ISSN: 2086-3446 (print) 2621-508X (online) Journal homepage: http://ejournalunb.ac.id/index.php/JSN

JURNAL SAINS NATURAL

Publish by: Universitas Nusa Bangsa, Indonesia

ISOTHERM ADSORPTION OF ION PHOSPHATE FROM VINASSE WASTE USING QUATERNARY AMMONIUM POLYMER AS ADSORBENT IN TERM EFFECT OF TEMPERATURE

Veranica[1)], Aster Rahayu[1)]*, Maryudi[1)], Dhias Cahya Hakika[1)], Lee Wah Lim[2)], Lia Anggresani[2)]

[1)] Department of Chemical Engineering, Faculty of Industrial Technology, Ahmad Dahlan University, Jl. Jend. Ahmad Yani, Banguntapan, Bantul, Yogyakarta, Indonesia 55166

[2)] Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu, Japan, 501-1193

ARTICLE INFO

Article history:
Received 15 Mar 2024,
Revised 18 Mar 2024,
Accepted 29 Apr 2024,
Available online 29 May 2024

Keywords:

- ✓ *Vinasse*
- ✓ *Phosphate*
- ✓ *Adsorption*
- ✓ *Polymer*
- ✓ *Isotherm Langmuir*

**corresponding author:*
aster.rahayu@che.uad.ac.id

Phone: -
https://doi.org/10.31938/jsn.v 14i2.720

ABSTRACT

Vinasse liquid waste is a waste product resulting from the ethanol distillation process. Phosphate in high concentrations can harm the environment, such as by polluting water sources and underground surfaces. In this research, adsorption of phosphate ions was carried out in vinasse waste to remove these pollutants using quaternary ammonium polymers. The study examined the effect of vinasse waste sample temperature on the adsorption of phosphate ions. The first step in this work was to create a quaternary ammonium polymer utilising a one-pot technique using 2-[methacryloyloxy)ethyl trimethylammonium chloride solution, also referred to as META. Subsequently, the adsorption process was performed using temperature variations of 25, 30, 40, 50, and 60 ℃. Phosphate ion adsorbance was measured with UV-Vis spectrometers at a wavelength of 880 nm. The quaternary ammonium polymer succeeded in adsorbing the phosphate ion content of the vinasse waste at an optimal temperature of 40 ℃, with an adsorption capacity of 3.78 mg/L and a removal efficiency of 75.70%. The adsorption isotherm model for phosphate ions onto quaternary ammonium polymer was studied using the Freundlich and Langmuir equations. The obtained data indicated that the Langmuir isotherm model, with an R^2value of 0.9921, is well-suited for describing the adsorption behaviour in this research.

INTRODUCTION

One of the most significant environmental issues facing the globe today is water contamination caused by nutrients like phosphate ions. A phosphate concentration of 100 µg/L can lead to river eutrophication or excessive algal growth. The main effect of this phenomenon is a decrease in the quantity of carbon dioxide and sunlight that enters the water, thereby diminishing the amount of dissolved oxygen (Schindler et al, 2016). Phosphate compounds contribute to the accumulation of deposits in water pipes, leading to obstruction and potentially impeding the release of hazardous pollutants, such as arsenic (Legasari et al., 2023). In the industrial sector, the presence of phosphate compounds in drinking water leads to high maintenance costs. A significant portion of these pollutants comes from industries producing liquid waste. For example, the sugar business produces large amounts of vinasse, a liquid waste, and bagasse, a solid waste (Colin et al., 2016). Vinasse is a liquid waste produced at a sugar factory during the ethanol distillation process, typically involving a heating procedure ranging from 85 to 90 ℃ (Moraes et al., 2015). Vinasse waste contains the following: water, esters, alcohols, phenolic compounds, fermented sugars, organic acids, and furans (Lorenzo-Santiago et al., 2023). According to Álvarez (2021), vinasse contains high organic matter, high lipid concentration, low pH, and high COD and BOD content (Hoarau et al, 2018). Consequently, its discharge poses environmental problems, leading to water pollution, which usually occurs in irrigation on agricultural land (Álvarez et al., 2021; Christofoletti et al., 2013; Fagier et al., 2016). Therefore, disposing of unprocessed vinasse in aquatic and terrestrial environments can pose environmental risks (Reis et al., 2019; Fito et al., 2019). Phosphate contamination is an anionic pollution of surface and subsurface water sources, posing risks to both natural ecosystems and human health due to

