International Journal of Multidisciplinary Research and Publications
ISSN (Online): 2581-6187

Calamansi Peels *(Citrus macrocarpa)* as Biosorbent for Phosphate Removal from Simulated Wastewater

Julie Rose T. Baillo[1], Engr. Ilde B. Deloria[2]
[1]Department of Sanitary Engineering, Western Mindanao State University, Zamboanga City, Philippines-7000
[2]College of Engineering and Technology, Western Mindanao State University, Zamboanga City, Philippines-7000
Email address: julieroset.baillo02@gmail.com, ilde.deloria@wmsu.edu.ph

***Abstract*—** *Excessive phosphate discharge from domestic sources, particularly laundry effluents, contributes to eutrophication and the degradation of aquatic ecosystems. This study evaluated the potential of calamansi peels (Citrus macrocarpa), an abundant agricultural waste in the Philippines, as a low-cost biosorbent for phosphate removal from simulated laundry wastewater. Non-activated calamansi peels (NACP) and caustic soda–activated calamansi peels (ACP) were prepared and compared through batch adsorption experiments. Simulated laundry wastewater was formulated with an initial phosphate concentration of 30 mg/L and adjusted to pH 10 to represent typical conditions. Biosorbent dosages of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g/L were applied with a contact time of 60 minutes. Phosphate concentrations were determined using the ascorbic acid method and analyzed via UV–Vis spectrophotometry at 880 nm. Descriptive statistics and a paired t-test were used to evaluate removal efficiency and compare performance. Results showed that phosphate removal efficiency increased with increasing dosage for both biosorbents; however, NACP consistently exhibited higher adsorption capacity, achieving a maximum removal efficiency of 82.69% at 3.0 g/L, while ACP has achieved only 32.61%, indicating that the applied chemical activation did not enhance adsorption performance. Statistical analysis confirmed a significant difference between the two materials (p=0.000118). Although NACP effectively reduced phosphate concentration, the treated effluent remained outside the pH limits set by DENR Administrative Order No. 2021-19, necessitating further treatment. Overall, raw calamansi peel demonstrates strong potential as an economical biosorbent for phosphate removal. However, post-treatment pH adjustment is required to meet regulatory standards. Future studies should investigate alternative activation methods, improve filtration techniques, and validate findings using actual wastewater at a pilot scale while increasing sample size for enhanced reliability.*

Keywords— *Calamansi peels (Citrus macrocarpa); Phosphate removal; Biosorption; Simulated laundry wastewater; Domestic phosphate pollution; Caustic soda activation; non-activated calamansi peel (NACP); Activated calamansi peel (ACP); Phosphate adsorption efficiency; Agricultural waste valorization; Eutrophication control; Sustainable wastewater treatment; UV–Vis spectrophotometry; Ascorbic acid method; Low-cost environmental remediation.*

I. INTRODUCTION

Phosphate is an essential inorganic compound composed of a phosphorus atom bonded to four oxygen atoms. This molecular structure serves as a fundamental building block for many vital biological processes, including cellular signalling, DNA and RNA synthesis, and energy production. Beyond its biological importance, phosphates are also widely used in industrial applications such as fertilizers, food additives, and detergents, making them indispensable to both natural and human systems (Fernández-García et al., 2017).

However, while phosphate is crucial in small amounts, its excessive accumulation in aquatic environments has become a global concern. Agricultural runoff, detergent use, and industrial effluents frequently introduce high phosphate concentrations into water systems, leading to eutrophication—a condition that depletes dissolved oxygen, accelerates algal blooms, and disrupts the balance of aquatic ecosystems. Because of its ecological consequences, phosphate is recognized as one of the most alarming contaminants in global water supplies, highlighting the urgent need for efficient, low-cost, and sustainable removal strategies (United Nations Environment Programme, 2024).

To prevent eutrophication and maintain ecological balance, phosphate concentrations in water bodies are regulated under Department of Environment and Natural Resources Administrative Order (DAO) 2021-19. The allowable phosphate limit is 0.025 mg/L for Classes AA to C waters, 0.05 mg/L for Class D waters, and 0.1–0.4 mg/L for marine waters depending on classification.

