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The adsorption and kinetics studies of nitrate ions from bioethanol wastewater by ammonium-based ion exchange polymer

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ABSTRACT

Bioethanol wastewater contains complex inorganic and organic ions, posing a severe environmental problem. In this research, the removal of nitrate ion (NO_3^-) from bioethanol wastewater was conducted using ammonium polymers as adsorbents. Ammonium polymer was synthesized using the one-pot approach method using functional monomer with single thermal. This study aimed to analyze the performance of an ammonium polymer for removing nitrate ions (NO_3^-) from bioethanol waste, considering operational parameters (polymer mass, temperature, and contact time) by advanced characterization technique and determine the isotherm model for predicting adsorption behavior. The results of FTIR revealed significant functional groups, including N-H and C-N. SEM-EDX confirmed the effectiveness of adsorption by identifying each component, and elemental analysis confirmed the percentages of C, H, and N in the adsorbent. The optimal conditions for the adsorption process were achieved when 0.1 g of ammonium polymer was in contact with bioethanol wastewater for 60 minutes at 40 °C with a removal efficiency of 96.32% and an adsorption capacity of 0.58 mg/g. The adsorption isotherm analysis followed the Temkin model.

Keywords: isotherm, adsorbent, removal, characterization, performance.

INTRODUCTION

Environmental pollution has become a significant concern in the past decade, primarily driven by human and industrial activities. Water, essential for various aspects of life such as household use, agriculture, and industry, is increasingly affected by pollution from industrial wastewater and other human activities (Hossain et al., 2023). This wastewater often contains heavy metals, dyes, and other harmful substances contaminating soil, air, and water. The bioethanol sector is one industry experiencing significant growth worldwide, which holds promise as an alternative energy source. Bioethanol stands out as a particularly promising biofuel due to its environmental benefits. In 2016, global bioethanol production reached 100.2 billion liters. Bioethanol production continues to rise, with forecasts predicting an increase to approximately 134.5 billion liters by 2024 (Bušić et al., 2018). It is defined as a liquid residue in acidic conditions exhibiting a pH of less than 4, a brownish hue, and a characteristic odor. It possesses a chemical oxygen demand (COD) value of over 100,000 mg/L (Chowdhary et al., 2018; Rodríguez-Félix et al., 2018). Manufacturing one liter of bioethanol is predicted to generate 12 to 15 times more liquid wastewater (Chowdhary et al., 2018). The generated wastewater consists of complex inorganic and organic ion compositions with considerable contamination potential, including nitrates and phosphates. The characteristics of this wastewater indicate that it can adversely affect water bodies and soil

when disposed of improperly or released directly into the environment.

Various techniques for processing bioethanol wastewater, encompassing physical, chemical, and biological methods, have been extensively utilized to mitigate its toxic effects. These techniques include coagulation/flocculation, advanced oxidation, aerobic and anaerobic processes, and fungal or enzymatic treatments (Georgiou et al., 2016; Hakika et al., 2019, 2022). However, traditional processing methods often require additional chemicals, such as coagulants. They are less environmentally friendly due to the generation of by-products like effluent or sludge, necessitating further treatment stages. Additionally, some pollutants in bioethanol wastewater are resistant to chemical breakdown, which can render these conventional methods ineffective. Thus, there is a need to develop innovative methods or technologies to address the environmental impact of this wastewater better.

An alternative technology for treating bioethanol wastewater is adsorption, a versatile and effective method for removing organic pollutants, nutrients, and trace metals from wastewater. The effectiveness of adsorption depends on the choice of adsorbent, the characteristics of the contaminants, and the operational conditions. By selecting suitable adsorbents and optimizing the process, adsorption can offer a cost-efficient solution for managing bioethanol wastewater and reducing its environmental impact. Adsorption involves the interaction between a solid (adsorbent) and a liquid phase containing the adsorbate (Zein et al., 2024) [8]. This method is both cost-effective and easily regenerative (Balci et al., 2011). This study removes contaminants by contacting the wastewater with the adsorbent surface, where absorption occurs through ion exchange. Previous research has demonstrated the effectiveness of ion exchange in treating water and wastewater contaminated with nitrate and phosphate ions, making it a viable method for removing such pollutants from the bioethanol industry (Rahayu et al., 2023; Rahayu et al., 2023).