elevated concentrations of phosphate ions, that can adversely affect both humans and ecosystems. Clean water quality is one crucial factor that must be considered to preserve ecosystem balance and human health (Nguyen et al., 2014).

Utilizing conventional water treatment techniques, including filtering and softening with lime, to eliminate contaminants from water is difficult due to their high labor and expense requirements. Furthermore, it takes longer to maintain and replace chemicals or filter media. The removal of dissolved nutrients from water and wastewater has been studied using various physicochemical and biological techniques. The process of adsorption highlights the elimination of phosphate ions from wastewater. Even at comparatively low phosphorus concentrations, its excellent selectivity makes this a straightforward, affordable, simple to set up, and very effective technique, resulting in less sludge production (Loganathan et al., 2014). The wastewater treatment industry frequently uses adsorption as a treatment method, because of its ease of operation and potential for adsorbent reuse, which sets it apart from other approaches. When using the adsorption method, developing a cost-effective and efficient adsorbent to remove phosphate from water is essential.

Phosphate ion-contaminated water and waste have been treated using the ion exchange technique in multiple trials. This can lead to a decrease in the amount of contaminants present in wastewater. Using polymer adsorption media, the ion exchange technique separates contaminants found in wastewater. Certain heavy metals, both as ions and as organic molecules, can be adsorbed by this highly developed polymer. For the efficient adsorption of phosphate ions in aqueous solutions of 95.11%, a grafted polymer based on the monomer 2-[methacryloyloxy) ethyl] trimethylammonium chloride solution or META the one-pot approach method has been used to be synthesized (Rahayu et al., 2023). Furthermore, utilizing META to modify the surface of cocoa shells increased the proportion of phosphate ion adsorption by 92% (Rahayu et al., 2023). According to Aini's (2023) study, adding quaternary ammonium to CH-T resulted in a 96% removal effectiveness of phosphate and nitrate ions. Polymers have proven to be an effective tool for extracting dissolved organic substances (Aini, 2023), including phenols (Víctor-Ortega et al., 2016) and other aromatic compounds (Albatrni et al., 2019). Therefore, the quaternary ammonium polymer is expected to bind phosphate ions in vinasse waste as an adsorbent in this adsorption method. The present study aims to examine the temperature-dependent adsorption of phosphate ions in quaternary ammonium polymers synthesized by the one-pot approach method.

MATERIALS AND METHODS

Material and Apparatus

The primary material was monomer 2-[methacryloyloxy) ethyl] trimethyl ammonium chloride solution ($C_9H_{18}ClNO_2$) 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), trisodium phosphate (Na_3PO_4) from Wako 1st Grade, Japan. AIBN or 2,2'-azobisisobutyronitrile ($C_8H_{12}N_4$) were supplied by TCI (China). Methanol for analysis 99,95% (CH_3OH), ethanol for analysis 99,95% (C_2H_6O), potassium antimonyl (III) oxide tartrate ($K_2Sb_2C_8H_4O_{12}\cdot 3H_2O$), ammonium molybdate 99,98% ($(NH_4)_6Mo_7O_{24}$), ascorbic acid ($C_6H_8O_6$), sulfuric acid 95 % (H_2SO_4), and Fenolphthalei indicator ($C_{20}H_{14}O_4$), aquabides, and vinasse waste taken from the Madukismo sugar factory. The tools used in this research were a magnetic stirrer, Erlenmeyer, heating stove, Whatmann 42 paper, thermometer, cuvette, stopwatch, funnel, analytical balance, water bath, and UV-Vis spectrophotometer.

