash are Ca, K, Mg, Si, Al, Na, Mg and Mn and wood fly ash also contains trace metals such as Fe, Zn, As, Ni, Cr, Pb, Cu and Cd (Demeyer et al., 2001; Steenari & Linqvist, 1997). The use of a biomass fly ash in an aqueous system may be a concern for the environment due to the potential leaching of heavy metals (Reijnder, 2005). Leaching tests on wood ash has been conducted previously. Andersson et al. (2011) performed leaching tests on a wood fly ash in deionized water, and it was determined that the dominant elements in the filtrates were K, Ca, S, and Na. In another study by Laohaprapanon et al. (2010), leaching tests were conducted on a wood fly ash in distilled water at two different liquid to solid ratios (L/S) of 5 and 10 at 293 K and for 24 h. The trace metals that were detected to a significant extent in the leachate for the L/S 5 and 10 were 3.2 and 1.7 mg/L Cr, 0.4 and 0.3 mg/L Zn, 0.3 and 0.4 mg/L Ba, and 0.1 mg/L Pb, respectively. However, a review of the literature did not reveal any quality criteria or regulations regarding the use of biomass fly ash as an adsorbent for wastewater treatment.

Previous studies have indicated that the concentration of a specific metal leached into a system is dependent on its concentration in a fly ash, but no direct correlation on the extent of leaching is observed (Izquierdo & Querol, 2012; Saqib & Backstrom, 2016). Furthermore, leaching characteristics of a system appears to be dependent on a combination of various factors, such as the specific mineral present (e.g. oxides versus sulfides versus chlorides), the specific location of the metals (e.g. on the surface versus the interior), ionic strength of the solution and the pH of the system studied (Poykio et al., 2009). Furthermore, the impact of grinding has not been adequately studied (Karlfeldt & Steenari, 2007). Metals may leach more easily from fly ash samples with a smaller particle size, but the increased surface area may also aid in the adsorption of metals (Karlfeldt & Steenari, 2007). Many studies have been performed on the leaching of metals from coal fly ash and several common trends have been reviewed (Izquierdo & Querol, 2012). However, relatively few leaching studies have been conducted on biomass fly ash and observations related to the leaching from coal ash may not apply to that from a biomass fly ash

(Saqib & Backstrom, 2016). For example, leaching of Pb from coal does not appear to pose a significant environmental impact (Izquierdo & Querol, 2012), but significant leaching of Pb from biomass fly ash has been observed (Saqib & Backstrom, 2016). Since leaching processes are very complex, leaching tests must be conducted to determine the extent of leaching for a specific system.

Biomass fly ash is a non-hazardous solid waste in Ontario (EPA, 1990, Reg. 347). However, the composition of wood fly ash is highly variable (Vassilev et al., 2013; Demeyer et al., 2001) and some biomass fly ash may be considered as hazardous under stricter regulations (Ribbing, 2007). Currently, a solid waste that is to be disposed of in a landfill in Ontario should meet the acceptability criterion set by the Canadian Regulation 347 of the Ontario Ministry of Energy and Environment, which is assessed by the laboratory test, US EPA TCLP Method 1131 (EPA, 1990, Reg. 347). In Previous studies, the toxicity characteristic of leaching procedure (TCLP) had been tested on wood fly ash. In one study by Zhou et al. (2000), the results indicated that the wood fly ash studied was non-hazardous, but in another study by Consigli et al. (2016), one of the three wood fly ash samples studied was considered hazardous. Thus, the development of a biomass-based fly ash adsorbent treatment requires confirmation that the biomass fly ash would not pose an environmental concern. However, standard leaching tests may under or overestimate the actual leaching conditions and leaching behaviour tests should also be conducted for the system under investigation (Wang & Wu, 2006; Reijnder, 2005). Thus, the development of a biomass-based fly ash adsorption treatment also requires an assessment of the potential environmental impact under representative conditions. To the best of our knowledge, the impact of leaching of a biomass fly ash in a TMP pressate was not conducted previously, and in fact is an objective of this chapter.

The purpose of this study was to assess the feasibility of using a biomass-based fly ash adsorbent with respect to its potential environmental impacts. The main novelty of this chapter was the assessment of the metals that leached into the resulting filtrate produced when a biomass fly ash was used as an adsorbent on a TMP pressate under different conditions. In this study, a biomass fly ash was fractionated and ground to yield two fly ash samples with a similar particle size range. This exercise was conducted to minimize the potential impact of particle size in order to provide a means for comparing the impact of their metal contents. Leaching experiments of the two fly ash samples were conducted using two L/S of 100 and 15 at neutral (pH 6) and alkaline (pH 12.5) conditions in both water and in a TMP pressate and the results were compared. The results were then evaluated against potential acceptability criteria related to wastewater effluent guidelines of the metal mining sector, since effluents of the pulp and paper sector are currently not regulated for metal content.

5.3 Materials and methods

5.3.1 Materials

A biomass fly ash and a TMP pressate were obtained from a pulp mill that is located in central Canada. The fly ash was the residue generated in a boiler that used a mixture of wood and wastewater sludge as fuel. The TMP pressate was filtered with a glass filter apparatus (Millipore) and a filter paper (Whatman No. 1), and the filtrates were collected for COD and lignin analyses and then stored in a refrigerator at 277 K prior to use. The fly ash was dried in an oven at 378 K, cooled and then stored in plastic bags at room temperature prior to use. Sodium hydroxide (98 wt. %), hydrochloric acid (37 wt. %), potassium hydroxide and glacial acetic acid (99 wt. %) were purchased from Sigma Aldrich Company. The Chemical oxygen demand (COD) kit (K-7365) was obtained from CHEMetrics Inc., USA.

5.3.2 Fractionation of biomass fly ash

The biomass fly ash was mechanically sieved using ASTM E11 sieves with mesh numbers of 10, 20 and 60, based on a method previously described (Zhu et al., 2013). In this fractionation step, 200 g of fly ash was sieved at a time using a mechanical sieve shaker (CSC Scientific, Meinzer II Sieve Shaker), and shaken for 10 min. The fly ash that was retained on the sieve with a mesh number of 10 was discarded and the fly ash that was retained on the sieves with mesh numbers

60 and 20 were collected. The fly ash samples were then ground separately for 20-30 seconds using a grinder (Bel-Art SP Scienceware micro-mill), sieved with mesh numbers of 200 and 400, and the fly ash retained on the sieve with the number 400 mesh were collected. The fly ash samples that were originally retained on the sieves with mesh numbers 60 and 20 were labelled as S1 and S2, respectively. In this study, S1 was selected, since it was previously determined that for the particular fly ash used, a particle size range of 0.250-0.841mm was optimum with respect to COD removal on a TMP pressate (Chapter 3); the metal compositions may have been an important factor with respect to the removal of COD and lignin from a TMP pressate (Chapter 4). The fly ash fraction S2 was chosen for a comparative analysis. The fly ash samples were ground and sieved to the same particle size range to minimize the impact of particle size in the leaching tests.

5.3.3 Toxicity characteristic leaching procedure (TCLP)

The TCLP was performed by a modified US EPA method 1311. In this method, a 1 L extraction fluid was added to 50 g of (S1) in a 1 L Erlenmeyer flask and the flask was sealed. The mixture was then shaken at 30 rpm in a Boekel water bath shaker at 298 K for 18 h. After the leaching treatment, the leachate was filtered with a glass filter apparatus (Millipore) and glass filter paper, and the filtrate was collected for ICP-OES analysis. The extraction fluid was prepared by mixing 5.7 mL of glacial acetic acid with deionized water to a volume of 1 L. The leaching test was repeated and the average results were reported.

5.3.4 Leaching tests in deionized water and TMP pressate

Biomass fly ash samples were added to 50 g of deionized water or TMP pressate in 250 mL Erlenmeyer flasks at a dosage of 10 or 67 mg/g fly ash/water or TMP pressate, the pH of the mixture was then adjusted to 6 or 12.5, and the flasks were sealed. The samples were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 2 h. After the leaching treatments, the samples were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1).

The filtrates were then collected for ICP-OES, COD and lignin analysis. The COD and lignin removals from the TMP pressate were determined using equation 1:

$$\text{Removal \%} = \frac{C_0 - C_F}{C_F} \times 100 \tag{1}$$

where C_O refers to the initial COD or lignin concentrations (i.e. after initial pretreatment) and C_F refers to the final COD or lignin concentrations in the filtrates after the leaching/adsorption treatments. All tests were carried out in triplicate and the average results were reported.

Unless indicated otherwise, the background metal contents in the TMP pressate were subtracted from the results of the leaching tests of S1 and S2 in a TMP pressate in this chapter. Furthermore, the analysis of the Na that leached into water and the TMP pressate by the addition of S2 was also omitted, since sodium hydroxide was added during the pH adjustment step.

5.3.5 Metal analysis

The metal content of fly ash and leachate samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro with CETAC ASX-510 Auto Sampler. In this modified EPA method 3051A, 0.2 g samples of fly ash were digested with aqua regia (i.e. nitric acid and hydrochloric acid in a 1:3 molar ratio) in a microwave (CEM Mars Xpress microwave) using an Xpress closed vessel. The digestion conditions consisted of a 20 min ramp time to a temperature of 448 K and 25 min digestion at 448 K. After digestion, the samples were cooled and then diluted with 40 mL deionized water prior to ICP-OES analysis. The leachate samples were analyzed by ICP-OES without pretreatment.

5.3.6 COD, Lignin and hemicellulose analysis

The COD analysis was carried out by adding 2 mL samples to COD vials obtained from CHEMetrics incubating them in a reactor (CR 2200 WTW thermoreactor) for 2 h at 423 K and measuring their COD by the spectrophotometric method at 620 nm using a spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific) as described by the COD kit. The lignin analysis was performed based on a spectrophotometric method described previously (Liu et al., 2011). The pH of the samples was adjusted to 7 (± 0.25) with 0.1 M NaOH or 0.1 M HCl prior to analysis at 205 nm (Saeed et al., 2012) using a UV-Vis spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific). The concentration of hemicelluloses in the TMP pressate was determined through ion chromatography (Dionex ICS 5000, Thermo Scientific, equipped with an electrochemical detector (ED) and a CarboPac™ SA10 column). The operating temperature of the column was 303 K, the eluent was 1.00 mM KOH and the eluent flow rate was 1.2 mL/min using an eluent generator (EGC 500 KOH, Thermo Scientific).

5.4 Results and discussion

5.4.1 Characterization of TMP pressate and biomass fly ash samples

In Table 5.1, the metal elements present in S1 and S2 is shown. The results indicate that the total metal content of S1 was 26.3 wt. % and that the major metals present were Ca, K, Mg, Mn, Al, Na and Fe. The rest of the metals represented less than 1 wt. % of the total weight and many of these metals were close or below their detection limits. The results of S2 indicates that the total metal content was 4.4 wt. % and that the major elements present were Ca and K. In another study, the weight percent of the main metals detected in a fly ash produced from a Kraft pulp mill located in Northern Alberta were 24.8 wt. % Ca, 6.5 wt. % K, 2.2 wt. % Mg, 0.6 wt. % Na, 0.6 wt. % Al and 0.4 wt. % Fe (Zhou et al., 2000).

In Table 5.1, the concentration of the metals detected in the filtered TMP pressate are given and the TMP pressate had 2318 mg/L COD, 1.95 g/L lignin, 0.7 g/L hemicelluloses and a pH of 6.1. The results in Table 5.1 indicate that the major metals present in the TMP pressate were K, Ca, Na, Mg, Mn and Si. In another study, it was determined that a TMP pressate had 1610 mg/L soluble COD, pH 4.2 and the average concentration of the main metals detected was 54.98 mg/L Na, 34.24 mg/L Ca, 33.00 mg/L K, 6.33 mg/L Mg and 2.32 mg/L Mn (Gao et al., 2011).

Table 5.1 Metal content in two biomass fly ash samples and a TMP pressate

Metal	**S1, mg/kg (dry wt.)**	**S2, mg/kg (dry wt.)**	**TMP pressate filtrate, mg/L**
Al	7894	713	0.14
As	2	<MDL	<MDL
Ba	2277	342	0.16
Be	<MDL	<MDL	<MDL
Ca	177450	29893	18.36
Cd	8	0	<MDL
Co	6	<MDL	<MDL
Cr	10	1	<0.01
Cu	82	9	0.07
Fe	4773	325	0.14
K	36445	8679	23.60
Mg	14774	1605	4.61
Mn	8014	1052	1.15
Mo	<MDL	<MDL	<MDL
Na	6612	1365	14.69
Ni	12	<MDL	<MDL
Pb	17	<MDL	<MDL
Si	1937	1443	3.17
Sr	526	86	0.07
Ti	184	10	<MDL
Tl	<MDL	<MDL	NM
V	9	<MDL	<MDL
Zn	1915	76	0.33

MDL = minimum detection limit NM = not measured

5.4.2 Toxicity characteristic leaching procedure (TCLP) test

Table 5.2 lists the metal concentrations in the leachate from the TCLP test for S1 as well as the landfill quality criteria. The results indicate that the concentration of As, Ba, Be, Cd, Cr, Ni and Pb in the TCLP leachate from the biomass fly ash were all below the regulatory limits. The thallium concentration was not measured in the TCLP leachate. The thallium concentration for S1 was below the MDL (Table 5.1). Based on a mass balance if 100 % was extracted assuming its MDL, its concentration would have been 0.1 mg/L in the TCLP leachate, and thus it was not expected to exceed the limit of 0.2 mg/L. Furthermore, based on a mass balance for S1, Ba, Cd, and Pb were the only metals that could have leached to an extent that would have been above the regulatory limit set by the Environmental Protection Act. The TCLP test was not conducted on S2 since based on a mass balance for As, Ba, Be, Cd, Cr, Ni and Pb, if 100 % were extracted, none would exceed the regulatory limit. Therefore, both of the biomass fly ash samples studied here would not pose an environmental concern with respect to landfill leachate generation. The TCLP test indicates that the biomass fly ash generated at the TMP mill would not be considered a hazardous solid waste according to a standardized test.

Table 5.2 Concentration of the metals detected in the TCLP leachate of S1

Metal	Fly ash leachate mg/L	Landfill criteria* mg/L
Al	0.73	-
As	0.04	5.00
Ba	1.83	21.00
Be	<MDL	1.22
Ca	2290.81	-
Cd	0.02	0.10
Co	0.08	-
Cr	0.02	0.60
Cu	0.14	-
Fe	0.05	-
K	987.63	-
Mg	57.79	-
Mn	20.85	-
Mo	<MDL	-
Na	269.14	-
Ni	0.10	11.00
Pb	<MDL	0.75
Si	58.42	-
Sr	10.60	-
Ti	<MDL	-
Tl	NM	0.20
V	0.05	-
Zn	2.29	-

* Environmental Protection Act R.R.O. 1990, Regulation 347

MDL = minimum detection limit, NM= not measured

5.4.3 Impact of leaching of biomass fly ash (S1 and S2) and L/S in water

Table 5.3 and Table 5.4 present the total amount of various metals that leached from the addition of S1 and S2, respectively, in water under the conditions of 298 K, 100 rpm, 2 h, with a L/S of 100 or 15 and a pH of 6 or 12.5. The L/S ratios and pH conditions were chosen based on the boundary conditions for the adsorption studies previously conducted, and the pH of 12.5 represents the pH influence of the S1 in water and TMP pressate (Chapter 3). A leaching time of 2 h was chosen to reflect the potential leaching that may occur in the use of a biomass-based fly ash adsorption process on a TMP pressate (Chapter 3). The results in Tables 5.3 and 5.4 indicate that the main metals that were detected in the filtrates of S1and S2, respectively, were Ca, K, Mg, Mn, Na and Si; and these results are consistent with results of leaching studies in water as previously reported (Andersson et al., 2011). In this study, the analysis of Na that leached into the water by the addition of S2 was omitted since the leaching at pH 12.5 required the addition of sodium hydroxide, and thus the leaching characteristics of Na from S2 cannot be determined in this study.

The results indicate that as the L/S ratio increased, the amount of K that was leached remained relatively constant (Tables 5.3 and 5.4) and the amount of Na that was leached remained relatively constant as well (Table 5.3). Furthermore, the concentration of K and Na in the leachates increased by a factor of 6.4-7.0 as the L/S ratio decreased from 100 to 15 at pH 6 and pH 12.5. Metals that were not limited by solubility generally exhibit a detectable concentration in the leachate that is inversely proportional to the L/S ratio even though the presence of other species can alter this to an extent (Dutre & Vandcasteele 1998; Martin-Torre et al., 2014; Reardon et al., 1995; Sabbas, et al., 2003). Furthermore, for availability controlled leaching (i.e. not limited by solubility), the concentration leached is relatively independent of pH (Sabbas, et al., 2003). Thus, the results suggest that the leaching of K and Na appear to have been availability-controlled under the conditions studied here.

The results of the leaching experiments of S1 and S2 in water indicate that metals such as As and Pb were not leached to a measurable extent. However, the results indicate that Al, Ba, Cd, Co, Cr, Cu, Sr and Zn were detected in the leachates from S1 and S2; and Ni was detected in the leachates from S1. Furthermore, as the L/S ratio increased, the metal contents of Ca, Mg, Mn, Si, Al, Ba, Sr, and Zn leached from S1 or S2; and those of Co, Cr and Cu leached from S1 increased.

For solubility-controlled leaching, the concentration in the filtrate is not related to the L/S, but the total amount leached increased with L/S (Martin-Torre et al., 2014). Therefore, the results suggest that the mechanism of leaching was solubility-controlled for Ca, Si, Ba, Sr, and Zn from S1 and S2, and for Mg in S1 under all conditions studied, for Al, Co and Cu from S1 at pH 6, and for Al from S2 at pH 12.5. The mechanism of leaching for Cd and Ni from S1, and for Cd, Co, Cr and Cu from S2, is unknown.

A comparison of the results in Tables 5.3 and 5.4 indicates that the overall amount of metal extracted from S1 in water was greater than that from S2 in water under similar conditions. These results were expected since the total metal content in S1 (26.3 wt. %) was significantly higher than that in S2 (4.4 wt. %). However, no correlation was observed for the extent of leaching with respect to the individual metal concentrations present in the samples. For example, the amount of Mn, Ba and Zn that leached from S1 and S2 in water was comparable despite there being a factor of 7.6, 8.5 and 23.9 times higher concentrations of these metals, respectively in S1 compared with S2.

Therefore, the results observed suggest that Mn, Al, Ba and Zn present in S2 may be more easily leached into water compared with those in S2 under similar leaching conditions. Several potential reasons or combinations thereof may explain the observations reported here. One possible reason may be that a greater extent of these metals in S2 were located on the surface of the biomass fly ash than in S1 and thus more readily available for leaching into water. Another possible reason may be that the Al mineral present in S1 was relatively insoluble whereas the Al mineral in S2 may have been relatively soluble (i.e. the Al mineral present may have been Al_2O_3 in S1 and $AlCl_3$ in S2). In Chapter 3, the mineral compositions of the same fly ash studied was analysed by XRD, and it was determined that various Ca minerals such as calcite were present, but other minerals could not be identified. A third potential reason may be that the combination of minerals present in S1 may have had a more significant impact on the leaching observed compared with S2. For example, adsorption mechanisms may have been more favorable for Al in S1 than in S2 (i.e. a greater extent of iron oxides may have been present on the surface of S1 compared with S2). Alternatively, the Al may have leached from S1 in water and then formed an insoluble mineral such as $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ (Izquierdo & Querol, 2012) and thus not detected in the filtrate. However, the specific leaching mechanisms and complex interactions that occurred in S1 and S2 in water are unknown.

Table 5.3 Leaching tests of S1 in water under various conditions

	Fly ash treatment			
	pH 6		pH 12.5	
L/S	**100**	**15**	**100**	**15**
Metal	**mg/kg (dry wt.)**			
Major metals				
Ca	97580	18749	103750	15793
K	35070	36366	35960	37910
Mg	6635	4739	4	1
Mn	658	339	<MDL	<MDL
Na	5294	5060	5534	5580
Si	1352	468	8	1
Trace metals				
Al	3.70	<MDL	<MDL	<MDL
As	<MDL	<MDL	<MDL	<MDL
Ba	65.00	42.04	48.50	10.86
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	0.39	<MDL	<MDL
Co	1.10	0.50	<MDL	<MDL
Cr	0.20	0.06	0.60	0.29
Cu	0.60	<MDL	<MDL	<MDL
Fe	<MDL	<MDL	<MDL	<MDL
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	0.71	<MDL	0.57
Pb	<MDL	<MDL	<MDL	<MDL
Sr	285.60	162.91	179.10	80.66
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	15.40	1.35	129.10	30.57
Total metal	146960	65929	145613	59407
Total trace metal	372	208	357	123

L/S = L/kg assuming a water density of 1 kg/L and (mg/kg)/(L/kg) = mg/L, MDL = minimum detection limit

Table 5.4 Leaching tests of S2 in water under various conditions

	Fly ash treatment			
	pH 6		**pH 12.5**	
L/S	**100**	**15**	**100**	**15**
Metal	**mg/kg (dry wt.)**			
Major metals				
Ca	16373	3734	15947	3009
K	7846	7979	7653	7998
Mg	1181	1140	<MDL	<MDL
Mn	599	491	<MDL	<MDL
Na	-	-	-	-
Si	277	181	221	31
Trace metals				
Al	<MDL	<MDL	146.90	52.69
As	<MDL	<MDL	<MDL	<MDL
Ba	105.10	15.35	18.10	6.85
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	0.03	<MDL	<MDL
Co	<MDL	0.09	<MDL	<MDL
Cr	<MDL	<MDL	<MDL	0.08
Cu	<MDL	0.11	<MDL	0.08
Fe	<MDL	<MDL	<MDL	<MDL
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	<MDL	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	48.90	35.29	13.60	8.11
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	4.60	2.76	13.00	1.55
Total metal	26434	13578	24013	11107
Total trace metal	159	54	192	69

L/S = L/kg assuming a water density of 1 kg/L and (mg/kg)/(L/kg) = mg/L, MDL = minimum detection limit

5.4.4 Impact of leaching of biomass fly ash (S1 and S2) in TMP pressate

Table 5.5 and Table 5.6 present the total amount of specific metals that leached from the addition of S1 and S2 in a TMP pressate under the same conditions studied in water as described in section 5.4.3. A comparison of the results in Tables 5.3 and 5.5 indicates that the total metal content leached from S1 was greater in water than it was in a TMP pressate by a factor of 1.1-1.9 for the same leaching conditions. Furthermore, the total trace metal content leached from S1 was greater in water than it was in a TMP pressate by a factor of 1.6 when the L/S was 15 at pH 6, and greater by a factor of 1.5 and 1.1 when the L/S was 100 and 15, respectively at pH 12.5. However, the total trace metal content leached from S1 was greater in a TMP pressate than it was in water by a factor of 1.5 when the L/S was 100 at pH 6. A comparison of the results in Tables 5.4 and 5.6 indicates that the total metal content and the total trace metal content leached from S2 was greater in water than it was in a TMP pressate by a factor of 1.4-2.7 and 1.5-2.9, respectively, under similar leaching conditions. Therefore, the results indicate that the extent of leaching in water was more pronounced from S1 and S2 than in a TMP pressate under all conditions studied except from S1 under the conditions of a L/S of 100 at pH 6.

The metals that appeared to leach to a significantly lower degree in a TMP pressate than in water under all conditions studied were Ca, Mg and Sr from S1 and S2, Fe and Cr from S1, and Ba and Zn from S2. Furthermore, the leaching of metals such as Ba from S1 and Mn and Cr from S2 were reduced at pH 6, and Mn, Si, Cu, Ni and Zn from S1 and Si and Al from S2 were reduced at pH 12.5 in a TMP pressate when compared with that in water. The results given in Tables 5.5 and 5.6 also indicate that the concentration of several of these metals were lower than that of the original TMP pressate. Thus, the metals that were originally present in the TMP pressate may have been adsorbed onto the biomass fly ash during the adsorption treatment of a TMP pressate.

Previous studies have indicated that wood fly ash could act as an adsorbent for metals (Hasan et al., 2000; Rahman et al., 2004; Seco-Reigosa et al., 2013; Orescanin et al., 2004; Heviankova et al. (2014). However, the leaching of metals such as Al, As, Cd, Co, Cu, Ni, V and Zn from S1 and Si, Al, Cu and Fe, from S2 was increased at pH 6 in a TMP pressate when compared with that in water.

The decreased leaching of S1 and S2 in TMP pressate when compared with that in water may be due to the presence of lignin and hemicelluloses in the TMP pressate. Previous studies have indicated that lignin has an affinity for metal ions and may be used as an adsorbent for metals (Guo et al., 2008; Hojaji, 2012; Wu et al., 2008, Zhuang et al., 2003). In other studies, it was reported that dissolved organic matter had an affinity for adsorbing metal ions (Weng et al., 2002; Wang & Mulligan, 2009; Fisher-Power et al., 2016). The main mechanism of metal ion adsorption on lignin appears to be attributed to electrostatic interactions with deprotonated hydroxyl phenolic groups and carboxylic acid groups on lignin (Guo et al., 2008). Since hemicelluloses contain carboxylic acid groups it was hypothesized that adsorption of metals may also have occurred on the hemicelluloses present in the TMP pressate. Furthermore, the complexation of lignin with metal ions has been reported to occur within 20 min (Guo et al., 2008). Since all of the leaching tests were conducted for 2 h, it was expected that there was sufficient time for the adsorption of metal on lignin to occur in this study. Thus, the reduced leaching observed from S1 and S2 in a TMP pressate may be due the adsorption of dissolved metals onto lignin and hemicelluloses followed by their subsequent indirect re-adsorption onto the fly ash as lignin, and hemicelluloses are adsorbed onto the fly ash.

Another possible explanation of the decreased leaching of metal in a TMP pressate may have been due to precipitation. Previous studies have indicated that the interaction of lignin and other dissolved organic matter increased the solubility and mobility of metals present in solution (Wang & Mulligan, 2009; Kalembkiewicz & Sitarz-Palczak, 2015; Weng et al., 2002). However, other studies have observed that the adsorption of metals ions on dissolved organic matter could form precipitates and thus the presence of dissolved organic matter might decrease the solubility and mobility of various metals (Jansen et al., 2002; Jansen et al., 2003; Kaiser, 1998). Therefore, lignin and hemicelluloses may have formed precipitates in the presence of some metals in this study. Thus, the observed decreased leaching of metals from S1 and S2 in the TMP pressate may have been due to the subsequent removal of lignin-metal and hemicellulose-metal precipitates from the solution in the filtration step.

5.4.5 Potential impact of pH on leaching from S1 and S2 in water and TMP pressate

The leaching results from S1 (Table 5.3) indicate that pH did not have a significant impact on the total amounts of metal and trace metal that leached into water when the L/S was 100. However, when the L/S was 15, the total metal and the trace metal contents that leached from S1 into water was significantly higher at a pH of 6 than at pH 12.5. The leaching results of S2 (Table 5.4) indicate that the total metal content that leached into water was significantly higher at pH 6 than at pH 12.5, but the total trace metal content that leached from S2 into water was significantly lower at pH 6 than at pH 12.5. Thus, the leaching characteristics of S1 and S2 differed significantly with respect to pH. Thus, these observations suggest that the mineral compositions in different fractions of a biomass fly ash may differ significantly.

The leaching results from S1 and S2 in a TMP pressate (Table 5.5 and 5.6, respectively) indicate that pH had a significant impact on the total metal and trace metal contents that leached. The results indicate that the total metal and trace metal contents leached from S1 and the total metal content leached from S2 into a TMP pressate were significantly higher at pH 6 than at pH 12.5. Therefore, although the magnitude of leaching observed in water and TMP pressate differed, the leaching trends observed with respect to pH were similar for S1 and S2.

In a previous chapter (Chapter 3), the adsorption of lignin on biomass fly ash was more favourable at pH 6 that at pH 12.5. Furthermore, comparison of the results in Tables 5.3 and 5.5 and Tables 5.4 and 5.6 suggest that the presence of dissolved constituents such as lignin appear to adsorb metal ions. Thus, it was expected that a greater adsorption of lignin at pH 6 than at pH 12.5 would promote the removal of metal ions to a greater extent. However, adsorption of metals on lignin may be more likely to occur at pH 12.5. Lignin present in a TMP pressate would not have been subjected to any significant chemical modification and thus was expected to resemble a fragmented native lignin, when compared with modified lignins such as Kraft lignin. Therefore, lignin present in a TMP pressate would contain phenolic hydroxyl groups and would not be expected to have a significant amount of carboxylic acid groups. The pKa of different phenolic hydroxyls present in softwood lignin can range between 6.2-11.3 (Ragnar et al., 2000). Thus, most of phenolic hydroxyl groups on TMP lignin would have been deprotonated at pH 12.5, and it was expected that at least 50 percent of the phenolic hydroxyls were protonated at pH 6. Therefore, electrostatic interactions between lignin's hydroxyl groups and the positively charged metals and hydrated species may have been more prevalent at pH 12.5 than at pH 6.

Therefore, it was expected that adsorption of metals on lignin would be relatively decreased at pH 6 compared with pH 12.5, and it was expected that the adsorption of lignin by fly ash would be relatively increased at pH 6 compared to pH 12.5. Thus, the presence of lignin in the solution may have been equalized with respect to its potential for aiding in the removal of metal ions at pH 6 and at pH 12.5 as was observed in the leaching from S2. However, it is unclear why the presence of constituents in a TMP pressate significantly increased the leaching of metals at pH 6 and L/S of 100. Overall, these results suggest that leaching tests performed in water may not be a suitable indicator of the amount of leaching that would occur in a complex solution such as TMP pressate.

