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Original Research

Synthesis and Characterization of Modified Lignin Flocculants for Congo Red and Methylene Blue Removal

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Abstract: This study aimed to synthesize lignin-based flocculants by grafting sulfonic acid (SA) and [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) using potassium persulfate as an initiator. The flocculants were characterized for particle size, thermal stability, surface morphology, and functional group analysis. Their dye removal performance was tested against Congo red and methylene blue at different pH levels. FTIR analysis confirmed successful grafting of METAC and SA groups on the lignin backbone for the lignin-METAC, lignin-SA, and lignin-METAC-SA. Particle size analysis showed an increase in particle size only with the Lignin-METAC-SA. Lignin modification leads to increased folding and the presence of raised structures in the modified flocculants. Compared to unmodified lignin (384°C), maximum thermal degradation occurs at relatively higher temperatures (400-500°C) for all modified lignin flocculants. Lignin modification enhanced the dye removal performance of the flocculant, with lignin-SA showing the highest removal efficiencies for both dyes. All lignin-based flocculants performed better against methylene blue at all pH levels, with lignin-SA (82.9%) and lignin-METAC-SA (82.3%) achieving the highest reduction efficiencies at pH 10. Higher removal efficiency (46-69%) was observed for Congo red in more acidic solutions (pH 4) for all lignin flocculants. These results highlight the potential of grafted lignin-based flocculants for dye wastewater treatment.

1. INTRODUCTION

As issues of water scarcity and pollution continue to intensify, advancements in wastewater treatment and management are necessary (Libralato et al., 2012). Wastewater is treated using chemical, biological, or physical processes, or a combination thereof, to reduce contamination and improve its water quality to fit the desired quality level (Englande et al., 2015). The textile dyeing and finishing industry is considered the 2nd top polluter of clean water, next to agriculture. Around 8000 chemicals are used in the textile manufacturing process, including dyeing and printing, with a significant fraction of these with known associated environmental and health risks (Kant, 2012; Yaseen & Scholz, 2019). Because of this, dye wastewater must be treated before release to receiving surface water bodies to minimize their negative impacts (Solayman et al., 2023).

Several treatment methods have already been studied and developed for dye removal. However, some of these methods are not capable of significantly reducing the levels of contaminants in wastewater, and some practical methods cannot be fully implemented due to disadvantages like high cost and potential for secondary pollution. An example of this is chemical precipitation, which is relatively simple and effective for high concentrations of pollutants but requires the heavy use of chemicals and produces a large amount of sludge. Another standard method is through adsorption or filtration, which is efficient for a wide range of contaminants and is flexible in terms of the setup; yet, it is restricted by the costs of the filtration material, maintenance to mitigate saturation and clogging, and the regeneration of the material (Crini & Lichtfouse, 2019). An ideal treatment method is something that can significantly reduce the dye concentration in wastewater without producing potentially hazardous by-products (Katheresan et al., 2018).

One of the well-studied dye removal processes is flocculation. Coagulation and flocculation are the processes of adding agents called coagulants, which will destabilize the forces separating the particles, and flocculants, which can promote the agglomeration of the contaminants into larger particles called flocs through bridging, thus accomplishing the separation of solids and liquids (Arockiam JeyaSundar et al., 2020). Flocculation does not bear such negative impacts and is commonly employed to reduce the turbidity of water through the removal of suspended solids, dissolved pollutants, and emulsified oil (Das et al., 2021). The treatment process can be further modified to reduce chemical use, sludge production, and treatment costs through direct flocculation, wherein only flocculants are added to treat the wastewater. For instance, such flocculants could be polyelectrolytes, which are polymers that contain either a cationic or anionic charge—like chitosan (Chatsungnoen & Chisti, 2019).

Synthetic polymer flocculants like polyacrylamide have been used in different industries because of their high molecular weight and exceptional performance for contaminant removal. However, they are non-biodegradable and can pose a hazard to living organisms (Siti Aisyah et al., 2014). Natural flocculants are attracting attention in several studies because of their comparable performance against synthetic flocculants (Ajao et al., 2018), safer use, and ability to produce organic sludge that is biodegradable and reusable as fertilizer in agriculture (Fauzani et al., 2021; Zaman et al., 2020). One of the common biopolymers used as a flocculant is the plant-derived lignin because of its natural abundance, biodegradability, and presence of functional groups that can effectively interact with contaminants during the flocculation process (Suryawanshi et al., 2025).

As flocculation involves chemical destabilization by overcoming repulsive forces between particles through complex bridging between particles (Gregory & O'Melia, 1989), lignin can be further modified to alter its surface charges by grafting different groups on the lignin backbone (Lee et al., 2014; Wang et al., 2008). In the study of Wang et al., (2018), lignin was modified by grafting [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) to make the flocculant more cationic. The produced Lignin-METAC flocculant showed effective dye removal against anionic dyes, Remazol Black B, and Remazol Brilliant Orange, through a bridging and charge neutralization mechanism. Alternatively, lignin can be made more anionic by adding negative groups like sulfone/sulfonate groups on the lignin backbone, resulting in more negative charge densities (Aro & Fatehi, 2017; Gao et al., 2019), and was tested to be effective in removing cationic dyes like methylene blue (Rahmawati et al., 2021). Furthermore, lignin can be modified to produce amphoteric flocculants, which can be effective in removing both cationic and anionic dyes (Yue et al., 2005). Wu et al., (2023) synthesized an amphiphilic lignin flocculant by grafting acrylamide and 3-chloro-2-hydroxypropyltrimethylammonium chloride on the kraft lignin backbone and found that it is capable of treating high turbidity wastewater. Eraghi Kazzaz and Fatehi (2020) studied the effect of cationization of lignin with (3-bromopropyl) trimethylammonium bromide and (5-bromopentyl) trimethylammonium bromide, coupled with polymerization with 3-sulfopropyl methacrylate, on its properties. However, its effect on flocculating performance was not studied. The Mannich reaction on acrylamide-modified lignosulfonate with amine and aldehyde was explored to produce the amphoteric lignin-flocculant LSDC, which was found to be effective in decolorizing a variety of dyes up to 80% under suitable conditions (Yue et al., 2005). These studies show the potential of incorporating both cationic and anionic groups on lignin to improve its flocculating and contaminant removal performance.