Methods

Synthesis of Quaternary Ammonium Polymer

Quaternary ammonium polymer produced through a one-pot approach polymerization process with optimum composition and conditions has been successfully used as an adsorbent (Rahayu et al., 2023). Before being filled into a cylindrical tube, the polymer solution consisting of 1.25 mL monomer META ($C_9H_{18}ClNO_2$), 0.375 mL EDMA ($C_{10}H_{14}O_4$), 0.35 mL ethanol (C_2H_6O), 1.4 mL poly (ethylene glycol) ((C2H4O)nH_2O), 1.75 mL isopropyl alcohol (C_3H_8O), and 0.005 g AIBN ($C_8H_{12}N_4$) was homogenized. Next, polymerization was left for 12 hours in a water bath at 70 ^oC (Rahayu et al., 2021). Figure 1 below is a reaction scheme for forming quaternary ammonium polymer, which will be used as an adsorbent to adsorb phosphate ions in vinasse waste.

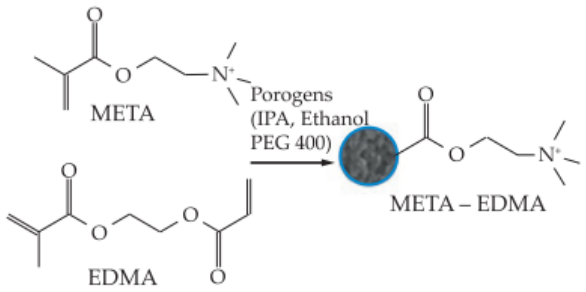


Figure 1. META Polymer Predicted Reaction Scheme (Rahayu et al., 2023)

$$q_e = \frac{(C0-Ce)x\,V}{w} \quad \ldots\ldots\ldots\ldots(1)$$

$$RE = \frac{C0-Ce\ x\ 100\,\%}{C0} \quad \ldots\ldots\ldots(2)$$

Where C_0 = initial concentration (mg/),
Ce = equilibrium concentration (mg/l)
W = adsorbent weight (g)
V = volume of solution (L)

RESULT AND DISCUSSION

The Adsorption Process Influences the Temperature of Vinasse Waste

Temperature variations were carried out to test the ability of quaternary ammonium polymers to remove phosphate e ions from vinasse waste. The adsorption process uses 3 grams of adsorbent mass with 100 mL of adsorbate solution, then shaken for 20 minutes with a temperature variation of 25, 30, 40, 50, and 60 °C, then filtered, and the filtrate added with phospho-molybdate reagent before being analysed by UV-Vis at 880 nm (Legasari et al., 2023). Equation 1 may be used to calculate the adsorption capacity (qe), and equation 2 can be used to calculate the percent removal efficiency (RE) value at equilibrium (mg/g and (%): (Rabiatul et al., 2020) (Aini et al., 2023).

Optimum Temperature of Phosphate Ions in Vinasse Waste

The optimum temperature is required for the adsorbent (quaternary ammonium polymer) during the maximum adsorption process of phosphate ions in vinasse waste until it reaches saturation. The temperature increase performed on vinasse waste samples shows the outcomes of examining phosphate ions in vinasse waste following adsorption using quaternary ammonium polymer with 25, 30, 40, 50, and 60 °C temperature variations. After reaching its optimum temperature, the amount of phosphate ions adsorbed will continue to rise until it does not exceed that point. The effect of temperature on phosphate ions in vinasse waste and ammonium polymer can be seen in Figure 2.

