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Original Research

Development of Ammonium-Based Ion Exchange Polymer for Phosphate Ions Removal

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Abstract

Polymers can exhibit adsorbent behavior and are used to remove pollutants from environments. Their adsorption properties can be tailored to capture specific contaminants effectively. In this research, an ammonium-based ion exchange polymer was developed using the one-pot approach method. It allows for simultaneous polymerization and functionalization, reducing the number of reaction steps and purification processes. The developed ammonium-based polymer is a novelty material for removing phosphate ions from an aqueous solution. Several essential factors (temperature, contact time, initial phosphate concentration, and adsorbent dosage) that affect the removal process of phosphate ions during adsorption were investigated. This research aims to develop a novel organic polymer using the one-pot approach for removing phosphate from aqueous solutions and performing adsorption behavior based on isotherm studies. The characterization of ammonium-based polymer was carried out using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM), which offered proof of chemical and physical adsorption. The optimum condition during phosphate adsorption using a developed ammonium-based polymer was at a temperature of 25°C, contact time of 20 minutes, initial phosphate concentration of 30 ppm, and adsorbent dosage of 0.05 g, which achieved adsorption capacity (Qe) of 2.99 mg/g and phosphate ion removal percentage of 99.73%. The Langmuir model describes the best adsorption isotherm of phosphate ions on the adsorbent with coefficient value (R2=0.9974). In the future, it can offer an alternative method for treating ion phosphate in aqueous solution or wastewater treatment.

Keywords: adsorption, isotherm, one-pot approach, phosphate, polymer

Introduction

Phosphate is a polyatomic ion or radical with the HOPO(OR) functional group consisting of one

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phosphorus atom and four oxygens with a 48 g/mol molecular mass, denoted PO_4^{3-}. Chemical industrial waste, such as phosphoric acid and bioethanol factories, can potentially contain high phosphate ion levels, which cause eutrophication [1]. However, when excessive amounts of phosphorus are introduced into the environment, typically through human activities, it can have several detrimental effects. The phosphorus overloading in ecosystems can lead to various environmental problems and negative impacts. Based on the Environmental Protection Agency regulation, the permissible maximum contaminant level of phosphate in freshwater is 0.1 mg/L. Environmental pollution caused by the accumulation of human activities, especially industrial ones, has become an essential concern in the last decade.

Direct disposal of industrial wastewater can lead to high concentrations of pollutants, including phosphates, in water bodies such as rivers. Thus, it is necessary to develop innovative methods or technologies to reduce this problem's negative environmental impact. Alternative technology can be applied by exploring advanced materials such as polymer-based adsorbents. Various analytical methods have been used to determine pollutant compounds in environmental and/or aquatic samples [2]. Phosphomolybdenum blue (PMB)-based spectrophotometry is applied as the standard method worldwide, while fluorescent and electrochemical (bio) sensors are gaining attention due to their versatility [3]. Primary instrumental analysis techniques, including chromatography and mass spectrometry, have been recognized as powerful tools for analyzing complex samples [3, 4].

Polymers are large molecules composed of interconnected monomers in the presence of cross-linkers. Many polymers have been researched and developed based on the type, main base material, and intended use of the polymer itself. Polymer production typically involves two phases: the polymerization step and the post-modification phase. The post-modification phase is focused on creating the specific active polymer sites required for the intended purpose and application in polymer manufacturing. Both organic polymers and inorganic polymers have found extensive application as a stationary phase in the separation of cations and the measurement of cation concentrations in drinking water [5], polar compounds [6], macro molecular compounds [7], and others in the chromatography method. Inorganic polymers have drawbacks, such as an extended overall production duration and a restricted range of materials for shaping. Methacrylate-based organic polymers incorporating amine groups through the epoxy methacrylate ring-opening technique have been effectively manufactured and employed for the adsorption of Cu (II) ions [8], phenol compound [9], and bisphenol A (BPA) [10]. The advanced modification stage in polymer preparation seeks to incorporate the specific active groups as the intended purpose and application [11].

Recent innovations in polymerization techniques have introduced the one-pot approach, a simple, efficient method for synthesizing organic polymers in a single step. This novel strategy not only streamlines the polymer preparation process but also enhances its application across diverse separation and adsorption objectives [12]. The one-pot method is recognized for its environmentally friendly nature, ease of development, and cost-effectiveness, as it eliminates the need for extensive modification steps often required in traditional polymerization methods [13]. This technique has gained traction in the production of stationary phase materials for liquid chromatography columns and has also shown potential in developing absorbent materials for wastewater treatment. Notably, ammonium polymers synthesized via the one-pot approach have been successfully utilized as stationary phases in chromatography [21] and explored for their efficiency in initial anion removal studies [13]. These advancements underline the versatility of the one-pot method in both analytical and environmental applications [14, 15].

