

Phosphate Adsorption from Aqueous Solution using Activated Carbon from Saba Banana Peels Impregnated with Ca^{2+}

Eden S. Erasga^{a,*}, Christine Joy D. Dimarucut^b, John Kyla M. Larino^b, Bren Julius T. Pablo^b

^aCollege of Arts and Science – Mapua Malayan Colleges Laguna –Brgy. Pulo, Diezmo Road, Cabuyao City, Laguna, 4025

^bDepartment of Chemical Engineering – Mapua Malayan Colleges Laguna –Brgy.Pulo, Diezmo Road, Cabuyao City, Laguna, 4025

eserasga@mcl.edu.ph

Untreated municipal wastewater with elevated phosphate levels can trigger eutrophication and the flourishing of algal blooms in surface waters. Among various phosphate removal methods, adsorption, especially with surface modifications, demonstrated enhanced adsorption capacity. This study examined phosphate removal from aqueous solution using activated carbon (AC) derived from saba banana peels (ACB) and AC derived from banana peels impregnated with Ca^{2+} from eggshells (ACB-C). Scanning electron microscopy (SEM) was used to examine the surface morphology of the adsorbents before and after adsorption. Batch adsorption experiments were conducted to investigate the effect of adsorbent dosage and effect of pH on phosphate removal, and to compare the performance ACB and ACB-C. The findings indicate that 0.5 g of ACB demonstrated the highest phosphate removal efficiency of 41.58 % with an adsorption capacity of 1.17 mg/g at pH 6 while 0.5 g of ACB-C exhibited superior performance, with a remarkable 96.42 % phosphate removal efficiency and an adsorption capacity of 2.43 mg/g at pH 8. These results were consistent under specific conditions: contact time of 1 hand agitation speed of 300 rpm. Adsorption kinetics adhered well to pseudo-second-order kinetics for both ACB and ACB-C. Isotherm analysis revealed that phosphate adsorption on ACB followed the Langmuir isotherm model, indicative of monolayer adsorption. These findings affirm that Ca^{2+} impregnation enhances the efficiency of phosphate removal by the adsorbent.

1. Introduction

Phosphorus in the form of phosphate (PO_4^{3-}) is an essential plant nutrient and is a major component of most agricultural fertilizers and animal supplements (Yang et al., 2022). High level of phosphates in municipal wastewater is one of the major contributors of increased eutrophication in lakes and natural waters. Eutrophication has posed a serious threat to most freshwater bodies and coastal ecosystems in recent years, as it promotes algal bloom, deteriorates water quality, reduces the dissolved oxygen levels, and adversely affects aquatic life (Kumar et al., 2010). Municipal wastewater can contain phosphorus as phosphate ranging from 4 to 15 ppm, as noted by Masindi et al. (2015). It's important to adhere to regulatory standards, such as the maximum allowable phosphate concentration in effluent, which is set at 1 ppm according to DAO 2016-08. Therefore, it's imperative to treat wastewater before its discharge into bodies of water. Commonly investigated treatment technologies for phosphate removal include chemical precipitation, biological treatment, electro dialysis, reverse osmosis and adsorption (Yang et al., 2018). Among these various methods, adsorption is widely employed and extensively studied due to its simplicity, cost-effectiveness, and high efficiency. The spent adsorbent, enriched with nutrients, can be repurposed as fertilizer and soil conditioner, adding to its value and environmental sustainability. In most recent studies, researchers are investigating the utilization of low-cost and locally available raw materials in wastewater treatment (Ali et al., 2021). Agricultural by-products, characterized by their cost-effectiveness, abundant availability, and effectiveness, serve as excellent precursor for producing activated carbon, a commonly used adsorbent. Banana peel is one of the biomass wastes that has potential to be used as a raw material to produce activated carbon due to its significant lignocellulose

content, estimated at around 50 % (Kabenge et al., 2018). In 2017 and 2018, the Philippines ranked among the top five banana exporters, with a production of 9.36 M t. Bananas are readily available year-round in the Philippine market and can even be harvested from nearby banana plants. Saba banana is the most used variety of banana for products sold as banana cues, banana chips, turon, and other products, and for that much waste is generated by the banana peels (Reginio Jr. et. al, 2020). About 70-75 % of wastes are generated in households and kitchens in Manila and fruit peels take up a portion of those. These resulting in a substantial amount of waste with minimal economic value but can serve as a valuable precursor for activated carbon production.