Currently, there is still no study that has reported on grafting anionic sulfonic acid and cationic METAC groups on lignin and investigated their dye removal activities. In this study, three lignin-based flocculants will be synthesized by grafting METAC and sulfonic acid (SA) groups to the lignin backbone using potassium persulfate as an initiator. The as-synthesized flocculants were characterized and tested for their dye removal performance against methylene blue and Congo red. All lignin-based flocculants tested in this study were effective in removing both Congo red and methylene blue dyes, highlighting their potential for treating dye wastewater.

2. MATERIALS AND METHODS

2.1 Materials

Alkali lignin, [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) (75 wt. % in H_2O), and potassium persulfate ($K_2S_2O_8$) with ≥99% purity were purchased from Merck Sigma-Aldrich. Linear alkyl benzene sulfonic acid (LABSA) was purchased from XERN Chemicals, Philippines. All reagents were used without further purification.

2.2 Synthesis of modified lignin flocculants

Three types of modified lignin flocculants were prepared by grafting METAC and sulfonic acid (SA) to the lignin backbone. The flocculants were prepared using the method of Liu et al. (2018) and Moore et al. (2021), with modifications. In summary, alkali lignin was dissolved in distilled water using a 1:20 solute-to-solvent mass ratio, and the mixture was stirred at 400 rpm until maximum dissolution. A 0.1 mol/L NaOH solution was then gradually added to the solution to adjust its pH to 11. The solution was then heated to 70°C for 30 minutes, and the pH was readjusted to 4 using 0.1 M H_2SO_4. The pH levels of the solution were adjusted to promote solubility and optimal reaction conditions for the synthesis. The solution was kept in a water bath at 75°C until the end of the synthesis and purged under a nitrogen atmosphere for 30 min. Afterwards, 0.015 g/g solute of the potassium persulfate was added as a free radical initiator to the solution while stirring at 400 rpm. Then, depending on the type of flocculant, METAC, SA, or both were added dropwise using a 1:2 solute-modifier mass ratio as summarized in Table 1. The solution was stirred for another 2.5 h to promote the reaction. After reaction completion, the solution was mixed with 80% (vol. ethanol/vol. water) to precipitate the flocculants. The precipitate was separated from the solution and then washed further with 80% ethanol twice before drying at 100°C.

Table 1. Mass ratios for the lignin and modifier used in the preparation of the different flocculants.

Type	**Lignin to METAC to SA Mass Ratio**		
	Lignin	METAC	SA
Unmodified Lignin	1	0	0
Lignin-METAC	1	2	0
Lignin-SA	1	0	2
Lignin-METAC-SA	1	2	2

2.3 Sample Characterization

Functional group analysis was done on the different flocculants using a Cary 360 FTIR Spectrometer from Agilent Technologies at the Philippine Science High School – Central Luzon Campus. IR spectra of the samples were obtained by measuring the % transmittance of the samples from 650 to 4000 cm^{-1} wavenumbers. The particle size of the different lignin-based flocculants was investigated using optical microscopy at the Department of Science and Technology – Industrial Technology Development Institute (DOST-ITDI), Material Science Division. Images were obtained for the different samples and were processed for image analysis to obtain the particle size distribution. Optical microscopy was chosen, as the samples were expected to fall within a 50–200-micron range, which is beyond the optimal range for Dynamic Light Scattering (DLS) analysis. Surface morphology of the different flocculants was studied using HITACHI TM4000Plus Scanning Electron Microscope (SEM) analysis at the Philippine Science High School – Ilocos Region Campus. Images were obtained at 800–1200x magnification. The thermal stability of the flocculants was studied using the Netzsch STA 2500 Regulus Simultaneous Thermal Analyzer. Samples were heated from 20°C to 600°C at a ramping rate of 40 K/min.

2.4 Dye Removal Performance against Congo red and methylene blue

A dye removal experiment was conducted following the protocol of Wang et al. (2018) and Wu et al. (2022), with some modifications. The different flocculants were tested against Congo red and methylene blue dyes at different pH conditions (pH 4, 7, and 10). These dyes were selected as they have differences in terms of charge, with Congo red being an anionic dye, while methylene blue is a cationic dye. The flocculants were tested by mixing the flocculant at a dosing rate of 100 mg/L with 50 ml of artificial dye wastewater with a concentration of 10 mg/L in centrifuge tubes. The samples were shaken for two hours in a linear shaker for 2 hours before leaving the samples to settle for another 2 hours. The supernatant was then filtered through a 0.45 μm pore size PTFE membrane, and the absorbance of the filtrate was measured using a Shimadzu UV-10008 UV-Visible spectrophotometer at 497 nm and 664 nm for Congo red and methylene blue, respectively. The dye removal performance of the flocculants was compared with RAFLOC 28 (cationic polymer flocculant) and ARFLOC 12 (anionic polymer flocculant).