Biosorption using agricultural by-products has emerged as a sustainable and cost-effective phosphate removal method. Citrus peels are particularly promising due to their cellulose, hemicellulose, lignin, and pectin content, which provide functional groups capable of binding phosphate ions through hydrogen bonding, ion exchange, and electrostatic interactions. Their porous structure and large surface area further enhance adsorption, while thermal or chemical activation can improve efficiency. Previous studies have reported phosphate removal efficiencies of up to 100% using lemon and mandarin peels.

This paper explored the effectiveness of non-activated and caustic soda-activated calamansi *(Citrus macrocarpa)* peels as biosorbents for phosphate removal from simulated laundry wastewater. Specifically, it seeks to determine and compare the phosphate adsorption efficiencies of both biosorbents under controlled conditions of 30 mg/L phosphate concentration, pH 10, varying dosages ranging from 0.5 to 3.0 g/L, and a contact time of 60 minutes. Furthermore, the study aims to assess the percentage reduction of phosphate achieved by each treatment and evaluate the resulting effluent quality based on the standards set by DAO 2021-19.

Therefore, this study will focus exclusively on phosphate removal, excluding other water quality parameters such as COD, BOD, nitrates, and heavy metals, since phosphate was

Julie Rose T. Baillo, and Engr. Ilde B. Deloria, M.Eng., "Calamansi Peels *(Citrus macrocarpa)* as Biosorbent for Phosphate Removal from Simulated Wastewater," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 9, Issue 1, pp. 1078-1082, June 2026.

identified as a primary contributor to eutrophication in aquatic ecosystems. As the study was conducted on a small laboratory scale, the findings had limited real-world applicability and required further validation for industrial implementation. Additionally, variations in calamansi peel characteristics—such as source, maturity, and preparation method—may have influenced adsorption efficiency, and simulated wastewater was used instead of actual wastewater due to equipment constraints.

II. METHODOLOGY

2. 1 Research Design

This study evaluated the efficiency of activated calamansi peel (ACP) and non-activated calamansi peel (NACP) in removing phosphate from simulated laundry wastewater. Experiments were conducted in the Department of Environmental Engineering laboratory. Phosphate concentrations were measured using an 880 nm UV-Vis spectrophotometer through the ascorbic acid method with adsorbent dosages ranging from 0.5 to 3 g/L were tested to determine the effect of biosorbent quantity on phosphate removal efficiency and pH.

2.2 Research Locale and Sampling Site

The experimentation process was conducted in a small-scale laboratory of the Department of Environmental Engineering, Western Mindanao State University, Zamboanga City. Simulated wastewater was used instead of actual wastewater to maintain constant phosphate concentrations, reduce the influence of external pollutants, and address equipment and instrumentation limitations.

2.3 Materials and Equipment

Calamansi *(Citrus macrocarpa)* peels were used as the raw material for biosorbent preparation, with chemical activation performed using a caustic soda solution. The peels were dried, ground, and sieved to obtain a uniform particle size, while an analytical balance ensured accurate dosage measurements.

Standard laboratory glassware was used for solution preparation, mixing, and filtration, and batch adsorption experiments were conducted using beakers and sampling containers. Phosphate concentrations were analyzed using the ascorbic acid method with an 880 nm UV-Vis spectrophotometer. Throughout the study, researchers wore appropriate personal protective equipment, including laboratory gowns, safety goggles, nitrile gloves, and face masks.

2.4 Preparation of Adsorbents

Approximately 8 kilograms of calamansi peels were collected from a local fruit stall in Barangay Tugbungan, Zamboanga City and were thoroughly cleaned using tap water before rinsing it with distilled water. The peels are divided into 2 batches. For NACP preparation, 3.62 kg of peels were weighed, divided into batches, sun-dried for 48 hours, and oven-dried at 110°C for 2 hours to reduce moisture content. The dried biomass, weighing 1.21 kg after drying, was cooled, ground, and sieved through a 40-mesh screen to obtain a uniform particle size. A total of 1.09 kg of powdered NACP was then stored in labeled airtight containers.

For ACP preparation, 3.81 kg of pre-treated peels were chemically activated using a 0.5 M sodium hydroxide (NaOH) solution prepared by dissolving 100 g of NaOH in 5 L of distilled water and applied at a 1:10 weight-to-volume ratio. The peels were immersed in the solution for 12 hours with periodic stirring, then drained, rinsed repeatedly with distilled water, and subjected to the same sun-drying and oven-drying procedures. After drying, the biomass weighed 1.32 kg and was subsequently cooled, ground, and sieved through a 40-mesh screen. The resulting 1.17 kg of ACP powder was stored in labeled airtight containers and kept in a cool, dry environment until use in the adsorption experiments.