Table 5.5 Leaching of S1 in TMP pressate under various conditions

	Fly ash treatment			
	pH 6		**pH 12.5**	
L/S	**100**	**15**	**100**	**15**
Metal	**mg/kg (dry wt.)**			
Major metals				
Ca	63004	10490	38004	2596
K	35760	38400	33810	37979
Mg	6619	1700	-456	-69
Mn	2877	1040	-63	-17
Na	4091	5495	3902	4879
Si	1283	771	-270	-48
Trace metals				
Al	17.80	20.69	1.90	-2.12
As	1.30	0.57	<MDL	<MDL
Ba	12.80	3.24	167.00	22.36
Be	<MDL	<MDL	<MDL	<MDL
Cd	2.45	0.43	<MDL	<MDL
Co	2.92	1.23	<MDL	<MDL
Cr	-0.20	-0.03	-0.20	0.21
Cu	3.90	0.47	-5.40	-0.90
Fe	-10.25	-1.87	-14.25	-2.14
Mo	<MDL	0.74	<MDL	<MDL
Ni	4.41	1.38	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	201.55	40.38	91.15	69.74
Ti	<MDL	<MDL	<MDL	<MDL
V	1.10	0.63	<MDL	<MDL
Zn	309.60	58.35	-0.90	25.90
Total metal	114182	58022	75166	45433
Total trace metal	547	126	239	113

L/S = L/kg assuming a water density of 1 kg/L and (mg/kg)/(L/kg) = mg/L, MDL = minimum detection limit

Table 5.6 Leaching of S2 in TMP pressate under various conditions

	Fly ash treatment			
	pH 6		**pH 12.5**	
L/S	**100**	**15**	**100**	**15**
Metal	**mg/kg (dry wt.)**			
Major metals				
Ca	6924	2066	704	352
K	5286	5826	8060	6112
Mg	720	1019	-244	-64
Mn	284	451	32	-4
Na	-	-	-	-
Si	360	269	194	16
Trace metals				
Al	6.57	3.75	111.05	48.91
As	<MDL	<MDL	<MDL	<MDL
Ba	89.40	11.96	-4.85	1.13
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	<MDL	<MDL	<MDL
Co	<MDL	<MDL	<MDL	<MDL
Cr	-0.20	-0.03	0.05	0.01
Cu	1.23	0.52	2.80	-0.24
Fe	1.42	0.87	4.55	-1.25
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	<MDL	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	-6.85	-0.98	4.05	2.95
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	1.93	2.09	-18.55	-4.49
Total metal	13668	9649	8845	6459
Total trace	94	18	99	47

metal

L/S = L/kg assuming a water density of 1 kg/L and (mg/kg)/(L/kg) = mg/L, MDL = minimum detection limit

5.4.6 Potential environmental impact of using S1 and S2 in a TMP pressate

Currently, effluents of the pulp and paper sector are not regulated in Ontario for their metal contents (EPA, 1990, O. Reg. 760/93). Table 5.7 shows the concentrations of various potentially environmentally significant metals detected in the filtrates after the addition of S1 and S2 in TMP pressate as collected (i.e. TMP pressate background levels were not subtracted). In Table 5.7, the COD and lignin removals observed and the daily and monthly average concentration limits for the metal mining sector are given. An assessment of the results indicates that all criteria would be met for the use of S1 as an adsorbent under the conditions of 10 mg/g fly ash/TMP pressate, pH of 12.5, 100 rpm and 2 h; and 46 % of COD and 38.2 % of lignin could be removed. An evaluation of the results for S2 in TMP pressate indicates that all acceptability criteria would be met for the use of S2 as an adsorbent for all conditions tested. Furthermore, the results indicate that 72.2 % of COD and 81.0 % of lignin could be removed under the conditions of 67 mg/g fly ash/TMP pressate, pH of 12.5, 100 rpm and 2 h. However, the environmental impact of using S1 or S2 as an adsorbent in a TMP pressate with respect to the potential leaching of other regulated chemical parameters such as mercury and polycyclic aromatic hydrocarbons (PAHs) (Masto et al., 2015) are unknown.

Table 5.7 Comparison of the leachates of S1 and S2 in TMP pressate with acceptability criteria of the metal mining sector

Metal	Fly ash treatment				Daily limit[a], mg/L	Monthly average limit[a], mg/L
	pH 6		pH 12.5			
	100 L/S	15 L/S	100 L/S	15 L/S		
	mg/L					
S1 in TMP						
As	0.01	0.04	<MDL	<MDL	1.0	0.5
Cu	0.11	0.10	0.01	0.01	0.6	0.3
Ni	0.04	0.09	<MDL	<MDL	1.0	0.5
Pb	<MDL	<MDL	<MDL	<MDL	0.4	0.2
Zn	3.43	4.22	0.33	2.06	1.0	0.5
Parameter	**Removal, %**					
COD	47.1	90.1	46.3	89.2		
Lignin	50.8	94.7	38.2	85.1		

Metal	Fly ash treatment				Daily limit[a], mg/L	Monthly average limit[a], mg/L
	pH 6		pH 12.5			
	100 L/S	15 L/S	100 L/S	15 L/S		
	mg/L					
S2 in TMP						
As	<MDL	<MDL	<MDL	<MDL	1.0	0.5
Cu	0.08	0.10	0.08	0.11	0.6	0.3
Ni	<MDL	<MDL	<MDL	<MDL	1.0	0.5
Pb	<MDL	<MDL	<MDL	<MDL	0.4	0.2
Zn	0.35	0.48	0.14	0.15	1.0	0.5
Parameter	**Removal, %**					
COD	30.8	71.9	29.7	72.2		
Lignin	43.5	89.1	33.2	81.0		

L/S as L/kg assuming a water density of 1 kg/L and (mg/L)(L/kg) = mg/kg, MDL = minimum detection limit

[a] Environmental Protection Act, 1990, O. Reg. 560/94

5.5 Conclusions

A biomass fly ash from a TMP mill was analyzed by TCLP and the results confirmed that the biomass fly ash was non-hazardous and that the ash would be safe for landfill disposal in Ontario. The major metals that were detected in the filtrates were Ca, K, Mg, Mn, Na and Si, the trace metals that were detected to a significant extent were Al, Ba, Sr and Zn and the concentration of the remaining metals studied such as As, Cd, and Cr were 0.2 mg/L or lower under the conditions tested. The extent of metals that leached from biomass fly ash was significantly different in water than in a TMP pressate. The amount of metals that leached into water was greater than that leached into a TMP pressate under the conditions of a L/S of 15 at pH 6 and a L/S of 100 and 15 at pH 12.5. The amount of metals that leached into a TMP was greater than that in water under the conditions of a L/S of 100 at pH 6.

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6 Chapter 6: Coagulation efficiency of calcium chloride, alum and a biomass fly ash leachate treatments of a thermomechanical pulping (TMP) pressate

6.1 Abstract

In this study, the coagulation performance of potassium chloride, calcium chloride, a biomass fly ash leachate (FLC) and alum on a thermomechanical pulping (TMP) pressate was assessed. Focused beam reflectance measurement (FBRM) analysis was used to monitor the effect of dosage, pH, and agitation speed on the mean chord length and cord length distribution of the resulting coagulant/TMP pressate solution. Furthermore, the impact of chemical pretreatment on the chemical oxygen demand (COD) and lignin removals were determined. It was observed that calcium chloride, FLC and alum coagulated the dissolved materials of the TMP pressate, but potassium chloride did not. A calcium chloride treatment on a TMP pressate removed 20.8 % of the COD and 30.8 % of the lignin under the conditions of 2894 mg/kg $CaCl_2$/TMP pressate, 200 rpm, pH 12.5 and 298 K for 30 min. The COD and lignin removals were 18.4 % and 26.9 %, respectively, when a FLC was added to a TMP pressate under the conditions of 5060 mg/kg FLC/TMP pressate, 200 rpm, pH 12.5 and 298 K for 30 min. The addition of alum removed 41.2 % of the COD and 40.6 % of the lignin from a TMP pressate under the conditions of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate pressate, 200 rpm, pH 6 and 298 K for 30 min.

6.2 Introduction

In thermomechanical pulping (TMP), wood chips are washed, pretreated with steam and then refined to produce TMP pulp (Sixta, 2006). The TMP pressate, which is the filtrate produced in the primary refiner stage, contains lignin, hemicelluloses, and some wood extractives (Zasadowski et al., 2014) and has a high chemical oxygen demand (COD) load (Andersson et al., 2008; Sumathi & Hung, 2006). The TMP process requires a considerable amount of water and thus an extensive wastewater treatment plant. The wastewater treatment of the pulp and paper industry often consists of an initial clarification stage followed by an activated sludge process. However, an activated sludge process is sensitive to toxicity and shock loading, and recalcitrant substances can remain in the effluent (Thompson et al., 2001).

In a review by Pokhrel & Viraraghavan, 2004, it was suggested that a combination of physicochemical and biological treatments may potentially offer a long-term solution for pulp and paper wastewater treatment operations. Various physicochemical treatments, such as membrane filtration, coagulation, adsorption and oxidation, were considered as suitable methods for removing recalcitrant compounds, such as lignin, from pulp mill effluents (Kamali & Khodaparast, 2015; Pokhrel & Viraraghavan, 2004; Sumathi & Hung, 2006). However, membrane filtration, adsorption and oxidation may be expensive. Furthermore, membrane filtration is susceptible to fouling and requires disposal of the concentrate. The regeneration of activated carbon for use in an adsorption treatment increases the complexity of the overall process and oxidation may be complicated. Coagulation processes may generate toxic sludges that require additional treatment, but the design of a coagulation process is simple and it can be used for primary or tertiary treatment (Teh et al., 2016).

Research on the treatment of a TMP pressate by coagulation and flocculation appears to be limited to the selective removal of wood extractives. In a United States patent by Roberts (1994), it was reported that up to 97 % of the fatty acids and 98 % of the resin acids were removed from a TMP pressate under the conditions of 50 mg/L alginate, 100 mg/L polyamide and 75 mg/L polyacrylamide addition. In a pilot trial study utilizing a dissolved air flotation unit, Opedal et al., (2011) determined that 76 % of the lipophilic extractives were removed from the TMP pressate under the conditions of 50 mg/L of equal mass of poly-(trimethyl(3-methacrylamidopropyl)-ammonium)chloride and poly-(N-N-dimethyldiallyl-3-4-ethylenpyrrolidonium) chloride addition, pH 6.6-7.1, 343 K and a 2 L/min flow rate of air-saturated water at 6 bar. In the study by Strand et al. (2012), which used a froth flotation unit, it was observed that 86 % of pitch, which includes fatty and resin acids, was removed from a TMP pressate under the conditions of 80 mg/L dodecythrimethylammonium chloride and pH 3.5 at 293 K. In another study that utilized a froth flotation unit, Singh et al. (2016) observed that 95 %

of the wood extractive were removed under the conditions of 80 mg/L dodecythrimethylammonium bromide, pH 5, 333K, 20 min, 4.5 L/min air flow, and 1300 rpm impeller speed.

Recently, Wu et al. (2016) investigated the removal of lignin from a prehydrolysis liquor using various coagulants while maximizing the retention of oligomeric xylose. The researchers determined that 44 % of lignin was removed and 98 % of the oligomeric xylose was retained under the conditions of 120 mg/L alum, 301 K and a stirring speed of 500 rpm for 60 min. Prehydrolysis liquor is the filtrate produced after wood chips are treated by steam or hot water, and thus may be similar to a TMP pressate. In another study by Stephenson & Duff (1996), coagulation was studied using various metals on a bleached chemithermomechanical pulping (BCTMP) effluent. The researchers determined that 90 % of the colour was removed for a 7.5 g/L dosage of ferric chloride and 90 % of the colour was removed for a dosage of 10 g/L aluminium chloride in the effluent. In the study by Chaudhari et al. (2010), coagulation process on a black liquor effluent was studied with polyaluminium chloride, aluminium chloride and copper sulphate. It was determined that 83 % of the COD was removed by polyaluminium chloride under the conditions of 8 mL/L at pH 5, 72 % of the COD was removed by aluminium chloride under the conditions of 5 g/L at pH 4 and 76 % of the COD was removed by copper sulphate under the conditions of 5 g/L at pH 6.

Sundin (2000) determined that calcium ions coagulated various kraft lignins, which had a molecular weight of more than 1000 g/mol, but no coagulation was observed when the molecular weight of lignin was less than 1000 g/mol. It was previously determined that the weight average and number average molecular weight of lignin in a TMP pressate was 2562 g/mol and 1088 g/mol, respectively (Chapter 3), and thus calcium ions may have a coagulating effect on lignin in a TMP pressate. Sundberg et al. (1994) observed that 0.01 mol/L of calcium chloride concentration completely removed the dissolved substances from a bleached TMP pulp suspension. However, Sundberg et al. (1994) also observed that a dosage of 0.002 mol/L of calcium chloride removed approximately 30 % of the substances from an unbleached TMP pulp suspension. He et al. (2014) investigated the coagulation of prehydrolysis of a kraft-based dissolving pulp process with various coagulants using focused beam reflectance measurement

(FBRM). It was observed that calcium chloride, magnesium chloride and iron chloride exhibited coagulated particles when mixed with prehydrolysis liquor, but sodium chloride and aluminium chloride did not. However, the addition of up to 1 mol/L of calcium chloride or sodium chloride did not coagulate particles of a magnesium bisulphite pulp and paper mill effluent (Yuliani et al., 2013).

In our previous research, the increase in calcium concentration of a fly ash was related to an increased adsorption capacity of lignin from a TMP pressate (Chapter 4) and the calcium concentration in the filtrate of the fly ash treatment in a TMP pressate was 5.5 times lower than that in the fly ash treatment of water (Chapter 5). Since lignin has an affinity for metal ions (Guo et al., 2008; Hojaji, 2012; Wu et al., 2008, Zhuang et al., 2003), it is hypothesized that the presence of calcium may have a coagulating effect on a TMP pressate and is in fact an objective in this study.

Research on the treatment of a TMP pressate by coagulation is limited and the previous coagulation studies on TMP pressate and prehydrolysis liquor were tailored to selectively remove wood extractives and lignin, respectively. Furthermore, the studies by Stephenson & Duff (1996) and by Chaudhari et al. (2010) were conducted on effluents that differed significantly from TMP pressate. To our knowledge, the effectiveness of a coagulation process for a TMP pressate is unknown and further studies are required. The second objective of this study was to investigate and compare the coagulation efficiency of a biomass fly ash leachate (FLC), calcium chloride and alum in the TMP pressate.

In this paper, the feasibility of the use of potassium chloride, calcium chloride, FLC and alum as potential coagulants for a TMP pressate was studied. The coagulating effect of these chemicals has not been studied previously on a TMP pressate and thus represents a novelty in the present study. The impact of coagulant dosage, pH, agitation speed and treatment time on the mean chord length and cord length distribution of the resulting coagulant/TMP pressate solution was monitored using FBRM analysis. Furthermore, the impact of coagulant dosage, pH, and agitation speed on the COD and lignin removals from a TMP pressate was determined.

6.3 Materials and methods

6.3.1 Materials

The TMP pressate and fly ash were obtained from a pulp mill that was located in central Canada. The fly ash was dried overnight in an oven at 378 K, sieved as described in section 6.3.2, and was then stored in a plastic bag at room temperature prior to use. The TMP pressate was initially analysed for its COD and lignin contents. The TMP pressate was then centrifuged at 1000 rpm for 10 min using a Thermo Scientific Sorvall ST 16 centrifuge to remove large undissolved particles, and was then stored in a refrigerator at 277 K prior to use. Sodium hydroxide (98 wt. %), hydrochloric acid (37 wt. %), sulfuric acid (95 wt. %), potassium chloride, calcium chloride and aluminium sulfate ($Al_2(SO_4)_3$, alum) were purchased from Sigma Aldrich Company. A 4 wt. % solution of sodium hydroxide, a 9 wt. % solution of potassium chloride, a 6 wt. % solution of calcium chloride, and a 5 wt. % solution of alum were prepared with deionized water. The Chemical oxygen demand (COD) kit (K-7365) was obtained from CHEMetrics Inc., USA.

6.3.2 Fractionation of biomass fly ash

The fly ash was mechanically sieved based on a method described previously (Zhu et al., 2013) using ASTM E11 sieves with mesh numbers of 60 and 400. In this method, the fly ash was sieved using a mechanical sieve shaker (CSC Scientific, Meinzer II Sieve Shaker), and fractionation was performed with 200 g samples for 10 min. The fly ash retained on the sieve with mesh # 60 was discarded and the fly ash retained on the sieve with mesh number 400 was used in this study.

6.3.3 Biomass fly ash leachate concentrate (FLC) preparation and characterization

Fly ash samples were added to 50 g of deionized water in 250 mL Erlenmeyer flasks at a dosage of 70 mg/g fly ash/water and the flasks were sealed. The mixtures were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 2 h. The mixtures were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1) and the fly ash leachate was collected. The metal content of the leachate samples was then analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro with CETAC ASX-510 Auto Sampler without pretreatment. Then, 1.25 L of the filtrate was concentrated in an oven at 378 K, which yielded a precipitate with a solid content of 7.71 g. The precipitates were then dissolved in water to a total weight of 100 g to produce FLC. The concentrations of its calcium, potassium and sodium concentrations of the FLC was determined via a mass balance. The concentration process was conducted to minimize the dilution effects for the experiments described in section 6.3.5.

6.3.4 Focused beam reflectance measurement (FBRM) analysis

The chord length of the colloids in the solutions were monitored using a FBRM instrument and Particle Track E25 probe (Mettler-Toledo AutoChem) as described previously (Fatehi et al., 2016). In this method, the probe and an impeller were mounted onto a shaft so that the blades of the impeller were 10 mm below the probe window and the impeller was offset at 65 mm with respect to the internal diameters of the probe and the impeller. The impeller used had 4 angled blades and the diameter made by the blades was 50 mm. The Particle Track E25 probe has a diameter of 25 mm and a scan circle diameter of 5 mm. The optical rotating laser scan speed was 2 m/s and data was collected every 3 s by the iC FBRM 4.3 control software into 90 log channels ranging from 1-1000 μm. The counts made by the instrument were counts per 2 m scan length and was reported as counts in this study. A moving average value of 15 was used on the data and all results reported were unweighted.

In the FBRM system, a rotating laser beam is projected through a sapphire window and light is reflected back through the sapphire window when the laser beam passes a particle. The software determines the chord length (i.e. the length between two edges of a particle) by multiplying the scan speed with the length of time of the reflected signal.

6.3.5 Coagulation experiments

In one set of experiments, the FBRM probe was immersed 20 mm below the solution level of 200 g samples of a TMP pressate in 400 mL glass beakers, and the TMP pressate was stirred at 200 rpm until steady state conditions were achieved. Then, various coagulant solution dosages of potassium chloride (546-4567 mg/kg KCl/TMP pressate), calcium chloride (1040-2770 mg/kg $CaCl_2$/TMP pressate), FLC (1897-5060 mg/kg FLC/TMP pressate), and alum (250-2500 mg/kg $Al_2(SO_4)_3$/TMP pressate) were added separately. The pH was adjusted to 6 for the alum experiments and to 12.5 for the potassium chloride, calcium chloride and the FLC experiments. The experiments were then repeated and the average results were reported. The coagulation efficiency of the coagulants studied was monitored by FBRM via quantifying the mean chord length and chord length distribution of particles produced in the samples after 30 min at 298 K.

In another set of experiments, the coagulation experiments were repeated under the same conditions, but with a calcium dosage of 2770 mg/kg $CaCl_2$/TMP pressate in the pH range of 6 and 12.5 and with an alum dosage of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate, in the pH range of 4.5 and 8.5. These experiments were also repeated at pH 6 for the alum treatments and at pH 12.5 for the calcium chloride treatments, under varied agitation speeds of 50, 100, 200 and 400 rpm for 30 min at 298 K, to investigate the impacts of agitation speed on the coagulation process.

6.3.6 COD and Lignin analysis

The COD analysis was conducted using a spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific) as described in the CHEMetrics COD kit. In this procedure, 2 mL samples were added to COD vials (CHEMetrics), and incubated for 2 h at 423 K in a reactor (CR 2200 WTW thermoreactor) prior to measuring the COD absorbance at 620 nm. The lignin concentration was determined by the spectrophotometric method at 250 nm (Saeed et al., 2012) as described previously (Liu et al., 2011) using a UV-Vis spectrophotometer (GENESY nm S 10S UV-Vis, Thermo Scientific). The pH of the samples was adjusted to 7 (± 0.25) prior to UV analysis, and the pH adjustment was conducted with 0.1 M NaOH or 0.1 M HCl.

6.3.7 COD and lignin removal measurements

After the coagulation experiments, all the samples were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1), and the filtrates were collected for COD and lignin analyses. The COD and lignin removals were determined using equation 1

$$\text{Removal}\ \% = \frac{C_0 - C_F}{C_0} \times 100 \tag{1}$$

where C_0 is the COD or lignin concentration in the filtrate of the control samples, and C_F refers to the COD or lignin concentration in the filtrate after the coagulation treatments. The concentration of the filtrates in the control samples was used instead of that of centrifuged TMP to account for the effect of filtration.

6.3.8 Hydrodynamic diameter analysis

The hydrodynamic diameter of lignin was determined based on a method previously described (Oveissi & Fatehi, 2015). In this method, the centrifuged TMP pressate was acidified to a pH of

1.5 with sulfuric acid (60 wt. %) and then shaken in a Boekel water bath shaker at 100 rpm and 298 K for 1 h. The solution was then centrifuged at 3000 rpm for 15 min (Thermo Scientific Sorvall ST 16 centrifuge) and the precipitate was collected. The lignin precipitate was suspended in deionized water, neutralized to pH 7, and then dried in an oven at 333 K. Then, a 1 wt. % lignin solution was prepared in a 0.5 mol/L sodium hydroxide solution and the solution was then stirred overnight. The hydrodynamic diameter of lignin under alkaline conditions was then measured by a static light scattering (SLS) instrument (Brookhaven, BI2000) at a scattering angle of 90° as described previously by Wang et al. (2006).

6.4 Results and discussion

6.4.1 Characterization of TMP pressate and fly ash leachate

Table 6.1 presents the characteristics of a TMP pressate before and after centrifugation and filtration treatments. The original TMP pressate had 2912 mg/L COD, 2.2 g/L lignin and a pH of 6.1. The results in Table 6.1 indicate that 6.3 % COD and 7.4 % lignin were removed after centrifugation at 1000 rpm for 10 min. The subsequent filtration removed an additional 23.5 % of the COD and 6.5 % of lignin, and no significant difference was observed when the pH of TMP pressate was adjusted to 4.5 or 12.5. Furthermore, the hydrodynamic diameter of the lignin present in the TMP pressate was determined to be 40 nm under alkaline conditions, which may suggest that self-aggregation of TMP lignin occurred under alkaline conditions (Ratnaweera et al., 2015). In our previous study (Chapter 4), the hydrodynamic diameter of a lignin from a TMP pressate was 8.5 nm at neutral pH. In another study, the hydrodynamic diameter of a prehydrolysis liquor lignin was determined to be 2.1 nm at pH 10 (Oveissi & Fatehi, 2015).

Table 6.1 Characteristics of the original TMP pressate and after pH adjustment and filtration

	TMP pressate			
Parameter	**Original**	**Centrifuged**	**Filtered**	
pH	6.1 ± 0.1	6.1 ± 0.1	4.5 ± 0.3	12.5 ± 0.3

COD, mg/L	2912 ± 63	2729 ± 72	2108 ± 37	2127 ± 35
Lignin, g/L	2.17 ± 0.04	2.01 ± 0.04	1.85 ± 0.02	1.87 ± 0.02

In Table 6.2, the concentrations of the metals in the biomass fly ash leachate are listed. The results indicate that under the conditions of 70 mg/g fly ash/water, 100 rpm and 298 K for 2 h leaching treatment, the main metals that were detected in the biomass leachate were Ca, K and Na. The trace metals that were detected to a significant extent were Ba, Mg, Mn, Si, Sr, and Zn and the remaining trace metals had a concentration of less than 0.1 mg/L or were below their minimum detection limit.

In this study, the biomass fly ash leachate was concentrated to produce FLC to evaluate its potential use as an alternative coagulant on a TMP pressate. The dosages of FLC applied to a TMP pressate were 1897-5060 mg/kg FLC/TMP pressate, which was equivalent to a calcium dosage range of 375-1000 mg/kg Ca/TMP pressate. The addition of a FLC to a TMP pressate at a dosage range of 1897-5060 mg/kg FLC/TMP pressate would also add trace metals to a TMP pressate, but at a slightly lower concentration than that indicated in Table 6.2 (on a mass balance basis). The pulp and paper sector is not currently regulated in Ontario for their metal contents (EPA, 1990, O. Reg. 760/93), and thus the acceptable limits for various trace metals in a pulp and paper effluent are unknown. However, the monthly average concentration limits for effluents in the mining sector are 0.5 mg/L for As, 0.3 mg/L for Cu, 0.5 mg/L for Ni, 0.2 mg/L for Pb and 0.5 mg/L for Zn (EPA, 1990, O. Reg. 560/94). Since the concentrations of As, Cu, Ni, and Pb in the biomass fly ash leachate were significantly below the acceptability limits for the metal mining sector, the results suggest that the potential use of a FLC coagulant on a TMP pressate at a dosage range between 1897-5060 mg/kg FLC/TMP pressate may not pose an environmental risk.

