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Fourier Transform Infrared (FTIR) Characterization of Sulfate Ion Adsorption on One-Pot Synthesized Quaternary Ammonium Polymer Derived from Vinasse Waste

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ABSTRACT: Vinasse is a major liquid waste generated from the bioethanol industry and contains a high concentration of sulfate ions that may cause environmental problems if not properly managed. This study investigates sulfate adsorption from vinasse wastewater using a one-pot synthesized quaternary ammonium polymer, with a focus on functional group interactions analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Quantitative adsorption experiments were conducted to confirm sulfate removal, while FTIR analysis was employed to examine changes in functional group characteristics before and after adsorption under various operating conditions. The quantitative results demonstrate that sulfate adsorption proceeds rapidly, achieving a removal efficiency of approximately 87.55 % with an adsorption capacity of 10.68 mg/g at a contact time of 20 minutes under the investigated conditions. FTIR spectra indicate that sulfate adsorption does not alter the main polymer structure and is primarily associated with changes in the intensity of bands related to quaternary ammonium groups and sulfate vibrations, suggesting non-covalent interactions dominated by electrostatic attraction, with possible contributions from hydrogen bonding. Overall, this study provides quantitative evidence of sulfate adsorption from real vinasse wastewater and demonstrates the usefulness of FTIR analysis in elucidating interaction behavior between sulfate ions and quaternary ammonium polymer functional groups.

Keywords: vinasse, sulfate ion, quaternary ammonium polymer, FTIR, one-pot synthesis, adsorption

1. Introduction

Vinasse is the main liquid waste generated from the ethanol fermentation process, particularly in sugarcane- and molasses-based bioethanol industries (Rahayu et al., 2021). The volume of vinasse produced is very large, reaching approximately 10–15 times the volume of ethanol generated, making its management a serious challenge for the bioethanol industry. Vinasse contains a high organic load as well as significant concentrations of inorganic compounds, including sulfate ions (SO_4^{2-}), phosphates, and other dissolved minerals (Nogueira et al., 2021). The sulfate concentration in vinasse has been reported to range from 2–5 g/L, which is far above industrial wastewater discharge standards (Tlaiaa et al., 2020).

The disposal of vinasse without proper treatment can increase biochemical oxygen demand (BOD) and chemical oxygen demand (COD), reduce dissolved oxygen levels, and contaminate soil and water bodies (Peraturan, 2021). High sulfate concentrations may also undergo biological reduction to hydrogen sulfide (H_2S), a toxic, malodorous, and corrosive gas. In addition, sulfate ions at high concentrations (>250 mg/L) can increase water acidity, accelerate metal corrosion, and inhibit the activity of aerobic microorganisms in biological treatment systems (Mukimin et al., 2018; Tlaiaa et al., 2020). Therefore, the removal of sulfate ions is an important aspect of vinasse wastewater treatment (Sahendra et al., 2021).

Various methods have been developed to reduce sulfate concentrations in wastewater, including chemical precipitation, electrodialysis, membrane filtration, and adsorption (Hou et al., 2022). Among these methods, adsorption is considered advantageous due to its operational simplicity, relatively low cost, regeneration potential, and minimal generation of secondary waste (Aini et al., 2023).
Functional polymers based on quaternary ammonium groups are promising adsorbents for the removal of anionic species such as sulfate because they contain positively charged functional groups ($-NR_4^+$) that can interact electrostatically with negatively charged ions (Rahayu, Jamilatun, et al., 2023). The structure of these polymers can be tailored to increase the number of active sites and improve stability under various environmental conditions (Pathak et al., 2021). The one-pot synthesis method is preferred because it

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can produce polymers with a homogeneous distribution of active functional groups, good chemical stability, and a simpler and more environmentally friendly process compared to multistep synthesis methods (Rahayu et al., 2025).

Fourier Transform Infrared Spectroscopy (FTIR) analysis is commonly used to identify functional groups involved in adsorption processes by observing changes in absorption band intensity and position before and after adsorption (Pellenz et al., 2023). Functional groups such as C–N and C=O, as well as O–H bands originating from bound or adsorbed water, have been reported to be associated with sulfate adsorption through electrostatic interactions, ion-exchange behavior, and hydrogen bonding (Alfi et al., 2025). However, systematic studies evaluating FTIR spectral changes under varying operating conditions during sulfate adsorption from vinasse wastewater remain limited.

Based on the above considerations, this study aims to analyze the functional group characteristics of a one-pot synthesized quaternary ammonium polymer during the adsorption of sulfate ions from vinasse wastewater using FTIR. The novelty of this study lies in the detailed investigation of functional group changes under variations in sulfate concentration, adsorbent mass-to-volume ratio, pH, temperature, and contact time, which have not been extensively reported in previous studies, particularly for applications involving vinasse wastewater.