2.5 Statistical Analysis

One-way analysis of Variance (ANOVA) with a 95% confidence level was used to evaluate the effect of the different flocculants in reducing the concentration of the two dyes investigated. Tukey's Honestly Significant Difference (HSD) post-hoc test was done to identify significant differences in the performance of the different flocculants against each other, including the positive controls.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

Fig. 1 shows the FT-IR spectra of the unmodified lignin and the different synthesized lignin-based flocculants (Lignin-METAC, Lignin-SA, and Lignin-METAC-SA). Characteristic peaks for hydroxyl moieties (-OH: 3400 cm^{-1}) and methyl and methylene vibration (alkyl -CH stretch: 2900 cm^{-1}) were present in all samples, suggesting the presence of many hydroxyl and methylene groups, highly associated with lignin (Guo et al., 2018). The different flocculants also exhibited prominent peaks at 1650 cm^{-1} and 1200 cm^{-1} associated with -C=C- of the characteristic conjugated alkene of lignin and the -CO stretching vibrations, respectively. Characteristic peaks for -C=O stretching (1750 cm^{-1}) and stretching vibration for $N^+(CH_3)_3$ (960 cm^{-1}) were observed for Lignin-METAC and Lignin-METAC-SA, suggesting successful incorporation of METAC in the structure of lignin (Guo et al., 2018). (Moore et al., 2021) described that the mechanism for modification is through METAC being grafted through the hydroxyl groups. This eventually translates to an apparent reduction in the -OH peak around 3300 cm^{-1}. Furthermore, peaks for the -C=O stretch around 1750 cm^{-1} were also more prominent in Lignin-METAC and Lignin-METAC-SA compared to Lignin-SA, which is expected as METAC contains a carbonyl group. On the other hand, peaks around 1020-1220 cm^{-1} associated with -S=O stretching due to sulfonate and sulfonic acid groups were observable in Lignin, Lignin-SA, and Lignin-METAC-SA, but highly diminished in Lignin-METAC (Karpukhina et al., 2023). These results confirm the successful grafting of METAC and sulfonic acid structures to the lignin backbone.

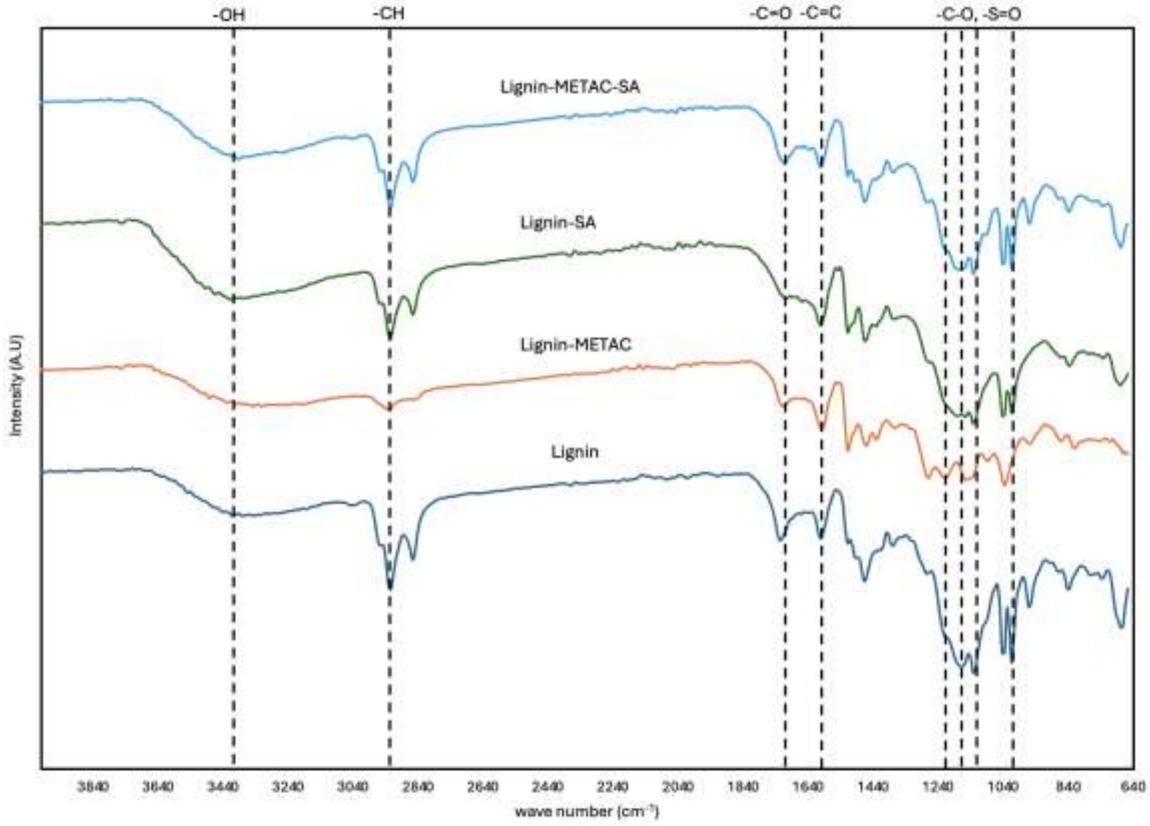

Fig. 1. *FTIR Spectra of unmodified lignin and synthesized modified lignin flocculants.*

3.2 Particle Size Analysis

Particle size of the different flocculants was determined using optical microscopy (Fig. 2). Particle size distribution analysis showed that lignin, lignin-METAC, and lignin-SA have similar particle sizes around 1.5-1.7 µm. Significantly larger particles were observed for the lignin-METAC-SA, which showed an abundance of particles with a Feret of 150 µm. The incorporation of METAC and SA into lignin may result in changes in the different inter- and intramolecular forces of attraction, resulting in possible folding within the structure and interlinking of individual lignin molecules with each other, resulting in increased particle size in lignin-METAC-SA. Specifically, electrostatic interactions between opposite charges within the structure of lignin-METAC-SA and the possible formation of inter- and intramolecular ionic bonds could result in a larger particle for lignin-METAC-SA compared to lignin-SA and lignin-METAC (Lekniute et al., 2013).