Adsorption has been known as one of the most effective methods of treating and removing contaminants contained in water and various kinds of waste. Several studies have tested ion exchange processes for treating water and waste contaminated with phosphate ions [16, 17]. This method effectively reduced these pollutant compounds. The ion exchange method is a reference for removing pollutant compounds contained in the liquid waste from industry with adsorption media based on advanced materials in the form of polymers. Several polymers have been employed as adsorbents for removing heavy metals in ionic forms and organic compounds. In previous studies, Cr(VI) ions were adsorbed using magnetic polymers containing amine groups [18]. Other organic polymers, derived from methacrylate and produced through the epoxy methacrylate ring-opening approach, have also been effectively utilized for the adsorption of metal ions [19].

In this study, a quaternary ammonium polymer was developed using a one-pot approach method for the removal of phosphate ions. The main objectives of this work are to synthesize and characterize quaternary ammonium polymers and then investigate the relationship between adsorption behavior and affected parameters, including isotherm studies. Synthesis of polymers is essential in the field of analytical chemistry due to the diverse applications and properties of polymers that can be utilized for analytical purposes [20]. These functional polymers showcase the versatility of polymers across various fields and their significance in addressing complex analytical challenges. Additionally, this research highlights the potential of polymer chemistry in developing solutions for analytical purposes.

Material and Methods

Materials

Materials used in this study consist of 2-[Methacryloyloxy)ethyl]trimethylammonium chloride solution (META), ethylene dimethacrylate (EDMA), isopropyl alcohol (IPA), methanol, and ethanol (Wako 1st Grade, Japan), while 2,2'-azobisisobutyronitrile and polyethylene oxide (PEG) 400 were purchased from Trade TCI Mark, Japan. All reagents used in this study were of analytical grade.

Synthesis and Characterization of Quaternary Ammonium Polymers

The preparation of organic polymer was started with an initial composition of 1.25 mL of META, 0.375 mL of EDMA, 1.75 mL of IPA, 1.4 mL of PEG 400, and 0.35 mL of ethanol, which were added to the vial. Then, 2 mg of 2,2'-azobisisobutyronitrile was added to the vial and stirred until a homogenous mixture was formed. The solution mixture was put into a glass cylinder, and both ends of the tube were covered. The solution was put in a water bath at 70°C for 24 hours during the polymerization process. Then, the polymer was rinsed with methanol and ethanol to remove unreacted reagents and residue. The quaternary ammonium polymers were obtained and are ready to be used for phosphate adsorption studies. The scheme of the expected reaction polymerization one-pot approach method is shown in Fig. 1. The scheme of expected reaction, in which a functional monomer introduces the quaternary ammonium in the organic polymer, shows the active group for the anion exchange [21].

The phosphate concentration was measured using a UV-Vis Spectrophotometer (Thermo Scientific-Genesys), while the polymer's functional groups were characterized using Fourier Transform Infrared (FTIR) Spectrum 400 Series (Perkin Elmer).

Adsorption Capacity

Adsorption experiments were carried out using the batch method. A certain amount of adsorbent was added to 25 mL of phosphate solution. The mixture was shaken thoroughly using a magnetic stirrer at 150 rpm, and the filtrate was analyzed for phosphate. To investigate the relationship between the adsorption behavior of polymers and affected factors, the adsorptions were conducted using various parameters: temperature, contact time, initial phosphate concentration, and adsorbent dosage. After contact, the samples were withdrawn and analyzed for residual phosphate concentration in the solution. The experiments were conducted in duplicate, and the reported adsorbed concentrations represent the averaged outcomes of these replicated experiments. The removal percentage of phosphate in the solution was calculated according to Equation (1), while the adsorption capacity of the adsorbent was obtained according to Equation (2):

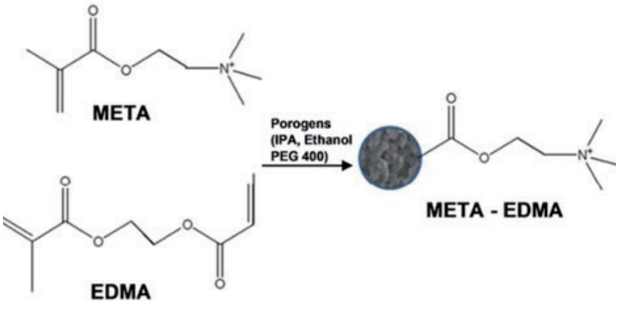


Fig. 1. Scheme of META polymer expected reaction [13].

$$Removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{2}$$

Where C_0 is the initial concentration (mg/L), C_e is the final concentration (mg/L), V is the solution volume (L), and m is the mass of adsorbent (mg).