Adsorption of nitrate ions from bioethanol wastewater is essential for reducing the environmental impact of nitrate contamination, which can lead to eutrophication of water bodies and other ecological issues (Li et al., 2022). Nitrate (NO₃) ions are a common by product of bioethanol production, mainly when fermentation processes use nitrogen-containing nutrients. Nitrate ion adsorption involves the removal of negatively charged

nitrate ions from the aqueous phase (bioethanol wastewater) by binding them to a positively charged or functionalized adsorbent (Hakika et al., 2019). Adsorption is an effective and practical method for removing nitrate ions from bioethanol wastewater. The success of this process depends on selecting the proper adsorbent, optimizing operational conditions, and managing the adsorbent's regeneration or disposal. With advanced materials such as ammonium polymers, adsorption can significantly reduce the environmental impact of nitrate in bioethanol wastewater. One of the advantages of adsorption for nitrate ions in bioethanol wastewater is that it is cost-effective, environmentally friendly, simple and scalable, and has high removal efficiency (Bellahsen et al., 2018).

In the adsorption process, adsorbent modifications that are often explored are advanced materials such as polymer-based adsorbents. Polymers are large molecules composed of a series of monomers that are interconnected by the presence of cross-linkers (Zhong et al., 2010). Many polymers have been researched and developed based on the type, primary base material, and intended use of the polymer itself. Two steps are typically involved in producing polymers: the polymerization stage and the post-modification stage. The advanced modification stage aims to develop the desired active side of the polymer by the desired goals and applications in making polymers (Simone et al., 2017; W. Wang et al., 2023). A satisfying development in polymerization methods is the one-pot approach, which accelerates the procedure by forming monolithic columns in a single step. This method, introduced as a more effective and advanced strategy, allows for synthesizing polymers with adsorptive properties in one integrated process rather than through a series of steps (Duan et al., 2023; Rahayu et al., 2015, 2021; Simone et al., 2017). The one-pot approach has become increasingly popular for developing polymers designed explicitly for adsorption applications.

In contrast to conventional polymerization techniques, this method offers a polymerization process that is environmentally friendly, straightforward, and conducive to development while minimizing time and complexity (Cwynar et al., 2022; Jiang et al., 2022). This method is also cost-effective as it eliminates the need for additional modification steps, unlike other polymerization techniques that typically necessitate further modifications at the final stage (Aini et al., 2023; Moravcová et al., 2003; Rahayu et al., 2015). The

one-pot approach method is increasingly adopted to produce stationary phase materials in liquid chromatography columns. Despite its potential, this polymerization method remains underutilized for producing absorbent materials intended for use as adsorbents, particularly in treating industrial liquid wastewater. Ammonium polymers are polymers that contain ammonium groups (NH4⁺) or ammonium-based functional groups in their structure. These polymers are commonly used in water treatment, ion exchange, antimicrobial agents, and pharmaceuticals (Haktaniyan et al., 2023). The ammonium groups can be introduced as quaternary ammonium salts or through the protonation of amine groups in the polymer backbone. Ammonium polymers, especially quaternary ammonium polymers, are widely used as flocculants and coagulants in water and wastewater treatment processes. They help aggregate suspended particles, making filtering and removing contaminants easier (Rahayu et al., 2023). They provide valuable properties such as antimicrobial activity, cationic charge for ion exchange, and flocculation, making them essential in many environmental and industrial applications.

Previous studies have demonstrated the successful application of ammonium polymer for the adsorption of nitrate, nitrite, and phosphate ions in aqueous solutions (Rahayu et al., 2023). Ammonium polymer is synthesized using 2-[(methacryloyloxy)ethyl]trimethylammonium chloride (META), which is a functional monomer based on quaternary ammonium. In this study, the experiments focus on applying the ammonium polymer to bioethanol wastewater processing, which focuses on removing specific pollutant compounds such as nitrate ions, which often experience obstacles due to the complex characteristics of the wastewater. Apart from that, the processing that has been tested is still limited to the application of traditional chemical and biological methods, which require additional chemicals and are less environmentally friendly due to the presence of by-products in the form of sludge. Therefore, the potential of ammonium polymer as an adsorbent medium for nitrate ions in bioethanol wastewater is an opportunity because few experiments have been conducted to develop this polymer.

