Abstract

In this research, two lignin-[2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) polymers were generated and assessed for their efficiency in treating municipally produced wastewater. The removals of chemical oxygen demand (COD) and turbidity were 47.5% and 71.2%, respectively, for the singular flocculation system at the dosage of 40–70 mg/L. For the dual coagulation/flocculation system, the polymer with a higher charge density (AM2) achieved higher COD and turbidity removals than the polymer with a lower charge density (AM1). To achieve the same organic removal from the wastewater, the alum use could be reduced from 150 mg/L in the single alum use to 35 mg/L in the dual system when used along with 65 mg/L of AM2. In both systems, lignin-METAC polymers exhibited better performance than the flocculant used at a local wastewater treatment plant. Lignin-METAC polymers could be used as bio-based flocculants for the replacement of petroleum-based flocculants and inorganic coagulants.

**KEYWORDS**

lignin, biorefining, biosolids, wastewater, sustainability, alum

1 | INTRODUCTION

Municipal wastewater is highly variable in composition and contains various organic and inorganic compounds (Ittisupornrat et al., 2015; Wang et al., 2020). It often contains high concentrations of phosphorous (4–15 mg/L) and nitrogen (12–50 mg/L), as well as varying concentrations of organic compounds (COD of 250–1000 mg/L) (Gupta, 2016). The primary wastewater treatment systems utilize chemical additives to facilitate the agglomeration and rapid sedimentation of particulates (flocs) (Sahu & Chaudhari, 2013). Various chemical additives, such as coagulants and flocculants, have been utilized in wastewater systems (Munshed et al., 2021; Sahu & Chaudhari, 2013; Teh et al., 2016). Coagulants, such as aluminium sulfate (alum), iron chloride and iron sulfide, are employed as the most successful chemicals for the phosphorous removal to reduce the potential eutrophication of water (Nir et al., 2009). Direct coagulation with lime and ferric chloride was also reported, but that would require much higher (>3.3 g/L) dosages and yield lower organic removals (Sarika et al., 2005). Generally, the direct coagulation is often criticized in the literature for its high dosage and low chemical oxygen demand (COD) removal (20%–40%) (Chen et al., 2015; Guida et al., 2007; Matilainen et al., 2010; Teh et al., 2016).

Alternatively, many reports have concluded that singular flocculation results in a high organic removal, low chemical use, sludge formation, and thus a reduced environmental impact, addressing limitations experienced by the singular coagulation method (Lee et al., 2014; Rashed et al., 2013; Sarika et al., 2005; Yu et al., 2008). It was determined that a complete total suspended solids (TSS) removal from olive mill effluents was achieved when a cationic polyacrylamides flocculant (>3 g/L) was used, whereas COD and BOD were reduced by 55% and 23%, respectively (Sarika et al., 2005). However, polymeric flocculants would inefficiently remove nutrients, such as phosphorous-containing compounds, from wastewater (Aguilar et al., 2002; Amuda & Amoo, 2007; Ginos et al., 2006; Sher et al., 2013).
Most wastewater treatment facilities adopt dual coagulation/flocculation treatment to ensure the effective removal of nutrients and organic compounds (Chen et al., 2015; Guida et al., 2007; Zhao et al., 2021). Synthetic polymers, such as polyacrylamides, polyacrylic acids, and polystyrene sulphonic acids and their derivatives, have been commonly used in the coagulation/flocculation process for decades to reduce coagulant dosages and the volume of sludge generated from the coagulant use (Bolto & Gregory, 2007). However, these polymers are oil-based, which are non-renewable and nonbiodegradable. They may also contain unpolymerized monomers and additives that are neurotoxic and carcinogenic (Brostow et al., 2009; Rudén, 2004). Consequently, there has been a growing interest in replacing oil-based flocculants with more sustainable bio-based alternatives.