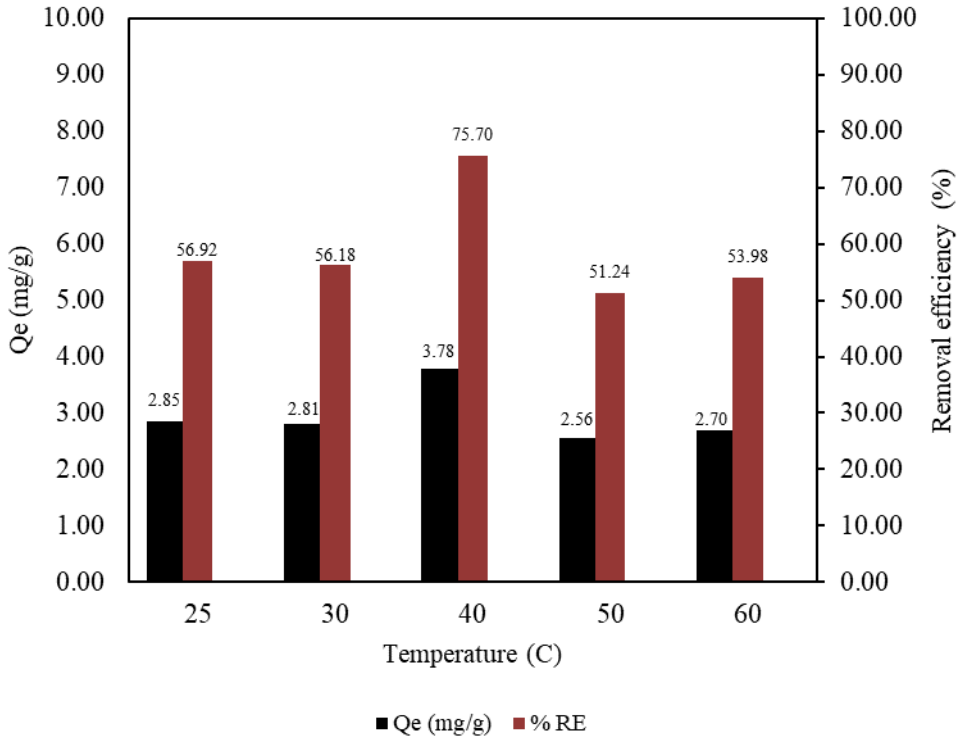


Figure 2. Effect of Temperature on Vinasse Waste and Quaternary Ammonium Polymer

Figure 1 shows the most significant concentration and efficiency of the phosphate ion adsorption at a temperature of 40 C, with a concentration of 3,78 mg/L and a phosphate adsorbent efficiency in vinasse wastes of 75.70%. Adsorption capacity shows the effect of temperature on the adsorption of phosphate ions contained in vinasse waste. Temperature has a significant influence on the efficiency of the adsorption process. The exothermic nature of the process was confirmed when it was discovered that the % phosphate removal dropped as the temperature rose from 40 to 60 °C. Increasing the temperature increases the system's thermal energy, increasing phosphate ions mobility, thereby encouraging increased desorption. As a result, the overall adsorption decreases (Mekonnen et al., 2020). The present study's findings are consistent with other investigations into the impact of temperatures ranging from 25 to 75°C on adsorption rates exceeding 60% (Zhang et al., 2021). The most efficient temperature for eliminating phosphate ions was 40 ºC, according to another study examining how temperature influences the adsorption of phosphate ions from rice husk (Yadav et al., 2015). An adsorption process will be carried out using other parameters to test different parameters, such as the time and mass of the quaternary ammonium polymer adsorbent.

One source of phosphate contamination in the environment is waste vinasse, which is usually produced from the manufacture of bioethanol from sugarcane, which often contains high concentrations of phosphates which is potential to harm the environment and human health, so new solutions are needed to deal with it. Thus, this research is expected to produce an effective and sustainable way to solve this problem. By using quaternary ammonium polymers as an adsorbent or ion exchanger, the phosphate content in vinasse waste can be reduced or eliminated. The innovation of this research is the creation of an ammonium quaternary polymer that is synthesized through a one-pot approach, which makes it more efficient to use as an adsorbent. We increased the phosphate adsorption capacity and composition with this polymer method. Furthermore, for the sustainability of this study, these synthetic ammonium quaternary polymers can be recycled after use with desorption methods to reduce the environmental impact.