2.5 Preparation and Analysis of Phosphate Solution

A phosphate stock solution was prepared by dissolving 1.005 g of potassium dihydrogen phosphate (KH_2PO_4) in 1 L of distilled water, with continuous stirring to ensure complete dissolution. Simulated laundry wastewater was then prepared by mixing 3 mL of the stock solution with 97 mL of distilled water in 100 mL beakers and stirring for 1 minute. The pH was adjusted to 10 by adding a sodium hydroxide (NaOH) solution, prepared by dissolving 0.4 g of NaOH flakes in 100 mL of distilled water, dropwise while monitoring with a pH meter. For phosphate analysis using the ascorbic acid method, the molybdenum blue reagent was prepared by sequentially mixing 50 mL sulfuric acid, 15 mL ammonium molybdate, 5 mL potassium antimonyl tartrate, and 30 mL ascorbic acid.

2.6 Experimental Setup and Procedure

The UV-Vis spectrophotometer was calibrated using phosphate standard solutions prepared from the stock solution prior to experimental procedure. Batch adsorption experiments were then conducted to evaluate the phosphate removal efficiency of non-activated calamansi peel (NACP) and activated calamansi peel (ACP) at biosorbent dosages of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g/L. The initial pH of each phosphate solution was measured before adding the biosorbents. The mixtures were stirred for 1 minute and allowed to stand for 1 hour at room temperature to facilitate adsorption. Each treatment was performed in duplicate, resulting in 24 samples, including the control. After adsorption, the samples were filtered using Whatman Grade 1 filter paper, and the final pH was recorded. A 25 mL portion of each filtrate was then reacted with 4 mL of molybdenum blue reagent and allowed to stand for 10 minutes for color development. Finally, 1 mL of the reacted solution was transferred into a cuvette, and the absorbance was measured at 880 nm using a UV-Vis spectrophotometer to determine the residual phosphate concentration.

III. RESULTS AND DISCUSSION

This chapter presents the results of phosphate removal using non-activated calamansi peel (NACP) and caustic soda–activated calamansi peel (ACP) as biosorbents in simulated laundry wastewater.

NACP and ACP underwent substantial weight reduction

Julie Rose T. Baillo, and Engr. Ilde B. Deloria, M.Eng., "Calamansi Peels *(Citrus macrocarpa)* as Biosorbent for Phosphate Removal from Simulated Wastewater," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 9, Issue 1, pp. 1078-1082, June 2026.

following the initial drying process due to the oven-drying method employed. NACP decreased from 3.62 kg to 1.21 kg, resulting in a moisture content of 66.58%, while ACP decreased from 3.81 kg to 1.32 kg, with a corresponding moisture content of 65.35%.

TABLE I. Weight Reduction and Moisture Content

Sample	Initial Weight (kg)	Final Weight (kg)	Moisture Content (%)
NACP	3.62	1.21	66.58
ACP	3.81	1.32	65.35

Linear regression analysis of adsorbance versus concentration yielded the equation y=0.0429x+0.3587, with a correlation coefficient (R=0.957). The high R^2 value indicates good linearity, suggesting that a large proportion of the variation in adsorbance is directly related to changes in concentration. This demonstrates that the method is capable of producing consistent and predictable results. To further assess the applicability of the calibration curve, an inverse relationship between concentration and adsorbance was also evaluated. The resulting regression equation, y=21.357x−5.5508, with the same correlation coefficient (R=0.957). These results demonstrate that the analytical method provides reliable and reproducible measurements within the tested concentration range.

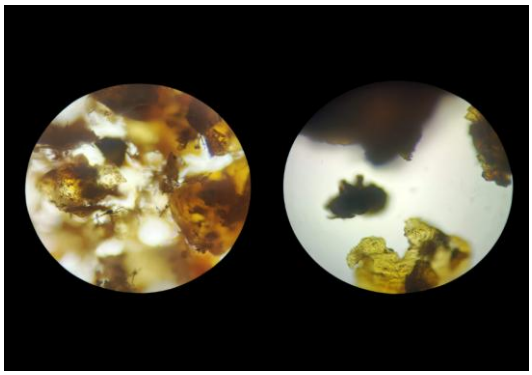

Fig. 1. Microscopic Analysis of NACP.