2. Materials and Methods

2.1. Materials

The primary materials used were monomer solution 2-[methacryloyloxy)ethyl]trimethylammonium chloride ($C_9H_{18}ClNO_2$) or META from Sigma Aldrich, crosslinker: EDMA or ethylene dimethacrylate ($C_{10}H_{14}O_4$), porogen: isopropyl alcohol (C_3H_8O), poly(ethylene glycol) ($(C_2H_4O)nH_2O$) with Mn = 400, ethanol (C_2H_6O), AIBN or 2,2'-azobisisobutyronitrile ($C_8H_{12}N_4$). Distilled water and vinasse. The tools used in this study were a magnetic stirrer, a volumetric flask, an Erlenmeyer flask, a heating stove, Whatman 42 paper, a thermometer, a cuvette, a stopwatch, a funnel, an analytical balance, a water bath, and an FTIR.

2.2. Synthesis of Quaternary Ammonium Polymer

The quaternary ammonium polymer produced via a one-pot polymerization process under the selected synthesis conditions and composition has been successfully used as an adsorbent. Prior to being placed into the cylindrical mold, the polymerization solution-consisting of 1.25 mL of META monomer, 0.375 mL of EDMA, 0.35 mL of ethanol, 1.4 mL of polyethylene glycol, 1.75 mL of isopropyl alcohol, and 0.005 g of AIBN was thoroughly homogenized. The polymerization process was then allowed to proceed for 24 hours in a water bath maintained at 70 °C (Rahayu, Hakika, et al., 2023). The reaction scheme for the formation of the quaternary ammonium polymer, which serves as an adsorbent for the removal of potassium ions from vinasse wastewater, is illustrated in Figure 1.

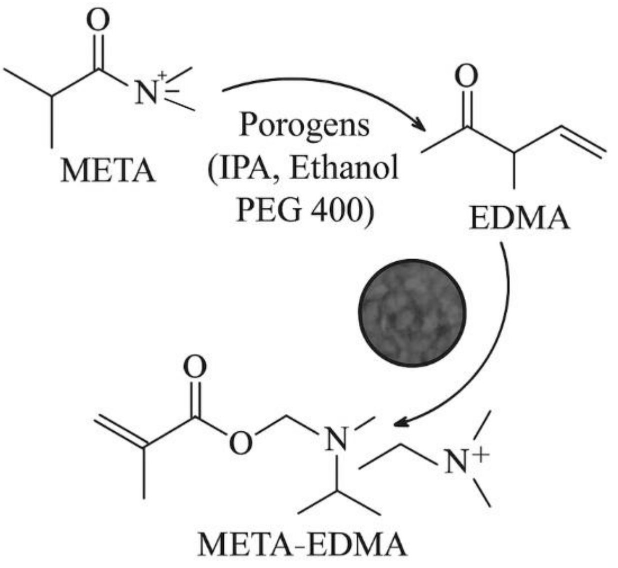

Figure 1. Synthesis of quaternary ammonium polymer (Rahayu, Hakika, et al., 2023)

2.3. Adsorption condition of sulfate (SO_4^{2-})

To evaluate the adsorption behavior of the quaternary ammonium polymer, two key parameters were calculated: the adsorption capacity (Qe) and the removal efficiency (RE %) state that the result is a percentage. The amount of sulfate ions retained per unit mass of adsorbent at equilibrium is indicated by the adsorption capacity. In contrast, the removal efficiency indicates the percentage of sulfate ions removed from the solution compared to the initial concentration. The following equations are used to determine these parameters:

$$q_e = \frac{(c_0 - c_e) \times V}{w} \quad \text{...} \ (1$$

$$RE = \frac{(c_0 - c_e)}{c_0} \times 100 \quad \text{...................................} \ (2$$

where C_0 and C_e represent the initial and equilibrium sulfate concentrations (mg/L), V is the solution volume (L), and W is the mass of adsorbent (g).

2.4 Adsorption Process on Vinasse Waste

The adsorption process was carried out under several experimental variables, including vinasse waste concentration (10, 25, 50, 75, and 100%), the ratio of adsorbent mass (g) to vinasse waste solution volume (mL) (0.75:100, 1.5:100, 2.25:100, 3:100, and 3.75:100), temperature (30, 40, 50, 60, and 70 °C), pH (4,5, 6,7 and 8), and contact time (20, 30, 40, 50, and 60 minutes). The adsorption experiments were conducted sequentially to evaluate the effect of each operating variable, while the remaining variables were maintained constant during each set of experiments. Selected operating conditions derived from these evaluations were subsequently used for further adsorption tests and FTIR analysis. All experiments were performed in duplicate to ensure reproducibility of the results.