Surface modifications of the activated carbon derived from biomass has the potential to enhance surface and adsorption chemistry by improving the interaction between the adsorbent surface and the adsorbate molecule. (Rosa et al., 2023). Impregnation involves incorporating a metal component into a porous material, which can be done through either dry impregnation or wet impregnation (Abegunde et al., 2020). An impregnated adsorbent is more stable and has higher surface area for enhanced adsorption capacity (Girish, 2018). Activated carbon and biochar exhibit strong adsorption capabilities for organic pollution and cations, but they are less effective for anionic pollutants like phosphates so enhancing their adsorption properties for anionic pollutants is necessary. Mitrogiannis et al. (2017) reported that metal cations, including Ca^{2+} , Al^{3+} , Fe^{3+} , and La^{3+} , exhibit a strong affinity for phosphates, resulting to enhanced the adsorption capacity in phosphate removal processes. Numerous studies have utilized chicken eggshells to produce calcium solutions, often employed as an economical activation agent for biomass or activated carbon. This approach serves to enhance the surface chemistry of the adsorbent, thereby augmenting its adsorption capabilities. About 94% of the dry eggshell is CaCO_3 (Faridi and Arabhosseini, 2018) so eggshell can be used as a low-cost source of Ca^{2+} . When calcium carbonate reacts with acetic acid, it produces carbonic acid and calcium acetate. Carbonic acid spontaneously decomposes to water and carbon dioxide leaving only Ca^{2+} and acetate ions in the aqueous solution.

This study aimed to remove inorganic phosphates from aqueous solution using two materials: (1) activated carbon derived from saba banana peels (ACB), and (2) activated carbon derived from saba banana peels impregnated with Ca^{2+} from chicken eggshells (ACB-C). Factors influencing phosphate adsorption, such as adsorbent dosage and pH, were examined. Additionally, adsorption isotherms and kinetics were analyzed by fitting the data to various isotherm and kinetic models.

2. Materials and Methods

2.1 Preparation of Activated Carbons (ACB and ACB-C)

The preparation of saba banana peels followed the methods outlined in the study by Chafidz et al. (2018), with some modifications. Initially, banana peels were collected, washed, diced, heated in an oven at 110 °C for 20 min, and ground using a blender. The unmodified activated carbon (ACB) was produced by subjecting 720 g of dried saba banana peels to activation in a furnace at 800 °C for 10 min. Before preparing the modified activated carbon (ACB-C), a calcium solution was initially prepared following the method outlined by Hernandez-Montoya et al. (2011). This involved immersing 100 g of prepared chicken eggshells in 1 L of 25 % (v/v) acetic acid. The mixture was agitated until all bubbles dissipated, and then the residual eggshells were filtered out. The resulting filtrate served as the calcium solution (1 L), wherein 600 g of dried saba banana peels were soaked, with intermittent stirring every hour, for 24 h at room temperature to impregnate the banana peels with calcium ions. The impregnated banana peels were then dried in the oven at 110 °C for 15 min before being activated at 800 °C for 5 min.

2.2 Characterization of the Activated Carbons

The microstructure and morphology of both ACB and ACB-C, which exhibited the highest phosphate removal efficiency, were examined through Scanning Electron Microscopy (SEM) Analysis before and after the adsorption process. Each sample underwent analysis at x1000 magnification and was observed at a voltage of 15 kV.