Adsorption Isotherms

Adsorption isotherms are mathematical relationships that describe the adsorption of a substance (adsorbate) onto a solid surface (adsorbent) to study the adsorption mechanisms. These isotherms help to understand how the adsorption process varies with changes in the adsorbate concentration [22]. Two isotherm models, Langmuir and Freundlich's isotherms, were studied in this study. The first model, Langmuir isotherm, assumes that adsorption occurs at specific, identical sites on the adsorbent's surface. It is based on the following assumptions: (i) adsorption takes place at a finite number of sites, (ii) once a site is occupied, no more adsorption can occur at that site, and (iii) all adsorption sites have the same affinity for the adsorbate [23]. Expressions for the Langmuir isotherm and its linear form are expressed in Equations (3) and (4), respectively:

$$q_e = \frac{q_t K_L C_e}{1 + K_L C_e} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{q_t K_L} + \frac{C_e}{q_t} \tag{4}$$

The second model, Freundlich isotherm, is an empirical equation that does not rely on specific site assumptions. It describes heterogeneous or multilayer adsorption by assuming that adsorption energy decreases as the adsorption sites become occupied. The Freundlich isotherm equations and the linearized form [23] are given in Equations (5) and (6), respectively, as follows:

$$q = K_F C_e^{1/n} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where q_e is the maximum adsorption capacity of the adsorbent (mg/g), q_t is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate in the gas or liquid phase (mg/L), K_L is Langmuir adsorption constant, K_F and $1/n$ are the Freundlich temperature-dependent constants.

Results and Discussion

Ammonium quaternary polymer is developed by conducting a 12-hour one-pot approach polymerization reaction. Ammonium quarter monolithic polymers are the result of the synthesis of 2-[(Methacryloyloxy) Ethyl] Trimethylammonium (META) and Ethylene Dimethacrylate (EDMA). This work promoted the polymer as an adsorbent for phosphate ion removal in an aqueous solution. The effect of various parameters, including temperature, contact time, initial phosphate concentration, and adsorbent dosage during adsorption, was investigated.

Characterization of Quaternary Ammonium Polymers

FTIR was performed to determine the presence of amino clusters in ammonium quaternary polymer samples. FTIR offers comprehensive insights into the functional groups found in the adsorbate. Identifying these groups allows for a better understanding of their interactions with the adsorbent. The spectrum of the FTIR analysis results on the polymer formed can be seen in Fig. 2.

Based on the FTIR spectrum data of the quaternary ammonium polymer sample, the results indicate the identification of amine salt groups (N–H Stretching) in the wavelength range of 1650 – 1580 cm^{-1}, characterized by a strong and broad waveform. Additionally, in the wavelength range of 1250 – 1020 cm^{-1} with a medium waveform, amine groups (C–N Stretching) were identified [1]. The amino group is known as the anion resin or anion exchanger group, where the amine group can exchange negative ions with phosphates classified as anions. From the FTIR results, it can be determined that the presence of amino groups in the polymer means it can be used as an adsorbent.

On the other hand, Scanning Electron Microscopy (SEM) is an effective method for examining ammonium polymers utilized in phosphate removal. It generates high-resolution images that reveal the surface morphology of these polymers. SEM also enables the measurement of particle size and distribution, factors that can significantly affect adsorption capacity and kinetics. Generally, smaller particles offer a greater surface area, which improves adsorption. Additionally, by assessing surface characteristics, SEM can identify potential sites for phosphate ion adsorption, providing valuable insights into the adsorption mechanism. SEM results are shown in Fig. 3.

Fig. 3 presents the SEM results at 500x magnification. The polymer exhibits a union size range of 0.386 to 0.701 µm, indicating the uniformity of the polymer structure. Additionally, macro pores are observed with sizes ranging from 0.336 to 1.243 µm. These macro pores are significant as they provide potential adsorption sites for phosphate ions, enhancing the effectiveness of ammonium polymer in phosphate removal. The combination of small particle size and the presence of macro pores suggests a favorable surface area for adsorption, supporting the application of polymer for adsorption.

Based on Rahayu [13] and according to the BET analysis, the polymer has a surface area, volume pores, and pores size of 5.6992 m2/g, 0.0044 mL/g, and 1.8225 nm, respectively. The percentage weights

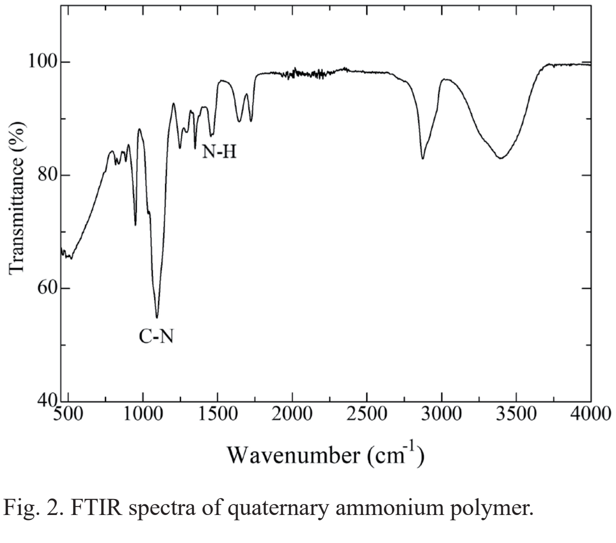


Fig. 2. FTIR spectra of quaternary ammonium polymer.