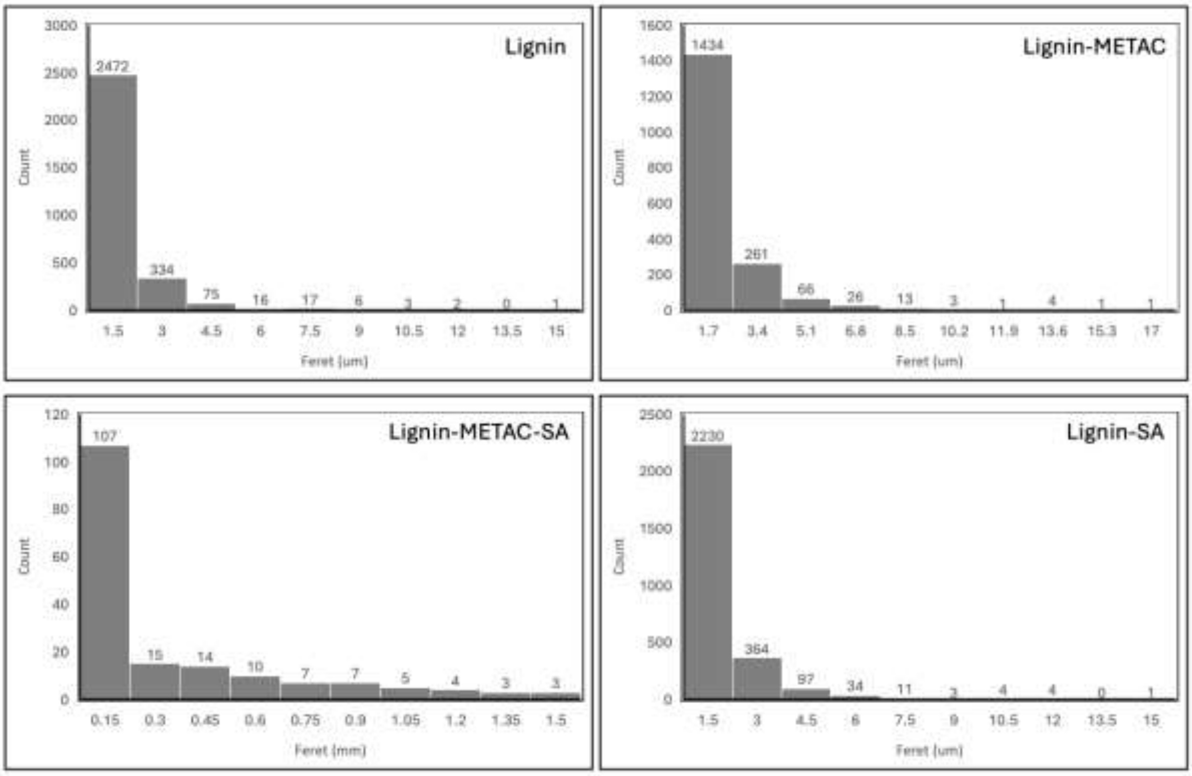

Fig. 2. *Particle Size Distribution of Pure Lignin and Modified Lignin Flocculants.*

3.3 Scanning Electron Microscopy

Scanning electron microscope images (Fig. 3) were obtained for the different flocculants. Unmodified lignin showed more uniform spherical structures that contain mounds and grooves, while lignin-SA and lignin-METAC showed some more porous microstructures. More folds and raised structures were also present in the modified lignin flocculants. The presence of crazing and cracks is characteristic of the formation of the plastic phase on the flocculants (Moustaqim et al., 2018). Furthermore, these changes in the surface morphology of the lignin may be attributed to the disruption in hydrogen bonding in the alkali lignin during the modification. This results in a collapse in the crystal structure of lignin and a consequential alteration in the surface of the flocculant (Li et al., 2024). This can be further confirmed by conducting molecular weight and zeta potential analysis, which was not done in the current study.