2.3 Preparation and Characterization of Aqueous Phosphate Solution

A 300 ppm phosphate stock solution was prepared by dissolving 300 mg of reagent grade KH_2PO_4 in 1 L distilled water. To achieve the desired inorganic phosphate concentration of 15 ppm in municipal wastewater, simple dilution of the stock solution was carried out. The actual phosphate concentration of the resulting working solution was determined using the Phosphate High-Range Checker® HC-HI717 by HANNA Instruments.

2.4 Effect of Adsorbent Dosage and Effect of pH

Batch adsorption experiments were conducted to investigate the phosphate adsorption capacity of both ACB and ACB-C. To determine the effect of adsorbent dosage, 0.1, 0.2, 0.3, 0.4, and 0.5 g of both ACB and ACB-C

were utilized for 100 mL of 15 ppm phosphate aqueous solution at pH 6, agitated using a magnetic stirrer set to 300 rpm, maintained at room temperature for a duration of 1 h. To evaluate effect of pH, 0.5 g of both ACB and ACB-C were used for 100 mL of 15 ppm phosphate aqueous solution. The pH of the solutions was adjusted to 6, 7, 8, 9, and 10 by adding 0.1 M NaOH. The mixtures were stirred with a magnetic stirrer at 300 rpm at room temperature for 1 h. Mixtures were then filtered using a 0.45 μm membrane syringe filter, and the phosphate concentration of the treated solutions was determined using the Phosphate High-Range Checker® HC-HI717 by HANNA Instruments. The adsorption experiments were conducted with two trials, each consisting of two replicates. These methodologies were adapted from the study conducted by Kumar et al. (2010) with some modifications.

2.5 Kinetics and Isotherm Experiment

In this experiment, 200 mL of phosphate aqueous solution with initial concentrations of 2, 4, 6, 8, and 10 ppm was employed. A 0.5 g of ACB at pH 6 and 0.5 g of ACB-C at pH 8 were utilized. Sample aliquots of 10 mL were collected at appropriate sampling times: a 1-min interval for the initial 5 min, a 5-min interval for the subsequent 10 min, a 10-min interval for the subsequent hour, and a 20-min interval until the solution concentration reached a steady state. This methodology was adapted from the research conducted by Cao et al. (2020) with some modifications.

3. Results and Discussion

3.1 Scanning Electron Microscopy (SEM) Analysis

SEM imaging analysis was employed to examine the features and surface structure of both ACB and ACB-C before and after adsorption. The surface morphology, as illustrated in Figure 1, reveals the surface area available for adsorption and illustrates its transformation following the adsorption process.

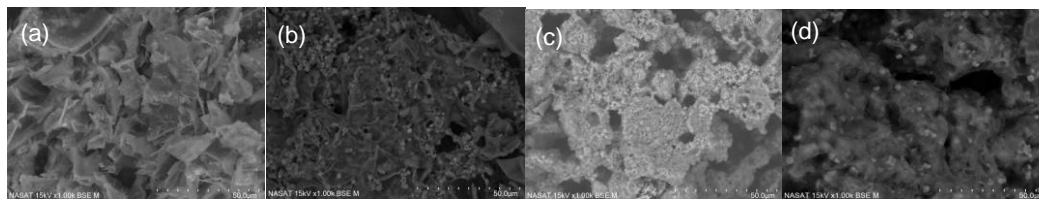


Figure 1: SEM micrograph of (a) ACB before adsorption; (b) ACB after adsorption; (c) ACB-C before adsorption; (d) ACB-C after adsorption. (Condition: $\times 1,000$ magnification)

The surface of ACB before adsorption, as shown in Figure 1a, is crystalline and has a distribution of shallow pores and cavities. Figure 1b illustrates ACB after the adsorption, where the surface of the activated carbon appears smooth due to the coverage of pores by phosphate molecules.