EXPERIMENTAL

Synthesis of ammonium polymer

A quaternary ammonium polymer synthesized using a one-pot polymerization method under optimal conditions has been effectively utilized as an adsorbent (Rahayu et al., 2023). The polymer solution, including 1.25 mL of monomer META $(C_9H_{18}CINO_2)$, 0.375 mL of EDMA $(C_{10}H_{14}O_4)$, 0.35 mL of ethanol (C₂H₆O), 1.4 mL of poly(ethylene glycol) ((C₂H₄O)nH₂O), 1.75 mL of isopropyl alcohol (C₃H₈O), and 0.005 g of AIBN (C₈H₁₂N₄), was subjected to homogenization then the solution was put into the cylindrical tube. Subsequently, polymerization was conducted for 12 hours in a water bath at 70 °C, as shown in Figure 1.

Adsorption of nitrate ion (NO₃⁻)

Adsorption experiments were carried out using the batch method. A certain amount of adsorbent was added to 100 mL of bioethanol wastewater. The mixture was shaken thoroughly using a magnetic stirrer at 150 rpm, as shown in Figure 2.

The solution was filtered and analyzed using a UV-Vis spectrophotometer. The adsorptions were conducted using various parameters: polymer mass, temperature, and contact time to determine the removal and adsorption capacity of nitrate in the solution was calculated according to Equation 1, while the adsorption capacity of the adsorbent was obtained according to Equation 2:

$$\% RE = \frac{Co - Ce}{Co} \tag{1}$$

where: RE – removal efficiency



Figure 1. Experimental step for synthesis of ammonium polymer



Figure 2. Experimental step for adsorption of bioethanol waste

$$Qe = \frac{Co - Ce}{m} \times V \tag{2}$$

where: *Co* is the initial concentration (mg/L), *Ce* is the final concentration (mg/L), *V* is the solution volume (L), and *m* is the mass of adsorbent (mg).

The Expected mechanism reaction for removing nitrate ion can be seen in Figure 3.

Adsorption isotherms

Adsorption isotherms are mathematical models that characterize how a substance (the adsorbate) adheres to a solid surface (the adsorbent). These isotherms are crucial for studying adsorption mechanisms, as they illustrate how the adsorption process changes with varying adsorbate concentrations (Al-Ghouti et al., 2020). Two isotherm models, Langmuir and Temkin isotherms, were investigated in this study.

Langmuir isotherm

The Langmuir isotherm model assumes that adsorption exists as a single layer on the outer

surface of the adsorbent, with the assumption that there are no interactions within the adsorbed molecules. This model predicts a uniform distribution of adsorption sites and does not account for lateral interactions among adsorbed particles (Mahmoodi et al., 2008). The linear form of the Langmuir model is expressed by Equations 3 and 4.

$$\frac{c_e}{q_e} = \frac{1}{b}Q_0 + \frac{c_e}{Q_0} \tag{3}$$

In this context, q_e represents the amount of dye adsorbed at equilibrium (mg/g), as determined using Equation 2.

$$q_e = \frac{Q_o \cdot C_e}{1 + b \cdot C_e} \tag{4}$$

This equation, Q_0 denotes the maximum adsorption capacity (mg/g). C_e represents the equilibrium concentration of the dye (mg/L), and *b* is the Langmuir constant related to adsorption energy (L/mg).

Temkin isotherm

The Temkin isotherm model addresses the reduction in the heat of adsorption as surface coverage increases, assuming a linear



Figure 3. Expected mechanism reaction for removing nitrate

relationship between heat and coverage. Its benefit systems with heterogeneous surfaces offer insights into the adsorption process's binding energy. Unlike other models that suggest a logarithmic decrease in heat, the Temkin isotherm assumes a linear decline (Shojaeipoor et al., 2016). The linear form of the Temkin isotherm is represented by Equations 5–8.

$$q_e = \frac{RT}{b} \ln(A_T C_e) \tag{5}$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b}\right) \ln C_e \tag{6}$$

$$\beta = (RT)/b \tag{7}$$

$$q_e = \beta \ln A + \beta \ln C_e \tag{8}$$

T is the absolute temperature in 298K. *R* is the universal gas constant of 8.314 J (mol K)⁻¹. *b* is the Temkin constant related to the heat of sorption (J/mg). *A* is the equilibrium constant corresponding to the maximum binding energy (L/g).