Table 6.2 Metal content of a biomass fly ash leachate (FLC) in water a biomass fly ash

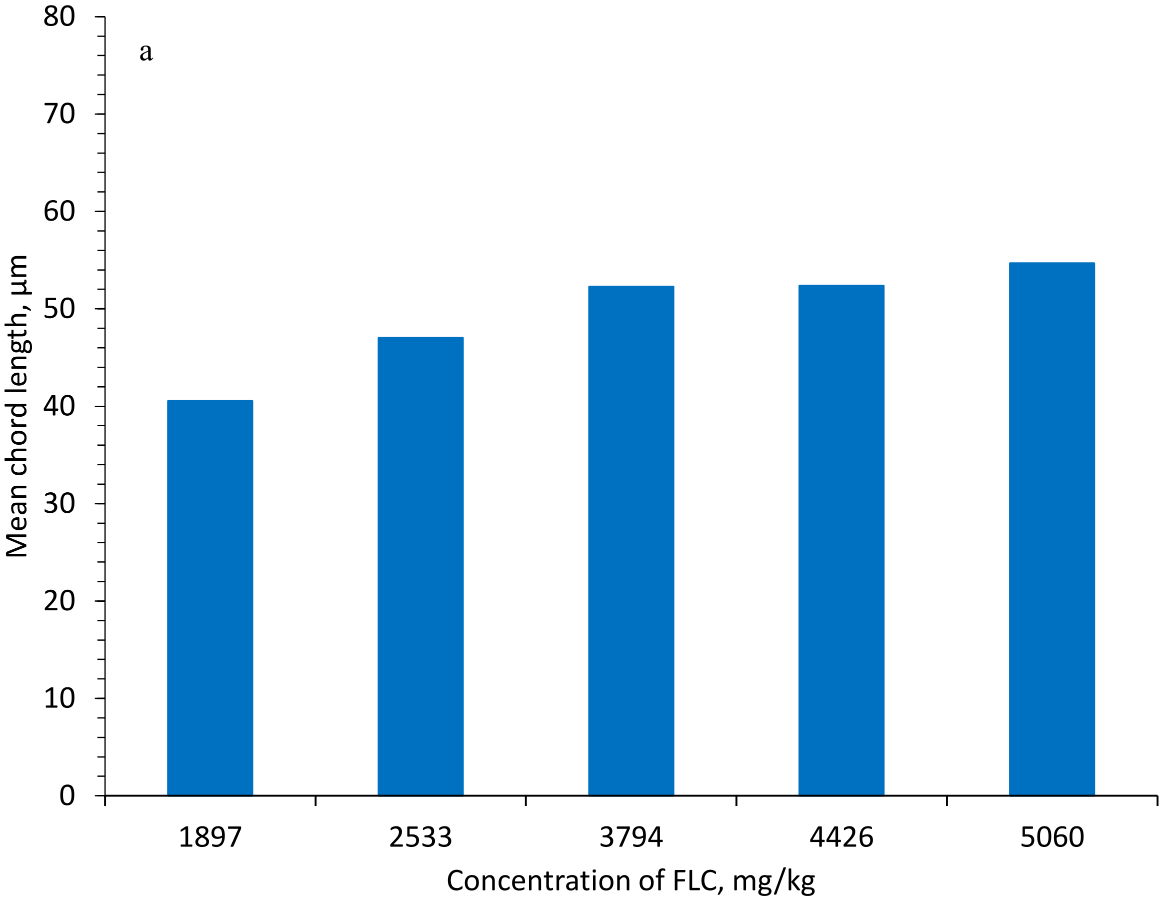
Metal	Fly ash leachate mg/L	Fly ash[a] wt. %
Major metals		
Ca	1218.70	19.16
K	2415.80	3.82
Na	464.76	0.70
Trace metals		
Al	0.07	0.94
As	<MDL	<0.01
Ba	0.25	0.14
Be	<MDL	<0.01
Cd	0.02	<0.01
Co	<MDL	<0.01
Cr	<MDL	<0.01
Cu	<MDL	0.01
Fe	0.01	0.59
Mg	0.78	1.48
Mn	0.16	0.79
Mo	<MDL	<0.01
Ni	0.05	<0.01
Pb	<MDL	<0.01
Si	0.31	0.09
Sr	2.14	0.05
Ti	<MDL	0.02
V	<MDL	<0.01
Zn	2.27	0.19

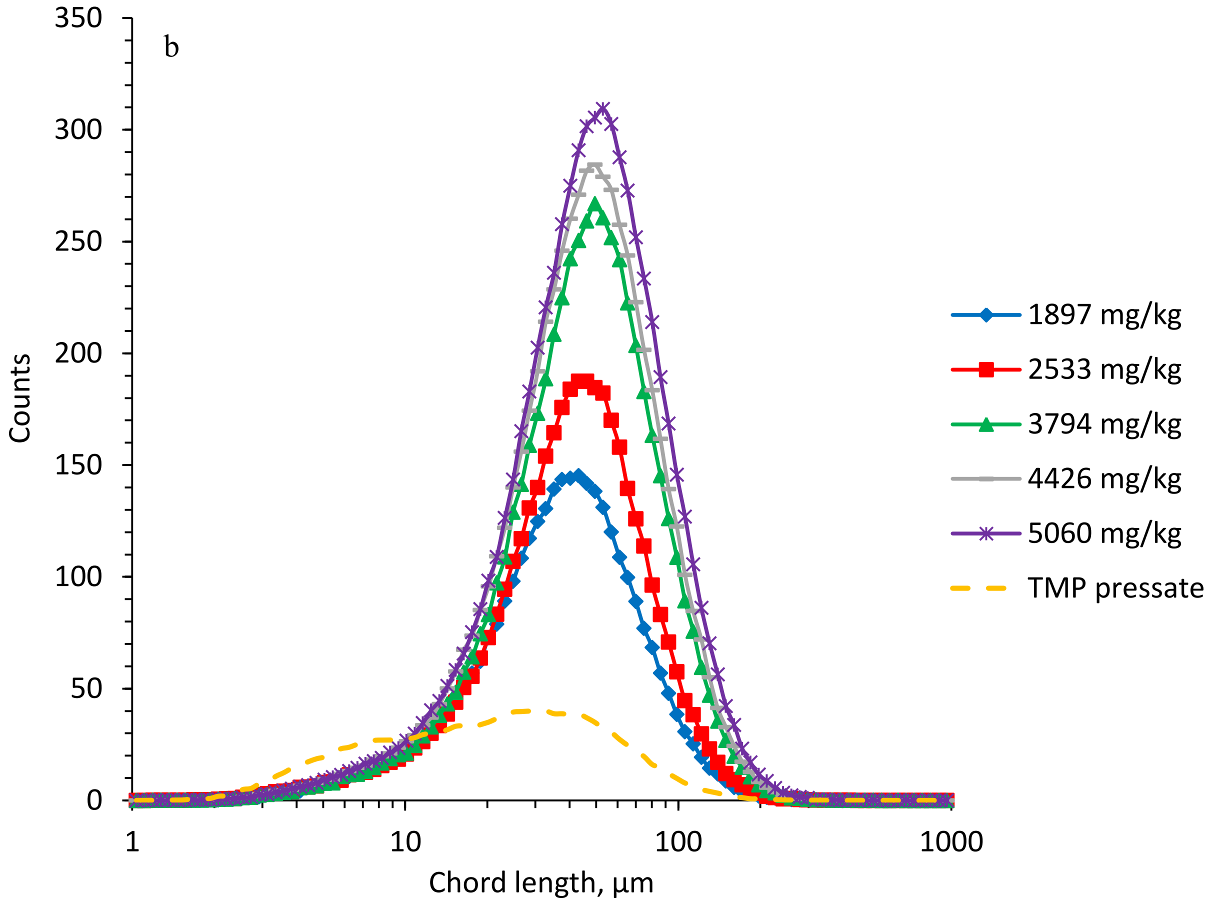
MDL = minimum detection limit

[a] The results were obtained from chapter 3

6.4.2 Potential use of a FLC, calcium chloride, potassium chloride and alum as coagulants for a TMP pressate

Figure 6.1a shows the impact of a FLC dosage on the mean chord length of a TMP pressate. It is seen that as the dosage of a FLC increased from 1897-5060 mg/kg FLC/TMP pressate, the mean chord length increased from 40.5 μm to 54.7 μm. Figure 6.1b shows the impact of FLC on the chord length distribution of the particles in the TMP pressate. It is seen that as the dosage of FLC increased from 1897 to 5060 mg/kg FLC/TMP pressate, the total number of counts and the peak chord length increased. In Figure 6.1c the impact of the FLC dosage on the COD and lignin removals from a TMP pressate are shown. The results indicate that as the dosage of the FLC increased from 1897 to 5060 mg/kg FLC/TMP pressate, the COD and lignin removals increased from 8.2 % to 18.4 % and from 22.3 % to 26.9 %, respectively. The addition of the FLC to the TMP pressate for a dosage range of 1897-5060 mg/kg FLC/TMP pressate corresponded to the addition of calcium in the range of 375-1000 mg/kg Ca/TMP pressate, potassium in the range of 744-1983 mg/kg K/TMP pressate and sodium in the range of 143-381 mg/kg Na/TMP pressate. Overall, the results in Figures 6.1 indicate that the FLC had a coagulating effect on the TMP pressate under the conditions of 200 rpm, pH 12.5 and 298 K for 30 min.


a
Mean chord length, µm
0
10
20
30
40
50
60
70
80
1897
2533
3794
4426
5060
Concentration of FLC, mg/kg


b
Counts
Chord length, µm
0
50
100
150
200
250
300
350
1
10
100
1000
1897 mg/kg
2533 mg/kg
3794 mg/kg
4426 mg/kg
5060 mg/kg
TMP pressate

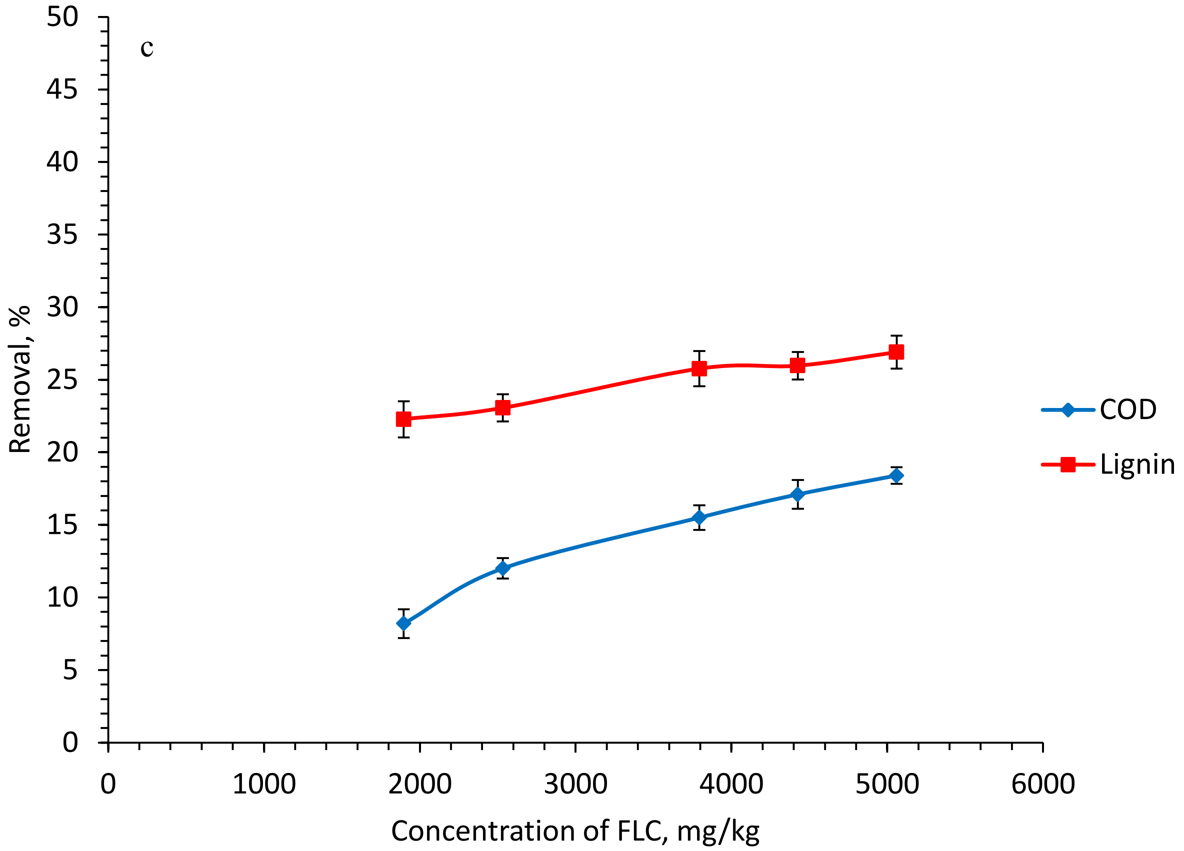
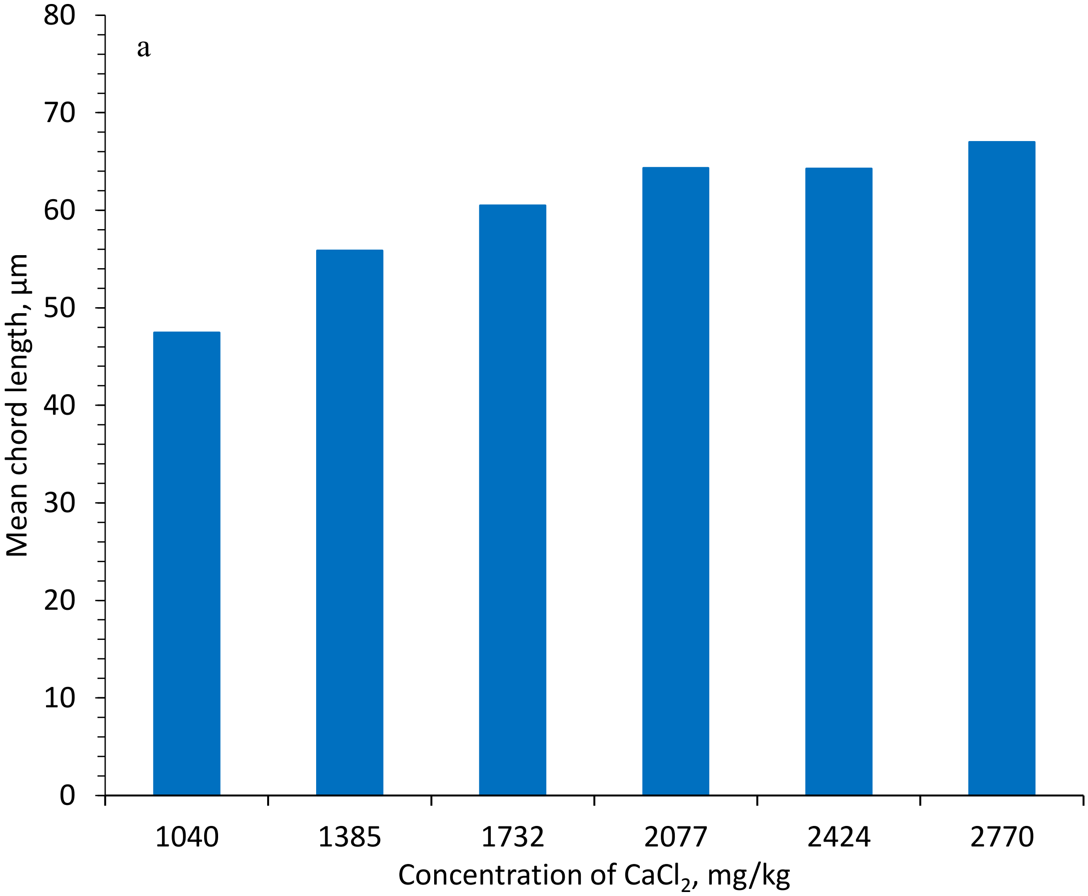
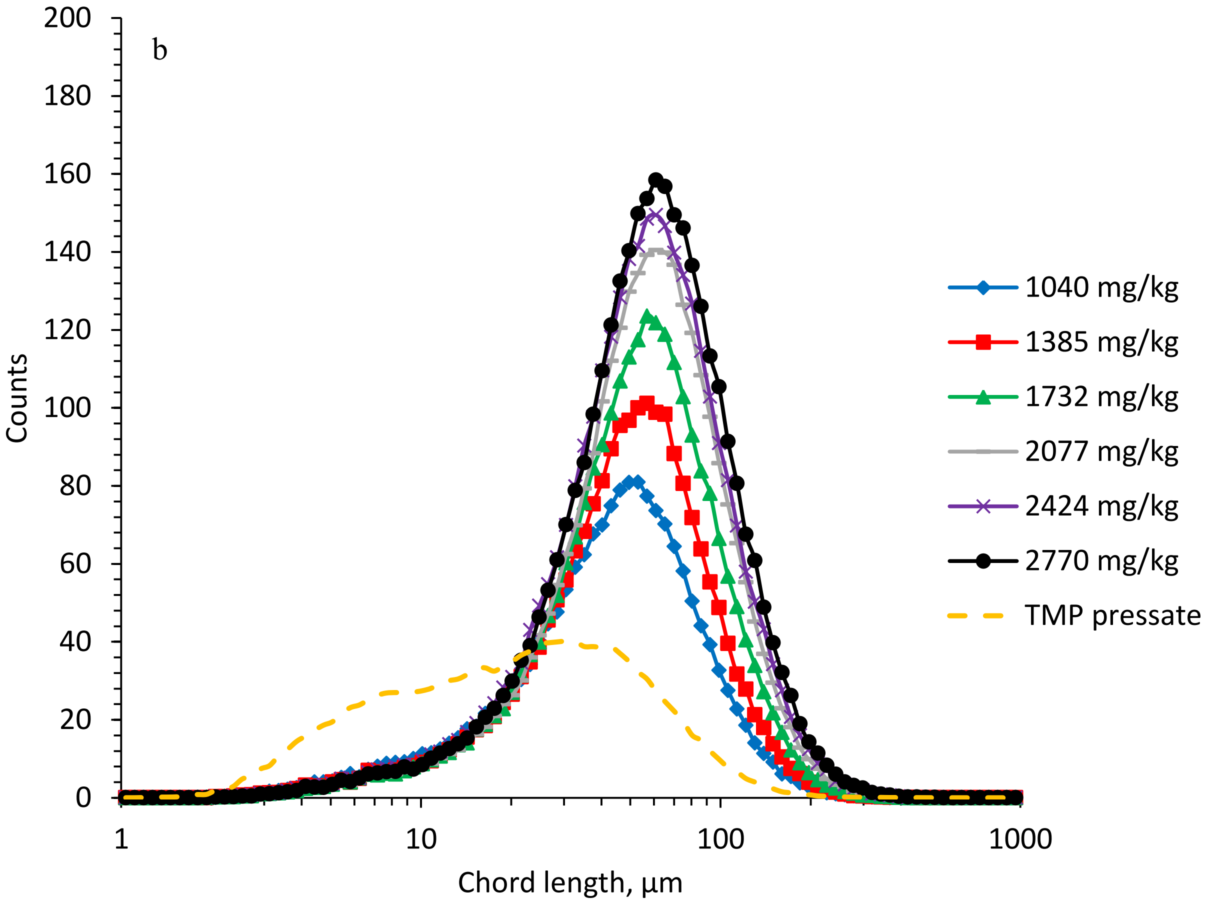


Figure 6.1 The impact of dosage of a FLC on a) the mean chord length b) the chord length distribution and c) the COD and lignin removals of a TMP pressate. The treatment conditions were 200 rpm, pH 12.5, and 298K for 30 min.

Figure 6.2a shows the impact of calcium chloride dosage on the mean chord length of the particles in the TMP pressate. It is seen that as the dosage of calcium chloride increased from 1040-2770 mg/kg $CaCl_2$/TMP pressate, the mean chord length increased from 47.5 µm to 67.0 µm. Figure 6.2b shows the impact of the calcium chloride dosage on the chord length distribution of the particles in the TMP pressate. The results indicate that as the dosage of calcium chloride increased, the total number of counts and the peak chord length increased. Thus, the results in Figure 6.2 suggest that calcium chloride had a coagulating effect on the constituents in the TMP pressate under the conditions of 200 rpm, pH 12.5 and 298 K for 30 min. In Figure 6.2c the impact of the calcium chloride dosage on the COD and lignin removals from a TMP pressate are shown. The results indicate that as the dosage of calcium chloride increased from 1040-2770 mg/kg $CaCl_2$/TMP pressate, the COD and lignin removals increased from 6.1 % to 20.8 % and 20.8 to 30.8 %, respectively.




b
Counts
0
20
40
60
80
100
120
140
160
180
200
1
10
100
1000
Chord length, µm
1040 mg/kg
1385 mg/kg
1732 mg/kg
2077 mg/kg
2424 mg/kg
2770 mg/kg
TMP pressate

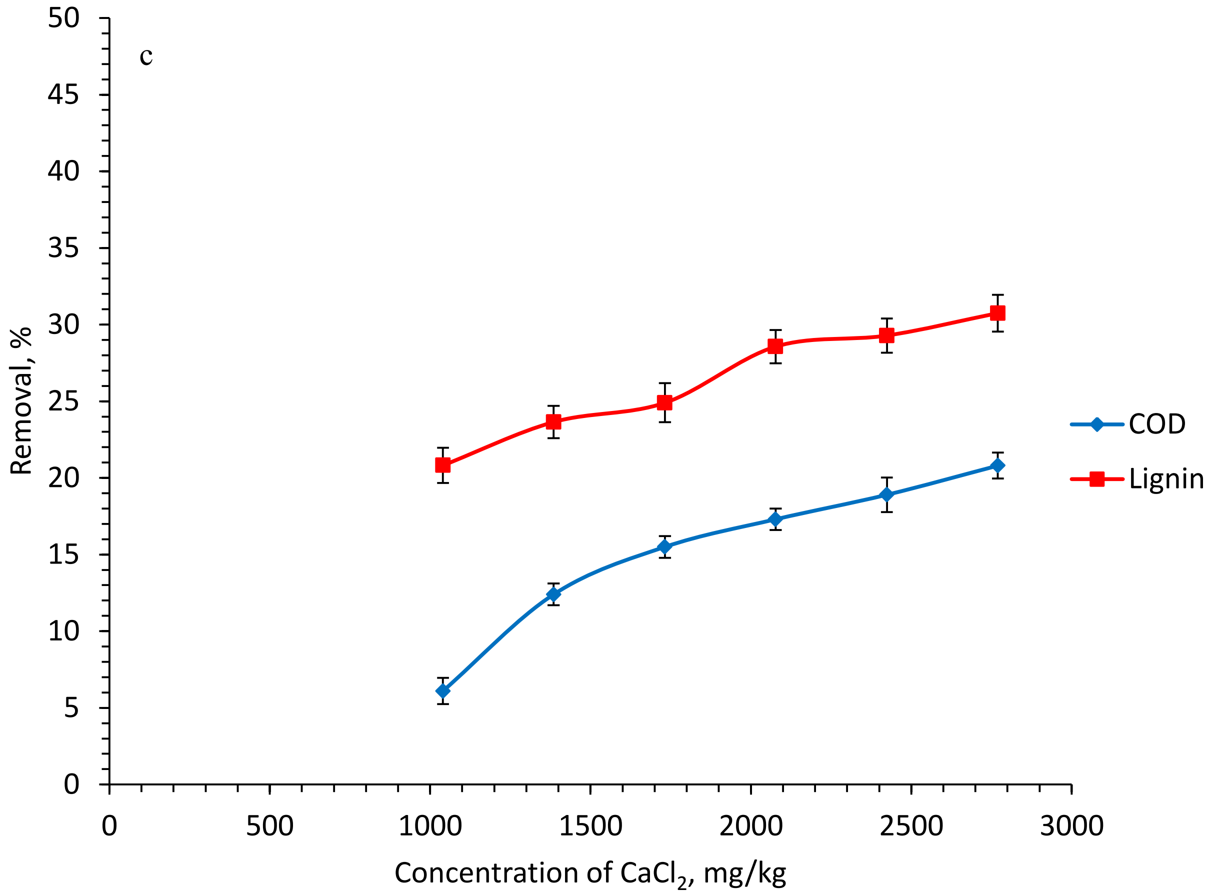


Figure 6.2 The impact of calcium chloride dosage on a) the mean chord length b) the chord length distribution and c) the COD and lignin removals of a TMP pressate. The treatment conditions were 200 rpm, pH 12.5, and 298K for 30 min.

In Figure 6.3, the impact of potassium chloride dosage on the chord length distribution of the TMP pressate is presented. The results indicate that the addition of potassium chloride in the range of 546-4567 mg/kg KCl/TMP pressate had no impact on the chord length distribution. The potassium dosage range added to the TMP pressate for the results in Figure 6.3 was equivalent to the addition of 767-6123 mg/kg FLC/TMP pressate, which indicates that potassium chloride in the FLC did not contribute to coagulation of the components of TMP pressate. According to the Schultz –Hardy rule, the critical coagulation is inversely proportional to the sixth power of the counter ion charge (Crittenden et al., 2012). Since the concentration of the sodium ions present in the FLC was significantly lower than the concentration of potassium ions, it was assumed that the sodium ions present in the FLC did not exert a coagulating effect on the TMP pressate. Thus, the results suggest that the coagulation observed when FLC was added to the TMP pressate may have been attributed to the presence of calcium ions.

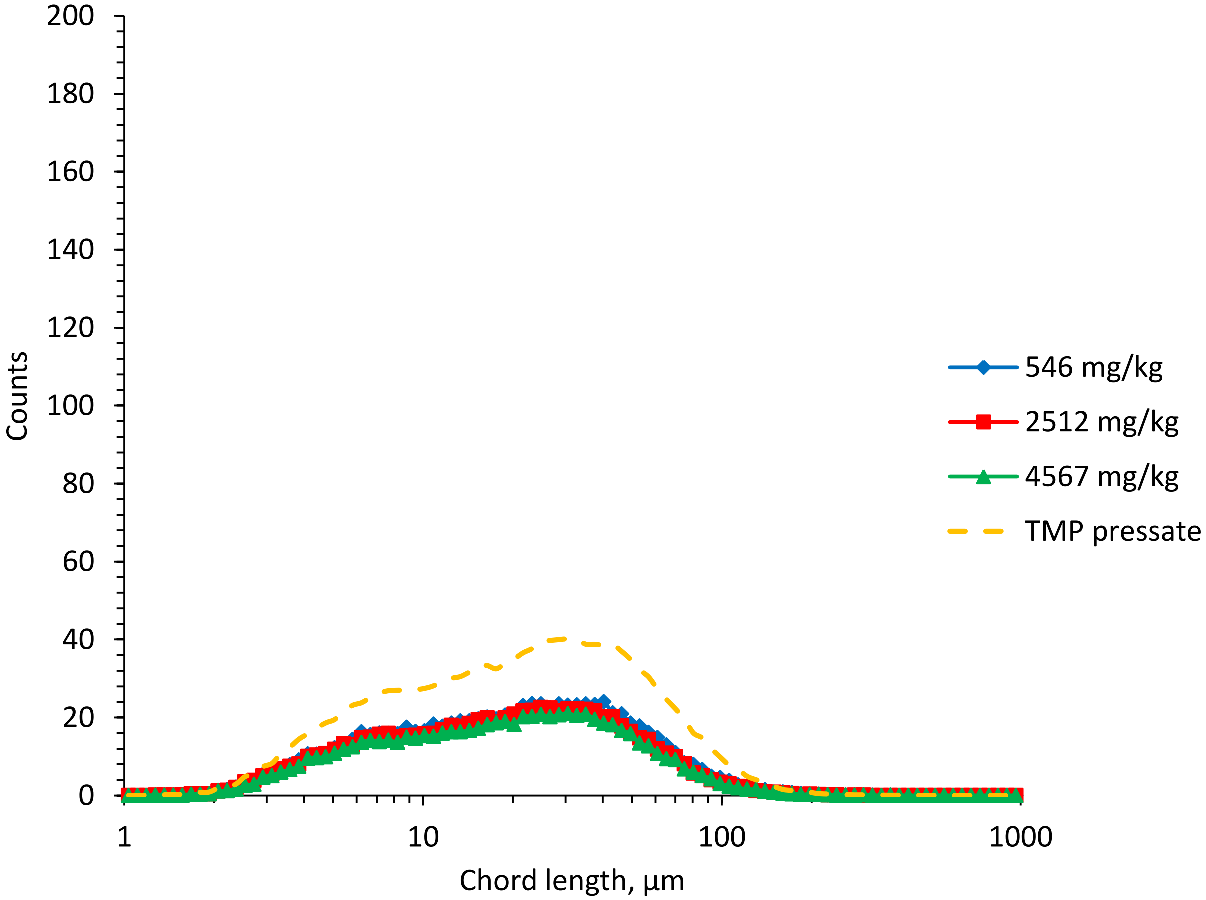
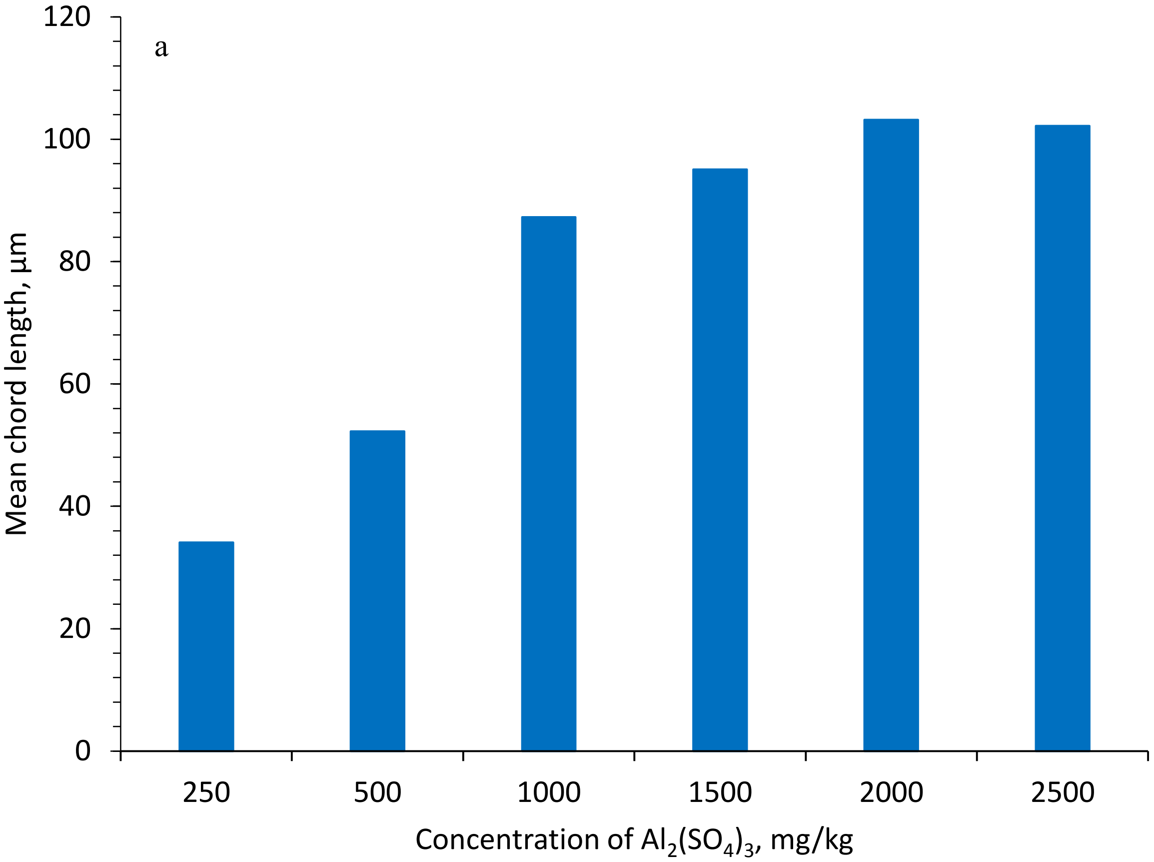
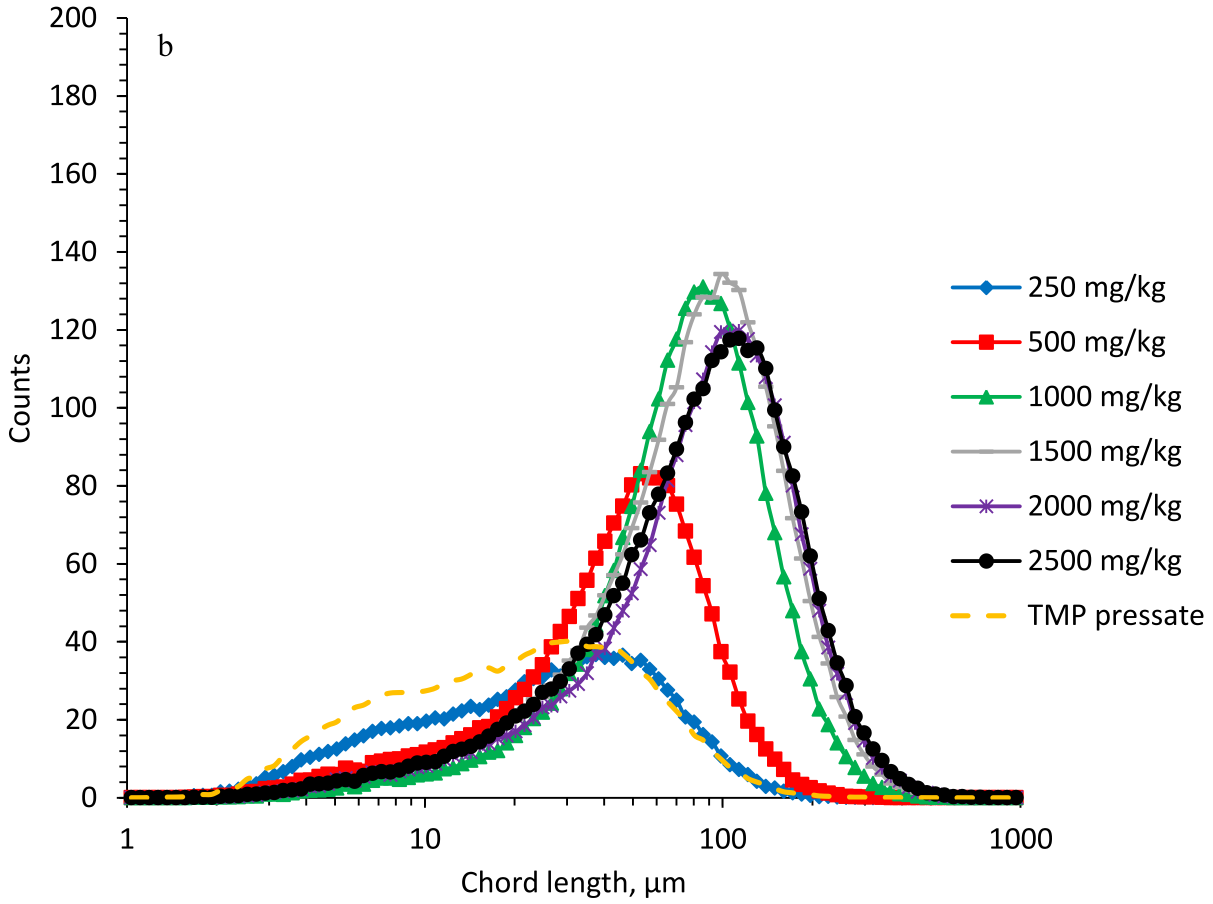


Figure 6.3 The impact of potassium chloride dosage on the chord length distribution of a TMP pressate. The treatment conditions were 200 rpm, pH 12.5, and 298K for 30 min.