The surface of ACB-C before adsorption, depicted in Figure 1c, shows amorphous-like structure with more visible pores that are deeper and larger. This suggests that the impregnation of Ca^{2+} enhances the surface morphology of the activated carbon by penetrating deeper into the structure of the saba banana peel, resulting to generation of internal pores. This increase in internal porosity leads to a larger surface area for the particles, ultimately enhancing their overall adsorption capabilities. Figure 1d displays ACB-C after the adsorption process, revealing that numerous pores on the surface are no longer visible. This suggests that these pores may have been occupied by phosphates during the adsorption, leading to their temporary or permanent obstruction. The phenomenon of Ca-P precipitation is also distinctly observed, potentially resulting from the formation of calcium phosphate crystals such as $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and CaHPO_4 . This occurs through the interaction between calcium oxide (CaO) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) with phosphates, as detailed in the study conducted by Cao et al. (2020).

3.2 Effect of Adsorbent Dosage

The influence of adsorbent dosage on phosphate removal, investigated across dosages ranging from 0.1 to 0.5 g under constant conditions of 1 h contact time, agitation rate of 300 rpm at room temperature, and at pH 6, is illustrated in Figure 2.

Results indicate that for ACB, as shown in Figure 2a, the highest removal efficiency of phosphate (40.24 %) is achieved with a dosage of 0.5 g. At a 95 % confidence level, there is a significant enhancement in phosphate removal as the dosage increases. This improvement is primarily due to the greater surface area and increased number of sorption sites provided by higher adsorbent dosages, which effectively enhances phosphate adsorption. This trend aligns with findings reported by Ouakouak and Youcef (2016).

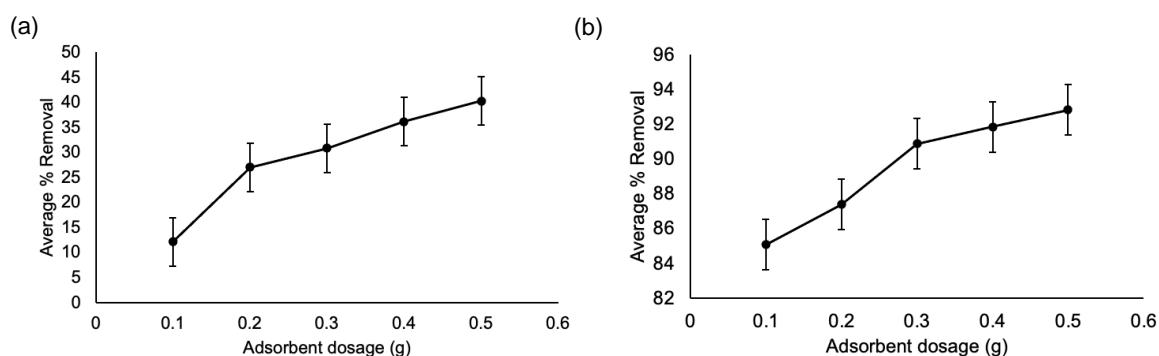


Figure 2: Effect of adsorbent dosage on the % phosphate removal of ACB (a) and ACB-C (b)

The results for ACB-C, depicted in Figure 2b, similarly indicated that the highest phosphate removal was achieved with 0.5 g of ACB-C, reaching 92.83 %. Similar pattern was also observed that there is a significant increase of phosphate removal as the dosage increases at 95 % confidence level. Notably, the impregnation treatment, incorporating Ca^{2+} into the adsorbent, resulted in a remarkable enhancement in phosphate removal efficiency compared to unmodified activated carbon. This improvement is attributed to the binding of phosphate ions to Ca^{2+} ions, utilizing metal-ligand interactions to augment adsorption efficiency as elucidated in the study conducted by Mitrogiannis et al. (2017). Modifying the surface of activated carbon with metal cations increases phosphate removal. The likely mechanism of phosphate ions onto the surface of the adsorbent involves not only ion interaction, which entails interactions between hydrogen ions and phosphate anions, but also ligand-metal interaction, which entails interactions between calcium ions and phosphate.