Lignin is a biomaterial that is produced as a waste product of the pulp and paper industry (Couch et al., 2016; Fang et al., 2010; Wang et al., 2014). Increased interest in the application of lignin as a flocculant has emerged due to its functionality and availability (Couch et al., 2016; Fang et al., 2010; Wang et al., 2014). Previous studies conducted by Wang and associates outlined the polymerization of lignin with [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) and reported the exceptional performance of the products for flocculating anionic azo-dyes and kaolin particles (Wang et al., 2018a, 2018b). The lignin polymer derivatives were also reported to be efficient flocculant in treating industrial wastewaters produced in the mining, textile (Zhang et al., 2013), and pulp and paper industries (Couch et al., 2016). However, to our best knowledge, the efficiency of lignin-based polymeric flocuants in municipal wastewater (RMW) has not been studied. As municipal wastewater contains different microorganisms and colloidal particles from other colloidal systems (Meerbergen et al., 2017), the results generated in other systems of industrial wastewater treatment cannot depict the impact of lignin-based polymers on municipal wastewater systems.

Also, the properties of lignin produced industrially may change batch by batch due to lignin’s variability in plant resources and pulping and extraction process conditions (Gigli & Crestini, 2020; Rutkowska et al., 2009), and such variability in lignin properties may affect its polymerization and thus performance. In this study, two industrially produced unmodified kraft lignin were polymerized with METAC under the same polymerization reaction conditions to evaluate the impact of the lignin source on the properties of the produced lignin-METAC polymers and their flocculation performance. The objectives of this study were to (1) produce and characterize lignin-METAC polymers from two different sources; (2) assess the effectiveness of two lignin-METAC polymers as flocculants in real municipal wastewater; and (3) analyse the coagulation/flocculation treatment of municipal wastewater in the dual systems of lignin-METAC polymers with alum.

2 | MATERIALS AND METHODS

2.1 | Materials

In this work, 100 L of municipal wastewater sample was collected from a water pollution control plant in a city in northern Ontario, Canada, on 15 April 2017. Two different acid-washed softwood kraft lignin (AKL) samples were supplied by FPlnovations. An acrylamide acrylic acid copolymer (AP) was supplied by a local wastewater plant. [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (METAC), (poly)diallyldimethylammonium chloride (PDADMAC with an M_w of 100–200 kg/mol), potassium persulfate (>99.0%), hypochlorite, sodium hydroxide (reagent grade), sodium salicylate, sodium nitroferricyanide, ammonium persulfate, ammonium molybdate, potassium antimonyl tartrate, ascorbic acid, ethanol and sulfuric acid (95–98 wt.%) reagent grade were purchased from Sigma Aldrich. The water-soluble alum (Al_2(SO_4)_3⋅18H_2O) with a molar mass of 666 was also purchased from Sigma Aldrich. Anionic polyvinyl sulfate (PVSK; M_w of 100–200 kg/mol; 97.7%) was purchased from Wako Pure Chem. Ltd Japan.

2.2 | Lignin METAC synthesis

The polymerization of lignin and METAC was conducted under the same conditions of pH 4.0, METAC/lignin ratio of 1.8 mol/mol, 3 h, 80°C, 0.3 mol/L of lignin concentration, and 1.5 wt% of K_2S_2O_8 initiator dosage as described in our previous study (Wang, Kong, Gao, & Fatehi, 2018b). Upon completion, the reaction medium was cooled, neutralized (pH ~ 7), and purified via ethanol precipitation (Wang, Kong, Gao, & Fatehi, 2018b). The precipitates were dried in an oven (105°C) overnight. The samples generated from different lignin samples of AKL1 and AKL2 were denoted as AM1 and AM2, respectively.

2.3 | Charge density, solubility and molecular weight analyses

The solubility of the product was determined following a previously established method (Couch et al., 2016; He et al., 2016). The charge density of the samples was determined using a Particle Charge Detector (Mutek, PCD 04, Germany) as described in the past (Couch et al., 2016; He et al., 2016).