Figure 6.4a presents the impact of alum dosage on the mean chord length of a TMP pressate. The results indicate that as the concentration of the alum increased from 250 to 2000 mg/kg $Al_2(SO_4)_3$/TMP pressate, the chord length increased from 34.1 to 103.2 µm, but a further increase of the alum dosage to 2500 mg/kg $Al_2(SO_4)_3$/TMP pressate seemed to insignificantly impact the chord length. Figure 6.4b presents the impact of alum dosage on the chord length distribution of a TMP pressate. The results indicate that a dosage of 250 mg/kg $Al_2(SO_4)_3$/TMP pressate resulted in a small reduction in the number of counts in the 1-50 µm chord length range and a subsequent slight increase in number of counts in the 50-150 µm chord length range. As the alum dosage was increased to 1500 mg/kg $Al_2(SO_4)_3$/TMP pressate, the number of counts in the 50-150 μm and 150-300 μm chord length ranges increased. Then as the alum dosage was further increased to 2000 mg/kg $Al_2(SO_4)_3$/TMP pressate, the number of counts in the 50-150 μm chord length range decreased and the number of counts in the 150-300 μm chord length range slightly increased. However, as the alum dosage was increased to 2500 mg/kg $Al_2(SO_4)_3$/TMP pressate, no significant change in the chord length distribution was observed. Thus, the results in Figure 6.4 indicate that alum exhibited a coagulating effect on the TMP pressate, but that the increase in dosage from 2000-2500 mg/kg $Al_2(SO_4)_3$/TMP pressate did not appear to significantly increase the coagulation effect on a TMP pressate.

Figure 6.4c depicts the impact of alum dosage on the removal of COD and lignin from a TMP pressate. As the dosage of alum increased from 250-2500 mg/kg $Al_2(SO_4)_3$/TMP pressate, the COD and lignin removals increased from 5.6 % to 43.9 % and 11.3 to 41.5 %, respectively, under the conditions of 200 rpm, pH 6 and 298 K for 30 min treatment. Furthermore, the results in Figure 6.4c indicate that an increase in the alum dosage greater than 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate insignificantly improved the coagulation process of a TMP pressate with respect to COD and lignin removals.


a
Mean chord length, µm
0
20
40
60
80
100
120
250
500
1000
1500
2000
2500
Concentration of Al2(SO4)3, mg/kg


b
Counts
0
20
40
60
80
100
120
140
160
180
200
1
10
100
1000
Chord length, µm
250 mg/kg
500 mg/kg
1000 mg/kg
1500 mg/kg
2000 mg/kg
2500 mg/kg
TMP pressate

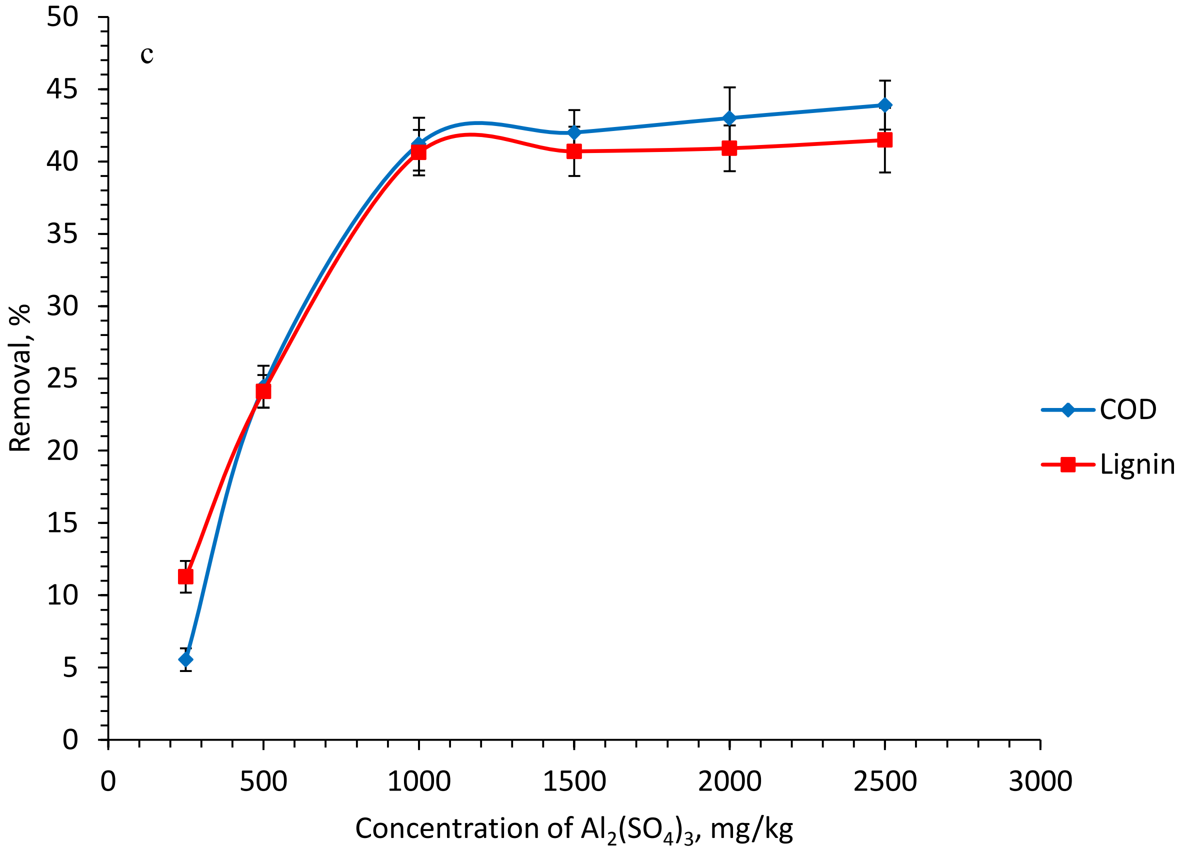
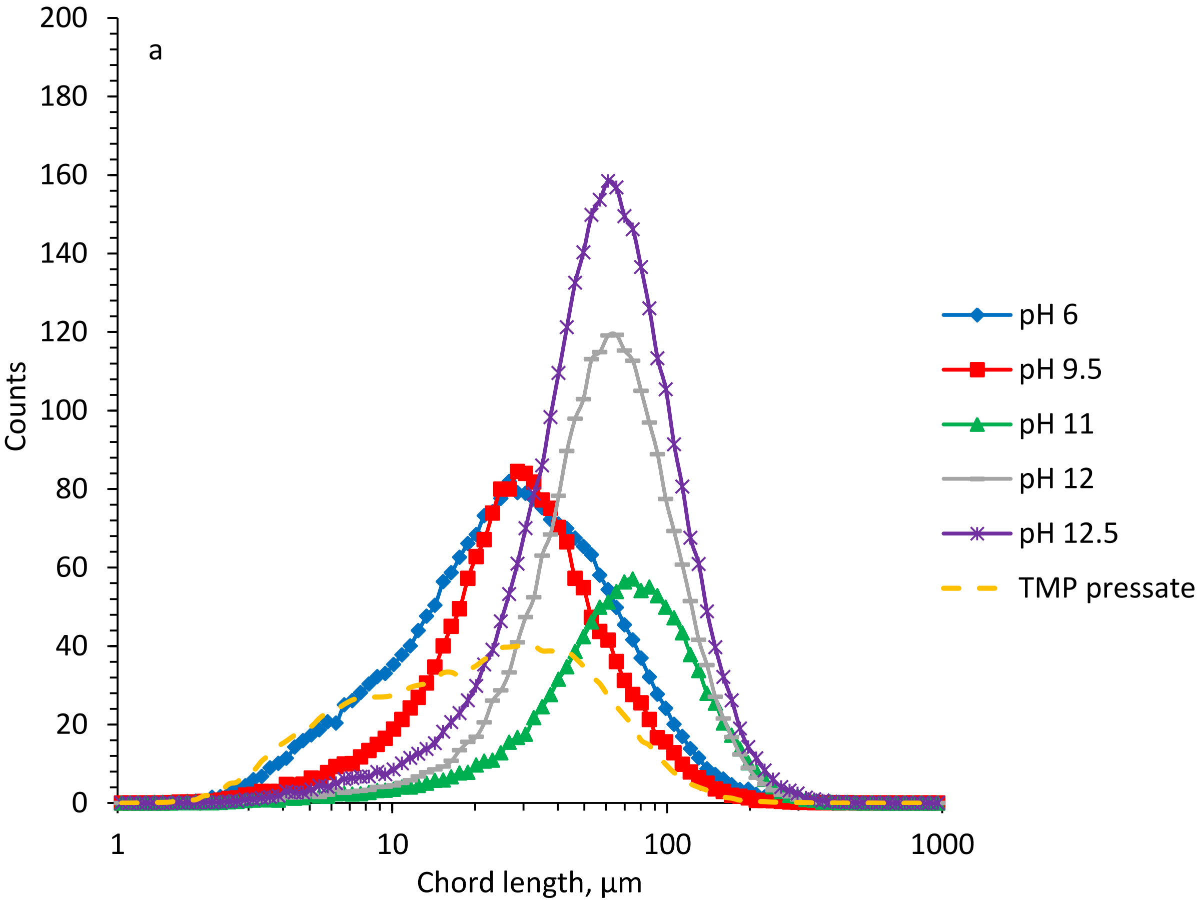


Figure 6.4 The impact of alum dosage on a) the chord length b) the chord length distribution and c) the COD and lignin removals of a TMP pressate. The treatment conditions were 200 rpm, pH 6 and 298K for 30 min.

The results in Figure 6.4a also suggest that the narrowest chord length distribution was obtained when the dosage was 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate. A narrow particle size distribution may improve the settleability of the resultant floc (Benjamin & Lawler, 2013). Thus, the alum dosage of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate was chosen as the optimum dosage for alum coagulation treatment of a TMP pressate. A dosage of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate would produce aluminum hydroxide precipitates, and therefore the coagulation mechanism would involve destabilization through enmeshment (Bratby, 2016; Crittenden et al., 2012). The mechanism of enmeshment is not thoroughly understood. However, it is believed that the process of enmeshment involves the nucleation of metal precipitates on the surface of particles, which then grow forming an amorphous solid, thereby entrapping particles during the growth process (Crittenden et al., 2012).

6.4.3 Impact of pH

Figure 6.5 presents the effect of pH on the chord length distribution of a TMP pressate when calcium chloride or alum were used as a coagulant. In Figure 6.5a, it is seen that the optimum pH for a calcium chloride-based coagulation treatment of a TMP pressate would be 12.5 since the chord length distribution at pH 12.5 corresponded to the greatest number of counts in the range of 50-150 μm. The results in Figure 6.5b indicate that the coagulation treatment of a TMP pressate with alum would be less effective at a pH below 4.5 and less effective at a pH greater than 6.5 since the number of counts in the 50-150 μm chord length range was significantly reduced at these pH ranges. The results in Figure 6.5b also suggest that the impact of pH on the extent of coagulation would be estimated to be similar at pH 5.5 and pH 6.


a
Counts
0
20
40
60
80
100
120
140
160
180
200
1
10
100
1000
Chord length, µm
pH 6
pH 9.5
pH 11
pH 12
pH 12.5
TMP pressate

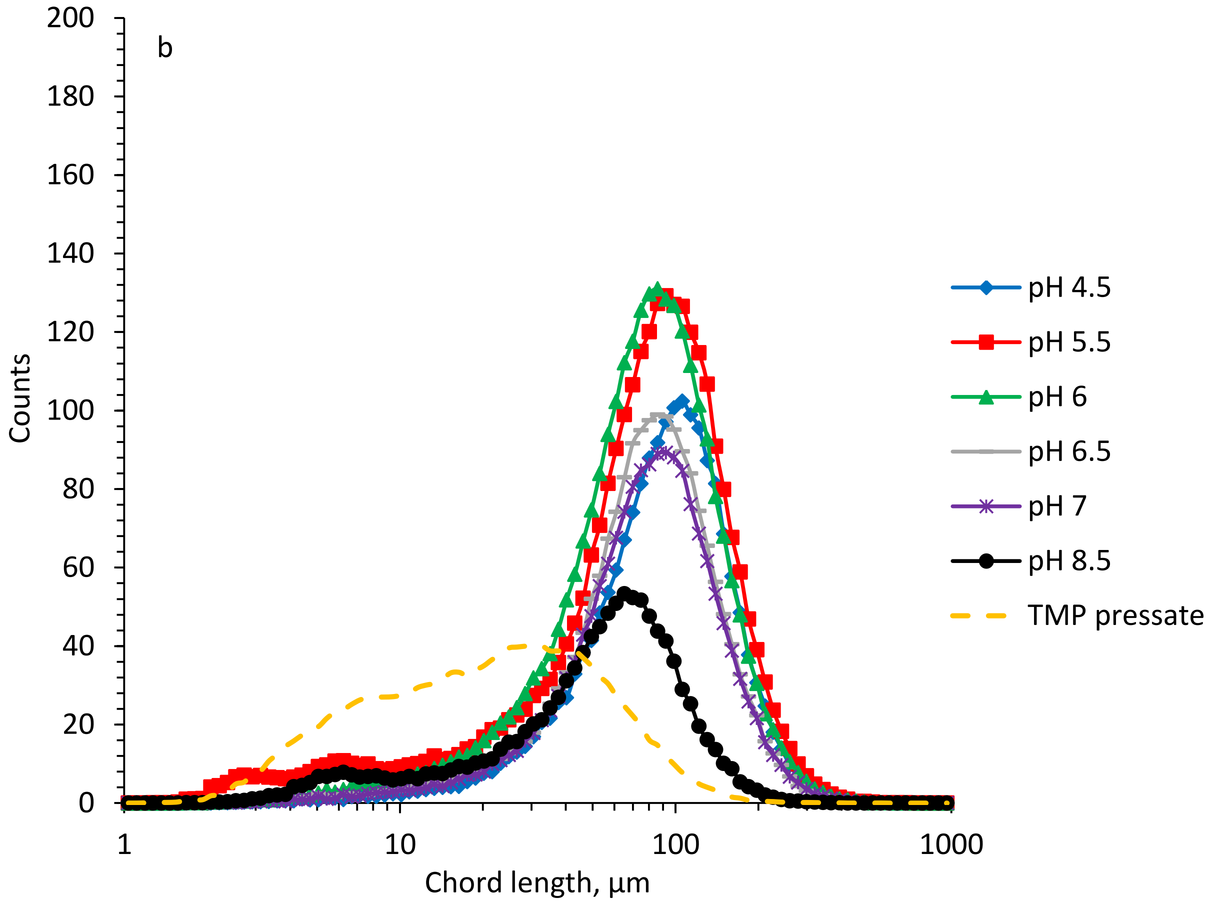
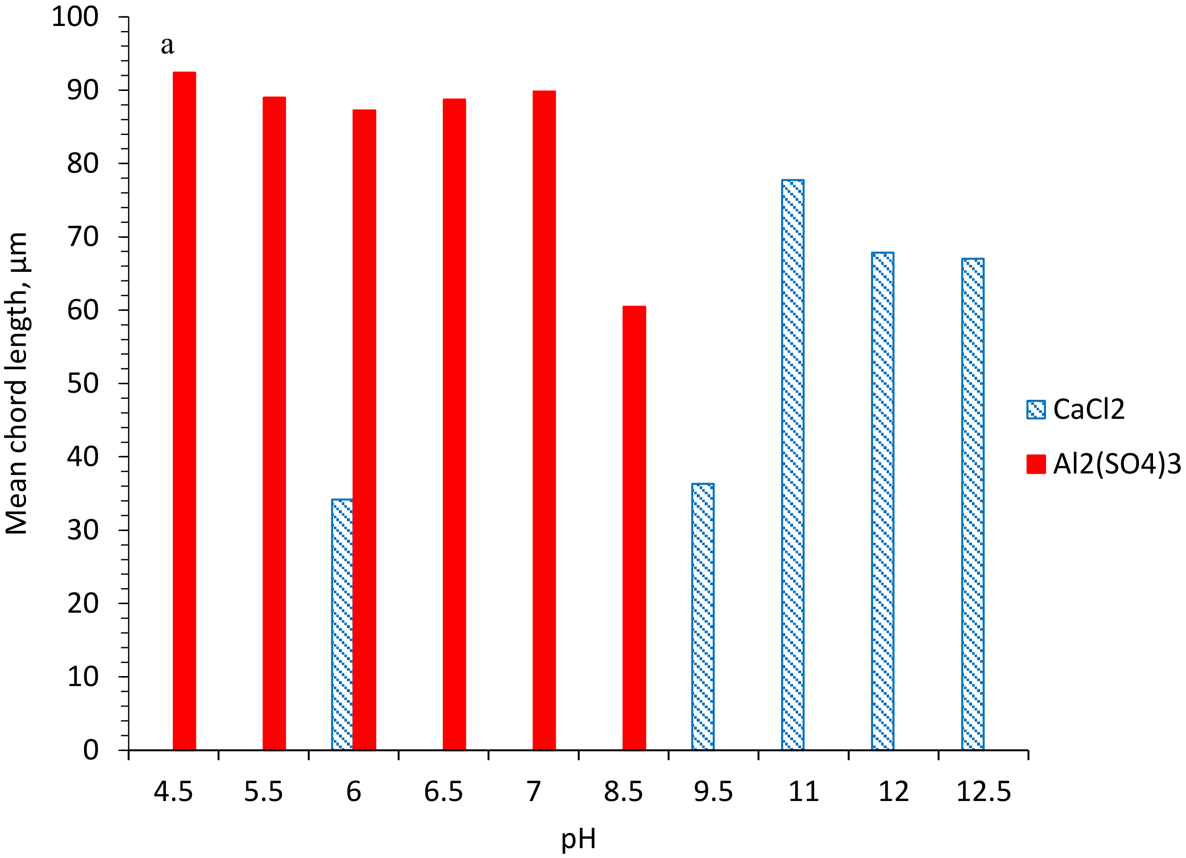


Figure 6.5 The impact of pH on the chord length of the coagulation treatment of TMP pressate. a) calcium chloride, 2770 mg/kg $CaCl_2$/TMP pressate b) alum, 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate and all coagulation conditions were 200 rpm, 298 K and 30 min.

Figure 6.6a shows the impact of pH on the mean chord lengths of a TMP pressate when calcium chloride or alum coagulants were used. The results in Figure 6.6a indicate that the largest chord lengths were observed when the pH was 11 for a calcium chloride-based treatment and pH 4.5 for an alum-based treatment. Figure 6.6b presents the impact of pH on the COD and lignin removals from a TMP pressate when calcium chloride or alum were used as coagulants. The results in Figure 6.6b indicates that for a calcium chloride-based treatment on a TMP pressate, as the pH increased from 6 to 12.5, the COD and lignin removals increased from 13.6 % to 20.8 % and 14.0 % to 30.8 %, respectively. A possible explanation for the improved removal of lignin under alkaline conditions may be due to aggregation of lignin molecules with calcium hydroxide at a high pH. As stated earlier, the hydrodynamic size of TMP pressate lignin significantly increases from 8.5 nm to 40 nm as the pH increases from neutral to alkaline conditions. This may indicate that lignin molecules self-aggregated to some extent. This self-aggregation may also help with coagulation with calcium hydroxide. Since a dosage of 2770 mg/kg $CaCl_2$/TMP pressate was used for the experiments in Figures 6.5 and 6.6, a portion of the calcium chloride was expected to have precipitated under alkaline conditions, and the improved lignin removal may have occurred via mechanism of enmeshment.

The results in Figure 6.6b indicates that when alum was used as a coagulant on a TMP pressate, the lignin removal was 39.7 % at pH 5.5 and 40.6 % at pH 6 and thus the coagulation for lignin removal was similar at pH 5.5 and pH 6. However, the results in Figure 6.6b indicate that the COD removal of an alum-treated TMP pressate was 33.1 % at pH 5.5 and 41.2 % at pH 6. Thus, the results indicate that a variation in the pH from 5.5 to 6 had a significant effect on the coagulation efficiency with respect to the COD removal for an alum-based treatment of a TMP pressate. The results in Figure 6.6b also indicate that the optimum pH for an alum-based treatment on a TMP pressate was 6. Overall, the results of the impact of pH on the alum coagulation experiments are in agreement with the literature results since the optimum pH range for coagulation using alum was expected to be between 5.5 and 7.7 (Crittenden, 2012; Bratby, 2016; Benjamin & Lawler, 2013).


a
Mean chord length, µm
0
10
20
30
40
50
60
70
80
90
100
4.5
5.5
6
6.5
7
8.5
9.5
11
12
12.5
pH
CaCl2
Al2(SO4)3

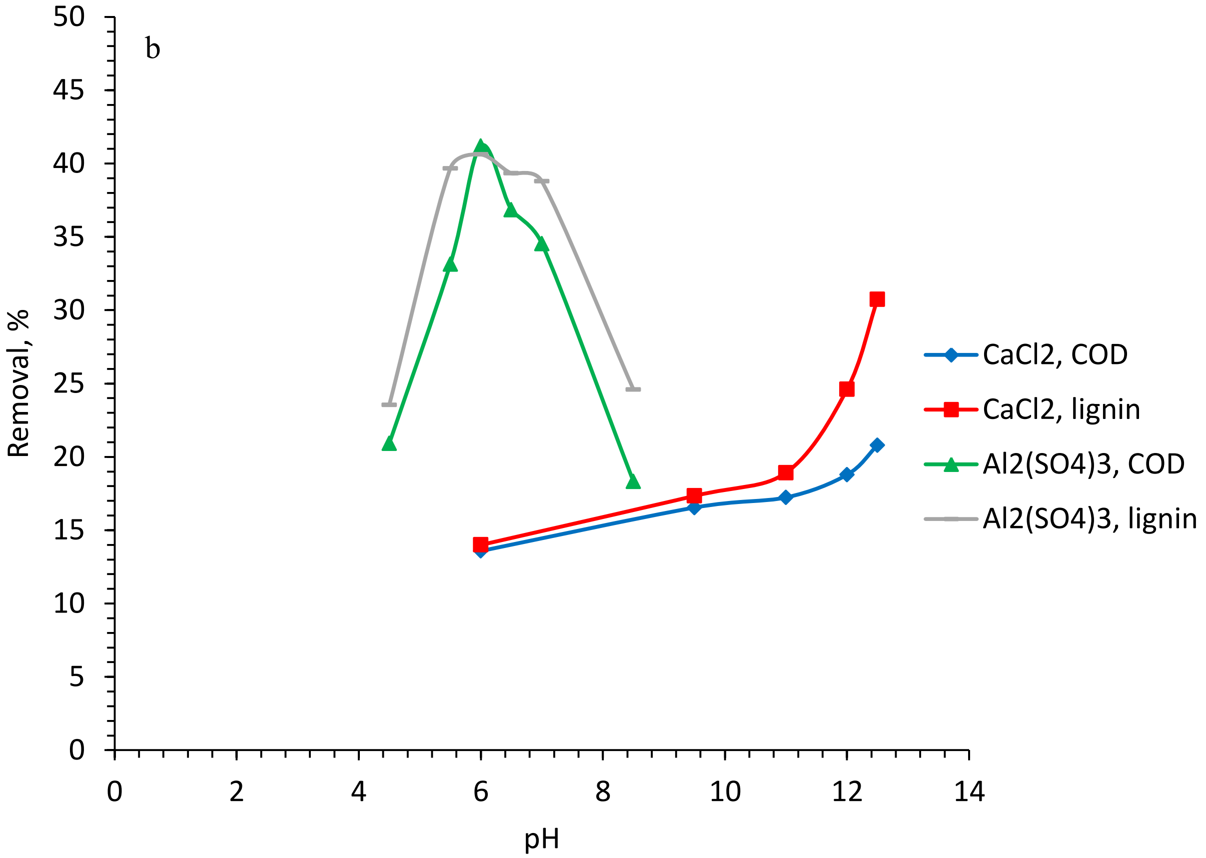


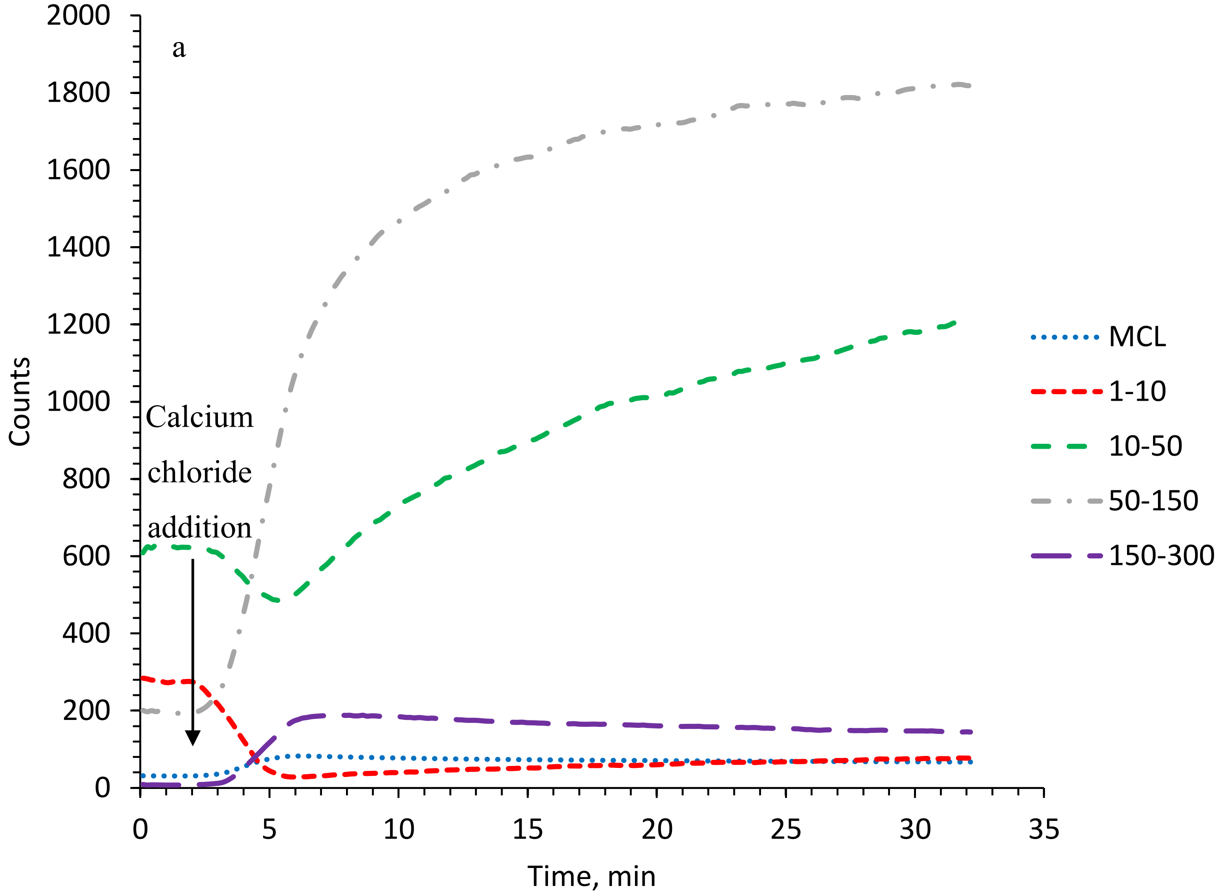
Figure 6.6 The impact of pH on a) the mean chord length and b) the COD and lignin removals from a TMP pressate when calcium chloride or alum were used as coagulants. The treatment conditions were 2770 mg/kg $CaCl_2$/TMP pressate or 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate, and 200 rpm, 298K and 30 min.