RESULT AND DISCUSSION

Characterization of ammonium polymer

Fourier transform infrared (FTIR) is a valuable technique for identifying chemical bonds and molecular structures by examining how a sample absorbs infrared light. In the case of ammonium-based polymers, FTIR analysis can reveal detailed information about the functional groups present within the polymer (Nandiyanto et al., 2023). The radiation absorbed by the sample is converted into the rotational energy of its molecules. This energy change is detected and recorded, and the resulting signal is processed into a spectral format (Mokari et al., 2023). FTIR analysis of ammonium-based polymers will confirm the presence of ammonium groups, reveal details about the polymer structure, and identify interactions between ammonium groups and other functional groups in the material. Figure 4 shows the FTIR results for the ammonium polymer both before and after adsorption.

Figure 4 shows several peaks in the FTIR spectra of ammonium polymers before and after the adsorption process. The first peak at 3359.62 cm⁻¹ within the range 3328–3402 cm⁻¹ corresponds to the vibration of the O-H group, originating from moisture or hydroxyl groups within the polymer. The second peak at 2946.13 cm⁻¹, in the range of 2858–2945 cm⁻¹, corresponds to CH group vibrations, indicating the presence of alkyl or hydrocarbon chains. The third peak at 1645.59 cm⁻¹, within the range of 1643–1650 cm⁻¹, represents NH group vibrations, highlighting the presence of amine or ammonium groups. The fourth peak at 1242.02 cm⁻¹, in the 1220–1247 cm⁻¹ range, corresponds to CN group vibrations essential for chemical interactions during adsorption. Then, the last peak at wave number 1149.44 cm⁻¹, within the range 1140–1160 cm⁻¹, corresponds to C-O group vibrations, indicating that the polymer contains oxygen (Aini et al., 2023; Rahayu, Alfi, et al., 2023; Rahayu, Hakika, Alfi, et al., 2023).



Figure 4. FTIR characterization of ammonium polymer for before and after adsorption

The peak reflected on the FTIR shows a difference in peak sharpness in the ammonium polymer functional group before and after adsorption. All functional groups, especially those related to nitrate in ammonium polymer, which has been used as an adsorbent in bioethanol wastewater, have sharper peaks than before adsorption. This indicates that the adsorption process to remove nitrate ions in bioethanol wastewater has been successfully bound with ammonium polymer. The adsorption mechanism of nitrate ions onto ammonium polymers involves several key interactions and processes. The quaternary ammonium groups in the polymer are positively charged, which attract the negatively charged nitrate ions (NO_{2}) through electrostatic forces, which serve as the primary mechanism for the adsorption process (Gizaw et al., 2021).

Furthermore, the elemental analysis (EA) was carried out to determine the percentage of hydrogen, carbon and nitrogen contained in ammonium polymer before and after, as shown in Table 1. Elemental analysis of hydrogen (H), carbon (C), and nitrogen (N) is essential in the adsorption process, as it provides critical insights into the changes in the sample's composition and chemical properties during the process. Markers or baselines for modifications are hydrogen, carbon, and nitrogen. Elements can provide information about the reactions that occur during the adsorption process. Fluctuations in the EA % indicate the presence of reaction transformations within the sample. Additionally, the presence of specific adsorbates or molecules that are adsorbed onto the sample is evidenced by the substantial increases in H, C, and C concentrations. This facilitates the chemical identification of molecules that are involved in the adsorption process.

Table 1 presents the elemental analysis results, revealing that ammonium polymer has a chemical composition of 7.57% H, 43.05% C, and 2.87% N. However, when in contact with bioethanol wastewater, the composition changes to H 3.97%, C 23.74%, and N 3.49%. This change indicates that the percentage of nitrogen (N) in the ammonium

polymer after adsorption is more significant. Thus, ammonium, the primary functional group in nitrates, is effectively absorbed into the polymer, increasing nitrogen content. The polymer contains nitrogen, forming a quaternary ammonium molecule that functions as a potent anion exchanger. The adsorption process entails interactions between the ammonium polymer and the adsorbate. Adsorbed molecules may interact with the sample surface to alter the elemental composition (Rahayu et al., 2023). Moreover, this robust anion exchanger likely interacted with a negatively charged site from nitrate ions in bioethanol wastewater.