Adsorption Isotherm

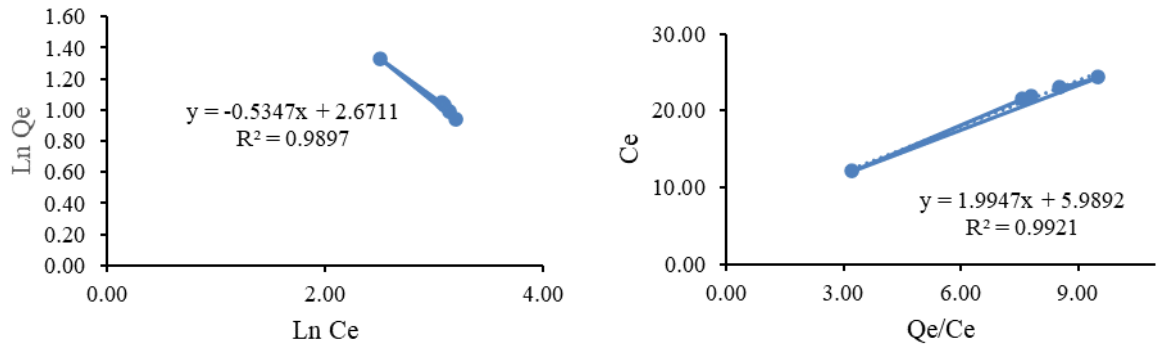
The temperature difference between the adsorbate in the liquid (25–60 ºC) and the amount of adsorbate adsorbed per unit mass of the adsorbent at a fixed time of 20 minutes produces an isotherm that helps explain the adsorption process. To illustrate the link between the amount of substance adsorbed by the adsorbent at different temperatures, this study uses the Freundlich and Langmuir adsorption isotherm equations. To illustrate the Freundlich isotherm model, look at equation 3 (Meila et al, 2021).

$$\text{Log qe} = \log K_f + 1/n \log \text{Ce} \quad \ldots\ldots\ldots (3)$$

where Ce is the solution's equilibrium concentration (mg/L), K_f is the adsorption constant in the multilayer, 1/n is the indicative constant of the adsorption intensity, and qe is the amount of phosphate adsorbed per mass of adsorbent (mg/g). Equation 4 below depicts the Langmuir isotherm model (Meila et al., 2021).

$$\frac{ce}{qe} = \frac{1}{KLqm} + \frac{1}{qm}\text{Ce} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

According to the Langmuir adsorption isotherm model, adsorption has the same adsorbate affinity, and adsorption at one location is independent of adsorption at an adjacent location. The following equation displays the Langmuir isotherm.



a) Isoterm Freundlich b) Isoterm Langmuir

Figure 3. The Plot of Freundlich and Langmuir's Adsorption Isotherm

The Langmuir equation assumes the adsorbent surface is homogenous, which means that the adsorption process spreads uniformly throughout the surface and that only one adsorbent molecule is adsorbed on one side of the adsorbent. On the other hand, the Freundlich equation contends that the surface of the adsorbent is heterogeneous. This research's equilibrium equation model, which best captures the reactions that occur, is shown by the correlation coefficient (R^2). The Freundlich isotherm model has a lower R^2 value than the Langmuir model, which is closer to 1. The picture 3b. above shows that the R^2 value for the Langmuir isotherm is 0.9921, which is higher than the Freundlich isotherm, namely 0.9897. The linear equation y = 1.9947x + 5.9892 is obtained from the Langmuir isotherm image. As shown in Table 1 below, the values of K_f and n, as well as the constant values of the equation, will be obtained.

Table 1. Phosphate Adsorption Isotherm Model on Vinasse Waste

Langmuir Adsorption Isotherm		
R^2	K_f (L g^{-1})	N
0,9921	0,1669	3,002

Table 1 concludes that the Langmuir adsorption isotherm model, whose graph is displayed in Figure 3b, is the more appropriate adsorption isotherm model for the adsorption of phosphate ions in vinasse waste on ammonium polymers. This indicates that phosphate ion adsorption occurs as a monolayer adsorption process on the surface of the quaternary ammonium polymer. It is presumed that the polymer surface's active sites are uniform or have an equal capacity to adsorb adsorbate. The findings of this study are pertinent to earlier investigations into the monolayer adsorption process that took place during the phosphate anions' adsorption with bentonite (Rabiatul et al., 2020).