After the adsorption process, Fourier Transform Infrared (FTIR) spectroscopy was employed to investigate the functional group characteristics of the quaternary ammonium polymer before and after sulfate adsorption.

FTIR spectra were recorded using a Shimadzu FTIR-8400S spectrometer equipped with an attenuated total reflectance (ATR) accessory. Spectra were collected over the wavenumber range of 4000–400 cm⁻¹ with a spectral resolution of 4 cm⁻¹, and each spectrum was obtained by averaging 32 scans to improve the signal-to-noise ratio. Prior to FTIR analysis, samples were air-dried at room temperature to remove excess surface moisture. Background spectra were recorded under the same conditions and automatically subtracted from the sample spectra. FTIR measurements were performed for the pristine polymer and for samples after sulfate adsorption under various operating conditions, including variations in vinasse concentration, adsorbent mass-to-solution volume ratio, temperature, pH, and contact time (Steiger et al., 2025).

3. Results and Discussion

3.1. Characterization of Vinasse Wastewater

The initial characteristics of the vinasse wastewater used in this study were evaluated based on parameters relevant to sulfate adsorption. The analyzed parameters included sulfate concentration and chemical oxygen demand (COD), which represent the target contaminant and the organic load of the wastewater, respectively. The results are summarized in Table 1.

Table 1. Selected initial characteristics of vinasse wastewater

Parameter	Unit	Value
Sulfate	mg/L	58.95
COD	mg/L	67.72

The measured sulfate concentration of 58.950 mg/L confirms that the vinasse used in this study contains a substantial amount of sulfate and is suitable for adsorption investigation. The high COD value of 67.727 mg/L indicates a complex wastewater matrix with significant organic content, which may influence adsorption behavior through competitive interactions. Therefore, sulfate removal under these conditions provides relevant insight into the adsorption performance of the quaternary ammonium polymer in treating real vinasse wastewater. These initial characteristics serve as a basis for interpreting both the quantitative adsorption results and the FTIR-based interaction analysis.

3.2. Quantitative Sulfate Adsorption Performance

Contact time was evaluated as the final operating parameter to provide quantitative evidence of sulfate adsorption and to support the FTIR-based interaction analysis. All quantitative adsorption experiments were conducted under selected operating conditions that were previously evaluated through FTIR analysis, while only the contact time was varied. The initial sulfate concentration (C_0) was maintained at 121.98 mg/L, and other experimental parameters were kept constant The quantitative sulfate adsorption results at different contact times are summarized in Table 2.

Table 2. Effect of contact time on quantitative sulfate adsorption performance

Co (ppm)	Contact Time (minutes)	Ce (ppm)	Qe (mg/g)	Removal efficiency (%)
121.98	20	15.18	10.68	87.55
121.98	30	15.76	10.62	87.07
121.98	40	23.17	9.88	81.00
121.98	50	19.32	10.26	84.15
121.98	60	15.18	10.67	87.54

As shown in Table 2 and Figure 2, sulfate adsorption occurred rapidly during the initial stage of contact. At a contact time of 20 minutes, the equilibrium sulfate concentration (C_e) decreased to 15.1827 mg/L, corresponding to an adsorption capacity of 10.6800 mg/g and a removal efficiency of 87.5534%. Increasing the contact time to 30 minutes resulted in comparable adsorption performance, indicating that the majority of sulfate uptake had already occurred within the first 20–30 minutes (Aini et al., 2024).