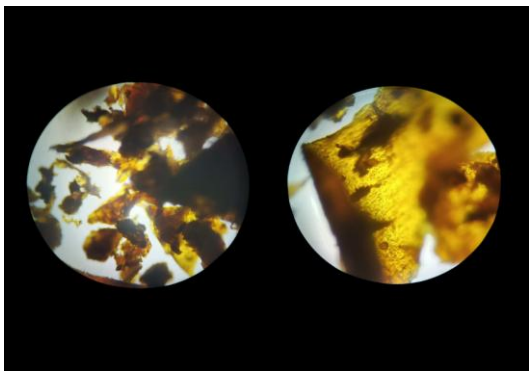

Fig. 2. Microscopic Analysis of ACP.

The physical characterization of the biosorbents showed clear differences between NACP and ACP. ACP exhibited a darker color due to sodium hydroxide activation, which promotes partial carbonization and structural changes in the biomass. In contrast, NACP appeared lighter, finer, and more free-flowing, while ACP tended to form larger agglomerated particles as a result of chemical treatment and surface modification.

Microscopic analysis further highlighted these differences. NACP showed irregular, heterogeneous particles with darker and less uniform features, suggesting a less compact structure. Meanwhile, ACP displayed more defined, larger, and brighter particles with a more uniform and consolidated appearance, indicating improved structural modification after chemical activation.

TABLE III. Initial and Final pH Level of NACP

Dosage (g)	pH Level			
	Trial 1		Trial 2	
	Initial	Final	Initial	Final
0.5	10	5.76	10	4.83
1	10	5.38	10	4.5
1.5	10	4.5	10	4.52
2	10	4.33	10	4.41
2.5	10	4.33	10	4.37
3	10	4.81	10	4.87

TABLE IIIII. Initial and Final pH Level of ACP

Dosage (g)	pH Level			
	Trial 1		Trial 2	
	Initial	Final	Initial	Final
0.5	10	9.82	10	9.74
1	10	9.7	10	9.8
1.5	10	9.85	10	9.71
2	10	9.64	10	9.82
2.5	10	9.57	10	9.72
3	10	9.57	10	9.57

NACP significantly lowered the pH to approximately 4.3–5.8 across all dosages, indicating strong interaction with phosphate ions and possible proton exchange during adsorption. In contrast, ACP caused only a slight pH change, remaining in the alkaline range of about 9.6–9.9, likely due to buffering effects from chemical activation. Therefore, neither biosorbent consistently met DENR Class C water quality standards (pH 6.0–9.5). NACP caused excessive acidification, while ACP remained slightly above the allowable range. These findings suggest that although both materials can influence phosphate removal, additional optimization or post-treatment is necessary to ensure safe effluent pH levels.

TABLE IVV. Phosphate Adsorption Performance of NACP

Dosage (g)	Trial 1			Trial 2		
	Adsorbance	Concentration	Removal (%)	Adsorbance	Concentration	Removal (%)
0.5	0.927	14.248	52.507	1.44	25.204	15.985
1	0.874	13.116	56.280	1.219	20.484	31.719
1.5	0.764	10.767	64.111	0.947	14.675	51.083
2	0.719	9.805	67.315	0.817	11.899	60.338
2.5	0.607	7.413	75.289	0.726	9.955	66.817
3	0.694	9.272	69.095	0.312	1.113	96.291

Phosphate adsorption performance of NACP and ACP at dosages of 0.5–3 g/L showed that biosorbent dosage

Julie Rose T. Baillo, and Engr. Ilde B. Deloria, M.Eng., "Calamansi Peels *(Citrus macrocarpa)* as Biosorbent for Phosphate Removal from Simulated Wastewater," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 9, Issue 1, pp. 1078-1082, June 2026.

significantly influenced removal efficiency. For NACP, removal efficiency increased with dosage, ranging from 52.51% to 75.29% (Trial 1) and 15.99% to 96.29% (Trial 2), with corresponding decreases in phosphate concentration from 30 mg/L to as low as 1.113 mg/L. A slight deviation was observed at 3 g in Trial 1, but overall trends showed strong dose-dependent improvement due to increased available adsorption sites.