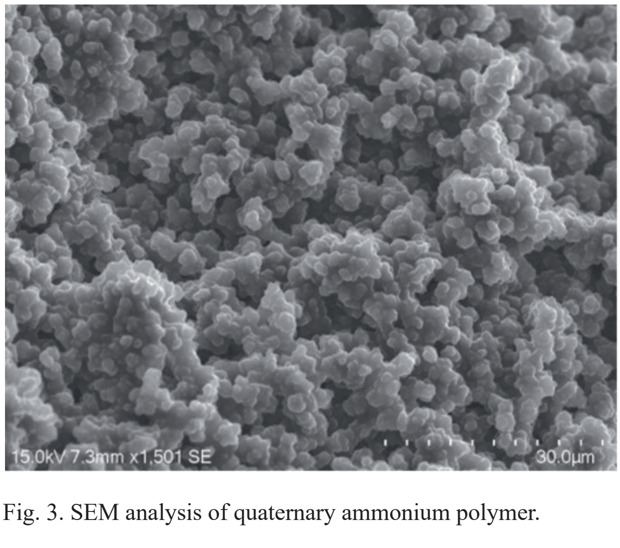


Fig. 3. SEM analysis of quaternary ammonium polymer.

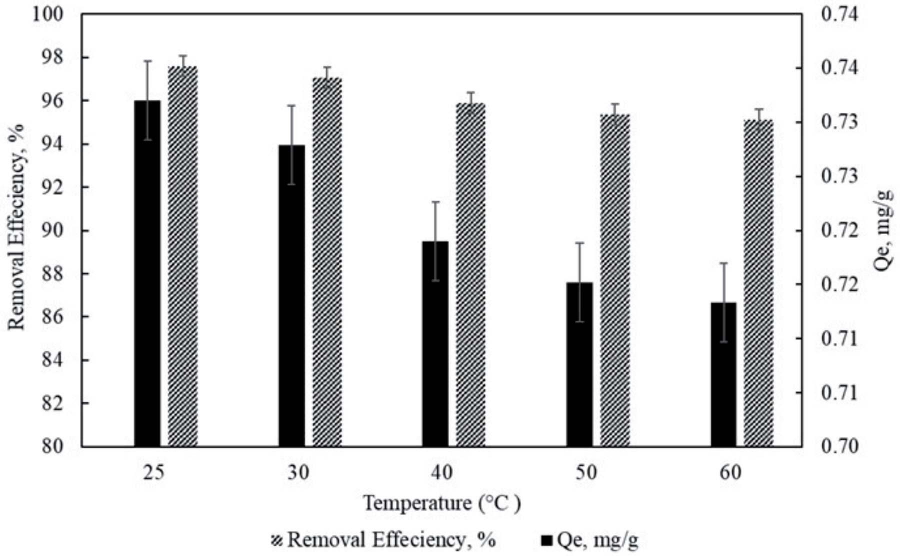


Fig. 4. Effect of temperature during phosphate adsorption.

of carbon, hydrogen, and nitrogen in META polymer were determined by elemental analysis. The percentage weights of carbon, hydrogen, and nitrogen were 8.57, 46.95, and 3.77, respectively. The polymer contains nitrogen, introducing a quaternary ammonium compound that acts as a strong anion exchanger [13].

Effect of Temperature on Adsorption

Studies have been conducted on the influence of temperature on ammonium quaternary polymers as absorbents on phosphate (PO_4^{3-}) absorption processes at various temperatures. The effect of temperature on phosphate adsorption is presented in Fig. 4.

Based on Fig. 4, the highest phosphate removal occurred at a temperature of 25°C, with a phosphate ion uptake of 97.60% and an adsorption capacity of 0.73 mg/g. This phenomenon is attributed to the fact that higher temperatures enhance the penetration of the aqueous solution into the adsorbent's pores, facilitating interactions. However, as phosphate ions and water compete in the solution, the adsorption capacity (Qe) decreases. Additionally, elevated temperatures promote desorption, which further reduces adsorption capacity. As temperature rises, adsorbents gradually detach from both the surface and the pores, primarily because the attractive forces between the adsorbent and phosphate ions weaken, leading to diminished adsorption capacity [24].