Assume the polymer has nitrogen present, for example, in various amine groups. In that case, the relative change in nitrogen content after nitrate adsorption will be more minor compared to a polymer with no nitrogen (Zhang et al., 2024). The more nitrate (NO3-) adsorbed onto the polymer, the higher the increase in nitrogen content, as each nitrate ion introduces an additional nitrogen atom. As the total mass increases, incorporating nitrate will reduce the relative percentages of carbon and hydrogen in the polymer. In contrast, the quantities of carbon and hydrogen remain unmodified. Polymers with functional groups like amines, hydroxyls, or carboxyls may exhibit higher nitrate adsorption due to more substantial interactions (e.g., hydrogen bonding or electrostatic attractions) (Bhatt et al., 2023). This can impact the final nitrogen percentage more than in polymers with fewer reactive sites.

Adsorption of nitrate can lead to crosslinking within the polymer structure, which can change the overall molecular weight, affecting how the percentages of C, H, and N are calculated (J. Wang et al., 2024) in solutions where nitrate is present with other anions (e.g., sulfate, chloride), competition between ions may reduce the amount of nitrate adsorbed, thus affecting the nitrogen percentage less than expected. This could also alter the overall mass balance of the polymer system, influencing the C and H percentages indirectly. The analysis of H, C, and N elements reveals

Table 1. Elemental analysis result of ammonium polymer

Treatment	Unit	Component			
		Н	С	N	
Before	% wt	7.57	43.05	2.87	
After		3.97	23.74	3.49	

insights into how the C and H samples interact with the adsorbent material during adsorption.

Elemental analysis offers a detailed overview of the chemical composition of the ammonium polymer, highlighting the initial nitrogen levels associated with the amine groups. In contrast, SEM-EDX enhances this understanding by illustrating how these groups engage with nitrate ions during adsorption and visualizing the morphological changes and surface interactions. The polymer surface morphology was examined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), as illustrated in Figure 5 before





Figure 5. SEM-EDX mapping result of ammonium polymer before adsorption

the adsorption process and Figure 6 after the adsorption process.

The SEM-EDX mapping of ammonium polymer before the adsorption performance is shown in Figure 5. Carbon (C), nitrogen (N), oxygen (O), aluminum (Al), chlorine (Cl), sulfur (S), phosphorus (P), silicon (Si), manganese (Mn), iron (Fe), copper (Cu) and zinc (Zn) are among the elements whose distribution has been illustrated by the elemental mapping. The majority of the elements carbon (C) and nitrogen (N) demonstrate the existence of the polymer's organic structure and amine groups. A great potential for ion exchange is offered by the high concentration of nitrogen 16.7% and carbon 67.7%, which the active amine groups cause. Oxygen element is equally essential since it contributes to the polymer's overall structure and functionality. It is most likely derived from hydroxyl groups or moisture. The trace elements (Al, Cl, S, P, Si, Mn, Fe, Cu and Zn) are found in lesser amounts and can be an effect of addition or impurities employed in the polymer synthesis procedure. Although their presence offers a comprehensive understanding of the material composition, it has little impact on the polymer performance.

Following the adsorption of nitrate ions, the SEM-EDX mapping of ammonium polymer is illustrated in Figure 6. The impact of the adsorption process is reflected in the alteration of the elemental distribution. Nitrogen rises to 17.2% during adsorption, while the carbon percentage significantly increases to 68.7%. Since the nitrogen in the nitrate corresponds to the total nitrogen amount of the polymer, this improvement indicates that the nitrate ions were successfully adsorbed. This suggests that the amine groups effectively acted as anion exchangers, facilitating the adsorption of nitrate ions while partially replacing the original nitrogen and carbon content. These findings highlight the ammonium polymer's ability to remove nitrates, confirming its suitability for environmental applications in the treatment of bioethanol wastewater. The decrease in nitrogen levels after adsorption further emphasizes the polymer's effectiveness in capturing nitrate ions, demonstrating its potential for enhanced ion exchange processes.