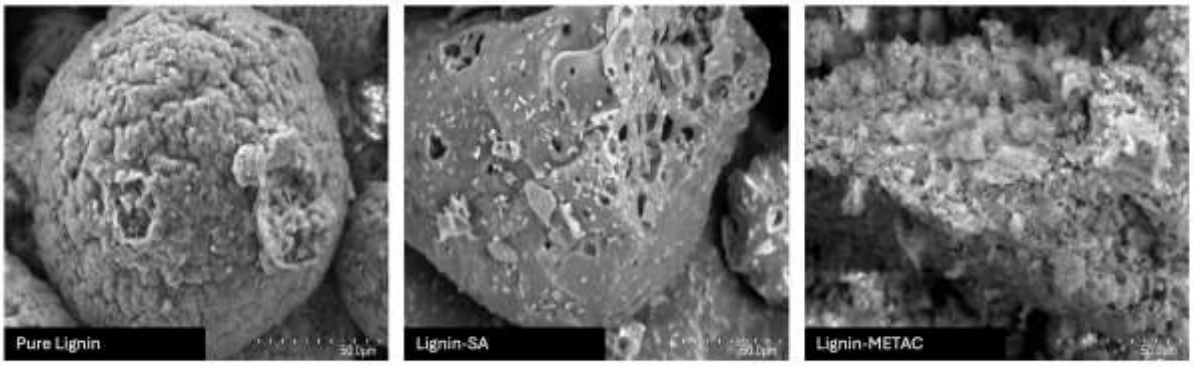

Fig. 3. *SEM Image of Lignin-based flocculants at 800x magnification.*

3.4 Thermogravimetry Analysis

Tests on the thermal stability of each flocculant were performed using a simultaneous thermal analyzer. The TGA graphs (Fig. 4) showed differences in the thermal profiles of the different flocculants, which is expected as new groups are incorporated into the structure of lignin. In general, patterns observed in the TGA and DTG graphs are similar for all flocculants, with DTG showing distinct peaks around 70-150°C and 250-500°C. The same are observed as apparent inflections in the thermograms for the different samples. Exothermic and endothermic peaks are apparent in the DTG curves, with maximum exothermic peaks present at higher temperatures in all modified lignin flocculants than in the unmodified lignin. DTG curves revealed three to four peak weight loss temperatures (T_p) for all flocculants, as summarized in Table 2. A slower rate of decomposition was observed at temperatures higher than 500°C for all flocculants.

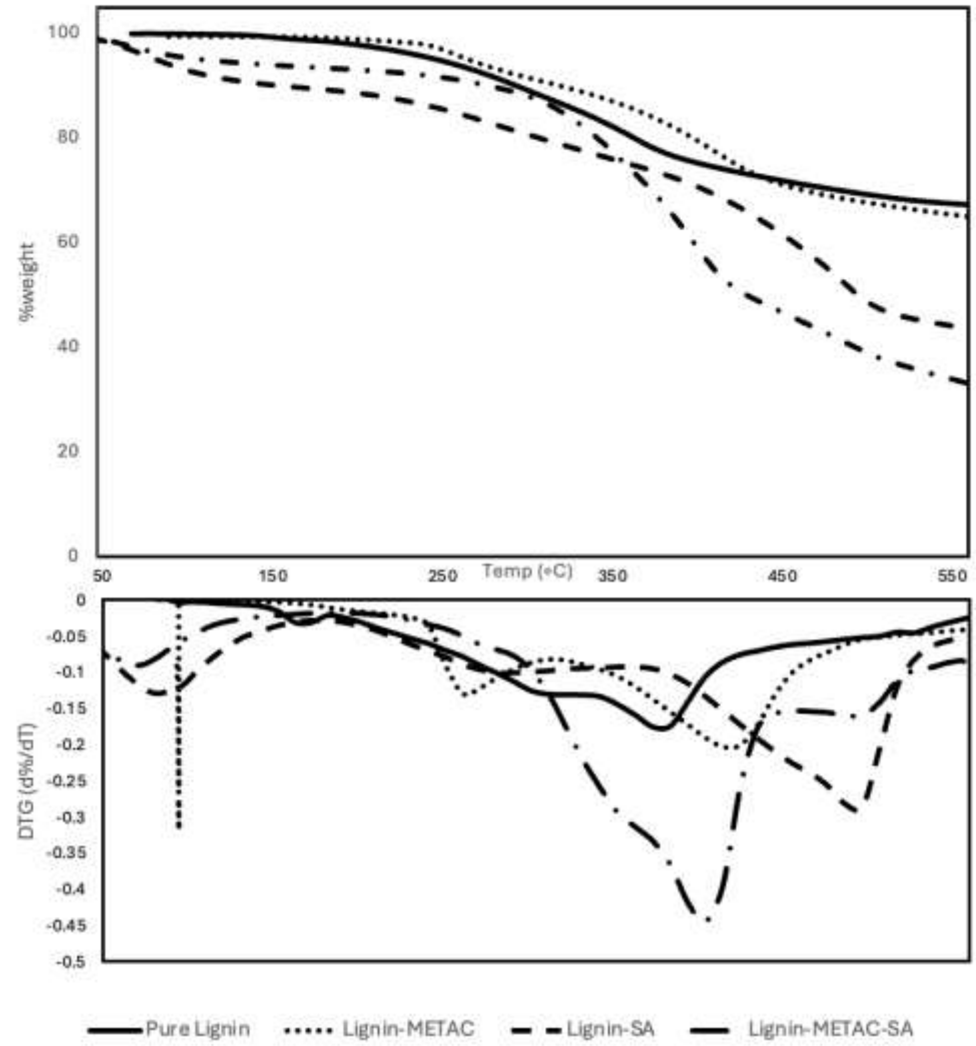

Figure 4. *TGA and DTG graphs for pure lignin, lignin-METAC, lignin-SA, and lignin-METAC-SA flocculants.*

The first peak (T_{P1}) in the DTG around 73–162°C is attributed to the loss of moisture, as much of the mass loss occurred around the vaporization point of water. The flocculants have differences in the 2nd to 4th peak temperatures owing to the differences in the structure. In the case of unmodified lignin, the formation of unsaturated chains, methane, carbon dioxide, and carbon monoxide occurs after dehydration. The process continues with the breaking of the methyl-aryl ether bonds around 300°C and phenol ring decomposition around 400°C (Moore et al., 2021; Sahoo et al., 2011). The mass loss at 304°C is also due to the cleavage of β-O-4 bonds of carbohydrate molecules (Chu et al., 2013; Kim et al., 2013; Moustaqim et al., 2018).