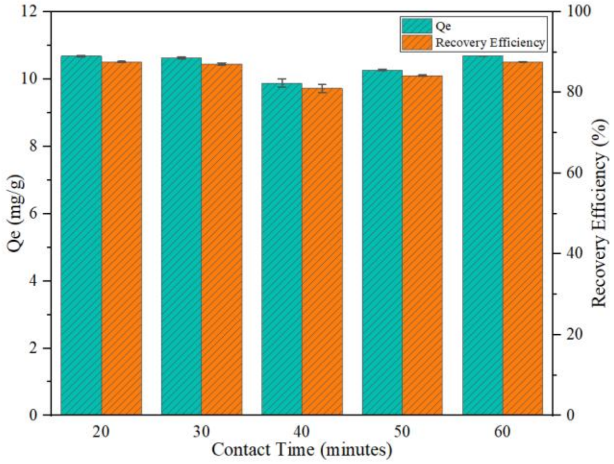

Figure 2. Effect of contact time on sulfate removal efficiency

At a contact time of 40 minutes, a temporary decrease in adsorption capacity (9.8807 mg/g) and removal efficiency (81.0006%) was observed, accompanied by an increase in (C_e). This behavior may be attributed to the dynamic adsorption desorption balance in the complex vinasse wastewater matrix, where the presence of competing species and mass transfer effects can influence the apparent adsorption performance (Zou et al., 2022). Upon further increasing the contact time to 50 and 60 minutes, the adsorption capacity and removal efficiency increased again, reaching 10.6793 mg/g and 87.5480%, respectively, at 60 minutes. However, the improvement in adsorption performance beyond 20 minutes was relatively marginal.

Overall, the quantitative results indicate that sulfate adsorption proceeds rapidly, and extending the contact time beyond 20 minutes results in only marginal changes in adsorption performance under the investigated conditions. Accordingly, a contact time of 20 minutes was found to provide effective sulfate removal under the investigated conditions in this study. These quantitative observations are consistent with the FTIR results, which show that the most evident spectral changes associated with sulfate–functional group interactions occur at shorter contact times. FTIR analyses under various operating conditions were therefore used to further investigate the interaction behavior between sulfate ions and the functional groups of the quaternary ammonium polymer.

3.3. FTIR Analysis of Adsorbent Before and After Adsorption

The broad band observed around 3380–3400 cm⁻¹ is attributed to adsorbed moisture or hydrogen-bonded OH groups, rather than to N–H vibrations, since quaternary ammonium groups do not contain N–H bonds.

3.3.1. FTIR Spectrum of the Adsorbent Before Adsorption

Before the adsorption process, it is essential to determine the initial functional group characteristics of the adsorbent surface. FTIR analysis was employed to identify functional groups that may potentially act as active sites for interaction with sulfate ions. These functional groups are known to be associated with interactions such as hydrogen bonding and electrostatic attraction, and may also be involved in ion-exchange interactions with anionic species in vinasse wastewater (Andreica et al., 2020). The obtained spectrum therefore serves as a reference for evaluating changes in chemical characteristics after the adsorption process.

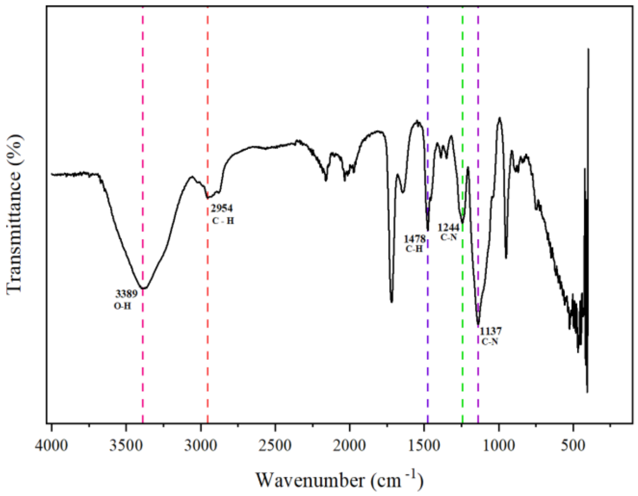

Figure 3. FTIR spectrum of the adsorbent before contact

The FTIR spectrum of the adsorbent before the adsorption process is presented in Figure 3. The spectrum exhibits several characteristic absorption bands that reflect the chemical structure of the quaternary ammonium polymer. A broad absorption band observed at 3389 cm⁻¹ is attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, rather than to N–H vibrations, since quaternary ammonium groups do not contain N–H bonds. The absorption band at 2954 cm⁻¹ corresponds to aliphatic C–H stretching vibrations of the polymer chains.
A distinct absorption band at 1723 cm⁻¹ is assigned to the stretching vibration of carbonyl (C=O) groups originating from the ester structure formed by the use of ethylene glycol dimethacrylate (EDMA) as a crosslinking agent. The band observed at 1478 cm⁻¹ is associated with aliphatic C–H bending vibrations. Strong absorption bands in the region of 1244 and 1137 cm⁻¹ are attributed to C–N stretching vibrations characteristic of quaternary ammonium groups within the polymer matrix. In addition, a weak band observed at 952 cm⁻¹ is associated with C=C vibrations of the polymer backbone. This initial FTIR spectrum serves as a reference for evaluating changes in functional group characteristics after sulfate ion adsorption under various operating conditions.