The amount of oxygen is relatively constant, indicating that the carbon and nitrogen elements are the principal targets of the adsorption process. The presence of trace elements (Al, Cl, S, P, Si, Mn, Fe, Cu, and Zn) is not significantly affected by the adsorption process, as evidenced by their constant distribution. However, during the adsorption process, their persistent presence confirms the polymer structure's integrity.

The morphology of ammonium polymer before and after the adsorption process exhibits a rounded shape with a particle size of 2 μ m. In its initial form, the polymer's surface looks quite smooth. Smaller particles have a larger surface area than larger particles, which provides more active sites for adsorption and enhances the adsorption capacity (Chouchane et al., 2021). After the adsorption process, the surface gets rougher, indicating that the polymer's surface shape has changed due to the nitrate ion adsorption.

Effect of polymer mass

The mass of the polymer in an adsorption process greatly influences its efficiency and dynamics. This study treated bioethanol wastewater at 361.5 ppm with initial polymer masses of 1, 2, 2.5, 3, and 3.5 g, agitated at 25 °C for 10 minutes. Figure 7 illustrates how polymer mass affects the removal percentage (%RE) and adsorption capacity (Qe).

Figure 7 demonstrates that increasing the ammonium polymer enhances the surface area and creates more active binding sites for nitrate ions, though it also results in decreased adsorption capacity and efficiency. The research found that the highest nitrate ion removal of 94.00% occurred at a mass of 1 g, with an adsorption capacity of 0.8496. The relationship between changes in polymer mass and absorption efficiency is nonlinear. Furthermore, variations in the mass of cocoa shells throughout the reaction may affect the duration needed to achieve equilibrium. These findings are consistent with Gorzin et al. (2018), who suggest that equilibrium decreases as the mass of the adsorbent increases (Gorzin and Bahri Rasht Abadi, 2018). This indicates that an increase in the polymer mass allows for the adsorption of more contaminants or molecules up to the saturation point.

Increasing the mass of the polymer can increase the available surface area and adsorption sites, potentially enhancing the adsorption capacity (Amiri et al., 2023). However, a larger mass of polymer may create diffusion barriers, leading to slower diffusion of molecules or adsorbates into the deeper layers of the polymer (Roopnarine et al., 2023). This can reduce the efficiency of the adsorption process, especially if the polymer particles are densely packed or poorly dispersed. A higher polymer mass may initially increase the



Lsec: 72.4 0 Cnts 0.000 keV Det: Element-C2 Det



Figure 6. SEM-EDX mapping result of ammonium polymer after adsorption

adsorption rate due to the availability of more active sites (Vievard et al., 2023). However, beyond a certain mass, the effect on kinetics may decrease as the system reaches equilibrium, and further mass might not significantly speed up the process. After a certain mass, the adsorption rate can stabilize when all available binding sites are filled, leading to saturation. At this point, adding more polymer mass will not increase the amount of adsorption since the polymer's adsorption sites are fully occupied (Wang and Giammar, 2013). Optimizing the mass of the polymer used in the



Figure 7. Effect of polymer mass for nitrate removal and adsorption capacity

adsorption process is critical to achieving high efficiency without overloading the system or incurring unnecessary costs.

Effect of adsorption temperature

Temperature significantly influences the adsorption process, affecting removal efficiency and capacity. In this variation, a 361.5 ppm bioethanol wastewater solution with a mass of polymer 1 g was agitated at initial temperatures of 25, 30, 40, 50, and 60 °C for 10 minutes. Figure 8 illustrates that the adsorption temperature influences removal efficiency (%RE) and the adsorption capacity (Qe). Figure 8 depicts the impact of temperature on the adsorption of nitrate ions in bioethanol wastewater. According to the research findings, the highest nitrate ion removal occurred at 40 °C, where the removal efficiency for nitrate ion was 96.07% with an adsorption capacity of 0.71. This meant that a higher temperature would increase thermal energy, but if the temperature is too high, it can result in the desorption of the ammonium polymer. Additionally, elevated temperatures during adsorption can enhance the adsorption rate due to faster ion diffusion. This observation is consistent with studies by Qu et al. (2022) and Aini et al. (2023), which investigated the effect of



Figure 8. Effect of temperature adsorption for nitrate removal and adsorption capacity

temperature on nitrite ion removal. Their research found that nitrate removal was most efficient at 40 °C (Aini et al., 2023; Qu et al., 2022).