CONCLUSION

The research that has been done leads to the conclusion that temperature significantly impacts the adsorption process's efficiency. With a removal efficiency of 75.70% and an adsorption capacity of 3.78 mg/L, the ideal contact temperature is 40 C. The Langmuir isotherm, with values of N = 3.002 and K_f = 0.1669 mg/g, is the adsorption isotherm of the phosphate ion adsorption system on vinasse waste follows. Drawing from this, the adsorption of phosphate by the ammonium polymer is mainly explained by the Langmuir isotherm model, indicating that the adsorbent surface forms a monolayer by binding the adsorbate molecules. Future research on this adsorbent should focus on determining the impact of the quaternary ammonium polymer's mass and contact time, and characterizing the adsorbent is also anticipated.

ACKNOWLEDGMENT

Grant Number 0003/PFR/LPPM UAD/VI/2023 from the Ministry of Education, Culture, Research, and Technology Indonesia's Directorate of Research, Technology, and Community Service is warmly acknowledged by the authors for providing financial support for this research.

REFERENCES

Aini, N., Mufandi, I., Jamilatun, S., & Rahayu, A. (2023). Exploring Cacao Husk Waste – Surface Modification, Characterization, and its Potential for Removing Phosphate and Nitrate Ions. *Journal of Ecological Engineering*, *24*(12), 282–292. https://doi.org/10.12911/22998993/174003

Albatrni, H., Qiblawey, H., Almomani, F., Adham, S., & Khraisheh, M. (2019). Polymeric adsorbents for oil removal from water. *Chemosphere*, *233*, 809–817. https://doi.org/10.1016/j.chemosphere.2019.05.263

Álvarez, O. E. R., Nicolás Vázquez, M. I., Oñate-Garzón, J., & Arango, C. A. (2021). Validation by molecular dynamics of the major components of sugarcane vinasse, on a surface of calcium carbonate (Calcite). *Molecules*,*26*(8),1–11. https://doi.org/10.3390/molecules26082353

Christofoletti, C. A., Escher, J. P., Correia, J. E., Marinho, J. F. U., & Fontanetti, C. S. (2013). Sugarcane vinasse: Environmental implications of its use. *Waste Management*, *33*(12),2752–2761. https://doi.org/10.1016/j.wasman.2013.09.005

Colin, V. L., Juárez Cortes, Á. A., Aparicio, J. D., & Amoroso, M. J. (2016). Potential

application of a bioemulsifier-producing actinobacterium for treatment of vinasse. *Chemosphere*, *144*, 842–847. https://doi.org/10.1016/j.chemosphere.2015.09.064

Fagier, M. A., Ali, E. A., Tay, K. S., & Abas, M. R. B. (2016). Mineralization of organic matter from vinasse using physicochemical treatment coupled with Fe2+-activated persulfate and peroxymonosulfate oxidation. *International Journal of Environmental Science and Technology*, *13*(4),1189–1194. https://doi.org/10.1007/s13762-016-0963-x

Fito, J., Tefera, N., & Van Hulle, S. W. H. (2019). Sugarcane biorefineries wastewater: bioremediation technologies for environmental sustainability. *Chemical and Biological Technologies in Agriculture*, *6*(1), 1–13. https://doi.org/10.1186/s40538-019-0144-5

Hoarau, J., Caro, Y., Grondin, I., & Petit, T. (2018). Sugarcane vinasse processing: Toward a status shift from waste to valuable resource. A review. *Journal of Water Process Engineering*, *24*(January), 11–25. https://doi.org/10.1016/j.jwpe.2018.05.003

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and recovery of phosphate from water using sorption. *Critical Reviews in Environmental Science and Technology*, *44*(8), 847–907. https://doi.org/10.1080/10643389.2012.741311