Effect of Contact Time on Adsorption

Time optimization is used to determine the optimum time required by the adsorbent and evaluate the limits

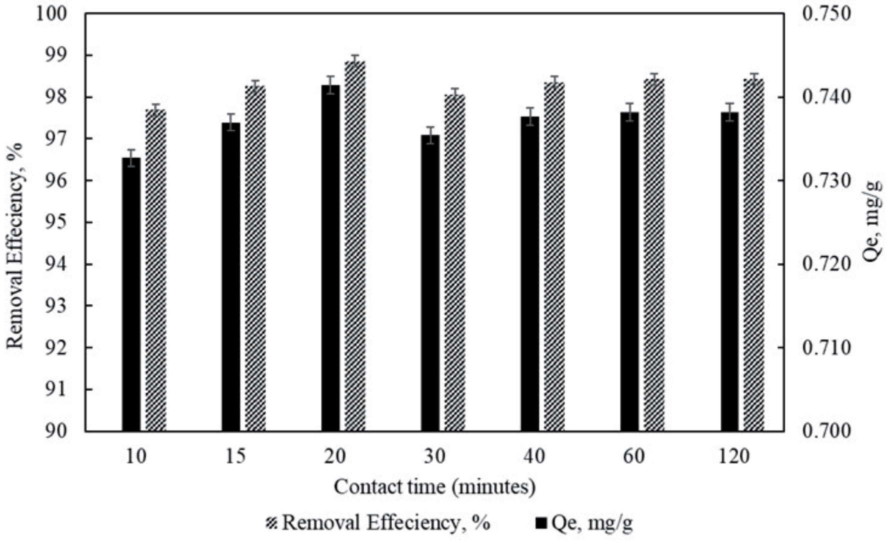


Fig. 5. Effect of contact time during phosphate adsorption.

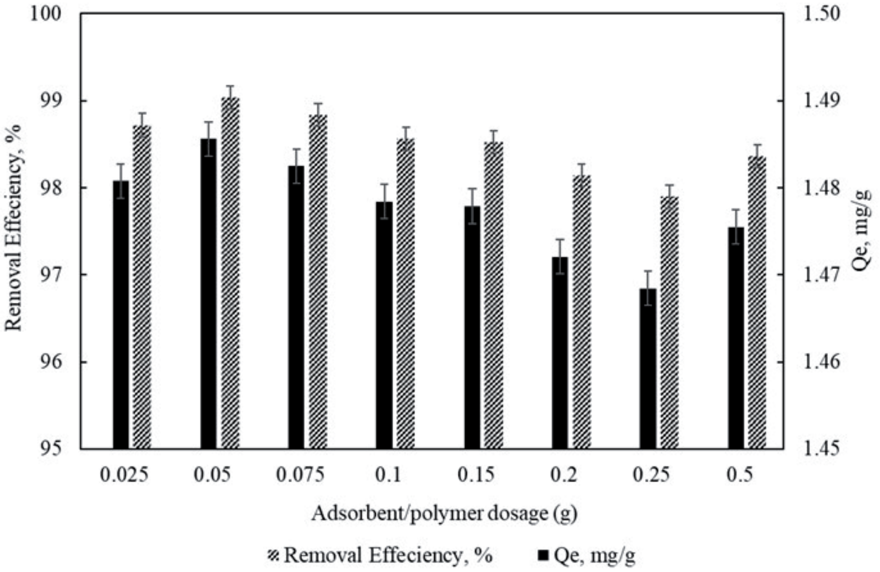


Fig. 6. Effect of adsorbent dosage during phosphate adsorption.

of its capability to absorb phosphates. The optimization was performed at various contact times ranging from 10 to 120 minutes at optimal temperature. The effect of contact time during phosphate adsorption is shown in Fig. 5.

Contact time is an important factor in the biosorption process. As shown in Fig. 5, the highest phosphate removal was achieved when the solution was in contact with the polymer for 20 minutes, resulting in a phosphate ion removal rate of 98.86% and an adsorption capacity of 0.741 mg/g. The results indicate that extending the contact time increases the percentage of phosphate ion removal through adsorption up to an optimal point. In this study, the highest adsorption capacity and phosphate removal percentage were achieved at 20 minutes, with a noticeable decline in both metrics at 30 minutes. Contact time is essential in the adsorption process as it affects the equilibrium between the adsorbent and adsorbate. Longer contact times allow more adsorbent particles to interact with the active sites, facilitating the establishment of equilibrium [25]. A decrease in adsorption is observed as a consequence of desorption or the release of the adsorbate, which occurs because of the weak interaction between the adsorbent and the adsorbate attached to the surface. Desorption also occurs during the adsorption of phosphate ions using iron oxide as an adsorbent in aqueous solution, where after an increase from 10 to 40 minutes, there is a decrease from 40 to 60 minutes [26].