In the case of Lignin-METAC, T_{P2} occurred at a lower temperature (261.9°C), which can be due to the decomposition of the quaternary ammonia group. At the same time, T_{P3} is due to the decomposition of the

Lignin-METAC backbone (Moore et al., 2021). The same pattern of decomposition was observed with Lignin-METAC-SA, but at a higher temperature, due to the incorporation of both the METAC and SA groups. T_{P3} for all modified flocculants occurred at temperatures between 400 and 500°C, which is due to the saturation reaction of the aromatic ring, C-C bond breakage, and release of water, carbon dioxide, and carbon monoxide by-products during rearrangements and removal of functional groups (Jakab et al., 1991; Wibowo & Park, 2023).

Table 2. Peak weight loss temperature (T_P) of pure lignin, lignin-METAC, lignin-SA, and lignin-METAC-SA.

	Peak Temperatures (°C)			
	T_{P1}	**T_{P2}**	**T_{P3}**	**T_{P4}**
Unmodified lignin	162	302	384	-
lignin-METAC	94.7	261.9	425	-
lignin-SA	88.06	281	496.8	-
lignin-METAC-SA	72.6	363	404.6	497.1

3.5 Dye Removal Performance

The effect of pH on the flocculating performance of the different flocculants was tested against Congo Red dye and is summarized in Fig. 5. Results showed that all lignin-based flocculants were effective in removing Congo red at pH 4 and 7. In acidic pH, unmodified lignin, lignin-METAC, and lignin-METAC-SA showed similar values for their reduction efficiencies around 46-52%. Lignin-SA performed best among the synthesized flocculants, with an average reduction efficiency of 69.4%. At neutral pH, all lignin-based flocculants showed similar performance at 37-40% reduction. In contrast to this, no significant reduction in dye concentration was observed at pH 10 for all lignin-based flocculants. In all pH conditions, superior performance was obtained by the positive control groups, RAFLOC and ARFLOC, with average reduction efficiencies at pH 4, 7, and 10 around 88-94%, 73-86%, and 61-76%, respectively.

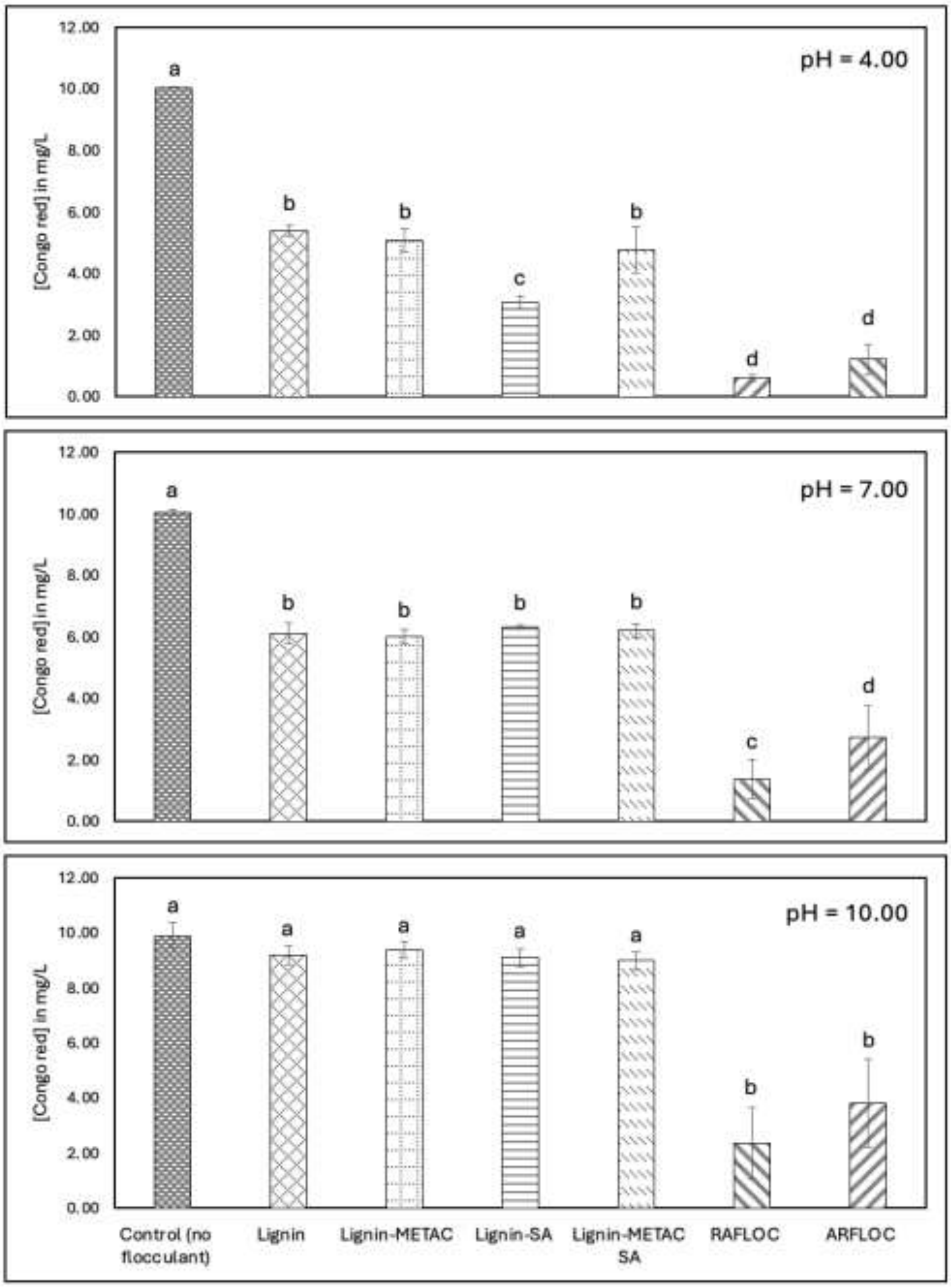

Fig. 5. Effect of pH on the dye removal performance of unmodified lignin, Lignin-METAC, Lignin-SA, and Lignin-METAC-SA flocculants against Congo red dye. Letters above the bars represent a significant difference among treatment groups based on ANOVA ($p < 0.05$) and Tukey's HSD test. Similar letters mean no significant difference between treatments. Error bars indicate standard deviation (n = 3).