TABLE V. Phosphate Adsorption Performance of ACP

Dosage (g)	Trial 1			Trial 2		
	Adsorbance	Concentration	Removal (%)	Adsorbance	Concentration	Removal (%)
0.5	1.636	29.391	2.031	1.55	27.554	8.154
1	1.487	26.208	12.639	1.374	23.795	20.684
1.5	1.384	24.008	19.972	1.327	22.791	24.030
2	1.37	23.709	20.969	1.277	21.723	27.590
2.5	1.263	21.424	28.586	1.245	21.040	29.868
3	1.258	21.317	28.942	1.155	19.117	36.275

In contrast, ACP showed much lower but gradually increasing performance, with removal efficiencies ranging from 2.03% to 28.94% (Trial 1) and 8.15% to 36.28% (Trial 2), and concentrations only decreasing to about 19.117–21.317 mg/L at 3 g. Although increasing dosage improved ACP performance, its adsorption capacity remained significantly weaker than NACP.

Hence, NACP consistently outperformed ACP due to its stronger phosphate affinity and greater reactivity, while ACP showed limited adsorption despite dosage increases. These contrasting results highlight the superior efficiency of NACP for phosphate removal under the experimental conditions.

TABLE VI. Paired t-Test Results

Dosage	Removal % (NACP)	Removal % (ACP)	p-Value
0.5	34.246	5.093	0.000118
1	44.000	16.662	
1.5	57.597	22.001	
2	63.827	24.279	
2.5	71.053	29.227	

The comparative evaluation of NACP and ACP showed that NACP consistently outperformed ACP in phosphate adsorption under all tested dosages and trials. NACP achieved much higher removal efficiencies (52.51%–96.29%) and significantly reduced phosphate concentration due to its ability to shift the solution to acidic conditions (pH 4.3–5.8), which enhanced electrostatic attraction and adsorption. In contrast, ACP showed lower efficiencies (2.03%–36.28%) because it remained alkaline after treatment, limiting phosphate uptake despite dosage increases. Statistical analysis confirmed that the difference was significant (p=0.000118). Overall, NACP demonstrated superior phosphate removal performance, while ACP showed limited effectiveness under the experimental conditions.

IV. CONCLUSION

This chapter presents the conclusions and recommendations from the study conducted on NACP and ACP as biosorbents for phosphate removal in simulated laundry wastewater. The findings and discussions presented in the preceding chapters form the basis for the insights discussed herein. Additionally, this chapter highlights the theoretical and practical implications of the study and provides recommendations for future research.

The laboratory results reveal that NACP exhibited significantly higher phosphate removal efficiency compared to ACP across all tested dosages (0.5–3.0 g/L). NACP achieved removal efficiencies ranging from 52.51% to 82.69%, with phosphate concentration reduced from 30 mg/L to as low as 5.19 mg/L, demonstrating strong adsorption performance. In contrast, ACP showed much lower removal efficiencies ranging only from 2.03% to 32.61%, with higher residual phosphate concentrations remaining in the treated solution. These results indicate that non-activated calamansi peel is more effective for phosphate adsorption than its chemically activated counterpart under the experimental conditions.

Based on the findings, the comparative evaluation of NACP and ACP using a paired t-test confirmed a statistically significant difference in performance (p=0.000118), with NACP consistently outperforming ACP across all dosage levels. The study further revealed that while NACP significantly reduced phosphate levels, the treated effluent still did not fully comply with DENR Administrative Order No. 2021-19 for Class C water bodies, particularly due to pH imbalance observed after treatment. NACP caused a shift toward acidic conditions, while ACP remained within the alkaline range, both of which indicate limitations in achieving regulatory pH standards.

The study concludes that although NACP shows strong potential as an effective and low-cost biosorbent for phosphate removal, its application alone is insufficient to ensure full compliance with environmental standards. The results highlight the need for additional treatment steps, particularly pH adjustment and process optimization, before practical application in real wastewater treatment systems.

APPENDICES

Fig. 3. Collected Calamansi Peels from Local Stall.

Julie Rose T. Baillo, and Engr. Ilde B. Deloria, M.Eng., "Calamansi Peels *(Citrus macrocarpa)* as Biosorbent for Phosphate Removal from Simulated Wastewater," *International Journal of Multidisciplinary Research and Publications (IJMRAP)*, Volume 9, Issue 1, pp. 1078-1082, June 2026.