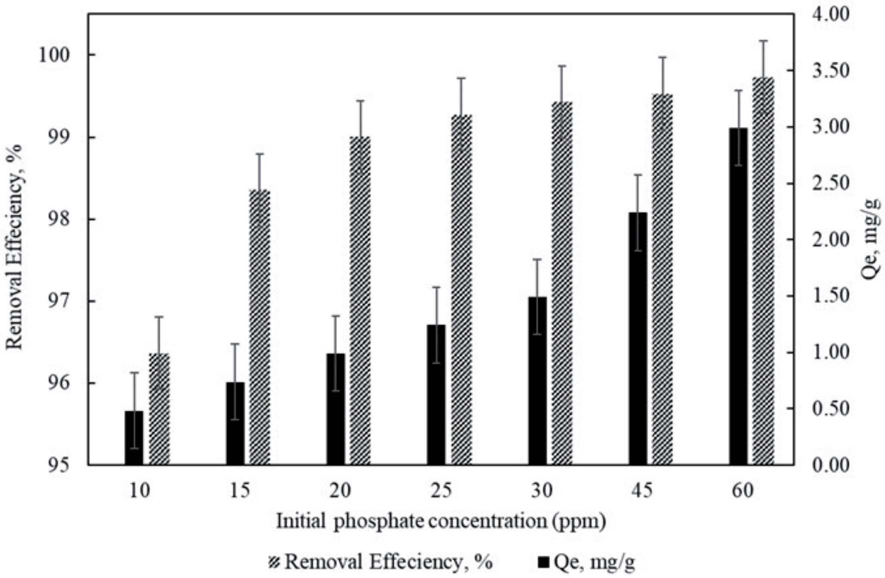
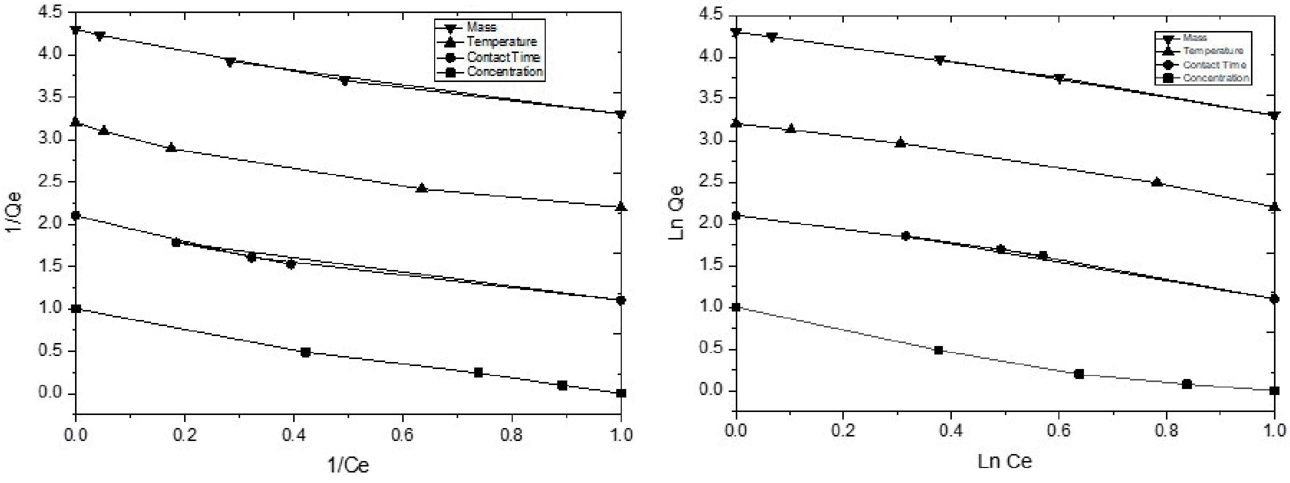


Fig. 7. Effect of initial phosphate concentration during phosphate adsorption.



a)

b)

Fig. 8. Normalize plot of adsorption isotherm (a) Langmuir (b) Freundlich.

Effect of Adsorbent Dosage on Adsorption

The effect of adsorbent dosage on phosphate ion adsorption on polymer as adsorbent is demonstrated in Fig. 6. To investigate the effect of adsorbate concentration, the adsorption was conducted in various polymer dosages (0.025, 0.05, 0.075, 0.1, 0.15, 0.20, 0.25, and 0.50 g).

The greatest phosphate removal occurred with a polymer dosage of 0.05 g, achieving a phosphate ion removal rate of 99.04% and an adsorption capacity of 1.49 mg/g. The removal percentage and adsorption capacity decreased with the increase of adsorbent mass. A decrease in the adsorption capacity indicated that the adsorbent dosage was too high during adsorption [27]. This is due to the low use of sorbent adsorption sites available in the adsorbent. The thickness of the aqueous solution might also affect adsorption performance, as there was a possibility of overlapping mechanisms between potential adsorption sites due to the excessive density of adsorbent particles. As a consequence, the area available for adsorption is reduced.