3.3 Effect of pH

The effect of pH on the removal of phosphate was observed from pH 6 to 10 using 0.5 g of ACB and ACB-C is summarized in Figure 3.

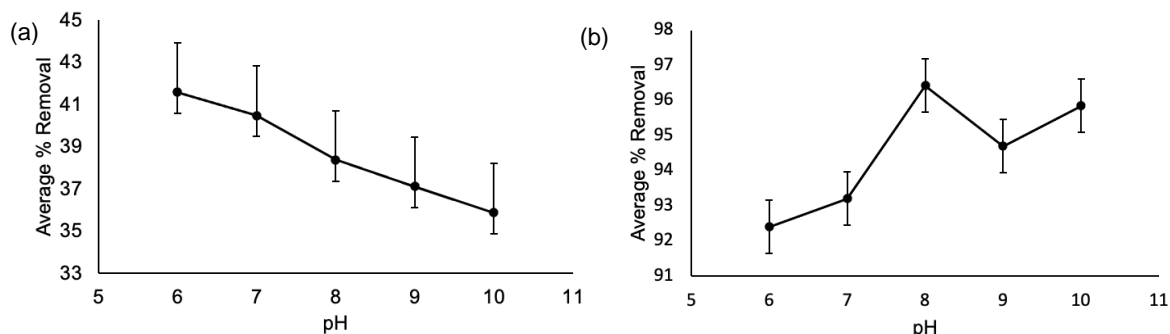


Figure 3: Effect of pH on the % phosphate removal of ACB (a) and ACB-C (b) (Conditions: adsorbent dosage = 0.5 g, contact time = 1 h, stirring rate = 300 rpm)

The highest percent removal for ACB is 41.58 % at pH 6. At 95 % confidence level, there is a significant decrease in phosphate removed after pH 6 as shown in Figure 3a. Under acidic conditions, the hydrogen ions (H^+) in the solution competes with the sorption sites of the adsorbent. There is probably an electrostatic attraction between H_2PO_4^- and H^+ . Whereas, under basic conditions, the hydroxide ions (OH^-) occupy the sorption sites of ACB. Since HPO_4^{2-} is also an anion, electrostatic repulsion and competition occurs between these ions for the adsorption sites of ACB. This would possibly explain why pH 10 has a lowest percent phosphate removal. Similar results were confirmed in the study of Ouakouak and Youcef (2016), where the maximum removal of phosphate ions occurred at pH 2 and the adsorption efficiencies decrease with increasing pH at pH ranging from 2 to 10. As pH decreases, more H^+ ions attract phosphate ions through electrostatic attraction. But in basic pH, more negative charges on the surface hinder phosphate ion removal because of electrostatic repulsion.

Results for ACB-C, as depicted in Figure 3b, showed that the highest percent removal is 96.42 % at pH 8. At 95 % confidence level, the percent removal is significantly different at different pH. Under acidic conditions,

some H^+ occupy the sorption sites of ACB-C, which $H_2PO_4^-$ then binds to the cations on the adsorbent. Due to the presence of Ca^{2+} , there is a competition between the cations in the solution which makes phosphates bind to the excess H^+ instead of the adsorbent surface. Moreover, $H_2PO_4^-$ favors interaction with H^+ than with Ca^{2+} because of their valency. Under basic conditions, there is an electrostatic repulsion between OH^- ions and HPO_4^{2-} in the solution. While the repulsion is not favorable for adsorption, Ca^{2+} plays a vital role in the adsorption process by strong chemical interaction. HPO_4^{2-} binds with Ca^{2+} of the adsorbent and there is a strong attraction between them.

3.4 Adsorption Kinetics

The kinetics of adsorption processes are often described using two common models: the pseudo first-order and pseudo second-order models. The pseudo first-order model suggests that the adsorption process involves physical adsorption, and the pseudo second-order model proposes that the adsorption process is driven by chemical adsorption. Experimental data can be graphed to assess which model offers a superior fit for the kinetic model. A higher R^2 value associated with a model indicates a closer fit to the data and is generally regarded as more favorable for describing the kinetics of the process.