Both RAFLOC and ARFLOC positive controls showed significantly higher reduction compared to the lignin-based flocculants. This is expected, as both are commercially used flocculants for treating industrial wastewater. Still, except at pH 10, all the lignin flocculants exhibited significant dye removal activity. The isoelectric point of Congo Red is at pH 3 (Litefti et al., 2019). Thus, it has been observed to ionize into a more positive charge ion below pH 3 and exhibits a more negative charge at values above pH 5.3 (Alarifi et al., 2021). It is expected that the anionic flocculant Lignin-SA will perform the best due to its ability to neutralize and destabilize the dye contaminants, reducing electric repulsion, which will lead to an efficient aggregation of flocs (Ghernaout & Ghernaout, 2012). In addition to this, sulfonation also generally increases the solubility of polymers in water, which increases the ability of the flocculant to adsorb onto the dye particles and bridge them together (Lufrano et al., 2013).

Lignin-METAC, on the other hand, with its cationic nature, would tend to perform flocculation via polymer bridging. This relies on several additional factors, including the agitation of the particles and the flexibility of the polymer, as well as the surface charges, branches, and functional groups that can serve as interaction points, which may lead to weaker flocculation performance (Hogg, 2013). This may also explain why lignin-METAC-SA performed better than lignin-METAC but worse than lignin-SA, as the amphoteric nature may have diminished some of its ability to neutralize the dye contaminants. Still, its polymer bridging capability remains due to the polymeric nature of grafted flocculants. Unmodified lignin was also able to perform flocculation at a comparable efficiency to lignin-METAC. This is likely due to the exact mechanism that these two flocculants utilized, except that Lignin-METAC had additional functional groups that can still interact with the contaminants through intermolecular forces, increasing the likelihood of bridging. At pH 7 and 10, RAFLOC still performed best for dye removal, which can be attributed to its cationic nature, which can effectively neutralize Congo red, which is anionic at these pH levels, through charge neutralization. Like other polyacrylamide flocculants, sweeping effects and enmeshment allow for the removal of the Congo red dye through possible adsorption and bridging mechanisms of both RAFLOC and ARFLOC flocculants (Khan et al., 2020).

The dye removal performance of the different flocculants was also tested against the methylene blue dye. Fig. 6 showed that in all pH levels, the unmodified lignin and all modified lignin flocculants showed significant dye removal performance. At pH 4.00, Lignin-METAC, Lignin-SA, and Lignin-METAC-SA flocculants showed high average reduction efficiencies at 49.63%, 79.15%, and 56.04%, respectively. Unmodified lignin and the two positive controls did not show a significant reduction at this pH level. The same with that at pH 4.00, no significant reduction in the dye concentration was observed for unmodified lignin and the two positive controls. Highest average reduction efficiencies were observed for Lignin-SA (61.5%) and Lignin-METAC-SA (60.7%), respectively. Lignin-METAC also showed significant dye removal performance at 31.1%. At pH 10, all flocculants, except for the RAFLOC control, showed significant flocculation performance. Lignin-METAC showed the lowest average reduction at 22%, followed by ARFLOC (31.7%) and unmodified lignin (42.9%). Lignin-SA and lignin-METAC-SA showed the highest average reduction efficiencies at 82.9% and 82.3%, respectively.