Effect of Initial Phosphate Concentration on Adsorption

To investigate the effect of adsorbate concentration, the adsorption was conducted in various initial phosphate concentrations (10, 15, 20, 25, and 30 ppm). The results of this variation are depicted in Fig. 7.

The highest phosphate removal was achieved using a 60 ppm aqueous solution, resulting in a phosphate ion removal rate of 99.73% and an adsorption capacity of 2.99 mg/g. This indicates that both adsorption capacity and removal percentage increase with higher initial phosphate concentrations. An elevated initial concentration of phosphate as the adsorbate enhances the number of molecules that can be adsorbed by the polymers, leading to greater interaction between them [28]. According to the maximum value of adsorption capacity and removal percentage, the optimum initial concentration of phosphate in this study was 30 ppm.

However, the optimum condition from the adsorption can be scaled up to practical application, considering several factors such as cost-effectiveness, regeneration potential of the polymer as adsorbent, and compatibility with the real wastewater, in this case, was vinasse. Polymer adsorbents are one of the advanced materials being widely developed, and not many polymer adsorbents have been developed and applied for these issues. Polymer-based adsorbents offer several advantages for wastewater treatment due to their versatility, efficiency, and cost-effectiveness [13].

Polymers have been used as a potential adsorbent to absorb phosphate ions, and they can be used several times. The regeneration can be performed through different pathways, including temperature swing regeneration (TSR), pressure swing regeneration (PSR), reactive regeneration, or changing the medium surrounding the adsorbent to a fluid (e.g., supercritical CO_2) that extracts the adsorbate. Among the aforementioned techniques, TSR and PSR are common methods of adsorbent regeneration [29].

Furthermore, the polymer could be applied to vinasse wastewater from the bioethanol industry. It is characterized as a liquid residue in acidic conditions with a pH of less than 4, a brownish color, and a distinctive odor. It contains a high chemical oxygen demand (COD) value of more than 100,000 mg/L. It was estimated that in producing one liter of bioethanol, 12 to 15 times as much liquid waste is produced [30, 31]. This waste also contains complex inorganic and organic ion compositions with high pollution potential, such as phosphate and nitrate [1].

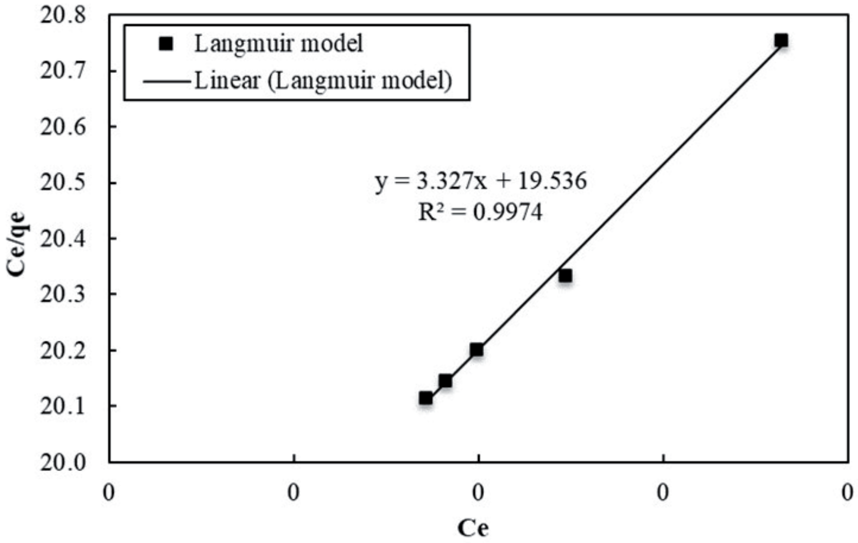


Fig. 9. Adsorption isotherm of the phosphate ions onto the adsorbent according to the Langmuir model.

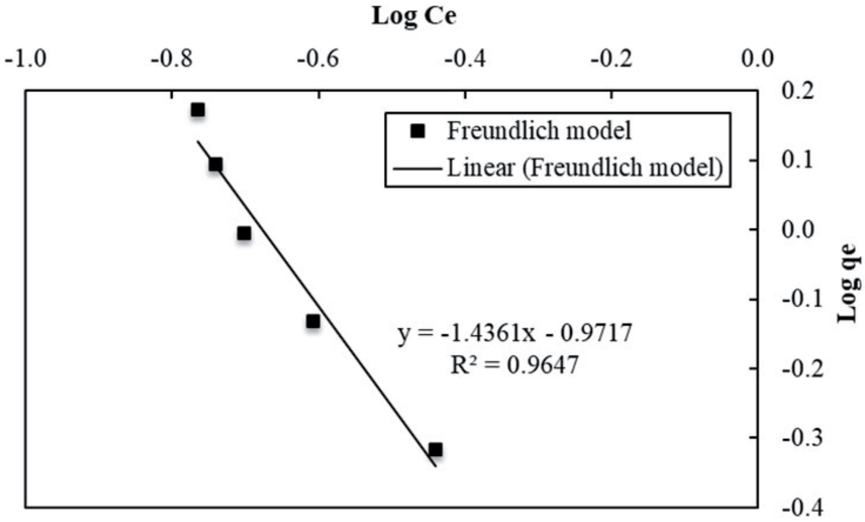


Fig. 10. Adsorption isotherm of the phosphate ions onto the adsorbent according to the Freundlich model.