The kinetics data, as presented in Table 1, demonstrate that the pseudo-second order model provides the most accurate fit for the adsorption of phosphate using ACB and ACB-C, indicating chemisorption as the predominant mechanism. The chemisorption happened because of electrostatic attraction between phosphate and impregnated calcium ions on the surface of the adsorbent.

Table 1: Rate Constants of Pseudo-first Order and Pseudo-second Order Kinetic Model for ACB and ACB-C

ACB			ACB-C					
Co (mg/L)	Pseudo-first order model		Pseudo-second order model		Pseudo-first order model		Pseudo-second order model	
	k_1 (min^{-1})	R^2	k_2 ($g/mg \cdot min^{-1}$)	R^2	k_1 (min^{-1})	R^2	k_2 ($g/mg \cdot min^{-1}$)	R^2
2.1	-0.0009	0.8651	0.2579	0.9901	-0.0015	0.8738	0.4092	0.9984
4.0	-0.0006	0.8780	0.1054	0.9870	-0.0006	0.9266	0.2472	0.9984
6.2	-0.0007	0.9059	0.0772	0.9920	-0.0004	0.8130	0.2523	0.9967
7.9	-0.0005	0.8601	0.0664	0.9964	-0.0002	0.7147	0.2681	0.9998
10.2	-0.0005	0.8738	0.0472	0.9944	-0.0003	0.7748	0.1620	0.9999

3.5 Adsorption Isotherms

Adsorption isotherms are used to relate adsorbent to its adsorbate when it reaches equilibrium. The Langmuir Isotherm Model and the Freundlich Isotherm Model are both widely used to describe the relationship between the amount of adsorbate adsorbed onto the surface of the adsorbent and the amount of the adsorbate remaining in the solution.

Langmuir isotherm assumes a monolayer adsorption with a homogeneous surface. The Freundlich model, on the other hand, suggests that multilayer adsorption takes place on heterogeneous surfaces, where adsorption sites possess different energy levels. When comparing the R^2 values obtained for both models, the model with a higher R^2 value indicates a better fit to the experimental data and is considered more favorable as an isotherm model.

The adsorption of phosphate onto unmodified activated carbon derived from saba banana peels was notably well described by the Langmuir model, evidenced by a significantly higher coefficient of determination (R^2) value of 0.9909, as compared to the Freundlich model, which yielded an R^2 value of 0.9833, as indicated in Table 2.

Table 2: Adsorption isotherm constants for ACB

Isotherm Model	Parameter	Constant	Isotherm Model	Parameter	Constant
Langmuir	q_{max}	29.4985	Freundlich	K_f	0.4419
	K_L	0.0150		$1/n$	0.9611
	R_L	0.9694		R^2	0.9833
	R^2	0.9909			

Adsorption on ACB follows a monolayer adsorption where all adsorbates form a single molecular layer around the surface of the adsorbent. There is no interaction between the adsorbed molecules on the other sites that are in proximity and all adsorption sites of ACB are homogeneous (Ashfaq et. al., 2020).

4. Conclusions

This study shows that activated carbon derived from saba banana peel impregnated with Ca^{2+} from chicken eggshells is an effective and low-cost adsorbent for the removal of phosphates from aqueous solution. The highest phosphate removal efficiency of 96.42 % was achieved at 0.5 g adsorbent dosage of ACB-C, pH 8, contact time of 1 h and stirring rate of 300 rpm. The mechanism of adsorption on both ACs was controlled by the electrostatic interaction and ion exchange reaction between phosphate anions and the adsorbent. ACB-C has greater adsorption performance than ACB due to the enhanced interaction of Ca^{2+} on the surface and the adsorbate, aside from the sorption sites that were already present on the adsorbent. The adsorption of phosphate onto ACB followed the Langmuir isotherm. The adsorption process onto ACB and ACB-C obeyed the pseudo-second order kinetic model.