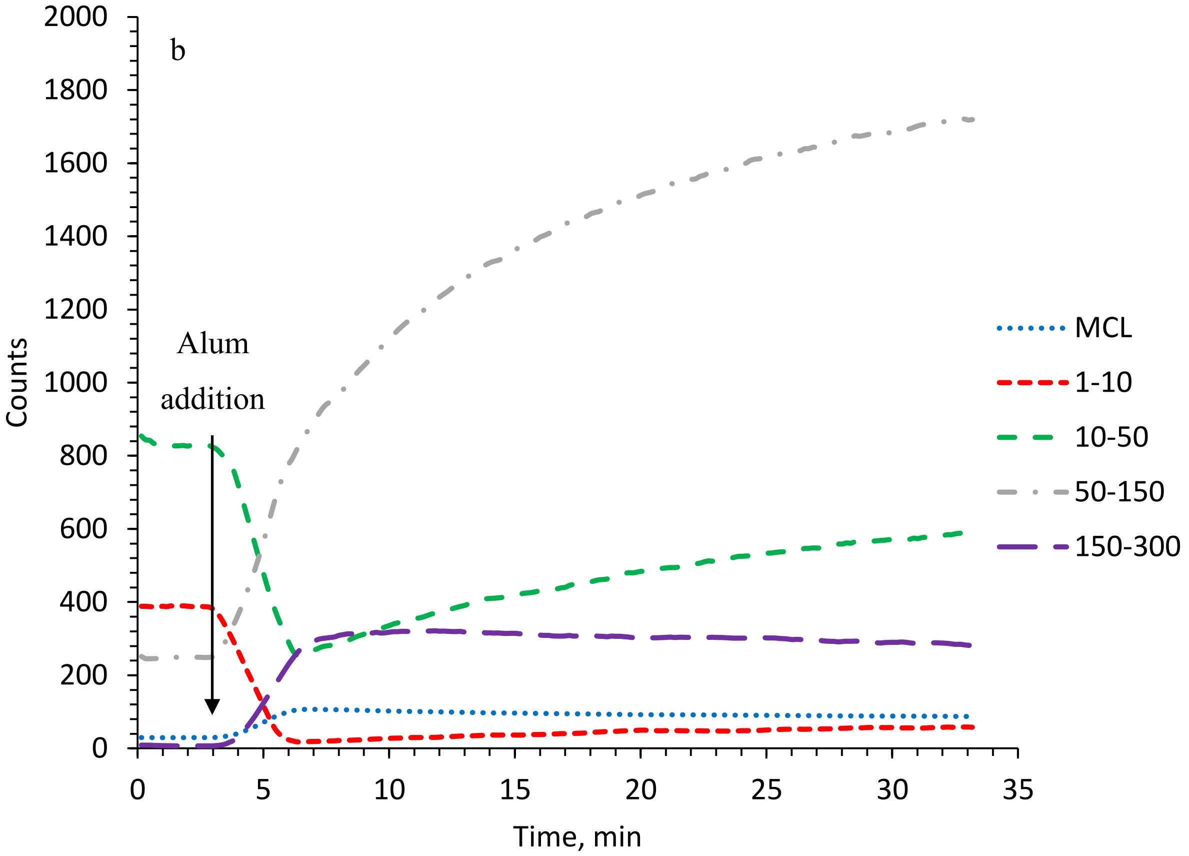
6.4.4 Impact of coagulation time

Figure 6.7a shows the impact of the coagulation time on the number of counts for various chord length ranges when calcium chloride was used as a coagulant on a TMP pressate. It is seen that calcium chloride addition to the TMP pressate led to a significant reduction in the number of counts in the 1-10 μm and 10-50 μm chord length ranges and a subsequent significant increases in number of counts in the 50-150 μm and 150-300 μm chord length ranges. The results suggest that the colloids in the 1-50 μm and 50-150 μm chord length rapidly coagulated to yield large flocs. It was also observed that the mean chord length reached a maximum of 82.5 µm after a coagulation treatment of approximately 4 min.

Figure 6.7b presents the impact of the coagulation time on the number of counts for various chord length ranges on a TMP pressate, when the coagulant used was alum. A similar coagulation trend as that for calcium chloride addition was observed. A comparison of the results given in Figure 6.7a and 6.7b suggests that the progression of the coagulation process by calcium chloride or alum on a TMP pressate were similar. It was also observed that the mean chord length reached a maximum of 106.6 µm after a coagulation treatment of approximately 4 min.

Figure 6.7c shows the impact of the coagulation time on the number of counts for various chord length ranges when a FLC was used as a coagulant on a TMP pressate. The results indicate that after the FLC was added to the TMP pressate, a significant increase in the number of counts in the 1-10 µm, 10-50 µm and 50-150 µm chord length ranges and a moderate increase in number of counts in the 150-300 µm chord length range occurred. It was also observed that the mean chord length reached a maximum of 60.0 µm after a coagulation treatment of approximately 7 min. The results in Figure 6.7 may indicate that the coagulation of the colloids in the 1-50 µm chord length range occurred continuously for the FLC-treated TMP pressate (Figure 6.7c), but the conversion to larger sized aggregates was slower when compared with the coagulation by calcium chloride (Figure 6.7a) or alum (Figure 6.7b).


a
Calcium chloride addition
Counts
Time, min
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
5
10
15
20
25
30
35
MCL
1-10
10-50
50-150
150-300


b
Counts
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Alum
addition
Time, min
0
5
10
15
20
25
30
35
MCL
1-10
10-50
50-150
150-300

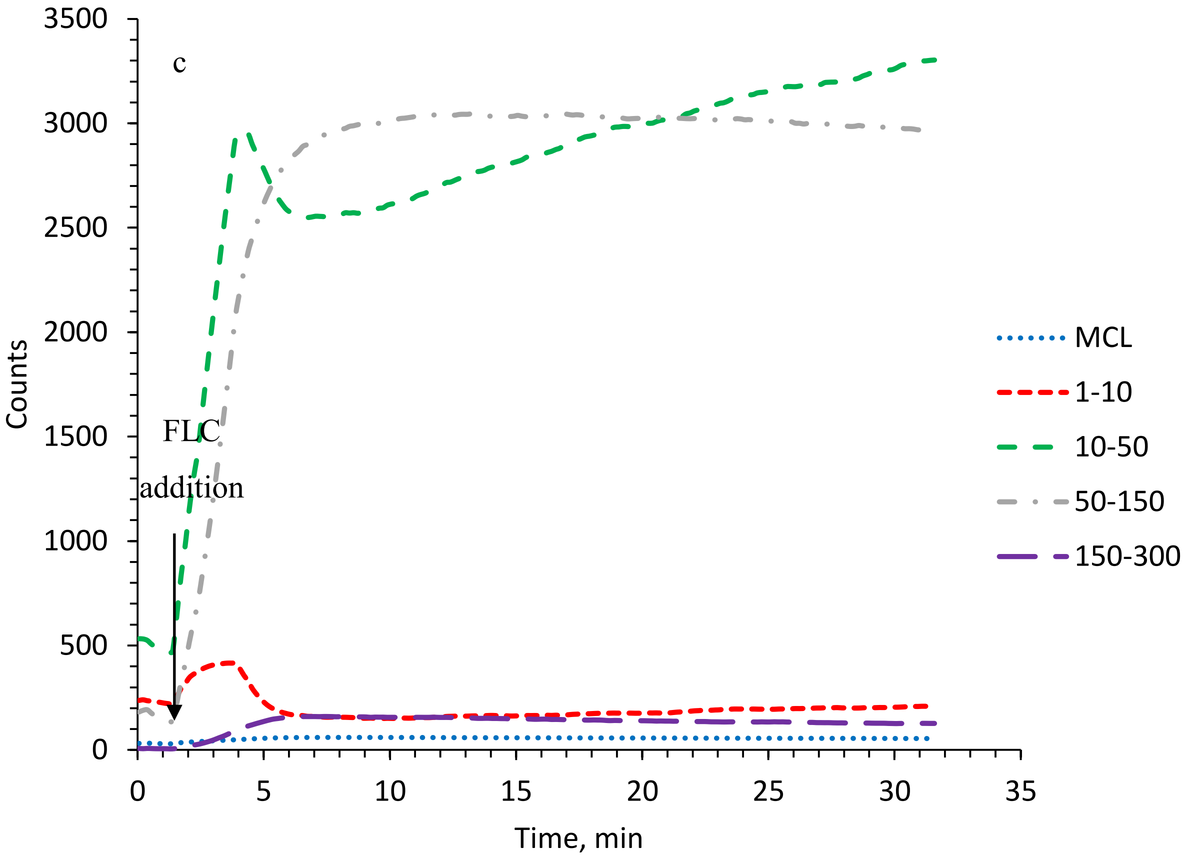
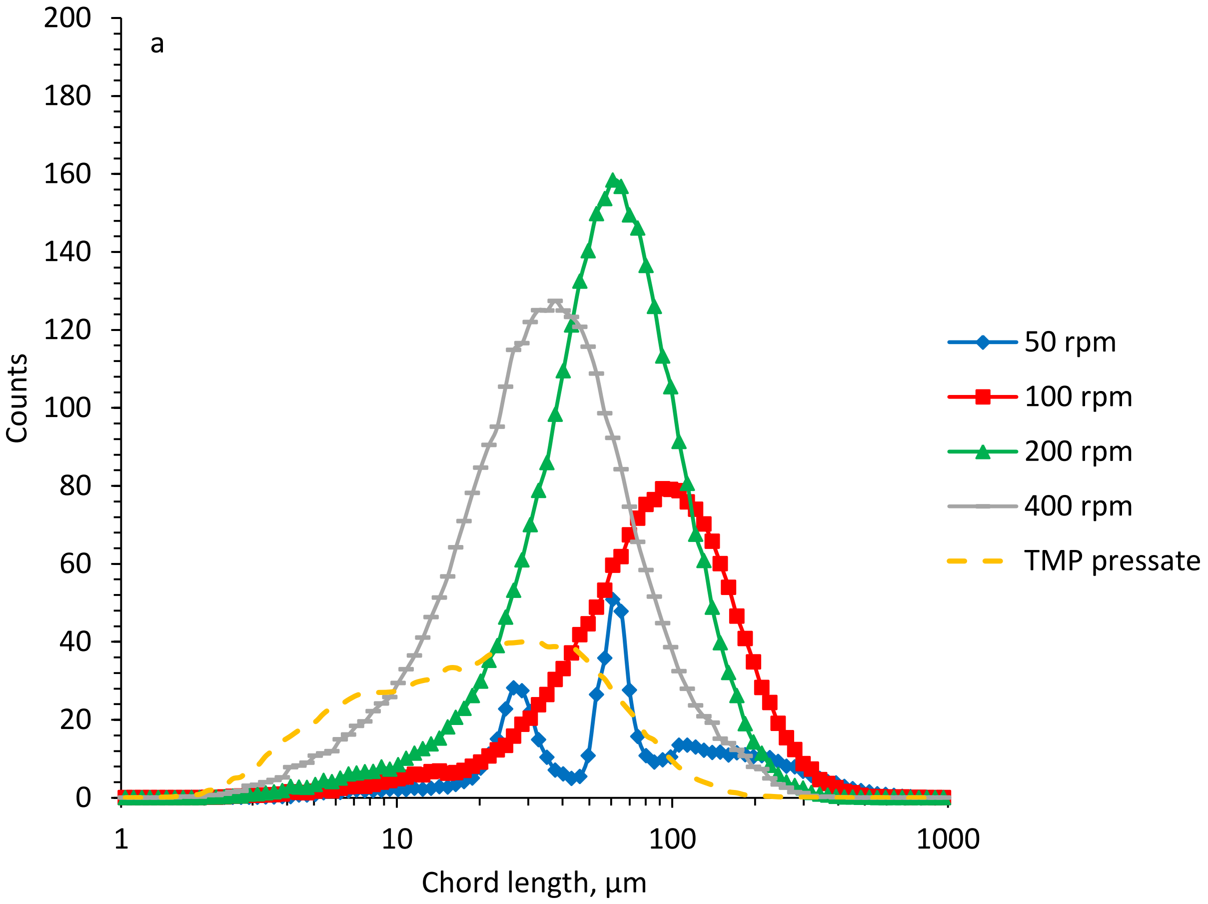


Figure 6.7 The impact of coagulation time on the chord length ranges in a TMP pressate a) calcium chloride, 2770 mg/kg $CaCl_2$/TMP pressate at pH 12.5 b) alum, 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate at pH 6 and c) a FLC, 5060 mg/kg FLC/TMP pressate at pH 12. All coagulation conditions were performed at 200 rpm, 298 K and 30 min. Mean chord length (MCL) and all chord length ranges are in µm.

As stated earlier, the analysis of the FBRM results in Figure 6.7 indicated that the particles in the 1-10 µm range were rapidly coagulated, forming larger aggregates when the coagulants used were alum or calcium chloride. Although the chord length information provided by the FBRM does not exactly relate the size of the particles, it still provides an estimation of the particle sizes. Since the pore size of the filtration unit used in this study was 11 µm (according to the manufacturer's specification), particles with a chord length greater than 11 µm were more likely retained via filtration. Therefore, the FBRM results suggest that the colloids in the TMP pressate with a chord length range between 1-10 μm were rapidly coagulated to form larger particles and subsequently removed via filtration when calcium chloride or alum were used.

6.4.5 Impact of agitation speed

Figure 6.8 shows the impact of the agitation speed in the coagulation treatments with calcium chloride or alum on the chord length distribution of a TMP pressate. The results in Figure 6.8a suggest that the optimum agitation speed was 200 rpm for the calcium chloride treatment since the greatest number of counts was observed for the particle size range of 50-150 μm. The results in Figure 6.8b indicate that the coagulation treatment at 100 rpm formed the largest particles, but the number of counts was relatively low and thus a relatively lower degree of coagulation occurred. At 200 rpm, a significantly greater number of counts were observed at a chord length range of 50-150 μm and thus a greater degree of coagulation occurred. The results for the treatment at 400 rpm did exhibit a chord length distribution with the highest number of counts, but the chord length range included significantly smaller particles, when compared with the other treatments. Thus, the results suggest that the agitation speed of 400 rpm may have been too intense and that either the aggregates disintegrated or the high shear exceeded that needed for the formation of larger aggregates. Therefore, the optimum agitation speed for the alum-treated TMP pressate appears to be 200 rpm.


a
Counts
0
20
40
60
80
100
120
140
160
180
200
1
10
100
1000
Chord length, µm
50 rpm
100 rpm
200 rpm
400 rpm
TMP pressate

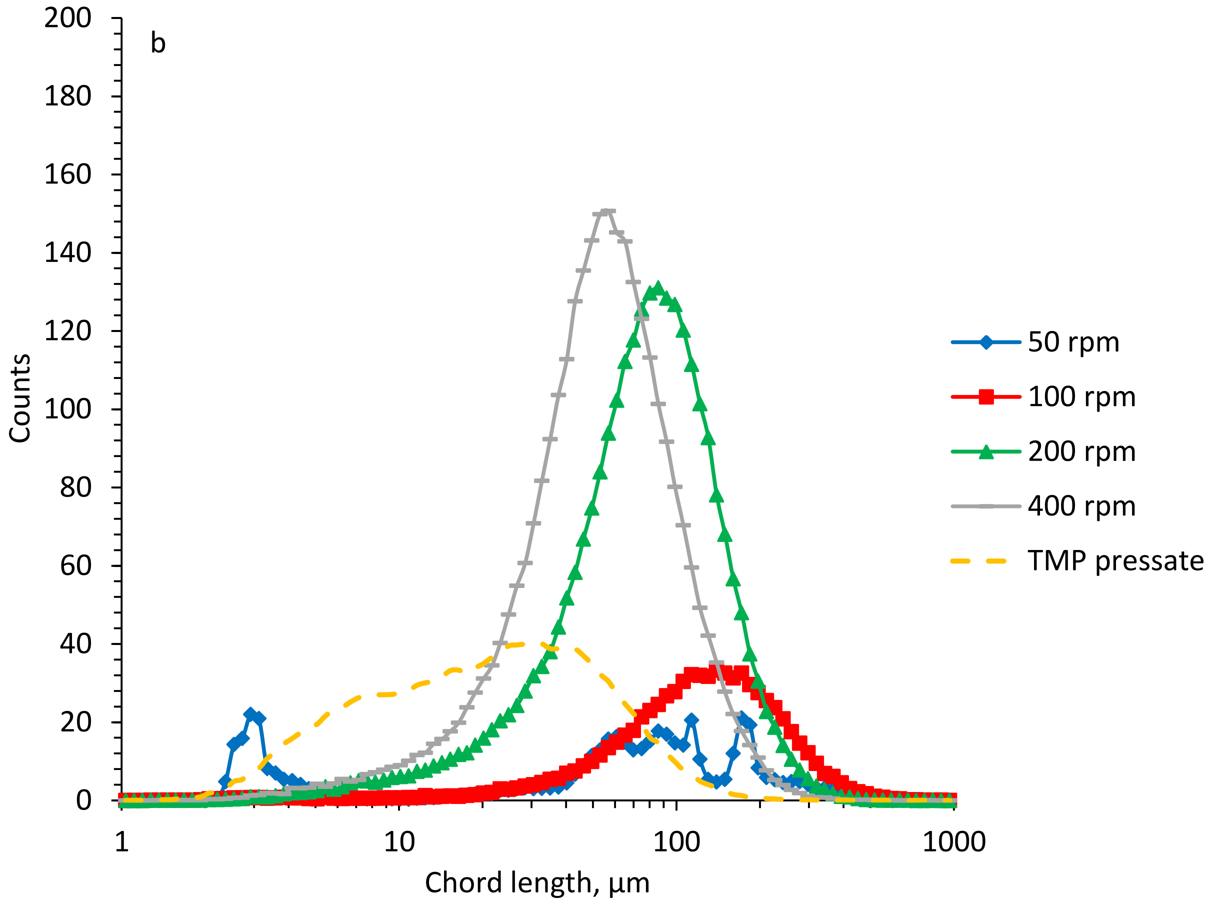
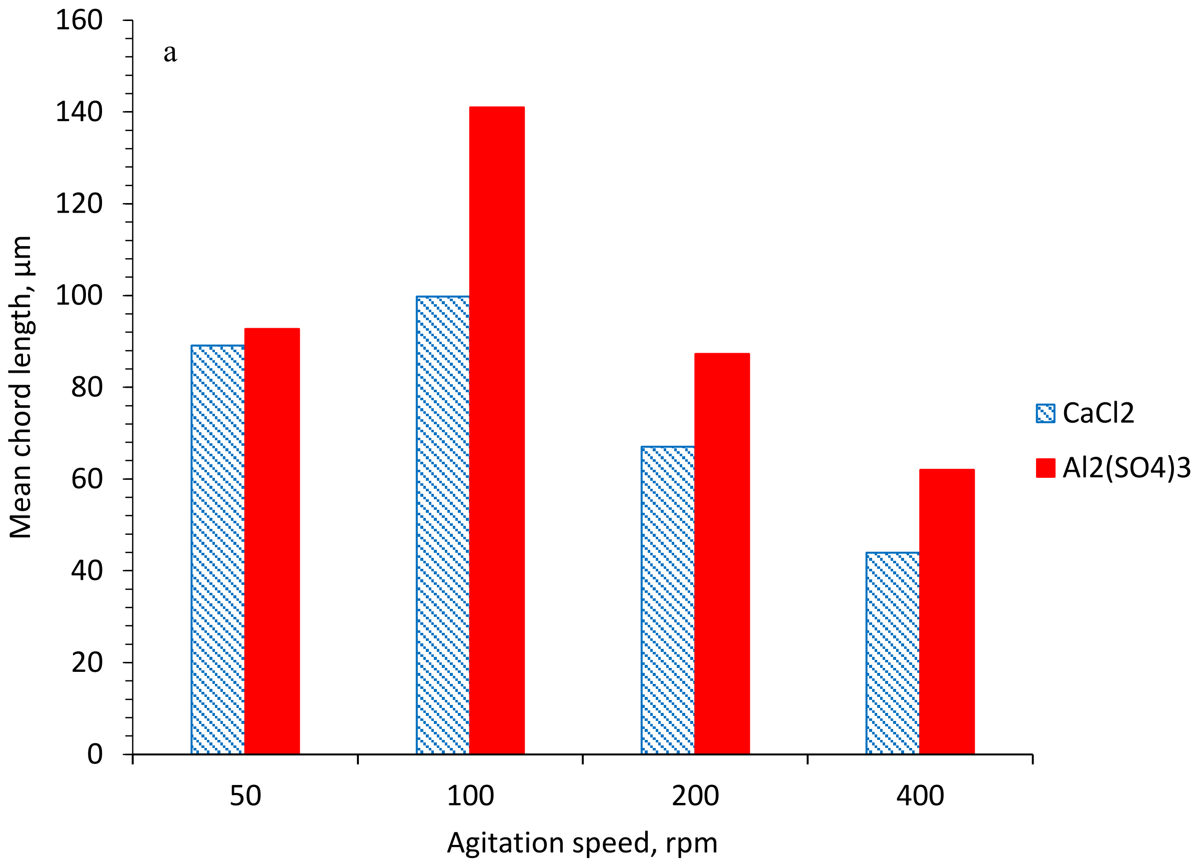


Figure 6.8 The impact of agitation speed on the chord length distribution of the coagulation treatment of TMP pressate. a) calcium chloride, 2770 mg/kg $CaCl_2$/TMP pressate at pH 12.5, b) alum, 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate at pH 6 and all coagulation conditions were at 298 K for 30 min.

Figure 6.9a shows the impact of the agitation speed in the coagulation treatments on the mean chord length and Figure 6.9b shows the impact of the agitation speed on the COD and lignin removals from a TMP pressate when calcium chloride or alum were used as coagulants. The results in Figure 6.9a suggest that the optimum agitation speed in the coagulation treatments was 100 rpm for both calcium chloride and alum treatments. However, the results in Figure 6.9b suggest that the variation of the agitation speed from 50 rpm to 400 rpm only had a slight impact on the COD and lignin removals. The optimum COD and lignin removals were observed when the agitation speed was 200 rpm under the conditions of 2770 mg/kg $CaCl_2$/TMP pressate and pH 12.5 for a calcium chloride treatment or 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate and pH 6 for an alum treatment at 298 K and 30 min. Under these conditions, it was observed that the removals of COD and lignin from a TMP pressate using a calcium chloride treatment was 20.8 % and 30.8 %, and using an alum treatment was 41.2 % and 40.6 %, respectively.



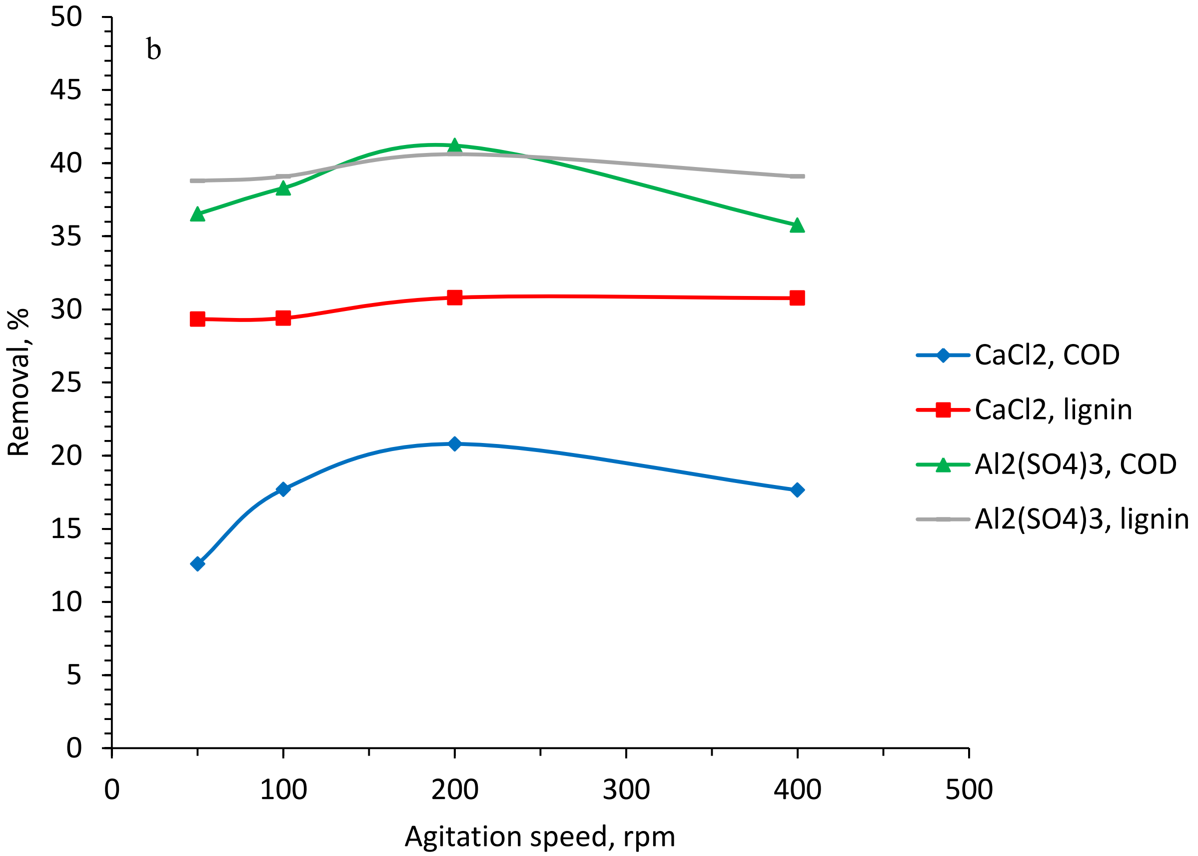


Figure 6.9 The impact of agitation speed on a) the mean chord length and b) the COD and lignin removals from a TMP pressate using calcium chloride or alum coagulants. The treatment conditions were 2770 mg/kg $CaCl_2$/TMP pressate at pH 12.5 or 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate at pH 6, and 298 K for 30 min.

6.5 Conclusions

It was determined that the addition of a FLC to a TMP pressate at a dosage range of 1987-5060 mg/kg FLC/TMP pressate would not be expected to pose an environmental concern with respect to heavy metal toxicity on the resultant effluent according to the acceptability limits for a metal mining sector. The coagulation studies indicated that alum, calcium chloride and a FLC coagulated the lignocelluloses dissolved in a TMP pressate, but potassium chloride did not. It was determined that a calcium chloride treatment of a TMP pressate removed 20.8 % of the COD and 30.8 % of the lignin under the conditions of 2770 mg/kg $CaCl_2$/TMP pressate, 200 rpm, pH 12.5 and 298 K for 30 min. It was also observed that a FLC treatment on a TMP pressate removed 18.4 % of the COD and 26.9 % of the lignin under the conditions of 5060 mg/kg FCL/TMP pressate, 200 rpm, pH 12.5 and 298 K for 30 min. It was determined that a coagulation treatment with alum removed 41.2 % of the COD and 40.6 % of the lignin from a TMP pressate under the conditions of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate, 200 rpm, pH 6 and 298 K for 30 min. It was observed that the sequential coagulation progression of the 1-10 µm, 10-50 µm, 50-150 µm and 150-300 µm chord length ranges was similar for calcium chloride and alum treatment. Furthermore, it was determined that coagulation of a TMP pressate using alum, calcium chloride or a FLC resulted in a significant increase in the number of counts in the 50-150 µm chord length range.

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7 Chapter 7: Overall conclusions and recommendations for future work

7.1 Overall conclusions

In this study two biomass fly ash samples, FA1 and FA2, were fractionated by mechanical sieving and it was determined that as the particle size of the fly ash decreased, the carbon content, total pore volume, micropore volume and the surface area decreased; while their metal content and the density increased. The grinding of FA1 had a negligible effect on its surface area and pore volume, but it increased the mesopore volume of FA1 by 5-65 %. The main metals present in the biomass fly ash samples were calcium, potassium and magnesium, and it was observed that the concentration of these metals was significantly higher in FA1 than in FA2. In this study, it was also observed that FA1 was a more effective adsorbent than FA2.

The most significant factor for the COD and lignin removals from a TMP pressate by FA1 and FA2 was determined to be the dosage of biomass fly ash applied. It was determined that the lignin removal increased when the pH of the biomass-based fly ash adsorption treatment on a TMP pressate was decreased, and the COD removal increased when the adsorption treatment time was extended. The optimum COD removal by FA1 was 91.3 % under the conditions of a biomass fly ash with the particle size of 0.43 mm, dosage of 70.0 mg/g FA/TMP pressate and adsorption treatment of 2 h. The optimal lignin removal by FA1 was 95.0 % under the conditions of a biomass fly ash with the particle size of 0.11 mm, dosage of 46.5 mg/g FA/TMP pressate and adsorption treatment at pH 6.