Lignin-METAC samples (50 mg) were dissolved in sodium nitrate (10 ml, 0.1 mol/L) and filtered with a 0.2 μm pore-size nylon filter. A gel permeation chromatography (GPC) analysis was conducted to determine the molecular weight of the samples using a Malvern GPCmax VE2001 Module + Viscotek TDA305 multi-detector (UV, IR, low angle and right-angle laser), which was equipped with PolyAnalytical PAC103 and PAC101 columns and 5% acetic acid solution as solvent/eluent. A flow rate of 0.50 ml/min and a column temperature of 35°C were utilized, and pullulan (47 300 g/mol) was used as a standard sample in the GPC analysis (Wang, Kong, Gao, & Fatehi, 2018b).

2.4 | Flocculation and coagulation of wastewater

A 40 ml aliquot of the wastewater sample was added to a 50 ml centrifuge tube. Various dosages (0–300 mg/L) of AMs, AP and alum were dispensed gravimetrically into the centrifuge tubes. The sample
was mixed in an Innova 3100 (Brunswick Scientific, Edison, NJ, USA) water shaker bath for 15 min and centrifuged in a Thermo Scientific Sorvall ST 16 centrifuge for 10 min at 1500 rpm. The supernatant was decanted into a clean dry tube and saved for further testing as outlined below. This process was repeated for flocculant/coagulation tests via adding alum first and the flocculant after 1 min.

2.5 Chemical oxygen demand (COD), turbidity and total suspended solids

The COD analysis was conducted using a COD test kit (0–1500 mg/L, CHEMetrics Inc) for samples collected before and after treatment with flocculants and coagulants according to the previously described method (Dashtban et al., 2014). The turbidity of the centrifuged wastewater samples before and after flocculation and coagulation was assessed using a Turbidimeter 2100AN, (Hach, Co. Co, USA) at room temperature (Dashtban et al., 2014).

Approximately, 50 ml of treated wastewater was filtered through a 55 mm diameter isoSPEC ProWeight® filter paper. The filter paper was then dried in a 105°C oven overnight. The final mass of the filter paper was recorded, and the total suspended solids (TSS) (mg/L) was calculated via Equation 1.

\[
TSS = \frac{(w_2 - w_1) \times 10^6}{V}
\]

where \(w_2\) denotes the weight (g) of the filter paper and residues, \(w_1\) denotes the weight (g) of the filter paper and \(V\) denotes the volume of the sample (ml).

2.6 Total organic carbon (TOC)

The TOC of the wastewater samples was determined using a Vario TOC Cube (Elementar Analysensysteme Gmb, Germany) via a nondispersive infrared (NDIR) detector (Chen et al., 2017).

2.7 Trace metal analysis

The metal components of the treated wastewater were analysed using an inductively coupled plasma emission spectrometer (ICP-OES) (Varian Vista Pro) in accordance with ISO 17025. The samples were digested with aqua regia (1:3 nitric acid: hydrochloric acid) in a CEM Mars Xpress microwave. A ramp time of 20 min was used to reach 175°C, and then the sample was kept at 175°C for an additional 25 min. After digestion, the samples were cooled and diluted with 40 ml of distilled deionized water before analysis.

2.8 Ammonia–nitrogen

Total ammonia as nitrogen (denoted as Ammonia-N) of the treated wastewater was determined in accordance with ISO 17025. The ammonia-silicate colorimeter assay was performed with a Skalar autoanalyser following the modified ammonia-silicate Berthelot reaction method (APHA, 1999). Briefly, an aliquot of wastewater was mixed with pre-prepared sodium hypochlorite solution and salicylate catalyst solution, which was digested for 5–10 min at room temperature, and the absorbance of the complex was measured at 660 nm with a Skalar autoanalyser.

2.9 Phosphorus

The total phosphorous content of the treated wastewater was identified in accordance with ISO 17025. Briefly, an aliquot of wastewater (50 ml) that contained (0.5 g) ammonium persulfate was digested at 97°C for 30 min. After cooling and neutralization, the digested solution was mixed with ammonium molybdate solution (1 ml, 40 g/L), potassium antimonyl tartrate solution (1 ml, 3.42 g/L) and ascorbic acid (1 ml, 0.1 M), producing a blue phosphomolybdic complex that was quantified at 880 nm with a Skalar Autoanalyser.