Lorenzo-Santiago, M. A., Rodríguez-Campos, J., Rendón-Villalobos, R., García-Hernández, E., Vallejo-Cardona, A. A., & Contreras-Ramos, S. M. (2023). Thermal Treatment to Obtain 5-Hydroxymethyl Furfural (5-HMF), Furfural and Phenolic Compounds from Vinasse Waste from Agave. *Molecules*, *28*(3). https://doi.org/10.3390/molecules28031063

Meila Anggriani, U., Hasan, A., & Purnamasari, I. (2021). Kinetika Adsorpsi Karbon Aktif Dalam Penurunan Konsentrasi Logam Tembaga (Cu) dan Timbal (Pb). *Universitas Sriwijaya*, *12*(02), 29–37. https://jurnal.polsri.ac.id/index.php/kimia/index

Mekonnen, D. T., Alemayehu, E., & Lennartz, B. (2020). Removal of phosphate ions from aqueous solutions by adsorption onto leftover coal. *Water (Switzerland)*, *12*(5), 1–15. https://doi.org/10.3390/W12051381

Moraes, B. S., Zaiat, M., & Bonomi, A. (2015). Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: Challenges and perspectives. *Renewable and Sustainable Energy Reviews*, *44*, 888–903. https://doi.org/10.1016/j.rser.2015.01.023

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Nguyen, T. V., Zhang, J., Liang, S., Chen, S. S., & Nguyen, N. C. (2014). A comparative study on different metal loaded soybean milk by-product “okara” for biosorption of phosphorus from aqueous solution. *Bioresource Technology*, *169*, 291–298. https://doi.org/10.1016/j.biortech.2014.06.075

Rabiatul, S., Islam, U., Alauddin, N., Sutarno, S., Mada, U. G., Suyanta, S., & Mada, U. G. (2020). *Indonesian Journal of Chemical Research Adsorption-Desorption Studies of Phosphate on CTAB Modified Bentonite Indonesian Journal of Chemical Research*. *January*. https://doi.org/10.30598/ijcr.2020.8-sra

Rahayu, A., Hakika, D. C., Alfi, N., Amrillah, Z., & Veranica, V. (2023). *Synthesis and characterization of ammonium polymer for anion removal in aqueous solutions*. *10*, 537–543. https://doi.org/10.14314/polimery.2023.10.3

Rahayu, A., Jamilatun, S., Fajri, J. A., & Lim, L. W. (2021). Characterization of Organic Polymer Monolith Columns Containing Ammonium Quaternary As Initial Study For Capillary Chromatography. *Elkawnie*, *7*(1), 119. https://doi.org/10.22373/ekw.v7i1.8764

Reis, C. E. R., Bento, H. B. S., Alves, T. M., Carvalho, A. K. F., & De Castro, H. F. (2019). Vinasse treatment within the sugarcane-ethanol industry using ozone combined with anaerobic and aerobic microbial processes. *Environments - MDPI*, *6*(1). https://doi.org/10.3390/environments6010005

Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E., & Orihel, D. M. (2016). Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science and Technology*, *50*(17), 8923–8929. https://doi.org/10.1021/acs.est.6b02204

Víctor-Ortega, M. D., Ochando-Pulido, J. M., & Martinez-Ferez, A. (2016). Phenols removal from industrial effluents through novel polymeric resins: Kinetics and equilibrium studies. *Separation and Purification Technology*,*160*. https://doi.org/10.1016/j.seppur.2016.01.023

Yadav, D., Kapur, M., Kumar, P., & Mondal, M. K. (2015). Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue. *Process Safety and Environmental Protection*, *94*(C), 402–409. https://doi.org/10.1016/j.psep.2014.09.005

Zhang, Y., & Li, R. (2021). Effect of Reaction Temperature on Adsorption Efficiency using Computer Mathematical Statistics Visible Spectorphotometer. *Journal of Physics: Conference Series*, *2083*(3), 0–6. https://doi.org/10.1088/1742-6596/2083/3/032072