3.3.2. Effect of Sulfate Ion Concentration Variation

The ion concentration in the solution is an important factor affecting the adsorption process, as it determines the availability of sulfate ions to interact with the active functional groups on the adsorbent surface. Increasing sulfate concentration generally enhances the interaction between adsorbate species and available active sites; however, at higher concentrations, the adsorbent surface may approach saturation as the number of available binding sites becomes limited (Mehrate et al., 2025; Zhao et al., 2020). Therefore, evaluating changes in functional group characteristics at different concentrations using FTIR provides valuable insight into the adsorption behavior and interaction mechanism of the quaternary ammonium polymer.

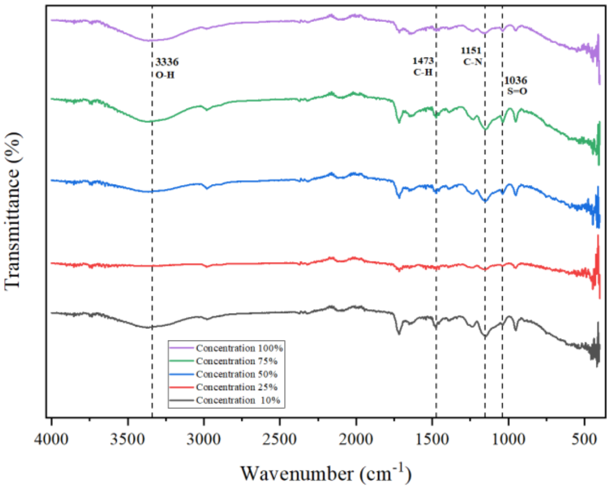

Figure 4. FTIR spectrum of the adsorbent after contact at different sulfate concentrations

The FTIR spectra of the quaternary ammonium polymer after contact with vinasse wastewater at various concentrations are shown in Figure 4. It can be observed that increasing the vinasse concentration from 10% to 100% leads to changes in several characteristic absorption bands of the adsorbent. A broad absorption band around 3336 cm⁻¹, attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, shows a gradual decrease in intensity with increasing vinasse concentration. This behavior suggests changes in the hydrogen-bonding environment associated with the adsorption process (Pellenz et al., 2023).

The absorption band at 1725 cm⁻¹, assigned to the stretching vibration of carbonyl (C=O) groups originating from the ester structure of the polymer, does not exhibit significant intensity changes, indicating that the main polymer framework remains stable during adsorption. In contrast, the band at approximately 1151 cm⁻¹, which corresponds to C–N stretching vibrations of quaternary ammonium groups, shows noticeable intensity variations with increasing vinasse concentration. These changes reflect alterations in the local chemical environment of the positively charged functional groups due to interactions with anionic species present in the vinasse wastewater.

Furthermore, the absorption band in the region around 1036 cm⁻¹, corresponding to the characteristic S=O stretching vibration of sulfate ions, becomes more pronounced at higher vinasse concentrations. The increased intensity of this band indicates a greater extent of sulfate ion interaction with the adsorbent surface. Although the sulfate-related band partially overlaps with polymer matrix bands in the fingerprint region, its presence can be clearly identified through comparison of spectra obtained at different concentrations. Overall, the observed intensity changes and spectral features suggest that sulfate adsorption is influenced by ion availability in solution and predominantly involves electrostatic interactions between sulfate ions and quaternary ammonium groups, with possible contributions from hydrogen bonding as a secondary interaction (Chaves et al., 2025).

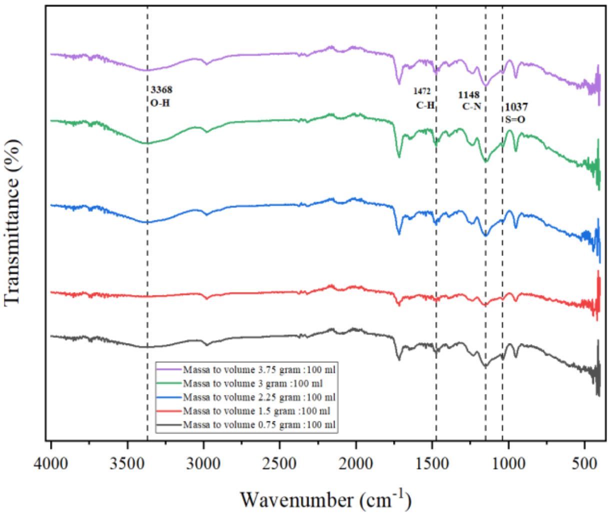

Figure 5. FTIR spectrum of the adsorbent after contact at different mass-to-volume ratios

3.3.3. Effect of Mass-to-Volume Ratio Variation

The mass-to-volume ratio (mass:volume) is an important parameter that influences the availability of active sites on the adsorbent surface for ion interaction. At a low mass-to-volume ratio, the number of available active sites may be limited, whereas at higher ratios, not all sites may effectively participate in the adsorption process due to the excess amount of adsorbent relative to the sulfate ions present in the solution (Kandil et al., 2022; Nicotera et al., 2022). Therefore, varying the mass-to-volume ratio is necessary to evaluate how changes in adsorbent dosage affect the interaction between functional groups of the quaternary ammonium polymer and sulfate ions, as reflected by FTIR spectral characteristics.