It was determined that the COD and lignin adsorption from a TMP pressate by various biomass fly ash fractions and pH adjustment to 6 followed the Freundlich isotherm model. Under the conditions of 298 K, pH 6, 100 rpm, and 24 h, the highest estimated Freundlich adsorption capacity for lignin from a TMP pressate was 149 mg/g fly ash/TMP pressate, which corresponded to a biomass fly ash with a metal content of 29.1 wt. %. It was also determined that the highest estimated Freundlich adsorption capacity for the COD from a TMP pressate was 212 mg/g fly ash/TMP pressate under the conditions of 298 K, no pH adjustment, 100 rpm, and 24 h, which corresponded to a biomass fly ash with a metal content of 24.6 wt. %. The pH of the biomass fly ash/TMP pressate system studied had a significant effect on the adsorption, but the ionic strength did not have a significant influence. An increase in the pH increased the lignin adsorption significantly under equilibrium conditions. Furthermore, it was observed that the metal contents of biomass fly ash, specifically calcium and potassium, had significant effects on the K_F for lignin and COD from a TMP pressate.

The analysis of the leachate from a Toxicity characteristic leaching procedure (TCLP) test on a biomass fly ash from a TMP mill confirmed that the biomass fly ash was non-hazardous and thus the ash would be safe for landfill disposal in Ontario. To study the leaching characteristics of metals from two biomass fly ash samples (S1 and S2), a set of experiments was conducted via mixing fly ash with water or a TMP pressate under various conditions and then comparing the concentrations of metals leached into the filtrates. The conditions studied in these leaching experiments consisted of a liquid/solid (L/S) of 15 or 100, a pH of 6 or 12.5, and an agitation speed of 100 rpm for 2 h at 298 K. It was determined that the major metals detected in the filtrates were Ca, K, Mg, Mn, Na and Si, and the trace metals detected to a significant extent were Al, Ba, Sr and Zn. The leaching experiments revealed that the extent of metals that leached from biomass fly ash in water differed significantly from that in a TMP pressate. Overall, the total amount of metals that leached from S1 and S2 into water was greater than that leached into a TMP pressate under the conditions studied.

The leachates of S1 and S2 in a TMP pressate were also evaluated with respect to the effluent guidelines of the metal mining sector, to assess their potential use as a biomass-based fly ash adsorbent for a TMP pressate. It was determined that the use of S1 under the conditions of 10 mg/g fly ash/TMP pressate, pH of 12.5, 100 rpm and 2 h, and the use of S2 under all conditions studied (L/S 15 or 100 at pH 6 or 12.5) would produce a leachate that meets the effluent guidelines of the metal mining sector.

In the coagulation studies, it was observed that calcium chloride, a biomass fly ash leachate concentrate (FLC) and alum coagulated the lignocelluloses dissolved in a TMP pressate, but potassium chloride did not. A calcium chloride-based treatment on a TMP pressate removed 20.8 % of the COD and 30.8 % of the lignin at a dosage of 2770 mg/kg $CaCl_2$/TMP pressate, under the conditions of 200 rpm, pH 12.5 and 298 K for 30 min. The coagulation treatment using a leachate, which was generated from mixing biomass fly ash with water, removed 18.4 % of the COD and 26.9 % of the lignin at a dosage of 5060 mg/kg FCL/TMP pressate under the conditions of 200 rpm, pH 12.5 and 298 K for 30 min. It was determined that a coagulation treatment with alum removed 41.2 % of the COD and 40.6 % of the lignin from a TMP pressate under the conditions of 1000 mg/kg $Al_2(SO_4)_3$/TMP pressate, 200 rpm, pH 6 and 298 K for 30 min. Furthermore, the sequential coagulation progression of particles with the chord length range of 1-10 μm, 10-50 μm, 50-150 μm and 150-300 μm was observed to be similar for calcium chloride and alum treatment of a TMP pressate. Overall, it was also determined that coagulation of a TMP pressate using alum, calcium chloride or FLC resulted in a significant increase in the number of counts in the 50-150 μm chord length range.

7.2 Future work

As discussed in chapter 5, a biomass fly ash may potentially leach other harmful substances in an aqueous system, such as mercury and polycyclic aromatic hydrocarbons (PAHs). The extent of leaching of mercury and PAHs from a biomass fly ash in a TMP pressate was not studied in this thesis and furthermore is unknown. Therefore, to ensure that the use of a biomass-based fly ash adsorption treatment of a TMP pressate is a viable option with respect to the impact on the environment, it is recommended that further analysis of the leachate produced, for mercury and PAHs, is conducted.

The work of this thesis indicated that the leachate from a biomass fly ash in water had a coagulating effect on a TMP pressate when added to TMP pressate, and that the coagulation observed may have been attributed to the presence of calcium ions. Therefore, it is recommended that future studies focus on the potential integration of a coagulation pretreatment and subsequent biomass-based fly ash adsorbent treatment on a TMP pressate, in which a portion of the filtrate from the latter stage is used as the source of the coagulant in the former stage. Alternatively, it is recommended that future studies focus on the optimization of the potential two stage treatment of a TMP pressate in which the first stage involves a coagulation pretreatment using a FLC, and the second stage consists of a biomass-based fly ash adsorbent treatment on the filtrate of the coagulant-treated TMP pressate.

8 Appendix

8.1 Design of the validation runs

Table 8.1 Parameters of the validation runs of the models for COD and lignin removals from a TMP pressate by fractionated FA1 and FA2

Run #	X_1 Wt.-based ave. particle size, mm	X_2 Dosage, mg/gTMP	X_3 Time, h	X_4 Temp., K	X_5 pH
1	0.11 (0.11)	60	2.0	328	12.5
2	0.11 (0.11)	30	1.0	308	6.0
3	0.11 (0.11)	45	1.5	318	10.0
4	0.43 (0.53)	45	2.0	298	6.0
5	0.43 (0.53)	15	1.0	318	12.5
6	0.43 (0.53)	30	0.5	328	10.0
7	1.01 (1.30)	15	1.5	328	6.0
8	1.01 (1.30)	60	1.0	298	10.0
9	1.01 (1.30)	45	0.5	308	12.5

Brackets indicate the weight-based average particle size for FA2

The agitation speed for all runs was 100 rpm

Table 8.2 Parameters of the validation runs of the models for COD and lignin removals from a TMP pressate by unfractionated FA1 and FA2

Run #	X_2 Dosage, mg/gTMP	X_3 Time, h	X_4 Temp., K	X_5 pH
10	20	0.5	328	6.0
11	20	1.5	298	12.5
12	45	1.5	298	10.0
13	45	0.5	318	12.5
14	60	1.0	328	6.0
15	60	2.0	318	10.0

The weight-based average particle size for FA1 and FA2 was 0.18 mm and 0.71 mm respectively

The agitation speed for all runs was 100 rpm

8.2 COD and lignin removals of the DSD experiments

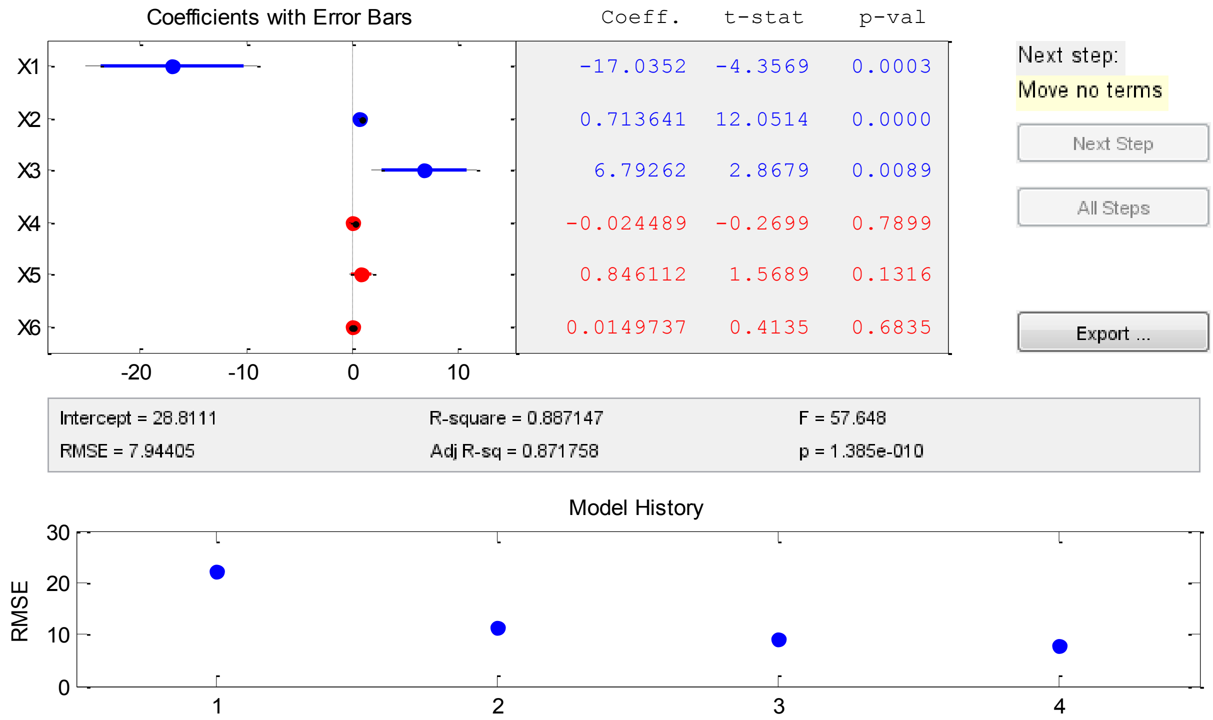
Table 8.3 COD and lignin removals of the DSD experiments

DSD	**FA1**				**FA2**			
run #	**COD removal, %**		**Lignin removal, %**		**COD removal, %**		**Lignin removal, %**	
1	73.6	76.5	97.5	97.5	50.9	52.7	86.0	87.6
2	47.2	50.9	45.0	49.0	5.5	6.8	11.2	11.3
3	41.5	42.0	60.7	62.1	11.4	12.2	15.8	16.5
4	64.1	61.1	96.3	96.3	45.9	52.2	86.5	82.9
5	28.7	32.8	58.8	65.8	20.3	21.2	43.2	43.8
6	64.3	71.5	83.4	79.2	30.5	34.5	34.9	35.7
7	90.0	88.7	94.5	94.5	39.4	39.3	45.9	47.6
8	15.9	19.9	42.0	45.3	12.6	9.5	27.2	25.3
9	29.0	31.4	39.2	38.9	25.7	30.6	22.4	25.7
10	76.5	77.8	97.0	96.0	55.7	52.5	83.1	80.0
11	76.9	76.3	98.0	97.0	52.9	54.4	86.5	87.7
12	45.2	43.5	42.8	42.4	9.5	7.7	10.0	13.3
13	77.0	77.8	94.7	93.5	34.2	33.9	62.0	62.9

8.3 Forward stepwise analysis for COD removal by FA1

Abbreviations

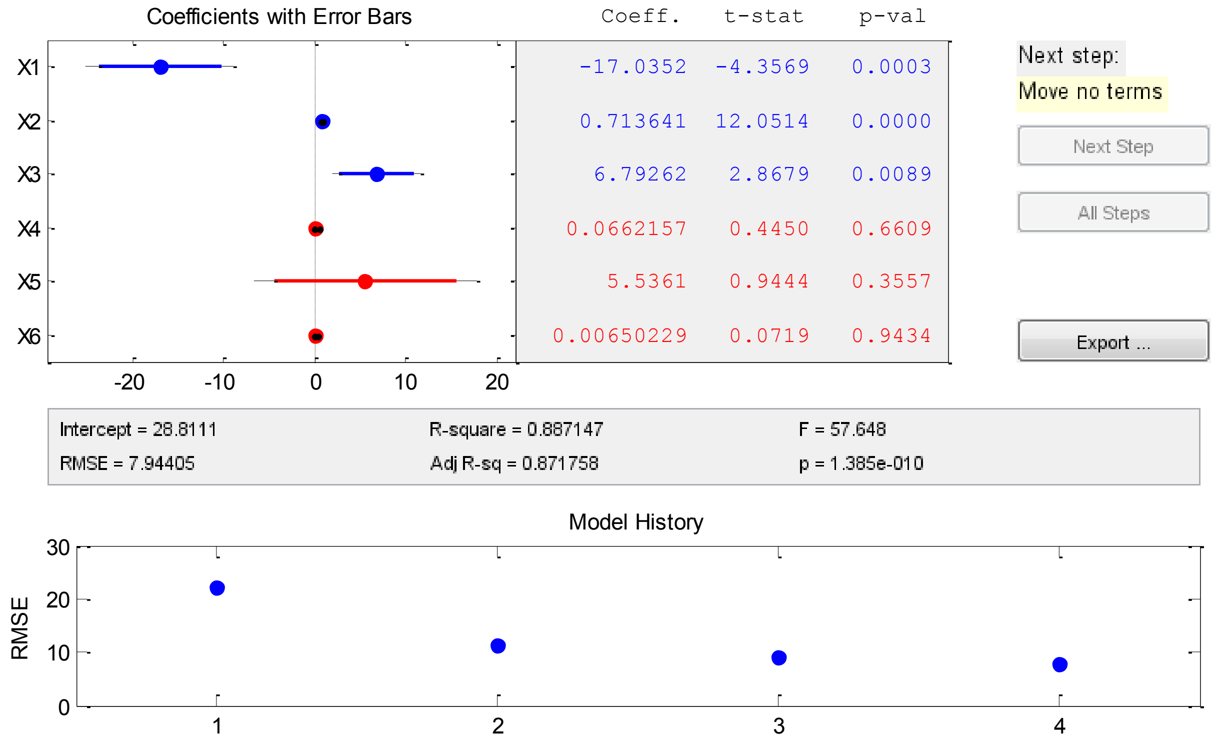
PS	particle size, mm
D	dosage, mg/g FA/TMP pressate
T	time, h
K	temperature, K
AS	agitation speed, rpm



```
  Coeff.       t-stat     p-val
-17.0352     -4.3569    0.0003
 0.713641    12.0514    0.0000
  6.79262     2.8679    0.0089
-0.024489    -0.2699    0.7899
 0.846112     1.5689    0.1316
0.0149737     0.4135    0.6835

Intercept = 28.8111        R-square = 0.887147       F = 57.648
RMSE = 7.94405             Adj R-sq = 0.871758       p = 1.385e-010
```

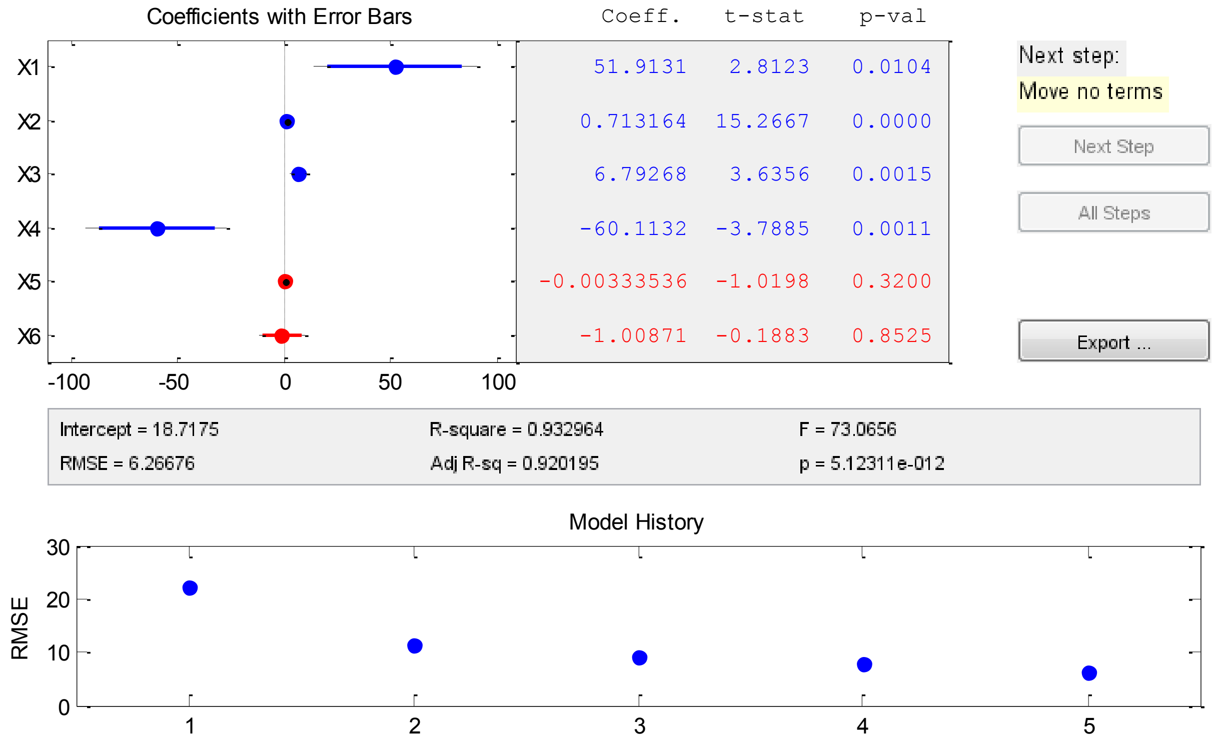
Figure 8.1 MATLAB stepwise output of lower order terms for the COD removal by FA1. X1) PS X2) D X3) T X4) K X5) pH X6) AS.



	Coeff.	t-stat	p-val
X1	-17.0352	-4.3569	0.0003
X2	0.713641	12.0514	0.0000
X3	6.79262	2.8679	0.0089
X4	0.0662157	0.4450	0.6609
X5	5.5361	0.9444	0.3557
X6	0.00650229	0.0719	0.9434

Intercept = 28.8111
RMSE = 7.94405
R-square = 0.887147
Adj R-sq = 0.871758
F = 57.648
p = 1.385e-010

Figure 8.2 MATLAB stepwise output for the significant lower order terms and their interactions for the COD removal by FA1. X1) PS X2) D X3) T X4) PS×D X5) PS×T X6) D×T.

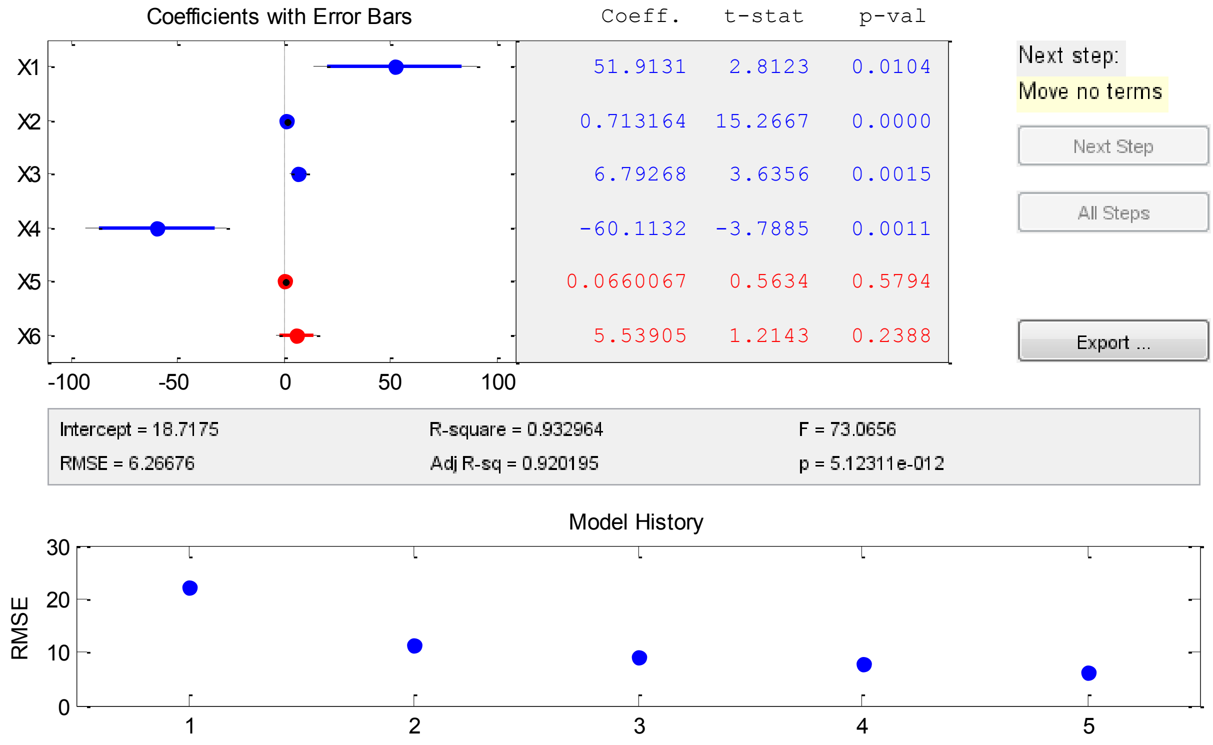


```
           Coeff.      t-stat     p-val
      51.9131      2.8123    0.0104
     0.713164     15.2667    0.0000
      6.79268      3.6356    0.0015
     -60.1132     -3.7885    0.0011
  -0.00333536     -1.0198    0.3200
     -1.00871     -0.1883    0.8525
```

Next step:
Move no terms

```
Intercept = 18.7175        R-square = 0.932964        F = 73.0656
RMSE = 6.26676             Adj R-sq = 0.920195        p = 5.12311e-012
```

Figure 8.3 MATLAB stepwise output for the significant lower order terms and their quadratic terms for the COD removal by FA1. X1) PS X2) D X3) T X4) PS^2 X5) D^2 X6) T^2.



```
   Coeff.      t-stat     p-val
  51.9131     2.8123     0.0104
 0.713164    15.2667     0.0000
  6.79268     3.6356     0.0015
 -60.1132    -3.7885     0.0011
0.0660067     0.5634     0.5794
  5.53905     1.2143     0.2388

Intercept = 18.7175        R-square = 0.932964      F = 73.0656
RMSE = 6.26676             Adj R-sq = 0.920195      p = 5.12311e-012
```

Figure 8.4 MATLAB stepwise output for the significant lower order terms, PS quadratic term and all PS interactions for COD removal by FA1. X1) PS X2) D X3) T X4) PS^2 X5) PS×D X6) PS×T.

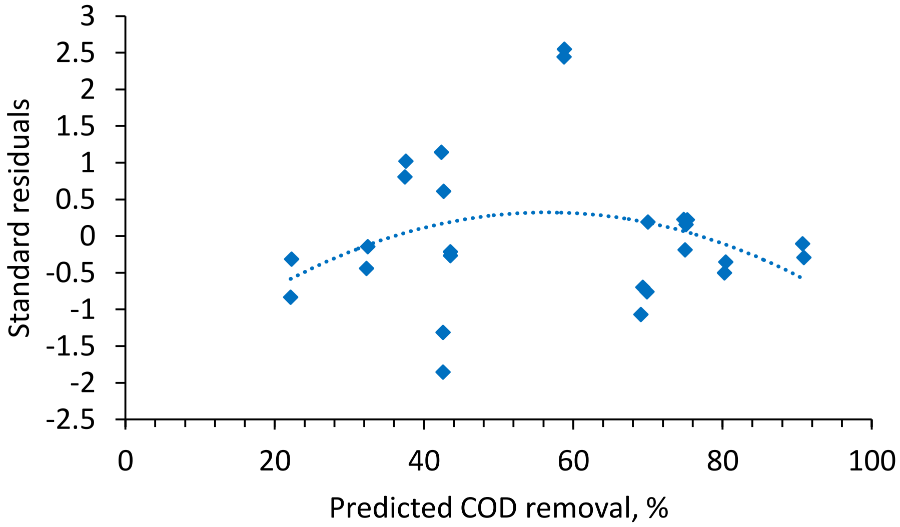


Figure 8.5 Residuals for the model Y = 28.811 + (-17.0352)PS + (0.7136)D + (6.7926)T

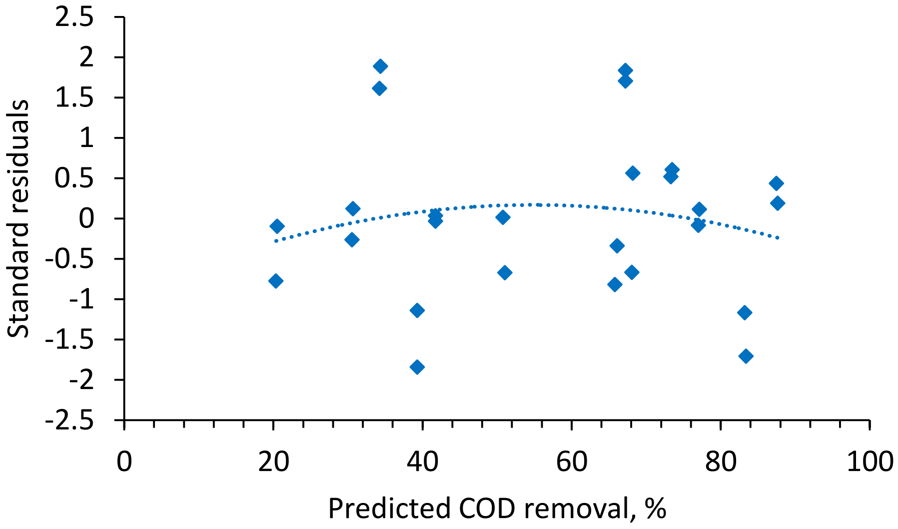
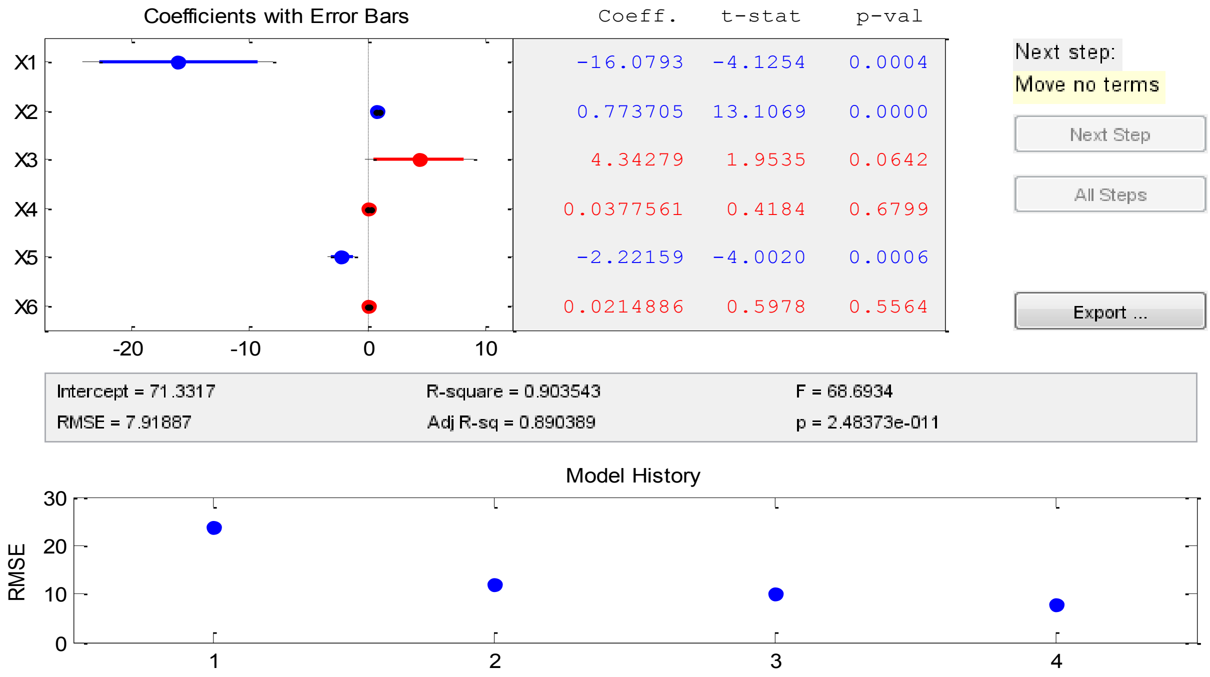


Figure 8.6 Residuals for the model Y = 18.7175 + (51.9131)PS + (0.7132)D + (6.7927)T + (-60.1132)PS^2