2.10 Acute toxicity

Aquatic toxicity tests were carried out at a single concentration via the biological test methods outlined by Environment Canada (Scroggins, 1990). Approximately, 26 L of distilled deionized water containing 65 mg/L of AM2 (selected due to its better flocculation performance) was prepared and aerated for 30 min at 6.5 ± 1.0 ml/min/L. Oncorhynchus mykiss (i.e. Rainbow trout) was introduced to the solution (25 L) and kept for 96 h, and Daphnia magna (i.e. Daphnia) was also added to the solution (1 L) for 48 h. Temperature (15 ± 2°C), pH (7.7), conductivity (102 μS/cm) and dissolved oxygen content (9.6 mg/L) was maintained throughout the test. After the appropriate time had elapsed, the surviving organisms were counted.

3 RESULTS AND DISCUSSION

3.1 Properties of wastewater and lignin–METAC polymers

Table 1 presents the characteristics of wastewater used in this study. It was found that the properties of wastewater were comparable with those of municipal wastewater found in the literature (Gupta, 2016). Municipal wastewater is largely impacted by the geographical size, infrastructure, population, and industry of municipalities, which can often change with the seasons and time of day (Gupta, 2016).

Two lignin–METAC polymers (i.e. AM1 and AM2) generated via polymerizing KL and METAC were used for flocculation treatment of the wastewater sample. The properties of these lignin–METAC polymers are listed in Table 2. The charge density and molecular weight of unmodified lignin samples of AKL1 and AKL2 were undetectable due to their low solubility at neutral pH. The solubility of AM1 and AM2
was less than 100%, which could be due to the presence of some unreacted and insoluble lignin in the product. The quantification of subunits and hydroxyl group content of lignin samples was accomplished using $^{31}$P NMR (Figure S1 and Table S1). Samples of AKL1 and AKL2 were determined to have 1.09 and 1.36 mmol/g coniferylhydroxyl units, respectively (Table 2), which is consistent with other reports about the composition of softwood lignin samples (Jiang et al., 2017). In addition, both phenolic and aliphatic hydroxyl group contents of AKL2 were higher than those of AKL1 (Table S1), leading to the higher charge density of AM2 than AM1 as the polymerization of KL with METAC mainly happened on the phenolic hydroxyl groups (Wang, Kong, Gao, & Fatehi, 2018b). The lower molecular weight of AM2 than AM1 could be attributed to the higher chance of collision or radial coupling termination as more radicals would be formed at a higher phenolic hydroxyl group content (Woodworth et al., 1998). Considering the same reaction conditions, the lignin properties were responsible for the difference in cationic charge densities and molecular weights of produced polymers, which could affect their flocculation performance. In addition, an acrylamide acrylic acid polymer (AP) used in the wastewater plant as a flocculant had a low molecular weight with a high anionic charge density (Table 2).

### 3.2 Singular flocculation and coagulation systems

Lignin METAC samples of AM1 and AM2 were implemented as floculants in the wastewater sample. The dosage of these floculants was optimized for their chemical oxygen demand (COD) and turbidity removals, as shown in Figure 1. The data revealed the optimum AM1 and AM2 dosages of 40–70 mg/L for the maximum removals of COD (45.3% and 47.5%) and turbidity (71.1% and 71.2%), respectively. The addition of AP to wastewater did not affect the COD or turbidity of the samples probably due to its relatively low molecular weight and negative charge density. It is believed that the floculants with high molecular weights are more effective than those with low molecular weights in bridging particles in suspension systems and thus flocculation development (Razali et al., 2011). Moreover, the high negative charge of AP could introduce repulsion in the colloidal system (with negative charges) of municipal wastewater, which would hamper its flocculation efficiency (Hameed et al., 2016). A slight increase in the COD of wastewater with increasing AP dosage was observed, and the turbidity remained unchanged. These results imply that both AM1 and AM2 were more effective than AP in treating municipal wastewater.

The optimum alum dosage to achieve the maximum turbidity removal was observed at 150 mg/L (Figure 1). An increase in the COD removal was observed with alum overdosing, potentially due to the stabilization of colloidal particles in the sample due to an increase in the overall ions of the wastewater (Guida et al., 2007; López-Maldonado et al., 2014).