The FTIR spectra of the quaternary ammonium polymer after adsorption at various adsorbent mass-to-solution volume ratios are presented in Figure 5. It can be observed that increasing the mass-to-volume ratio from 0.75 g: 100 mL to 3.75 g: 100 mL leads to changes in several characteristic absorption bands of the adsorbent. A broad absorption band around 3368 cm⁻¹, attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, shows a gradual decrease in intensity with increasing adsorbent dosage. This behavior suggests changes in the hydrogen-bonding environment associated with the adsorption process.

The absorption band observed at approximately 1718 cm⁻¹, assigned to the stretching vibration of carbonyl (C=O) groups originating from the ester structure of the polymer, does not exhibit significant intensity changes, indicating that the main polymer structure remains stable during adsorption. In contrast, the band at around 1148 cm⁻¹, which corresponds to C–N stretching vibrations of quaternary ammonium groups, shows noticeable intensity variations as the mass-to-volume ratio increases. These variations reflect changes in the local chemical environment of the positively charged functional groups due to interactions with sulfate ions (Duarte et al., 2023).

Furthermore, the absorption band in the region around 1037 cm⁻¹, corresponding to the characteristic S=O stretching vibration of sulfate ions, becomes more pronounced at higher mass-to-volume ratios. This observation indicates that increasing the amount of adsorbent provides a greater number of available interaction sites for sulfate ions. Overall, the FTIR spectral changes observed at different mass-to-volume ratios suggest that the adsorbent dosage influences the extent of sulfate ion interaction, which predominantly involves electrostatic interactions between sulfate ions and quaternary ammonium groups, with possible contributions from hydrogen bonding as a secondary interaction.

3.3.4. Effect of Temperature Variation

Temperature is an important parameter that influences the adsorption process by affecting ion mobility and the strength of interactions between adsorbate and adsorbent. At lower temperatures, ion diffusion toward the adsorbent surface may occur more slowly, whereas at higher temperatures, electrostatic interactions and hydrogen bonding can be affected by increased kinetic energy (Yamakawa et al., 2023). Therefore, evaluating FTIR spectral changes at different temperatures provides insight into how temperature influences the interaction behavior between sulfate ions and the functional groups of the adsorbent.

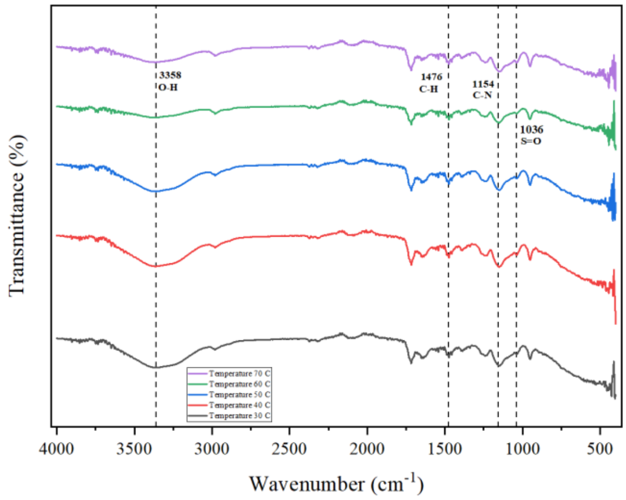

Figure 6. FTIR spectrum of the adsorbent after contact at different temperatures

The FTIR spectra of the quaternary ammonium polymer after the adsorption process at different temperatures are shown in Figure 6. Variations in the FTIR spectra are observed over the temperature range of 30–70 °C, particularly in absorption bands associated with the functional groups of the adsorbent and sulfate ions. A broad absorption band around 3358 cm^{-1}, attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, shows a slight decrease in intensity at higher temperatures. This behavior suggests changes in the hydrogen-bonding environment during the adsorption process (Ahmadi & Izanloo, 2023).

The absorption band observed at approximately 1722 cm^{-1}, assigned to the stretching vibration of carbonyl (C=O) groups, does not exhibit significant changes across the investigated temperature range, indicating that the main polymer structure remains stable during adsorption. In contrast, the band around 1154 cm^{-1}, which corresponds to C–N stretching vibrations of quaternary ammonium groups, shows minor intensity variations with increasing temperature. These variations reflect changes in the local chemical environment of the positively charged functional groups.