Fig. 4. Color Variation Between ACP and NACP Samples.

Fig. 5. Samples Undergoing Adsorption Process.


Fig. 6. Formation of the Molybdenum Blue Reagent.

ACKNOWLEDGMENT

The researcher expresses her sincerest gratitude to those who helped her make the execution of this study possible. First and foremost, she wishes to express her heartfelt appreciation to her thesis adviser, Engr. Ilde B. Deloria, for his guidance, unwavering support, and invaluable wisdom. His knowledge and commitment greatly influenced this research and enhanced the researcher's comprehension of the experimental process. The researcher remains profoundly grateful for his mentorship and the lasting impact it has had on her academic journey.

Secondly, the researcher sincerely extends her highest respect and appreciation to the Examination Committee Chairman, Dr. Lizamyl R. Laping and the panel members, Engr. Dwinsel Maramba and Engr. Anas L. Atal, for their insightful guidance and constructive feedback throughout the course of this research, as well as to Engr. Jeshier John H. Feliciano for his valuable recommendations and support that greatly contributed to the improvement of this study.

Moreover, the researcher sincerely extends her deepest appreciation to Engr. Anamie Rabongue and Engr. Richelle A. Ogdiman for granting her access to Environmental Engineering's laboratory and for their invaluable support and guidance throughout this research.

To Albert A. Salvador, Kenjie I. Ebol, Gracethyl Mae Acla, and the laboratory friends the researcher made during the experimentation process, without their support, guidance, and hospitality, this study would not be possible.

An extension of heartfelt appreciation to her amazing and ever-supportive girlies: Princess Jean L. Galabin, Jezca S. Niesas, Jocelyn S. Davalan, Mark Swen S. Morano, Kyla M. Damsik, and Cristine Faith C. Chavez. Their constant encouragement, friendship, and presence, has made this challenging endeavor more manageable. The researcher is forever grateful to each of you.

Lastly, the researcher sincerely extends her deepest gratitude and indebtedness to her parents, Roland R. Baillo and Jennifer T. Baillo, as well as her uncle, Engr. Benedick R. Tablon, her aunts, Rebecca T. Valerio, Claire T. Egeberg, and Ana Tablon for their unwavering love, moral support, financial assistance, and invaluable guidance throughout the course of this research endeavor. Special recognition to her aunt, Jocelyn B. Salvador and Mr. Winnie Atilano for their unwavering support and valuable assistance throughout the research process. Their support was the key to the successful completion of this study.

REFERENCES

[1] Department of Environment and Natural Resources. (2021) *DENR administrative order no. 2021-19: Updated water quality guidelines (WQG) and general effluent standards (GES) for selected parameters* [Administrative order]. Environmental Management Bureau.

[2] Fernández-García, C., Coggins, A. J., & Powner, M. W. (2017). A chemist's perspective on the role of phosphorus at the origins of life. Life, 7(3), Article 31.

[3] Milovanovic, Z., Lazarevic, S., Jankovic-Castvan, I., Radovanovic, Z., Cvetkovic, S., Janackovic, D., & Petrovic, R. (2023). *The removal of phosphate from aqueous solutions by sepiolite/ZrO_2 composites: Adsorption behavior and mechanism*. *Water, 15*(13), 2376

[4] Muhaisen, L. F. (2016). Lemon peel as natural biosorbent to remove phosphate from simulated wastewater. Journal of Engineering and Sustainable Development, 20(2), 163–173.

[5] Siangko, C. N. B., Escasinas, P. J. D., Florida, H. A. S., Gaudia, A. C. C., Vistan, J., Regala, J. E., Punzalan, J. M., & Argamino, C. R. A. (2021). *Biosorption optimization and kinetic modeling of Ni^{2+} and Zn^{2+} removal from aqueous solution using calamansi (Citrofortunella microcarpa) and dalandan (Citrus aurantium) peels*. Proceedings of the De La Salle University Research Congress 2021. De La Salle University.

[6] Tseng, R.-L. (2007). *Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation*. Journal of Hazardous Materials, 147(3), 1020–1027.

[7] United Nations Environment Programme. (2024, January 24). *What is phosphorus and why are concerns mounting about its environmental impact?* United Nations Environment Programme.