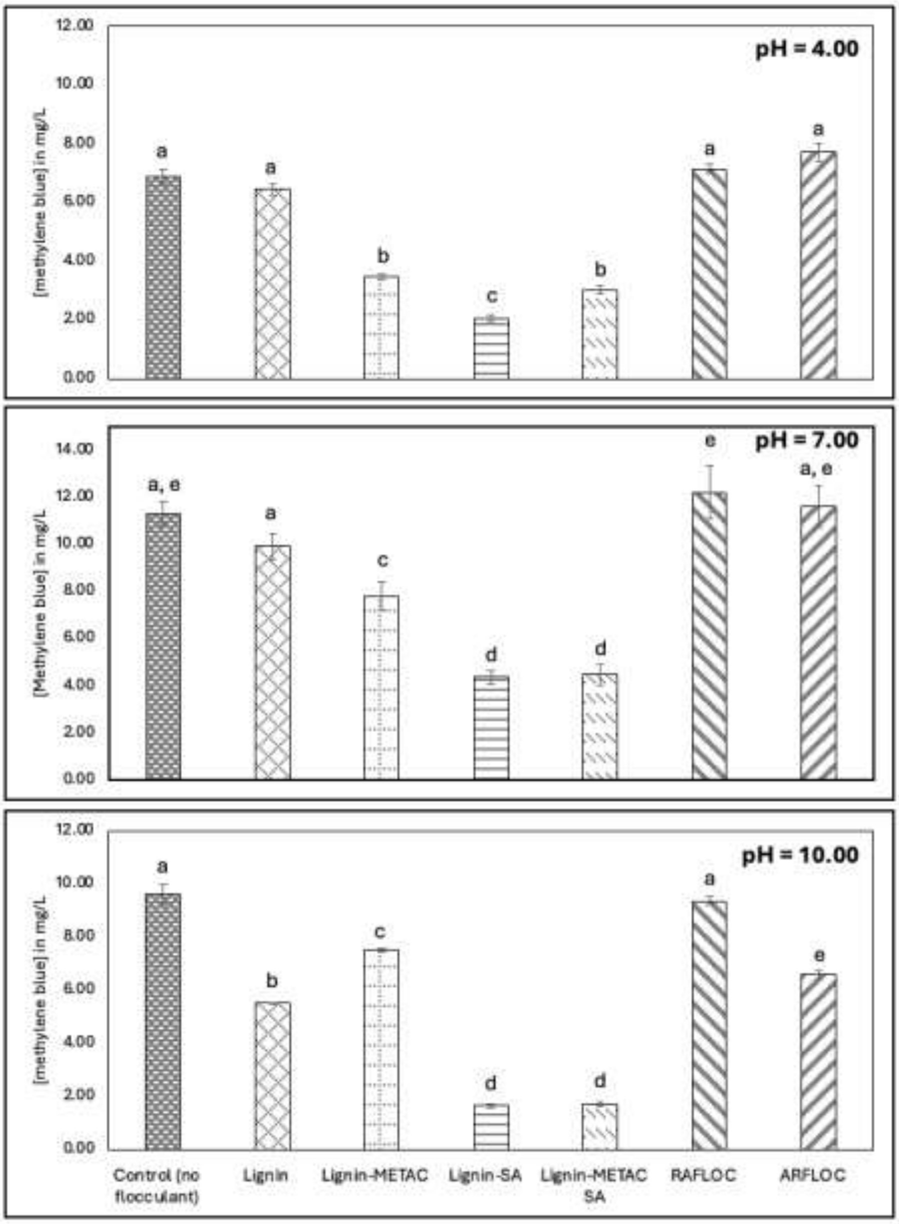

Fig. 6. Effect of pH on the dye removal performance of unmodified lignin, Lignin-METAC, Lignin-SA, and Lignin-METAC-SA flocculants against methylene blue dye. Letters above the bars represent a significant difference among

treatment groups based on ANOVA ($p < 0.05$) and Tukey's HSD test. Similar letters mean no significant difference between treatments. Error bars indicate standard deviation ($n = 3$).

The difference in trend observed for methylene blue and Congo red can be attributed to their differences in charge, with methylene blue being a cationic dye. More prominent dye removal was achieved by all lignin-based flocculants, compared to the positive controls RAFLOC and ARFLOC. The result of the methylene blue flocculation test highlights the positive impact of grafting cationic and anionic groups on the lignin backbone in improving the flocculating performance of lignin, as unmodified lignin did not show significant dye reduction at pH 4 and 7. Lignin with significant sulfonic acid modification (lignin-SA and lignin-METAC-SA) has more negative charge groups, which can effectively neutralize the positive charge of methylene blue. This is consistent with previous studies, where the presence of lignosulfonate shows high removal efficiency against methylene blue (Sotelo et al., 2024; Zhang et al., 2020). For lignin-METAC, it is likely that polymer bridging, along with the aid of intermolecular forces, was the primary mechanism at hand, resulting in weaker flocculation. Lignin-METAC-SA exhibited a mixture of the two mechanisms.

It can be observed that as the solution became more alkaline, the lignin-based flocculants with sulfonic acid groups significantly improved in terms of dye reduction. The basic environment likely neutralized the H^+ ions of the sulfonic acid functional group. This, therefore, leads to the formation of a negatively charged SO_3^- group after the dissociation of H^+, making it more efficient in neutralizing the positively charged methylene blue contaminant. In the same manner, the lower reduction efficiency for Lignin-METAC may be attributed to the neutralization of the positive charge of the quaternary ammonium group.

3.6 Limitations and Future Work

Although the current work has highlighted the performance of modified lignin for the removal of Congo red and methylene blue dyes, a critical limitation of the current research is the absence of substantive characterization of the synthesized flocculants. The lack of such makes elucidation of specific dye removal mechanisms difficult. For example, specific mechanisms like electrostatic charge neutralization, bridging, and sweeping effects cannot be confirmed without conducting additional characterization. Molecular weight determination needs to be done to know the polymer chain length, which is important in understanding the formation of interparticle bridging. Solubility and viscosity tests are required to establish the polymer's hydrodynamic volume and conformational stability in the dye solution. Zeta potential analysis is needed to map surface charge evolution of the dye-flocculant complex and confirm the point of zero charge for the flocculants. Until these parameters are established, the specific mechanism of dye removal of the different flocculants cannot be confirmed.

4. CONCLUSIONS

Lignin-based flocculants with varying modifiers were successfully synthesized through grafting of METAC and sulfonic acid groups on the lignin backbone. The modification resulted in increased surface functionality and the presence of folding and protrusion structures that can translate to increased interaction between the flocculant and target dye molecules. Lignin modification improved the dye removal performance of lignin flocculants for both Congo red and methylene blue dyes at all pH levels, with Lignin-SA and Lignin-METAC-SA achieving more than 80% removal efficiencies. The effectiveness of the lignin-based flocculant is affected by the pH of the solution. Higher removal efficiency was observed for Congo red at a more acidic pH, while methylene blue removal is favored in more alkaline conditions. Although the modified lignin flocculants were effective in removing both methylene blue and Congo red dyes, they were found to be less effective than industrial flocculants for removing Congo red in neutral and alkaline pH. To further understand the mechanism of dye removal, the synthesized flocculants may be subjected to further characterization, like molecular weight and zeta potential analysis. Testing its flocculating activity at different temperatures and dosing rates may also be done.

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