When adsorption capacity increases with temperature, it indicates an endothermic process, as higher temperatures enhance the mobility of molecules and the availability of active sites for adsorption. In contrast, a decrease indicates an exothermic process. This is likely due to the increased mobility of dye molecules and available active sites at higher temperatures. Reducing adsorption capacity with rising temperature supports Le Chatelier's principle, which states that higher temperatures shift equilibrium away from adsorption. At lower temperatures, adsorbate molecules have less kinetic energy, making them more prone to being captured on the adsorbent surface, particularly in exothermic processes (Lin and Murphy, 2017). However, if the temperature is too low, the diffusion of adsorbate molecules to the adsorbent's surface can become sluggish, reducing the overall efficiency.

At elevated temperatures, the kinetic energy of adsorbate molecules increases, which can improve diffusion rates and the likelihood of reaching adsorption sites (Vievard et al., 2023). However, higher temperatures can also enhance the mobility of adsorbate molecules, allowing them to overcome activation energy barriers and access deeper or less accessible adsorption sites. This can potentially increase both removal efficiency and adsorption capacity in specific cases. It should be noted that too-high temperatures are not recommended in the nitrate ion adsorption process.

Effect of contact time

The contact time between the adsorbent (e.g., polymer) and the adsorbate (substance to be removed, e.g., bioethanol wastewater) plays a crucial role in the efficiency of the adsorption process. In this variation, bioethanol wastewater 361.5 ppm solution with a mass of polymer 1g was agitated at 40 °C for initial contact times 10, 20, 30, 50, and 60 minutes. Figure 9 illustrates that the adsorption temperature impacts the removal efficiency (%RE) and the adsorption capacity (Qe).

Contact time is a crucial factor in the biosorption process. As shown in Figure 9, the percentage of nitrate ion removal increases with longer contact times. The highest removal efficiency reached 96.31% with an adsorption capacity of 0.58 mg/g at a contact time of 60 minutes. This indicates that longer contact times enhance the adsorption capacity of the ions (Rahayu, Alfi, et al., 2023). The reaction time for adsorption significantly impacts the effectiveness of the adsorbent. Extending the reaction time or contact duration between the adsorbent and ions in the aqueous solution generally increases the number of ions adsorbed. Additionally, sufficient reaction time ensures the system reaches equilibrium (Aini et al., 2023).

As contact time increases, more adsorption sites on the adsorbent get occupied (Li, Dong, et al., 2022). The process slows down as fewer active sites are available to attach the adsorbate. The adsorption rate decreases at this point, but the removal efficiency increases slowly. Eventually, the adsorption process reaches an equilibrium where



Figure 9. Effect of contact time for nitrate removal and adsorption capacity

no further adsorbate is removed, regardless of the increase in contact time. At this point, all accessible active sites are saturated, and the removal efficiency stabilizes. Extending the contact time beyond this equilibrium won't significantly improve removal efficiency (Ghanbarizadeh et al., 2022). If the adsorbent is porous, longer contact times allow adsorbate molecules to diffuse into deeper adsorbent layers. This can enhance the removal efficiency, particularly in cases where the adsorbate molecules require time to penetrate the pores. However, removal efficiency generally increases with contact time, but there is a diminishing return once equilibrium is reached.

Adsorption isotherm kinetics

Adsorption isotherms are mathematical models that explain how the amount of a substance adsorbate on a surface changes with its concentration in the fluid phase at specific temperature and pressure conditions (Ayawei et al., 2017). Calculating adsorption isotherms helps to understand and characterize the adsorption process of ammonium polymers on a surface. The insights gained from these isotherms also support the design of efficient adsorption systems by identifying optimal operating conditions. The data was adjusted to a standard scale to create a normalized plot, often to make different datasets comparable or to visualize data in relative terms rather than absolute values, such as in Figure 10.