References

- Abegunde, S.M., Idowu, K.S., Adejuwon, O.M., Adeyemi-Adejolu, T., 2020, A review on the influence of chemical modification on the performance of adsorbents, *Resources, Environment and Sustainability*, 1, 100001.
- Akbar, A., Hamideh, F., 2018, Application of eggshell wastes as valuable and utilizable products: a review, *Research in Agricultural Engineering*, 64, 104–114.
- Ali D.A., Al-Mansi N.M., Sadek, M.A., Aboelnasr, A.W., 2021, Simultaneous removal of nitrate and phosphate ions from aqueous solutions using fume dust from electric arc furnace industrial waste, *Chemical Engineering Transactions*, 88, 25–30.
- Ashfaq, M.Y., Al-Ghouti, M.A., Da'na, D.A., Qiblawey, H., Zouari, N., 2020, Investigating the effect of temperature on calcium sulfate scaling of reverse osmosis membranes using FTIR, SEM-EDX and multivariate analysis, *Science of the Total Environment*, 703, 134726.
- Cao, H., Wu, X., Syed-Hassan, S.S.A., Zhang, S., Mood, S.H., Milan, Y.J., Garcia-Perez, M., 2020, Characteristics and mechanisms of phosphorous adsorption by rape straw-derived biochar functionalized with calcium from eggshell, *Bioresource Technology*, 318, 124063.
- Chafidz, A., Astuti, W., Hartanto, D., Mutia, A.S., Sari, P.R., 2018, Preparation of activated carbon from banana peel waste for reducing air pollutant from motorcycle muffler, *MATEC Web of Conferences*, 154, 01021.
- Girish, C.R., 2018, Various impregnation methods used for the surface modification of the adsorbent: a review, *International Journal of Engineering and Technology*, 7(4.7), 330–334.
- Kabenge, I., Omulo, G., Banadda, N., Seay, J., Zziwa, A., Kiggundu, N., 2018, Characterization of banana peels wastes as potential slow pyrolysis feedstock, *Journal of Sustainable Development*, 11, 14.
- Kumar, P., Sudha, S., Chand, S., Srivastava, V.C., 2010, Phosphate removal from aqueous solution using coir-pith activated carbon, *Separation Science and Technology*, 45(10), 1463–1470.
- Mitrogiannis, D., Psychoyou, M., Baziotis, I., Inglezakis, V.J., Koukouzas, N., Tsoukalas, N., Markou, G., 2017, Removal of phosphate from aqueous solutions by adsorption onto $\text{Ca}(\text{OH})_2$ treated natural clinoptilolite, *Chemical Engineering Journal*, 320, 510–522.
- Ouakouak, A.K., Youcef, L., 2016, Phosphates removal by activated carbon, *Sensor Letters*, 14(6), 600–605.
- Reginio, F.C., Qin, W., Ketnawa, S., Ogawa, Y., 2020, Bio-properties of saba banana (*Musa 'saba'*, ABB Group): influence of maturity and changes during simulated in vitro gastrointestinal digestion, *Scientific Reports*, 10(1), 6701.
- Rosa D., Segneri V., Di Palma L., Vilardi G., 2023, Synthesis and CO_2 adsorption capacity of biomass waste functionalized by nanoparticles, *Chemical Engineering Transactions*, 101, 127–132.
- Yang, Q., Wang, X., Luo, W., Sun, J., Xu, Q., Chen, F., Zeng, G., 2018, Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. *Bioresource Technology*, 247, 537–544.
- Yang, Y., Li, Y., Mao, R., Shi, Y., Lin, S., Qiao, M., Zhao, X., 2022, Removal of phosphate in secondary effluent from municipal wastewater treatment plant by iron and aluminum electrocoagulation: efficiency and mechanism, *Separation and Purification Technology*, 286, 120439.