### 3.3 Dual coagulation/flocculation system

Figure 2 depicts the COD and turbidity of the wastewater sample as a function of alum dosage, whereas the dosage of AM1 and AM2 remained constant at 65 mg/L. The addition of 65 mg/L of polymers to alum-treated samples improved the COD and turbidity removals. The maximum turbidity removal for alum-AM1 and alum-AM2 was within 30–60 mg/L alum dosage (Figure 2), whereas 120–150 mg/L of alum dosage was needed to achieve a similar level of turbidity removal by the alum treatment alone (Figure 1). More importantly, both alum-AM1 and alum-AM2 systems showed higher COD removals than the singular alum system (Figures 1 and 2). For the dual systems, the COD removal decreased sharply after the addition of 1 mg/L alum and remained constant with increasing the alum dosage. The use of alum helped to destabilize and increase the size of the particles, facilitating their subsequent flocculation by AM1 and AM2. Considering the similar solubility of AM1 and AM2, the main causes of their different flocculation efficiency were related to the molecular weight and charge density. Although AM2 had a slightly lower molecular weight (i.e. less efficient in flocculating particles), AM2 achieved slightly higher COD and turbidity removals than the AM1 did probably due to its higher charge density leading to higher charge neutralization affinity of particles in wastewater effluents. It was reported in our previous work that AM1 and AM2 contained small amounts of inorganic elements (e.g. Al, Ca, Fe, Na and K), which originated from the woody material and the kraft pulping process (Table S2). These inorganic metal in the lignin samples may act as a potential coagulant to form small particles with pollutants in municipal wastewater (Duan & Gregory, 2003). Both AM1 and AM2 exhibited better flocculation performance than the commercial flocculant (AP) in the dual alum/polymer system (Figure 2).
3.4 | Comparative analysis

The ammonia, phosphorous, inorganic content and TSS of wastewater after singular and dual systems are presented in Table 3. A slight increase in the ammonia removal was observed when the wastewater was treated with AP, which could be attributed to the ammonium content of the flocculant itself. For both singular and dual systems of AM1 and AM2, the ammonia removal was limited (<15%) and consistent with literature reports (Aguilar et al., 2002). The ammonia was either dissolved in the water or adsorbed to the surface of the oppositely charged polymers/particles in the solution via electrostatic attraction. Coagulation–flocculation process removed these particles and thus indirectly caused the reduction of ammonia-nitrogen associated with them (Aguilar et al., 2002). Direct and efficient nitrogen removal is usually achieved by biological nitrification–denitrification processes, which target the conversion of ammonia to nitrate and finally to nitrogen gas (Yuan et al., 2016).

The phosphorous removal appeared to be significant in both systems. In the singular flocculation system, the total phosphorous could be removed through adsorption with the flocculated particles. In the singular coagulation system, the phosphorus could be removed via the formation of phosphate precipitates with the metal salts used as coagulants. In the dual systems, a complicated combination of both interactions facilitated phosphorus removal. Based on the current Canadian regulations, the phosphorous concentration in the municipal wastewater effluent should not exceed 1 mg/L with a 2040 objective of <0.5 mg/L (Environment Canada, 2001). This laboratory study achieved a value that was well below this requirement.

The total inorganic content of the wastewater sample (170 mg/L) decreased slightly after the flocculation with AM1 and AM2 to...
162 and 163 mg/L, respectively. AM1 and AM2 were ineffective in the inorganic removal, which could potentially be attributed to the limited interaction between inorganic metal ions and positively charged AM1 and AM2. The addition of AP resulted in a more remarkable decrease in the inorganic content to 134 mg/L. The dual system showed relatively lower inorganic removal than the singular system did, which is attributed to the presence of alum that potentially increased the inorganic concentrations of wastewater.