In addition, the absorption band in the region of approximately 1036 cm^{-1}, corresponding to the characteristic S=O stretching vibration of sulfate ions, appears more pronounced at intermediate temperatures (Maculewicz et al., 2025). The more evident spectral changes observed at these temperatures suggest that temperature influences the interaction behavior between sulfate ions and the active functional groups of the adsorbent, as reflected in the FTIR spectra.

3.3.5. Effect of pH Variation

The pH of the solution plays an important role in influencing the surface charge environment of the adsorbent and the interaction behavior between functional groups and sulfate ions. Under acidic conditions, the presence of a higher proton concentration can enhance the positive charge environment around the adsorbent surface, including quaternary ammonium sites and residual protonatable groups, thereby favoring electrostatic interactions with sulfate ions. Conversely, under basic conditions, the increased concentration of hydroxide ions may reduce the effectiveness of these interactions through charge screening and competitive effects, leading to weaker adsorption behavior (Kaczmarek et al., 2021; Rohman et al., 2011).

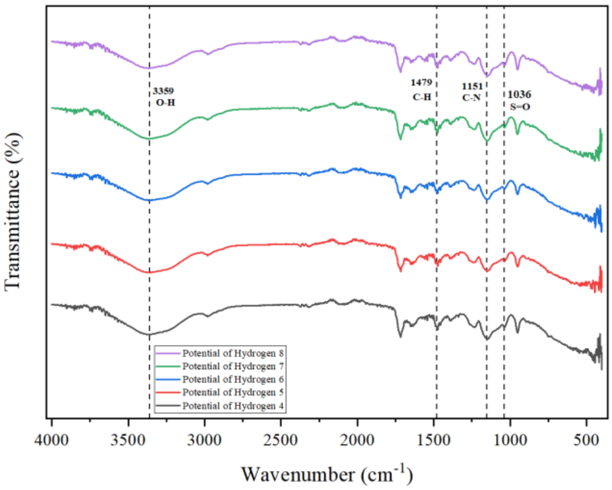

Figure 7. FTIR spectrum of the adsorbent after contact at different ph values

The FTIR spectra of the quaternary ammonium polymer after the adsorption process at different pH values are presented in Figure 7. Variations in solution pH influence the intensity of several characteristic absorption bands of the adsorbent, particularly those associated with functional groups and sulfate ions. A broad absorption band around 3359 cm^{-1}, attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, exhibits intensity variations with changes in pH. This behavior suggests alterations in the hydrogen-bonding environment on the adsorbent surface under different pH conditions (Rahayu et al., 2025).

The absorption band observed at approximately 1714 cm^{-1}, assigned to the stretching vibration of carbonyl (C=O) groups, does not show significant intensity changes across the investigated pH range, indicating that the main polymer structure remains stable during the adsorption process. In contrast, the band around 1151 cm^{-1}, which corresponds to C–N stretching vibrations of quaternary ammonium groups, exhibits more pronounced intensity variations under acidic to near-neutral pH conditions. These variations reflect changes in the local chemical environment of the positively charged functional groups.

Furthermore, the absorption band in the region around 1036 cm^{-1}, corresponding to the characteristic S=O stretching vibration of sulfate ions, shows intensity variations at different pH conditions. The more evident spectral changes observed under acidic to near-neutral pH suggest that this pH environment is more favorable for electrostatic interactions between quaternary ammonium groups and sulfate ions, as reflected in the FTIR spectra (Mach et al., 2020).

3.3.6. Effect of Contact Time Variation

Contact time determines the extent of interaction between sulfate ions and the active sites of the adsorbent. In the initial stage, interactions typically occur rapidly due to the availability of vacant active sites, while at longer contact times the extent of interaction tends to change more slowly as fewer sites remain available.

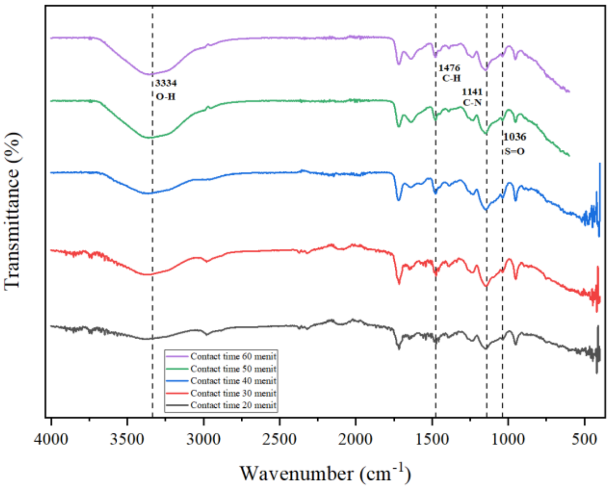

Figure 8. FTIR spectrum of the adsorbent after contact at different contact times