Adsorption Kinetics

Adsorption isotherm calculations that occur in polymer MET in this research are Langmuir and Freundlich, as shown in Fig. 8. Adsorption isotherm is a mathematical relationship that describes how the amount of substance adsorbed by a surface changes along with the concentration of the substance in the fluid phase at a certain temperature and pressure. In addition, information obtained from adsorption isotherms is determined by the normalized plot to understand the type of adsorption isotherm that is suitable for it.

Based on Fig. 8(a), Langmuir adsorption indicates that as the equilibrium concentration (Ce) increases, the ratio of equilibrium concentration to the amount adsorbed (Ce/qe) decreases. This trend signifies an efficient adsorption process. In contrast, Fig. 8(b) illustrates Freundlich adsorption, where the natural logarithm of the amount adsorbed (ln qe) increases while the natural logarithm of the equilibrium concentration in solution (ln Ce) decreases. However, the linearity of the plots differs: Fig. 8(a) exhibits a clear linear trend across all variables, while Fig. 8(b) shows less linearity with variations in contact time and adsorbent mass. This suggests that the Langmuir adsorption isotherm is more appropriate for this study, further supported by the isotherm parameters presented in Tables 1 and 2.

The experimental data for phosphate adsorption onto an ammonium quaternary polymer at the optimal contact time of 20 minutes were analyzed using the linear forms of Isotherm Equations (4) and (6) to determine the intrinsic parameters of the Langmuir and Freundlich models. Additionally, the kinetic sorption data were evaluated with the linear forms of first-order models, which assume that sorption is proportional to the difference between the sorption capacity and the

Table 1. Parameter results for the Langmuir isotherm model.

Isotherm model	Parameter		
	K_L	q_t	R^2
Langmuir	5.8719	0.0511	0.9974

Table 2. Parameter results for the Freundlich isotherm model.

Isotherm model	Parameter		
	K_F	$1/n$	R^2
Freundlich	0.0366	-0.9717	0.9647

adsorbed concentration [32]. The Langmuir–Freundlich isotherm incorporates the fundamental assumptions of the Langmuir model while also accounting for surface heterogeneity. This makes it a practical and valuable model for studying adsorption equilibrium [33]. The adsorption behavior of phosphate ions onto quaternary ammonium polymer as an adsorbent is graphically represented in Figs. 9 and 10 for the Langmuir and Freundlich models, respectively. The resulting intrinsic parameters are summarized in Tables 1 and 2.

Linearized plots in Figs. 9 and 10 indicated that the adsorption of phosphate ions onto the adsorbent conducted in this study was best described by the Langmuir isotherm. The Langmuir adsorption model relies on the presumption that the adsorbed layer is a single molecule in thickness and that all sites are uniform or identical. This model is suitable for representing adsorption on sites with a uniform or homogeneous surface [34, 35]. The comparison of the parameter results based on Tables 1 and 2 also shows that the Langmuir model has a better determination coefficient value (R^2=0.9974) compared to the Freundlich model, suggesting that the adsorption of phosphate ion toward ammonium quaternary polymer is attributed to monolayer adsorption.

Conclusions

This study investigated the development of an ammonium quaternary polymer using the one-pot approach, utilized the polymer as an adsorbent, and studied the adsorption behavior between phosphate ions and polymer. Experimental parameters such as temperature, contact time, initial phosphate concentration, and adsorbent dosage affected the adsorption capacity and removal percentage of phosphate ions. The optimum condition for phosphate ions adsorption using ammonium quaternary polymer was obtained at a temperature of 25°C, contact time of 20 minutes, initial phosphate concentration of 30 ppm, and adsorbent dosage of 0.05 g, which achieved an adsorption capacity of 2.99 mg/g and removal percentage of phosphate 99.73%. The Langmuir model best describes the adsorption isotherm of phosphate ions on the adsorbent. While this study presents optimized conditions for phosphate adsorption, further discussion on the underlying adsorption mechanism, such as specific interactions between phosphate ions and the polymer matrix, would enhance understanding and provide insight into potential improvement strategies.

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Conflict of Interest

The authors declare no conflict of interest.

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