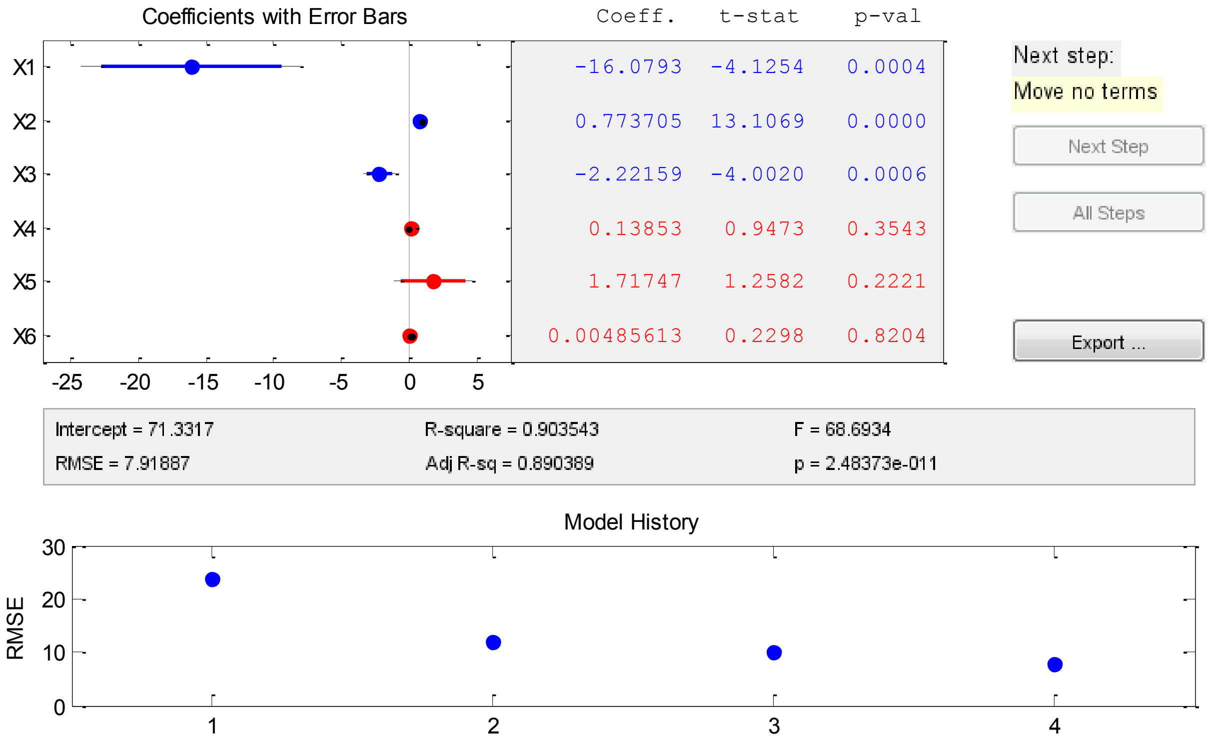
8.4 Forward stepwise analysis for lignin removal by FA1



	Coeff.	t-stat	p-val
X1	-16.0793	-4.1254	0.0004
X2	0.773705	13.1069	0.0000
X3	4.34279	1.9535	0.0642
X4	0.0377561	0.4184	0.6799
X5	-2.22159	-4.0020	0.0006
X6	0.0214886	0.5978	0.5564

Intercept = 71.3317
RMSE = 7.91887
R-square = 0.903543
Adj R-sq = 0.890389
F = 68.6934
p = 2.48373e-011

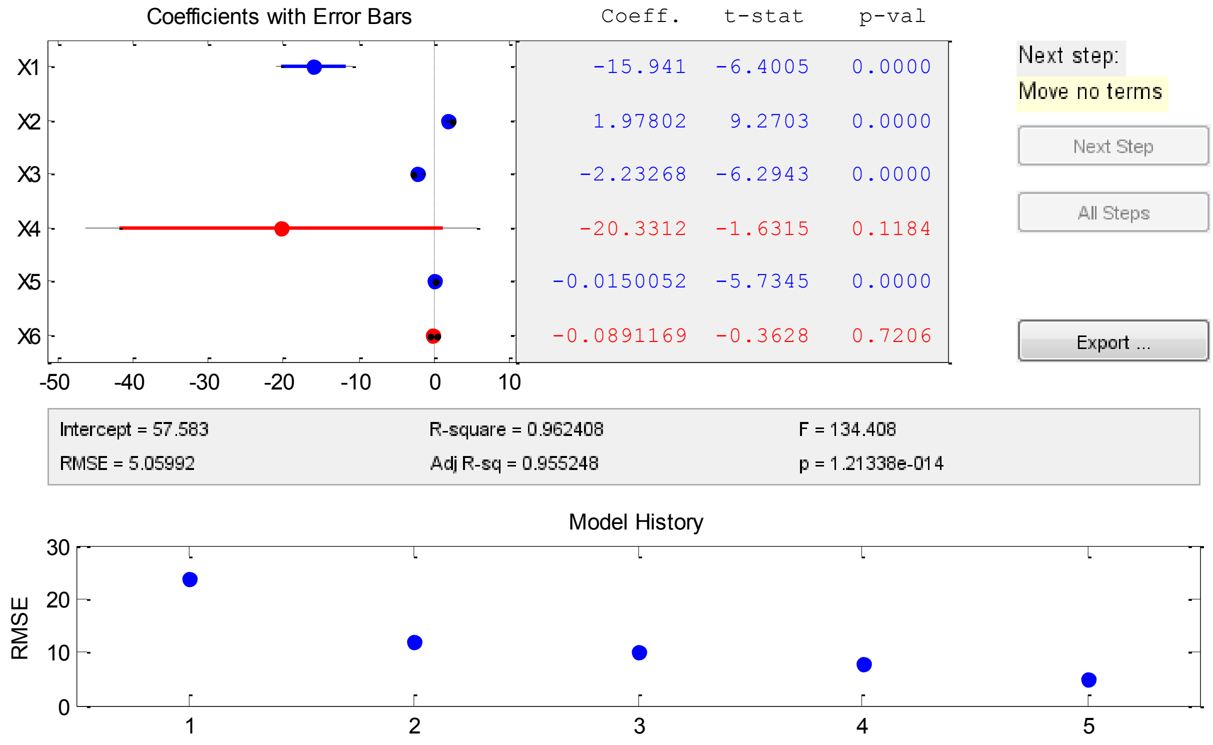
Figure 8.7 MATLAB stepwise output of lower order terms for the lignin removal by FA1. X1) PS X2) D X3) T X4) K X5) pH X6) AS.



```
     Coeff.       t-stat     p-val
 -16.0793      -4.1254    0.0004
 0.773705      13.1069    0.0000
 -2.22159      -4.0020    0.0006
  0.13853       0.9473    0.3543
  1.71747       1.2582    0.2221
0.00485613      0.2298    0.8204

Intercept = 71.3317       R-square = 0.903543       F = 68.6934
RMSE = 7.91887            Adj R-sq = 0.890389       p = 2.48373e-011
```

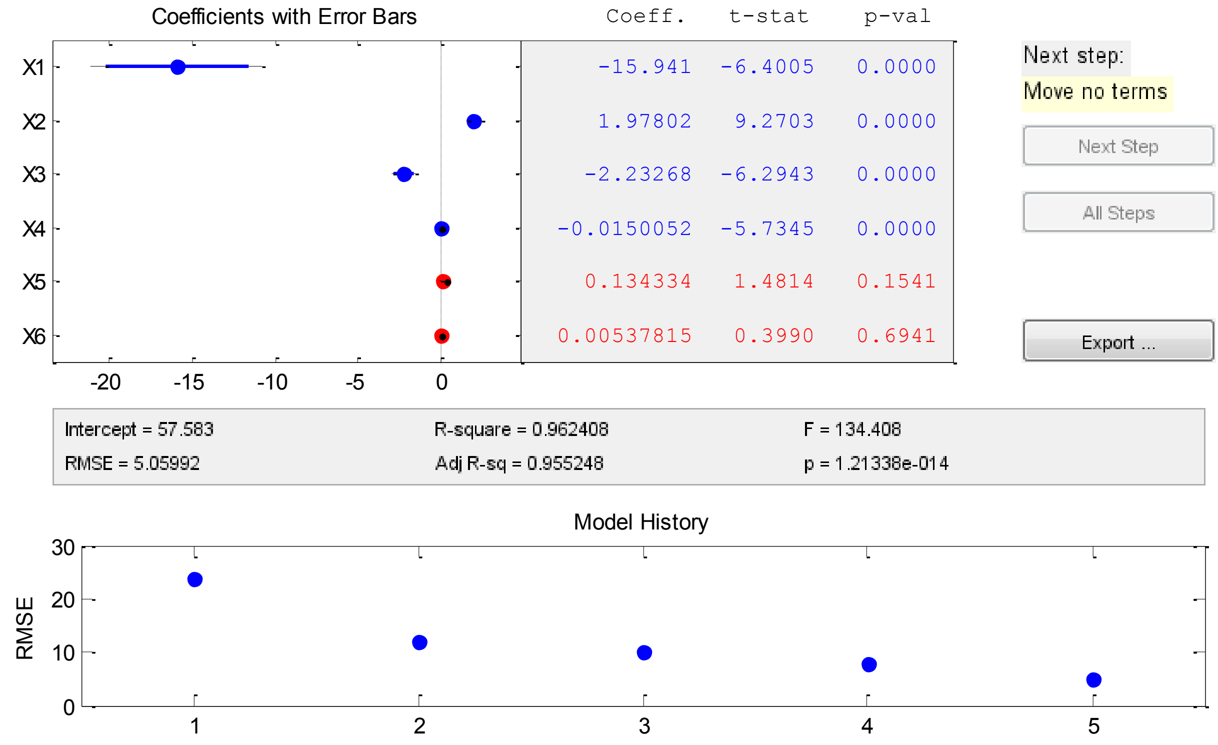
Figure 8.8 MATLAB stepwise output for the significant lower order terms and their interactions for the lignin removal by FA1. X1) PS X2) D X3) pH X4) PS×D X5) PS×pH X6) D×pH.



```
    Coeff.      t-stat     p-val
   -15.941     -6.4005    0.0000
   1.97802      9.2703    0.0000
  -2.23268     -6.2943    0.0000
  -20.3312     -1.6315    0.1184
-0.0150052     -5.7345    0.0000
-0.0891169     -0.3628    0.7206

Intercept = 57.583        R-square = 0.962408       F = 134.408
RMSE = 5.05992            Adj R-sq = 0.955248       p = 1.21338e-014
```

Figure 8.9 MATLAB stepwise output for the significant lower order terms and their quadratic terms for the lignin removal by FA1. X1) PS X2) D X3) pH X4) PS^2 X5) D^2 X6) pH^2.



```
     Coeff.     t-stat    p-val
    -15.941    -6.4005   0.0000
    1.97802     9.2703   0.0000
   -2.23268    -6.2943   0.0000
 -0.0150052    -5.7345   0.0000
   0.134334     1.4814   0.1541
 0.00537815     0.3990   0.6941

Intercept = 57.583          R-square = 0.962408         F = 134.408
RMSE = 5.05992              Adj R-sq = 0.955248         p = 1.21338e-014
```

Figure 8.10 MATLAB stepwise output for the significant lower order terms, D quadratic term and all D interactions for lignin removal by FA1. X1) PS X2) D X3) pH X4) D^2 X5) PS×D X6) D×pH.

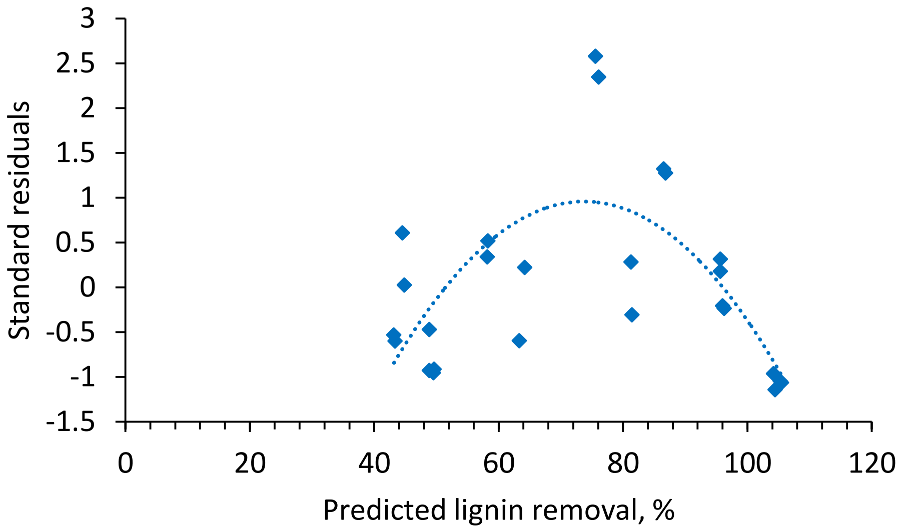


Figure 8.11 Residuals for the model Y = 71.3317 + (-16.0793)PS + (0.7736)D + (-2.2216)pH

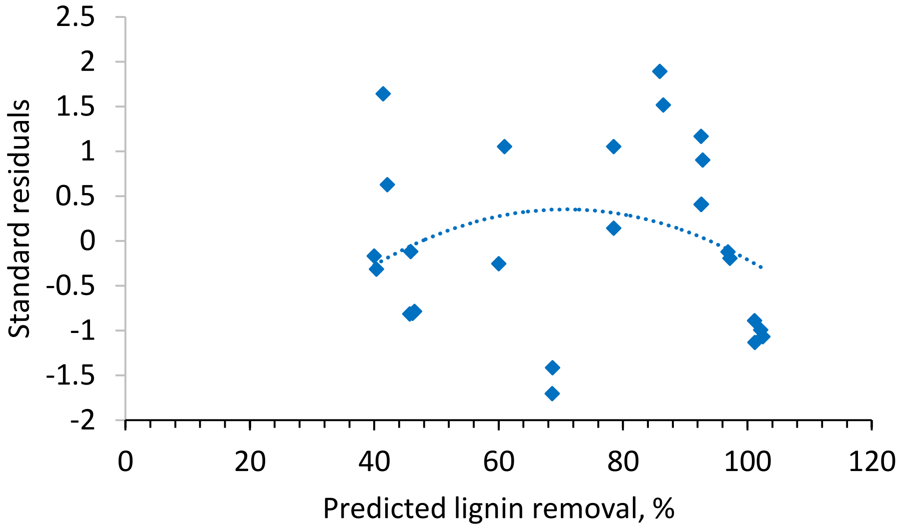
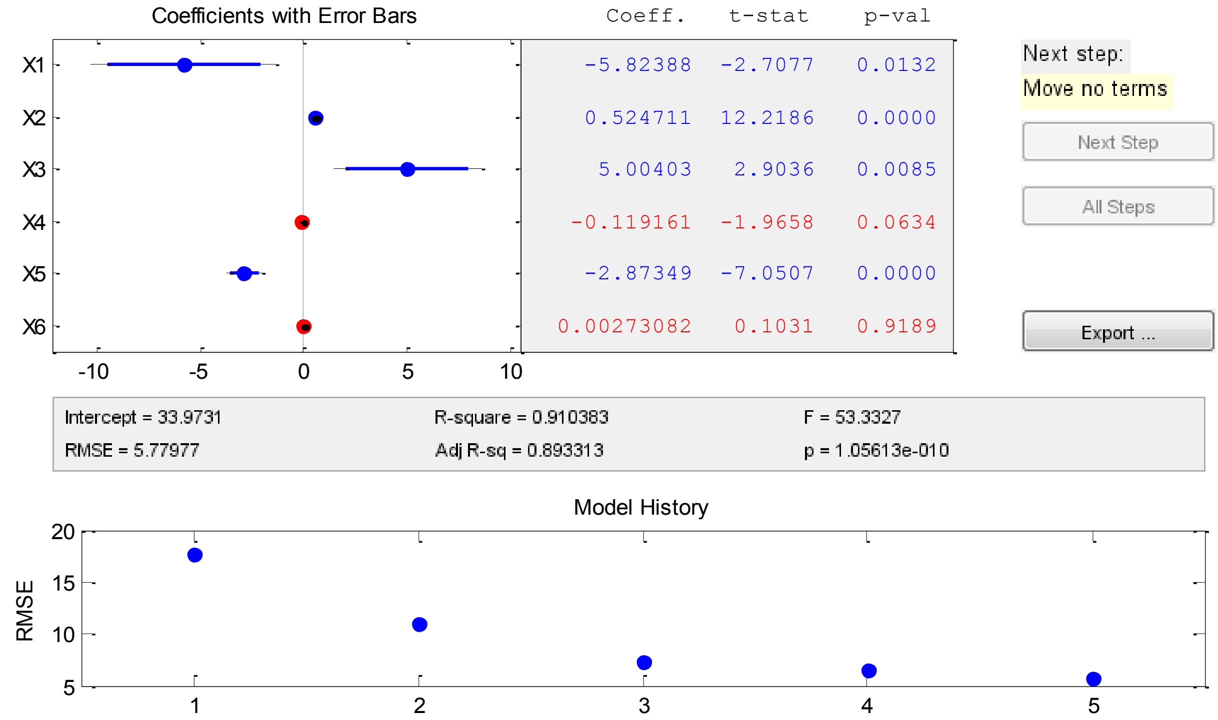


Figure 8.12 Residuals for the model Y = 57.5830 + (-15.9410)PS + (1.9780)D + (-2.2327)pH + (-0.0150)D^2

8.5 Forward stepwise analysis for COD removal by FA2

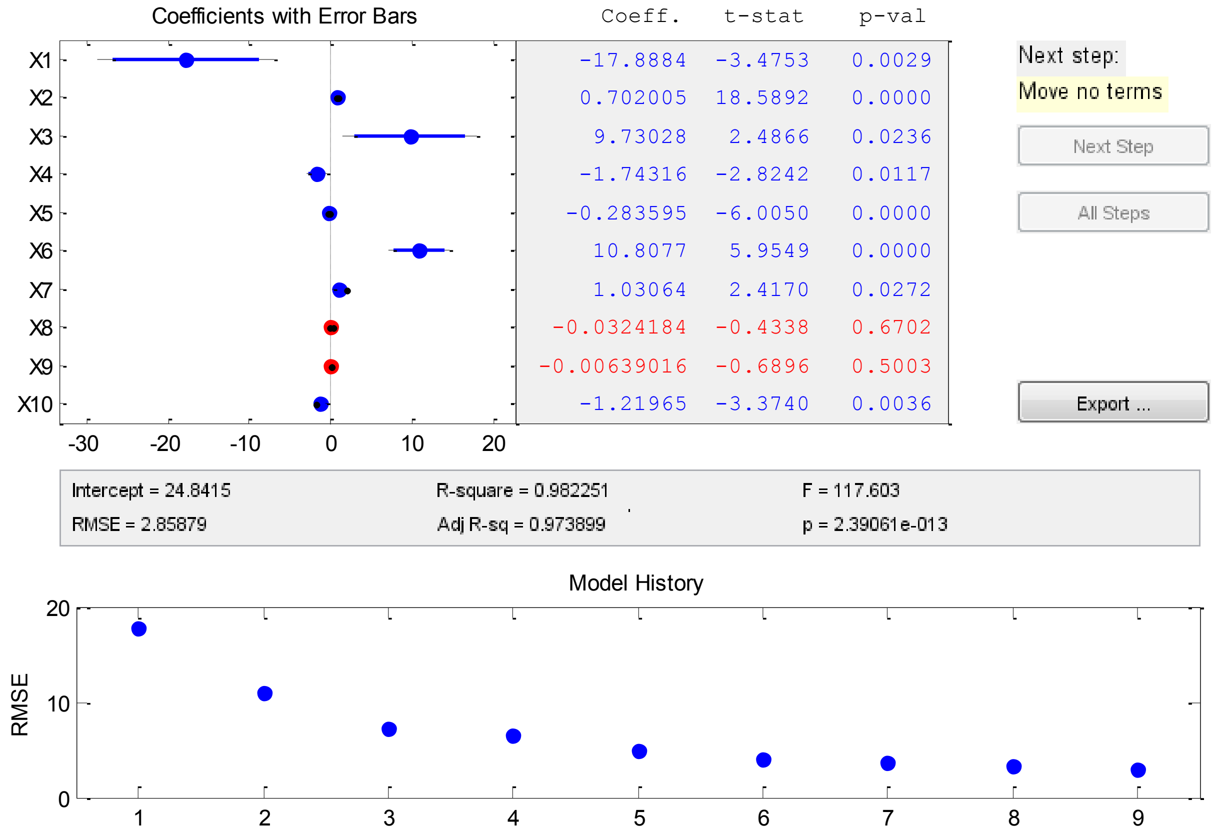


	Coeff.	t-stat	p-val
X1	-5.82388	-2.7077	0.0132
X2	0.524711	12.2186	0.0000
X3	5.00403	2.9036	0.0085
X4	-0.119161	-1.9658	0.0634
X5	-2.87349	-7.0507	0.0000
X6	0.00273082	0.1031	0.9189

Next step:
Move no terms

Intercept = 33.9731
RMSE = 5.77977
R-square = 0.910383
Adj R-sq = 0.893313
F = 53.3327
p = 1.05613e-010

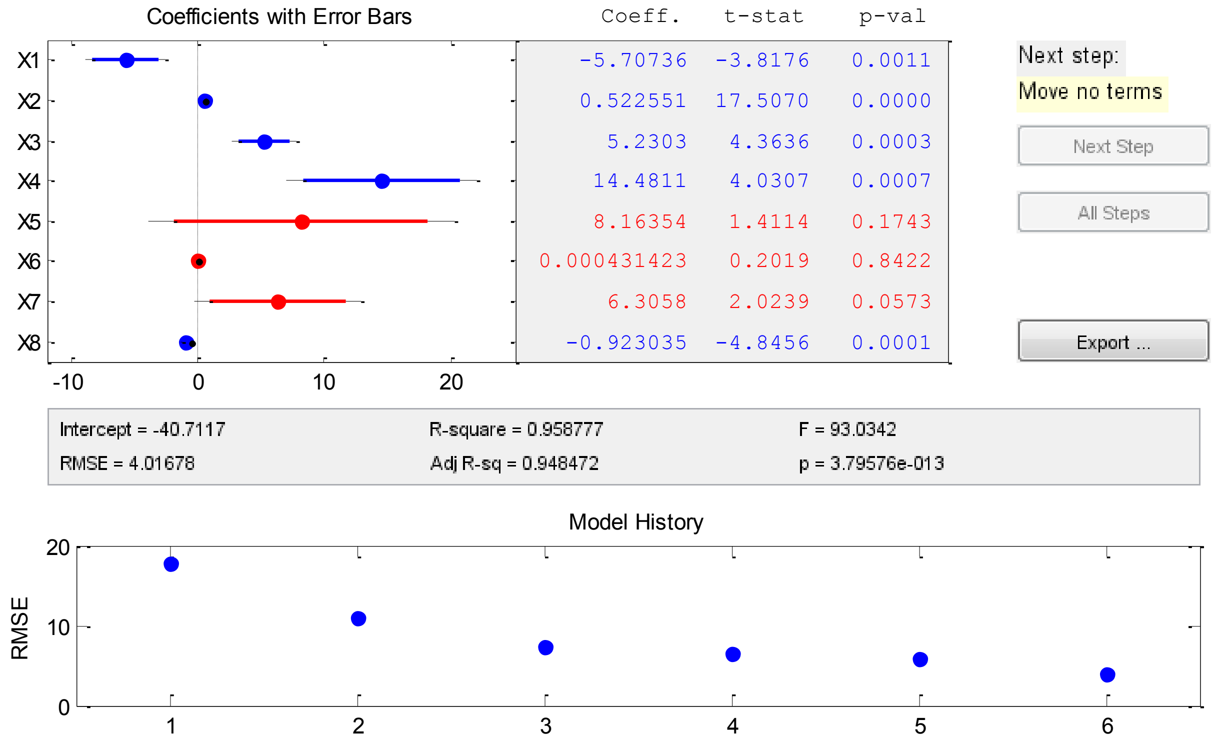
Figure 8.13 MATLAB stepwise output of lower order terms for the COD removal by FA2. X1) PS X2) D X3) T X4) K X5) pH X6) AS.



```
     Coeff.      t-stat     p-val
   -17.8884     -3.4753    0.0029
   0.702005     18.5892    0.0000
    9.73028      2.4866    0.0236
   -1.74316     -2.8242    0.0117
  -0.283595     -6.0050    0.0000
    10.8077      5.9549    0.0000
    1.03064      2.4170    0.0272
 -0.0324184     -0.4338    0.6702
-0.00639016     -0.6896    0.5003
   -1.21965     -3.3740    0.0036
```

```
Intercept = 24.8415     R-square = 0.982251      F = 117.603
RMSE = 2.85879          Adj R-sq = 0.973899      p = 2.39061e-013
```

Figure 8.14 MATLAB stepwise output for the significant lower order terms and their interactions for the COD removal by FA2. X1) PS X2) D X3) T X4) pH X5) PS×D X6) PS×T X7) PS×pH X8) D×T X9) D×pH X10) T×pH.

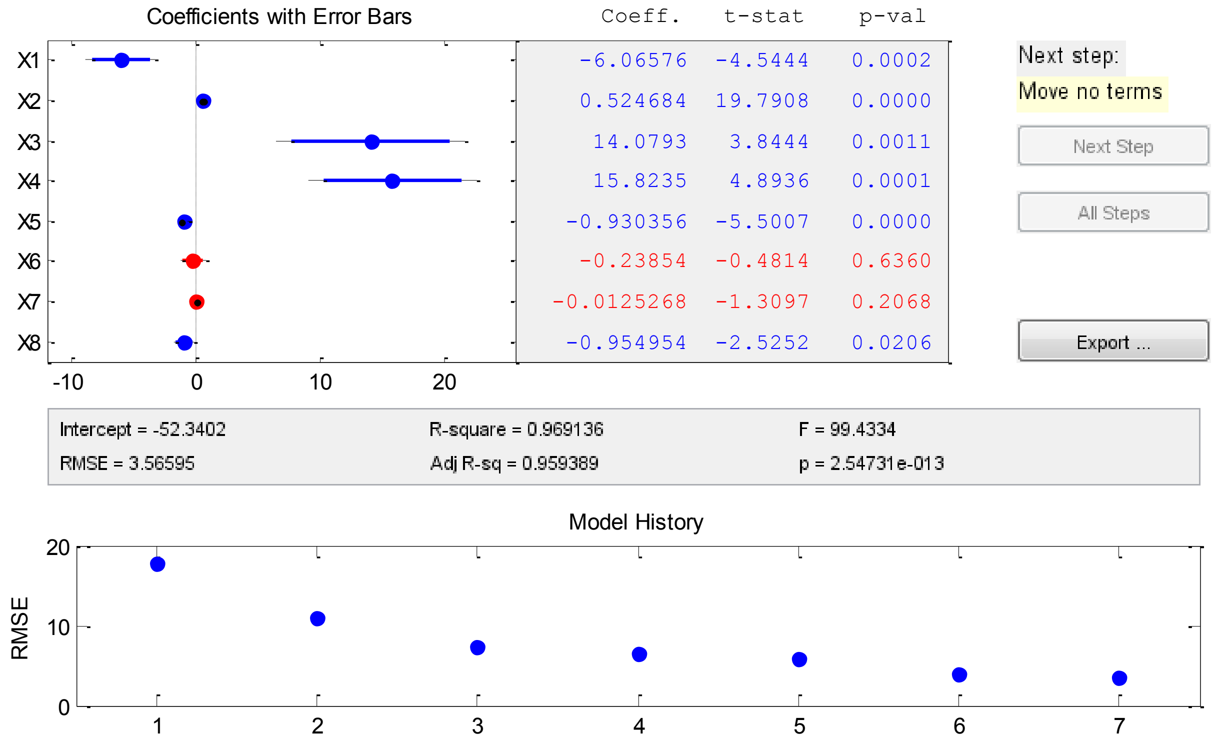


	Coeff.	t-stat	p-val
X1	-5.70736	-3.8176	0.0011
X2	0.522551	17.5070	0.0000
X3	5.2303	4.3636	0.0003
X4	14.4811	4.0307	0.0007
X5	8.16354	1.4114	0.1743
X6	0.000431423	0.2019	0.8422
X7	6.3058	2.0239	0.0573
X8	-0.923035	-4.8456	0.0001

Next step:
Move no terms

Intercept = -40.7117
RMSE = 4.01678
R-square = 0.958777
Adj R-sq = 0.948472
F = 93.0342
p = 3.79576e-013

Figure 8.15 MATLAB stepwise output for the significant lower order terms and their quadratic terms for the COD removal by FA2. X1) PS X2) D X3) T X4) pH X5) PS^2 X6) D^2 X7) T^2 X8) pH^2.



	Coeff.	t-stat	p-val
X1	-6.06576	-4.5444	0.0002
X2	0.524684	19.7908	0.0000
X3	14.0793	3.8444	0.0011
X4	15.8235	4.8936	0.0001
X5	-0.930356	-5.5007	0.0000
X6	-0.23854	-0.4814	0.6360
X7	-0.0125268	-1.3097	0.2068
X8	-0.954954	-2.5252	0.0206

Next step:
Move no terms

Intercept = -52.3402
RMSE = 3.56595
R-square = 0.969136
Adj R-sq = 0.959389
F = 99.4334
p = 2.54731e-013

Figure 8.16 MATLAB stepwise output for the significant lower order terms, pH quadratic term and all pH interactions for COD removal by FA2. X1) PS X2) D X3) T X4) pH X5) pH^2 X6) PS×pH X7) D×pH X8) T×pH.