Figure 10a shows that the Langmuir adsorption model depicts the relationship between the amount of adsorbate on the surface (Ce) and the equilibrium concentration (Ce/qe). The Ce/qe typically decreases as Ce increases, indicating the efficiency of the adsorption process, as evidenced by the decrease in Ce/qe. Figure 10b depicts the relationship between the adsorption amount (qe) and the logarithm of the equilibrium concentration (ln Ce). The Temkin plot provides insights into the energetic properties of adsorption and the maximum adsorption capacity. It shows a linear relationship with polymer mass, temperature, and contact time during adsorption. However, the Langmuir plot in Figure 10a reveals a less linear relationship concerning adsorbent mass, whereas the Temkin plot in Figure 10b demonstrates a clear linear trend for all variables. This suggests that the Temkin adsorption isotherm is more appropriate for this study, a conclusion further supported by the isotherm model parameters in Table 2.

The comparison of the parameter results in Table 2 shows that the Temkin model consistently has a better determination coefficient value than the Langmuir model. Even if it has a perfect R² temperature and time, the value of the mass parameter is too <0.99. On the other hand, K_L for mass and temperature has a negative value, even though it is a Langmuir constant expressed in L/mg (or any related unit), so it should not be harmful. Negative K_L means that adsorption does not follow Langmuir assumptions (Perwitasari et al., 2021). Finding a negative value means that Langmuir isotherm doesn't fit the experimental data correctly.

The Langmuir adsorption isotherm describes the adsorption of molecules onto a solid surface. This is based on the assumption that adsorption occurs at specific homogeneous sites on the surface, resulting in a monolayer of adsorbed molecules (Kalam et al., 2021). It is widely used to explain gas-solid adsorption and can be applied to various adsorption processes. The Temkin adsorption isotherm is another model that describes adsorption, particularly considering adsorbent-adsorbate

Figure 10. Normalize plot of adsorption isotherm (a) Langmuir (b) Temkin

Parameter	Langmuir			Temkin		
	K _L (L/mg)	Q _t (mg/g)	R ²	K _T (L/mg)	В	R ²
Mass	-0.84317	-0.27612	0.9382	3.94 × 10⁻ ⁶	-2.7508	0.9956
Temperature	0.01999	30.21148	1	2.47× 10 ⁻¹⁰	-0.0773	0.9996
Time	-0.0364	-15.083	1	9.37× 10 ⁻²⁵	-0.6176	0.9975

Table 2. Langmuir and Temkin parameters for nitrate ions removal using ammonium polymer

interactions. In contrast to the Langmuir isotherm, the Temkin isotherm assumes that the heat of adsorption decreases linearly with increasing coverage due to interactions between adsorbate molecules (Inyinbor et al., 2016).

CONCLUSIONS

The polymer ammonium-based was successfully prepared using the one-pot approach method with a single thermal. The removal of nitrate ions in bioethanol wastewater proceeded using an adsorption mechanism using ammonium polymers. The optimal conditions for the adsorption process occur when 0.1 gram of ammonium polymer comes into contact with bioethanol wastewater for 60 minutes at 40 °C. The removal efficiency and adsorption capacity of ion nitrate were 96.32% and 0.58 mg/g, respectively. The combined analysis of FTIR, elemental analysis, and SEM EDX reveals that the ammonium polymer effectively adsorbs nitrate ions, highlighting its potential for environmental remediation. FTIR results show critical functional groups, including O-H, CH, N-H, C-N, and C-O, with sharper peaks after nitrate adsorption, indicating successful binding. Elemental analysis demonstrates a significant change in composition upon contact with bioethanol wastewater, particularly an increase in nitrogen content, which enhances the polymer's capability as a strong anion exchanger. SEM-EDX findings indicate a slight decrease in nitrogen distribution after nitrate adsorption, confirming effective ion exchange. Analysis of adsorption isotherm shows that the Temkin model consistently has a better determination coefficient value than the Langmuir model and offers a comprehensive understanding of the adsorption process, which was previously lacking. This study makes significant contributions by addressing the specific challenge of nitrate ion removal from bioethanol wastewater. It provides substantial environmental benefits by reducing nitrate pollution

with regeneration, reusability and environmentally friendly polymer, offering economic advantages in the future.

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