Both singular flocculation or coagulation and the dual system of coagulation/flocculation showed similar TSS removals (72%–76%), except that alum achieved the highest TSS removal of 96%. Alum is a commonly used coagulant for water treatment and purification processes. However, the use of alum will induce 1%–3% sludge production based on the volumetric amount of the treated water (Zhao et al., 2009). Such a high production of alum sludge has been a concern worldwide due to the increasing demand for clean water with the rapid growth of the world population and urban expansion. Alum sludge has long been disposed of in landfills, which raises significant environmental concerns due to high dosage requirements (150 to 2000 mg/L) (Guida et al., 2007). The residual amount of aluminium compounds in water after treatment with alum is another great concern (Becaria et al., 2002; Bolto & Gregory, 2007; Lee et al., 2012; Matilainen et al., 2010). The results in this study suggested that AM could reduce the alum dosage from 150 to 35 mg/L in treating the wastewater while maintaining similar organic content reduction (Figure 2), which could potentially help to manage alum usage and final sludge disposal.

3.5 | Toxicity

The *Oncorhynchus mykiss* toxicity test was conducted with exposure to the AM2 (65 mg/L) solution. The *Daphnia magna* tests showed a non-lethal 48-h LC50 for the sample concentration with total mortality of 17%. However, 60%–30% of the organisms were immobile upon test completion. The high concentration and large particle size of AM2 may have resulted in organism suffocation (Belanger et al., 2005). Upon test completion. The high concentration and large particle size of AM2 may have resulted in organism suffocation (Belanger et al., 2021). Such a high production of alum sludge has been a concern worldwide due to the increasing demand for clean water with the rapid growth of the world population and urban expansion. Alum sludge has long been disposed of in landfills, which raises significant environmental concerns due to high dosage requirements (150 to 2000 mg/L) (Guida et al., 2007). The residual amount of aluminium compounds in water after treatment with alum is another great concern (Becaria et al., 2002; Bolto & Gregory, 2007; Lee et al., 2012; Matilainen et al., 2010). The results in this study suggested that AM could reduce the alum dosage from 150 to 35 mg/L in treating the wastewater while maintaining similar organic content reduction (Figure 2), which could potentially help to manage alum usage and final sludge disposal.

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It should be stated that the present study was conducted at the optimized AM2 concentration (i.e. 65 mg/L) in wastewater, assuming that lignin-METAC would not be removed with the particles. However, the vast majority of AM2 would be bound to solid particles (Liber et al., 2005); they are mainly coagulated/flocculated with organic and inorganic components of wastewater (Figures 1 and 2 and Table 3), and only a small amount of them may remain in wastewater. Therefore, they would be removed from wastewater before releasing the treated water into the environment, which implies that AM2 would not be available at 65 mg/L concentration to cause toxicity. However, more research is needed in this area to determine the LC50 of lignin-METAC and its use for cleaning open fields in the future.

**4 | CONCLUSIONS**

It is concluded that lignin-METAC polymers can be used as flocculants for municipal wastewater in singular flocculation and dual coagulation/flocculation systems. The optimum dosage range of lignin-METAC for achieving the maximum removals of COD (45.3%–47.5%) and turbidity (71.1%–71.2%) was 40–70 mg/L. The dual coagulation-flocculation analysis revealed that at the constant dosages of lignin-METAC (65 mg/L), the maximum COD (65.9%) and turbidity (88.5%) removals were achieved when 65 mg/L of AM2 and 30–60 mg/L of alum were used. The addition of lignin-METAC reduced the alum dosage by 82.5% for reaching comparable COD and turbidity removals when alum alone was used. Phosphorous removal (90.2%–97.5%) appeared to be highly effective in singular flocculation and dual coagulation/flocculation systems. Alum-AM2 system achieved slightly higher COD and turbidity removals than the alum-AM1 system, which is attributed to the higher charge density of AM2 and thus higher charge neutralization affinity for wastewater. Lignin-METAC polymers showed better flocculation performance in both singular and dual systems than commercial acrylamide-based polymers in terms of COD, turbidity and TSS removals. Additional research is needed to improve the inorganic removal efficiency and to determine the shelf life and toxicity of lignin-METAC polymers to promote its applications.

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**DATA AVAILABILITY STATEMENT**

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.

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