The FTIR spectra of the quaternary ammonium polymer after the adsorption process at different contact times (20–60 minutes) are presented in Figure 8. Overall, the most evident changes in the FTIR spectra are already observed at a contact time of 20 minutes, while further increases in contact time (30–60 minutes) result in relatively minor additional changes in absorption bands. A broad absorption band around 3334 cm^{-1}, attributed to O–H stretching vibrations from adsorbed or hydrogen-bonded water molecules, shows a decrease in intensity at the initial contact stage. This behavior suggests changes in the hydrogen-bonding environment during the early stage of the adsorption process.

In contrast, the absorption band observed at approximately 1725 cm^{-1}, corresponding to the stretching vibration of carbonyl (C=O) groups, remains relatively unchanged over the entire range of contact times, indicating that the main polymer structure remains stable during adsorption. In the fingerprint region, the absorption band around 1141 cm^{-1}, attributed to C–N stretching vibrations of quaternary ammonium groups, as well as the band around 1036 cm^{-1}, corresponding to the characteristic S=O stretching vibration of sulfate ions, exhibit intensity variations at different contact times (Salamah et al., 2024).

These FTIR results indicate that the primary spectral changes associated with sulfate adsorption occur at the initial contact stage, whereas extending the contact time leads to only limited additional spectral changes. This observation is consistent with the quantitative adsorption results, which show that sulfate uptake proceeds rapidly under the investigated conditions.

Based on FTIR analysis under various operating conditions, including vinasse concentration, adsorbent mass-to-solution volume ratio, temperature, pH, and contact time, the results suggest that sulfate adsorption on the quaternary ammonium polymer is dominated by non-covalent interactions. The FTIR spectra mainly exhibit variations in absorption band intensities without significant shifts in wavenumber, suggesting that no new chemical bonds are formed during the adsorption process (Wang et al., 2024).

More pronounced absorption bands in the region of approximately 1036–1038 cm^{-1}, associated with the S=O stretching vibration of sulfate ions, are observed with increasing vinasse concentration and adsorbent mass-to-volume ratio, reflecting enhanced sulfate–adsorbent interactions. Changes in the intensity of C–N bands in the range of 1140–1155 cm^{-1} indicate the involvement of positively charged quaternary ammonium groups in these interactions. Variations in temperature and pH influence the extent of spectral changes, with more evident interactions observed at intermediate temperatures and under acidic to near-neutral pH conditions, while weaker interactions are suggested under basic conditions due to possible ion competition effects. In addition, FTIR analysis of contact time variation indicates that most spectral changes occur at the initial contact stage, with only limited additional changes at longer contact times.

Overall, the FTIR results indicate that sulfate adsorption on the quaternary ammonium polymer predominantly involves electrostatic interactions between $-NR_4^+$ groups and SO_4^{2-} ions, with possible contributions from hydrogen bonding as a secondary interaction, as inferred from FTIR spectral features.

4. Conclusions

This study demonstrates that a one-pot synthesized quaternary ammonium polymer is capable of adsorbing sulfate ions from vinasse wastewater. Quantitative adsorption results confirm that sulfate removal occurs rapidly under the investigated conditions, achieving effective sulfate removal within a contact time of 20 minutes. FTIR analysis reveals that the adsorption process does not alter the main polymer structure and is associated with changes in the intensity of functional group vibrations related to quaternary ammonium groups and sulfate ions. These observations indicate that sulfate adsorption occurs predominantly through non-covalent interactions, mainly electrostatic attraction, with possible contributions from hydrogen bonding. The combined use of quantitative adsorption data and FTIR analysis provides insight into sulfate–polymer interactions in a complex vinasse matrix, highlighting the potential of quaternary ammonium polymers for sulfate removal studies based on interaction characterization rather than process optimization.

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Statement

At the time of writing this work, the author used Google Translate to improve their English. After using the service, the writer reviews and edits the content and takes full responsibility for the published material.

Credit Authorship Contribution Statement

Hutri Puspita Sari: Writing-original draft, Resources, Visualization, Investigation, Conceptualization. **Aster Rahayu**: Writing-review & editing, Conceptualization, Editing, Validation, Supervision. **Dhias Cahya Hakika**: Visualization, Formal Analysis.

Declaration of competing interests

The authors declare that there are no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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