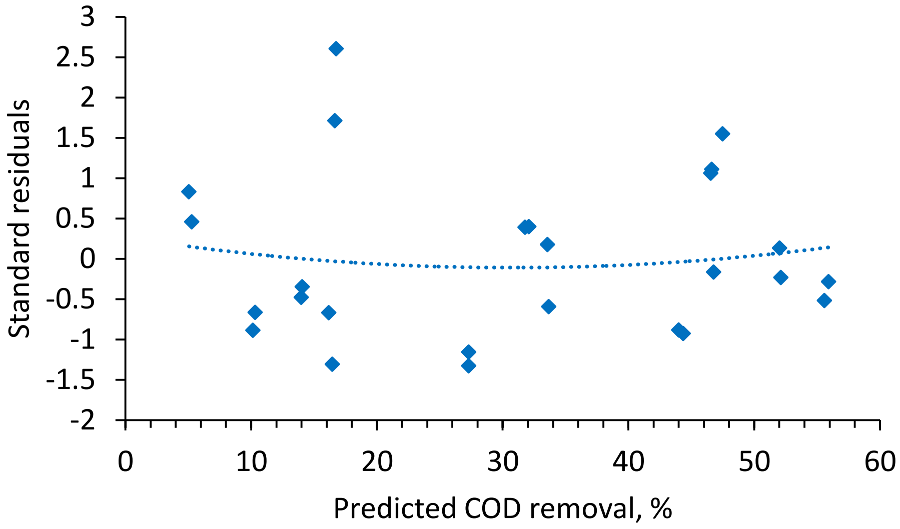


Figure 8.17 Residuals for the model Y = 33.9731 + (-5.8239)PS + (0.5247)D + (5.0040)T + (-2.8735)pH

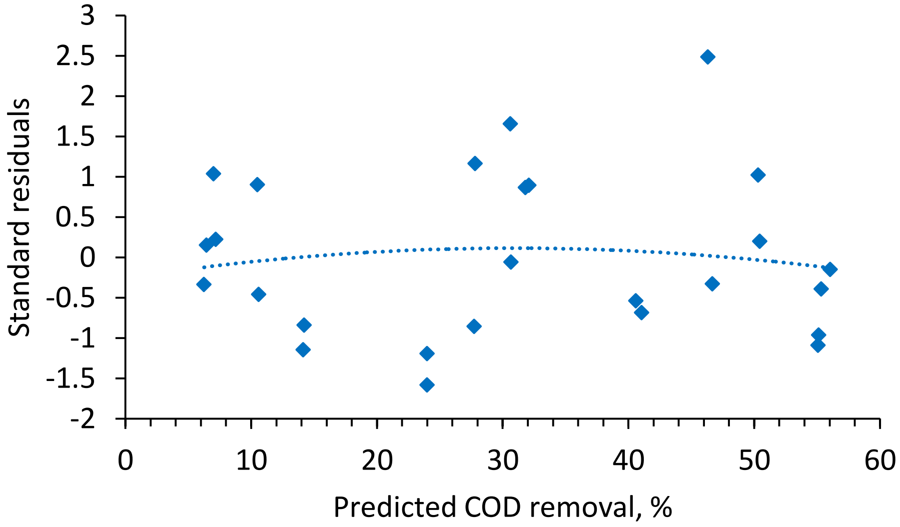


Figure 8.18 Residuals for the model Y = 2.84515 + (-17.8884)PS + (0.702)D + (9.7303)T + (-1.7432)pH + (-0.2836)PS×D + (10.8077)PS×T + (1.0306)PS×pH + (-1.2197)T×pH

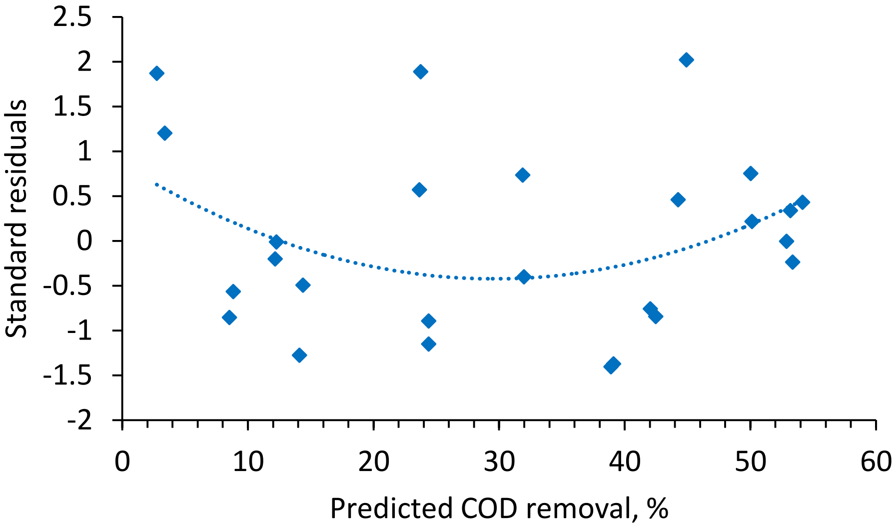


Figure 8.19 Residuals for the model Y = -40.7117 + (-5.7074)PS + (0.5226)D + (5.2303)T + (14.4811)pH + (-0.9230)pH^2

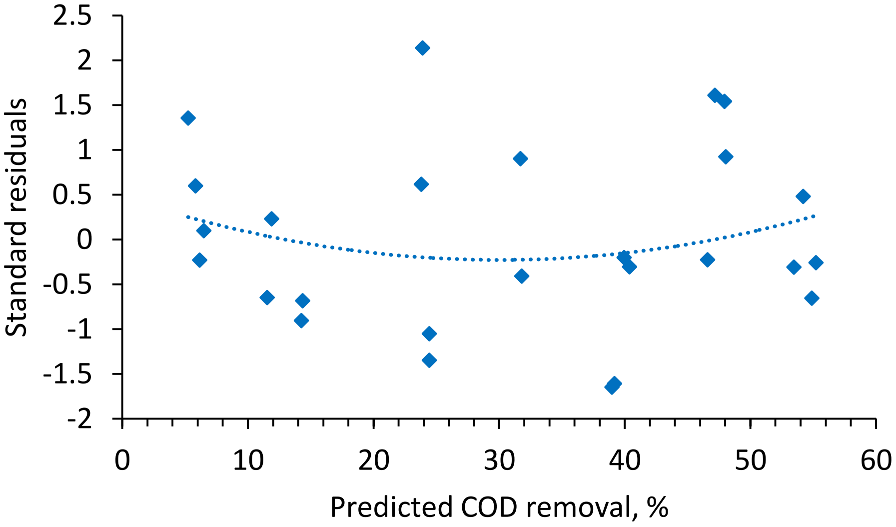
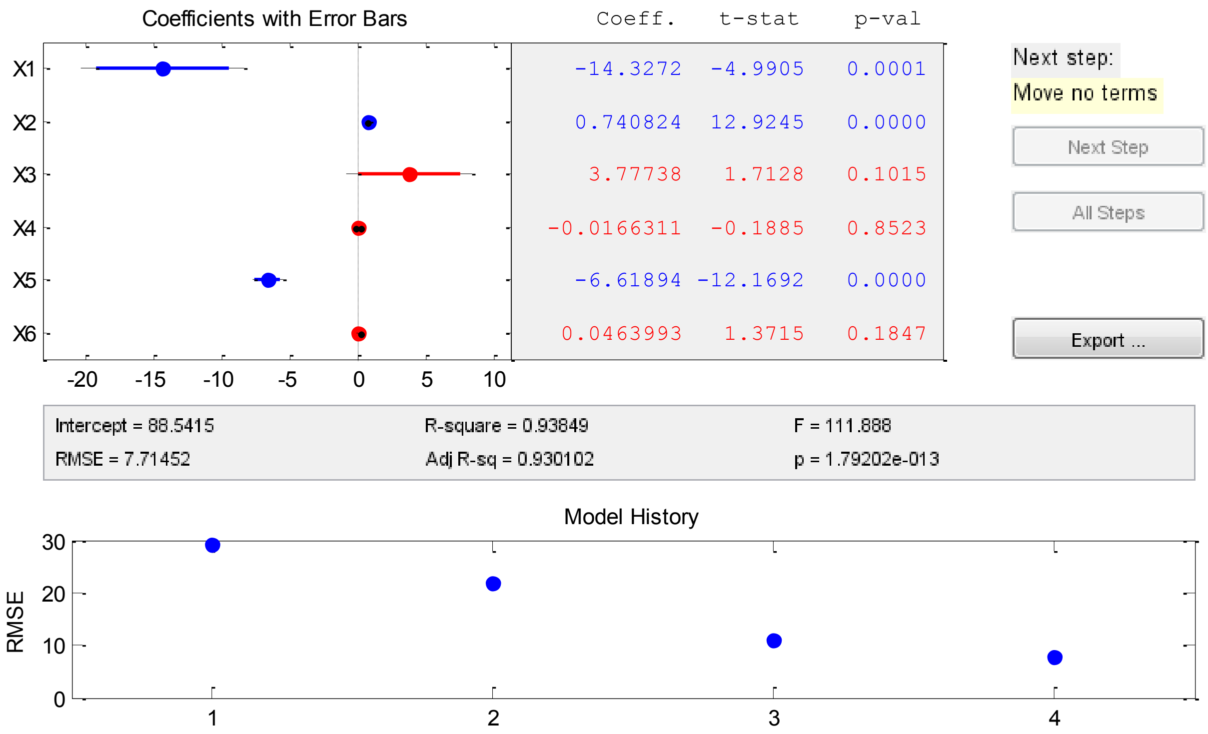


Figure 8.20 Residuals for the model Y = -50.3402 + (-6.0658)PS + (0.5247)D + (14.0793)T + (15.8235)pH + (-0.9304)pH^2 + (-0.9550)T×pH

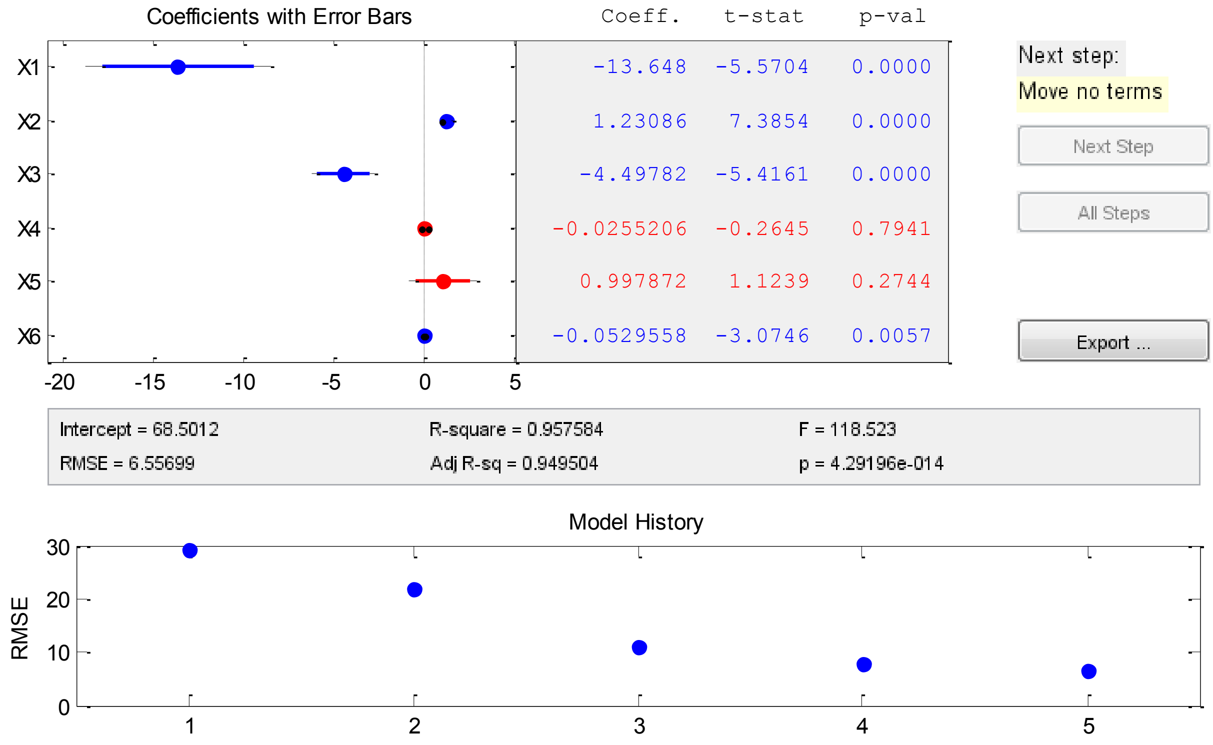
8.6 Forward stepwise analysis for lignin removal by FA2



```
    Coeff.      t-stat     p-val
  -14.3272    -4.9905    0.0001
  0.740824    12.9245    0.0000
   3.77738     1.7128    0.1015
-0.0166311    -0.1885    0.8523
  -6.61894   -12.1692    0.0000
 0.0463993     1.3715    0.1847
```

```
Intercept = 88.5415        R-square = 0.93849       F = 111.888
RMSE = 7.71452             Adj R-sq = 0.930102      p = 1.79202e-013
```

Figure 8.21 MATLAB stepwise output of lower order terms for the lignin removal by FA2. X1) PS X2) D X3) T X4) K X5) pH X6) AS.

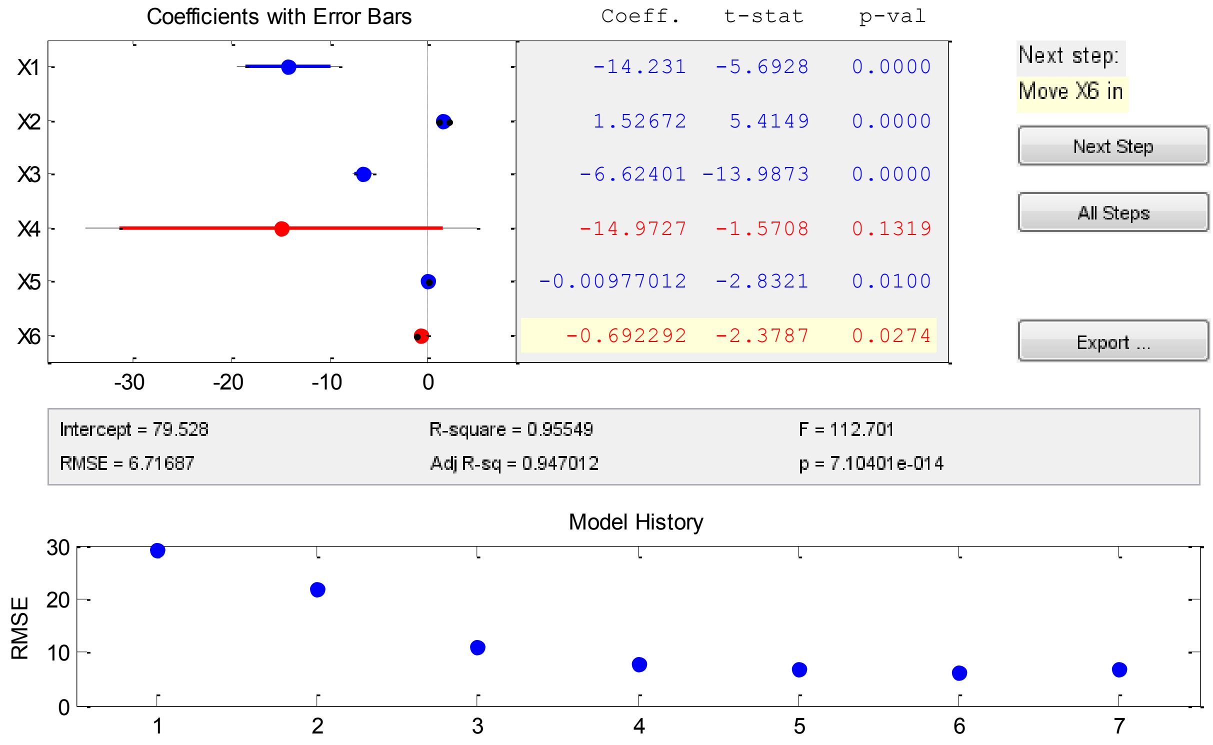


	Coeff.	t-stat	p-val
X1	-13.648	-5.5704	0.0000
X2	1.23086	7.3854	0.0000
X3	-4.49782	-5.4161	0.0000
X4	-0.0255206	-0.2645	0.7941
X5	0.997872	1.1239	0.2744
X6	-0.0529558	-3.0746	0.0057

Next step:
Move no terms

Intercept = 68.5012
RMSE = 6.55699
R-square = 0.957584
Adj R-sq = 0.949504
F = 118.523
p = 4.29196e-014

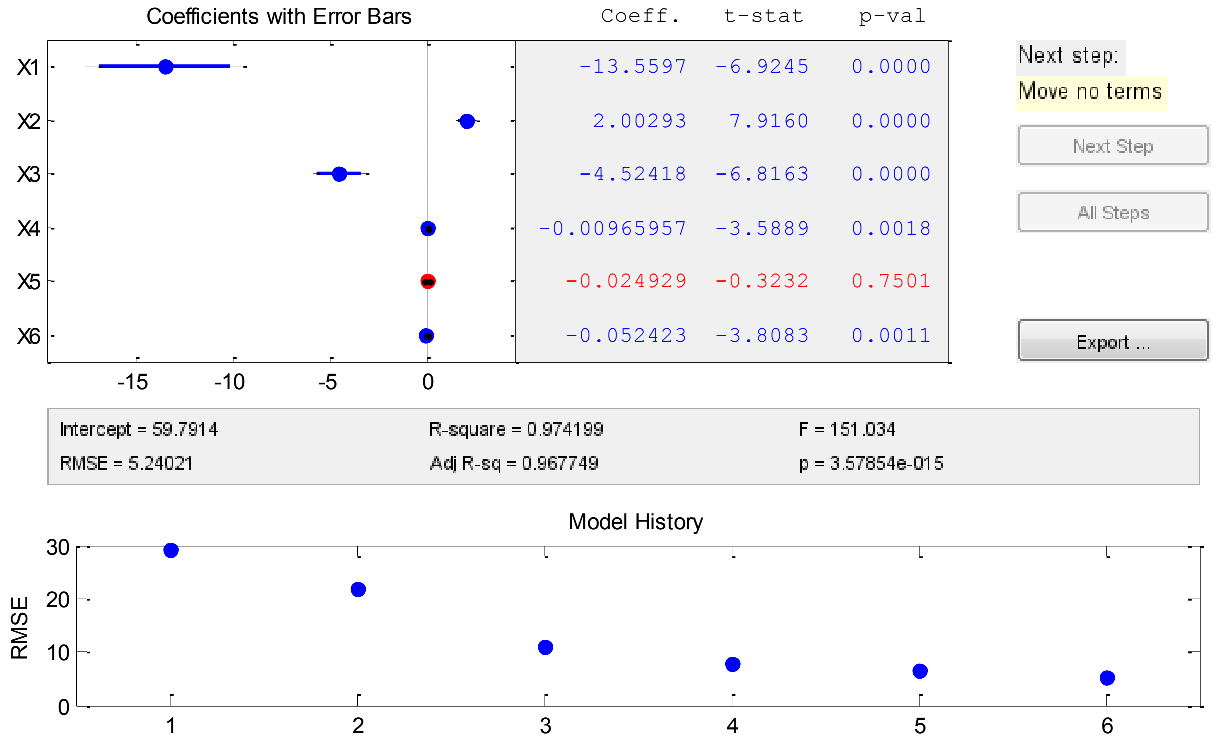
Figure 8.22 MATLAB stepwise output for the significant lower order terms and their interactions for the lignin removal by FA2. X1) PS X2) D X3) pH X4) PS×D X5) PS×pH X6) D×pH.



```
   Coeff.      t-stat     p-val
  -14.231     -5.6928    0.0000
  1.52672      5.4149    0.0000
 -6.62401    -13.9873    0.0000
 -14.9727     -1.5708    0.1319
-0.00977012   -2.8321    0.0100
-0.692292     -2.3787    0.0274
```

```
Intercept = 79.528     R-square = 0.95549     F = 112.701
RMSE = 6.71687         Adj R-sq = 0.947012    p = 7.10401e-014
```

Figure 8.23 MATLAB stepwise output for the significant lower order terms and their quadratic terms for the lignin removal by FA2. X1) PS X2) D X3) pH X4) PS^2 X5) D^2 X6) pH^2.



	Coeff.	t-stat	p-val
X1	-13.5597	-6.9245	0.0000
X2	2.00293	7.9160	0.0000
X3	-4.52418	-6.8163	0.0000
X4	-0.00965957	-3.5889	0.0018
X5	-0.024929	-0.3232	0.7501
X6	-0.052423	-3.8083	0.0011

Next step:
Move no terms

Intercept = 59.7914
R-square = 0.974199
F = 151.034
RMSE = 5.24021
Adj R-sq = 0.967749
p = 3.57854e-015

Figure 8.24 MATLAB stepwise output for the significant lower order terms, D quadratic term and all D interactions for lignin removal by FA2. X1) PS X2) D X3) pH X4) D^2 X5) PS×D X6) D×pH.

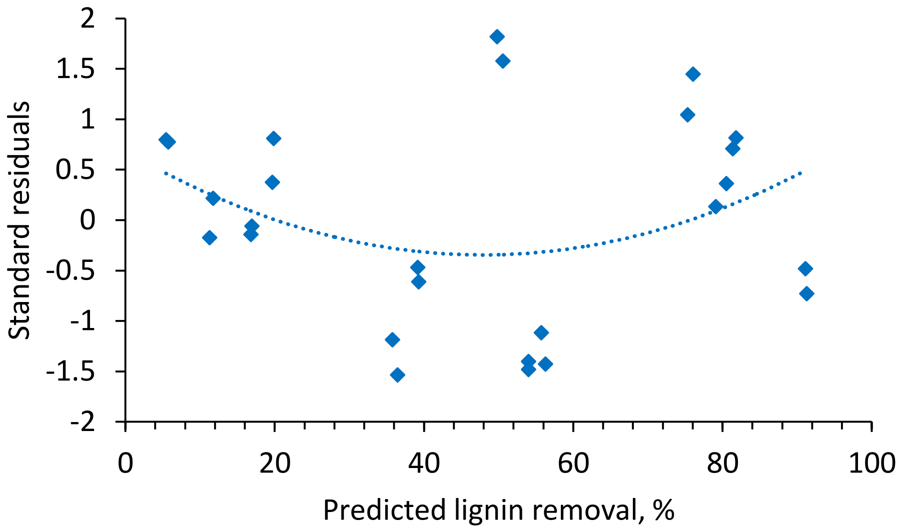


Figure 8.25 Residuals for the model Y = 88.5415 + (-14.3272)PS + (0.7408)D + (-6.6184)pH

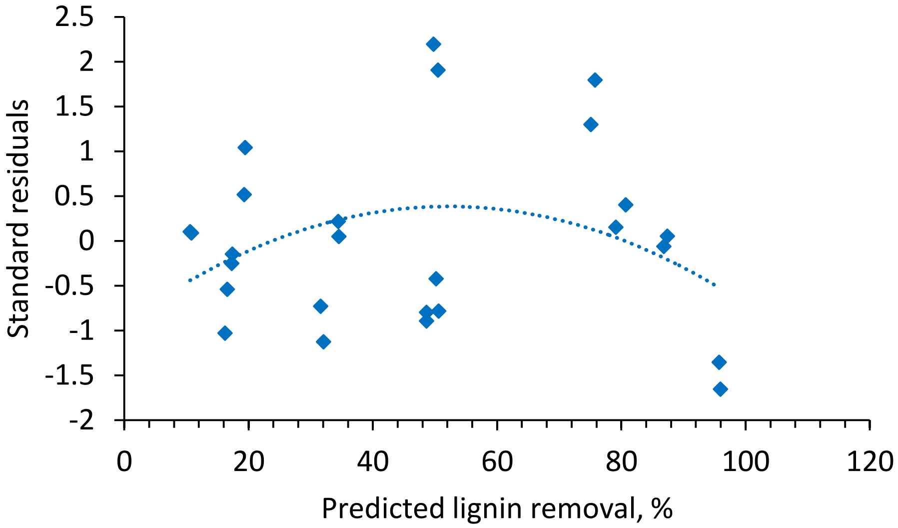


Figure 8.26 Residuals for the model Y = 68.5012 + (-13.648)PS + (1.2309)D + (-4.4978)pH + (-0.0530)D×pH

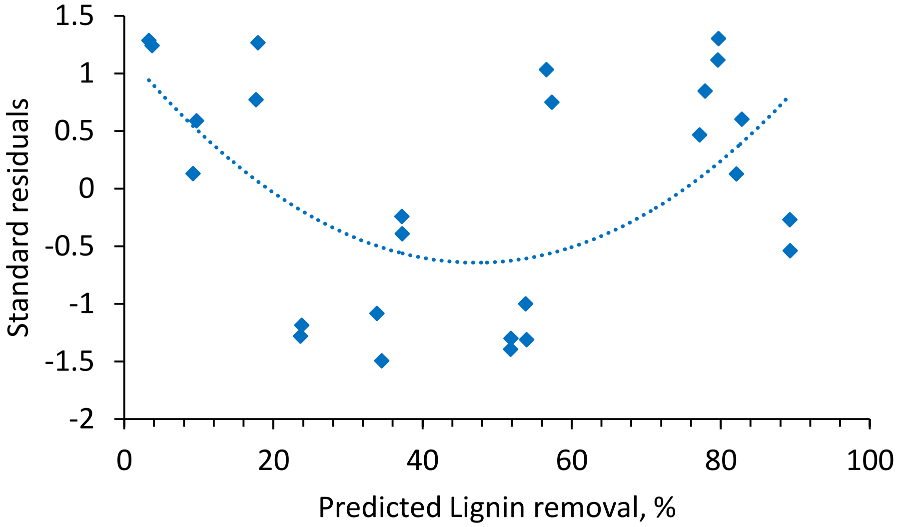


Figure 8.27 Residuals for the model Y = 79.528 + (-14.231)PS + (1.5267)D + (-6.6240)pH + (-0.0098)D^2

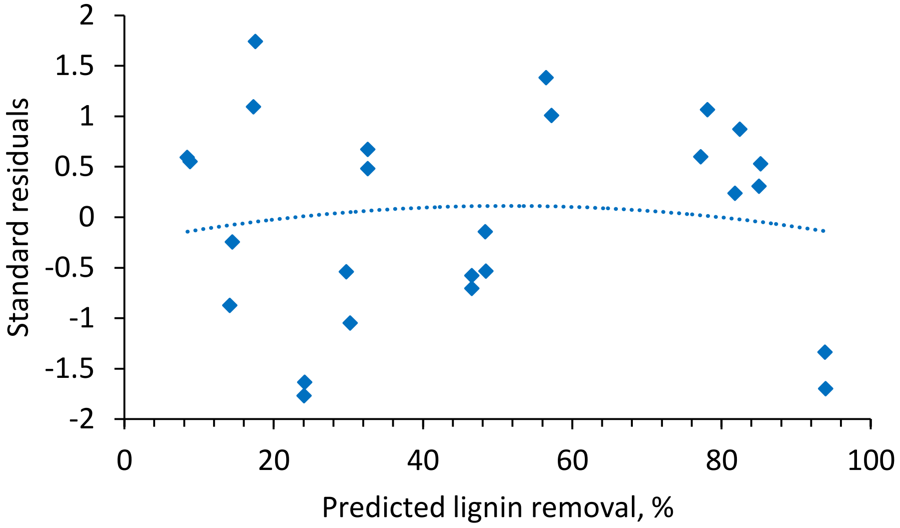


Figure 8.28 Residuals for the model Y = 59.7914 + (-13.5597)PS + (2.0029)D + (-4.5242)pH + (-0.0097)D^2 + (-0.0524)D×pH

8.7 Estimation of the diameter of TMP lignin

Lignin is considered to be a spherical molecule in aqueous solutions (Sjostrom, 1993). Therefore, the average weight based volume of a lignin molecule can be related by the following equation

$$V = \frac{\hat{V}M_W}{N_A} = \frac{4\pi(d/2)^3}{3} \tag{1}$$

where $\hat{V}$ is the specific volume (i.e. the inverse of density) of lignin, M_W is the weight based molecular mass of lignin, and N_A is Avogadro's number. Using the average density of a softwood lignin as 1.34 g/cm^3 (Stamm, 1969), the average diameter of a softwood lignin molecule can then be estimated from equation 1. Thus, the lignin molecules in the TMP pressate may be spherical in shape with an estimated average diameter of 1.8 nm.

More recently, Petridis & Smith (2016) suggest that oligomeric softwood lignins may exhibit a cylindrical conformation in aqueous solutions. The M_N of the lignin in the TMP pressate was

1088 g/mol and using coniferyl alcohol as the monomer of TMP lignin (Sixta, 2006), the average lignin present in the TMP pressate would have a degree of polymerization (N) of 6, and thus is oligomeric. Furthermore, Petridis & Smith (2016), determined that at 300 K, the radius of gyration (R_G) of softwood lignins in aqueous solutions with an N of less than 15 is related to the following equation.

$$R_G = 0.47\ \text{nm}\ N^{0.32} \tag{2}$$

Then, using equation 3, the dimensions of a cylindrical lignin molecule can be estimated from its R_G

$$R_G{}^2 = \frac{R^2}{2} + \frac{L^2}{12} \tag{3}$$

where R is the radius and L is the length. Since milled softwood lignin is expected to be a linear oligomer (Crestini et al., 2011), the diameter of a cylindrical TMP lignin oligomer may be as small as the diameter of one coniferyl alcohol monomer. However, since the concentration of lignin is low, it appears that a softwood lignin oligomer would not remain linear in solution and instead conforms to a width of two coniferyl alcohol monomers (Ratnaweera et al., 2015). The R_G of a coniferyl monomer is 0.32 nm (Petridis & Smith, 2016), and assuming that the monomer is spherical, equation 4 can be used to estimate the radius of the monomer from its R_G.

$$R_G{}^2 = \frac{3R^2}{5} \tag{4}$$

Therefore, on the basis of the literature and assumptions described above and using equations 2 through 4, the lignin in the TMP pressate may be cylindrical in shape with an estimated diameter and length of 1.7 nm and 2.1 nm respectively.

8.8 References

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