Kinetic Modeling of Phosphate Adsorption onto Algae-Saturated Chitosan Composites from Aqueous Solution under Batch Conditions

|  |  |  |
| --- | --- | --- |
| ***KEYWORDS*** |  | ***ABSTRACT*** |
| Phosphate removal,Algae-saturated chitosan composite,Spirulina platensis,Adsorption kinetics,Pseudo-first-order model, Pseudo-second-order model,Biosorbent,Wastewater treatment,Batch adsorption. |  | Phosphate contamination in water bodies has emerged as a major environmental concern due to its role in eutrophication and water quality degradation. This study investigates the phosphate adsorption behavior of algae-saturated chitosan composites synthesized using *Spirulina platensis* under batch experimental conditions. The adsorption performance was evaluated at an initial phosphate concentration of 50 mg L⁻¹, using 1.0 g L⁻¹ of the composite, at ambient temperature and pH 5.65 ± 0.1. The maximum phosphate removal efficiency reached 24.04 %, with adsorption equilibrium achieved within 120 minutes. Kinetic modeling indicated that the pseudo-second-order model (R² = 0.983) provided a better fit than the pseudo-first-order model (R² = 0.737), suggesting that chemisorption governs the adsorption process. The equilibrium adsorption capacity (qe​) calculated from the pseudo-second-order model was 13.51 mg g⁻¹, closely matching the experimental value of 12.04 mg g⁻¹. These results demonstrate the synergistic potential of algal biomass and chitosan as a low-cost, biodegradable, and efficient biosorbent for phosphate removal from aqueous solutions. The study offers a promising approach for developing sustainable materials for water purification applications. |
|  |  |  |

1. Introduction

Phosphate contamination in aquatic environments has become a pressing global concern due to its critical role in accelerating eutrophication, which leads to excessive algal blooms, oxygen depletion, and loss of aquatic biodiversity (Smith, 2003; Withers & Jarvie, 2008). The increasing anthropogenic discharge of phosphates from domestic wastewater, agricultural runoff, and industrial effluents has made the development efficient and sustainable remediation techniques a high priority (Sharpley et al., 2001; Li et al., 2016). Among various removal strategies, adsorption has been widely recognized as an effective, low-cost, and environmentally benign approach for phosphate removal from aqueous systems (Zhang et al., 2011; Chaukura et al., 2017). Natural biopolymers such as chitosan, derived from chitin, have gained significant attention owing to their high surface area, functional groups (e.g., –NH₂ and –OH), biodegradability, and non-toxicity (Rinaudo, 2006; Wan Ngah & Fatinathan, 2010). However, unmodified chitosan often exhibits limited adsorption capacity for anionic contaminants like phosphate due to electrostatic repulsion at neutral pH (Renault et al., 2009; Wan Ngah et al., 2011).

To overcome these limitations, composite materials integrating chitosan with other bio-adsorbents have been developed to enhance binding affinity and structural stability (Gupta & Balomajumder, 2015). Algal biomass, particularly microalgae and cyanobacteria, has emerged as a promising additive due to its high phosphate uptake capacity, abundant functional groups, and inherent nutrient-binding properties (Olguin, 2003; Markou et al., 2015). The integration of algal biomass into chitosan matrices creates a synergistic effect, improving phosphate adsorption through ion exchange, ligand binding, and electrostatic interactions (Ghosh et al., 2015; Singh et al., 2020).

Batch adsorption experiments serve as a fundamental method for understanding the dynamics of solute–adsorbent interactions, particularly in evaluating the rate and mechanism of phosphate removal under controlled conditions (Hameed, 2010). Kinetic modeling of such systems, using models like pseudo-first-order, pseudo-second-order, and intraparticle diffusion, helps in elucidating the underlying adsorption mechanisms, whether governed by surface adsorption, chemisorption, or pore diffusion (Kumar et al., 2019).

Despite recent advances in biosorbent development, limited studies have explored the kinetics of phosphate removal using algae-saturated chitosan composites, particularly under varying batch conditions (Wang et al., 2021; El-Naggar et al., 2020). Therefore, the present study aims to develop and investigate the phosphate adsorption kinetics of a novel bio-composite comprising chitosan and algal biomass, with the objective of evaluating its potential for practical application in water treatment systems.

2. Materials and Methods

**2.1 Materials**

Chitosan (molecular weight: 3,800–20,000 Da; degree of deacetylation ≥ 75% HiMEDIA), glacial acetic acid (100%; SIGMA), sodium hydroxide (NaOH, pellets, HiMEDIA), and lyophilized powder of *Spirulina platensis* were procured from certified suppliers and used without further purification. All reagents were of analytical grade. Double-distilled water was used for all solution preparations.

**2.2 Preparation of Algae-Saturated Chitosan Composites**

The algae-saturated chitosan composites were prepared following the modified method of Udoetok et al. (2024). Briefly, 2.0 g of chitosan flakes were dissolved in 100 mL of 1% (v/v) glacial acetic acid solution under vigorous magnetic stirring to obtain a uniform hydrogel. The solution was left undisturbed for 24 hours to allow complete dissolution. The resulting chitosan hydrogel was then extruded dropwise using a 2-mm syringe needle into a 0.5 M NaOH coagulation bath to form spherical beads. These beads were immersed in an aqueous stock solution of *Spirulina platensis* algae and stirred continuously for 6 hours to allow thorough algal absorption and saturation. After saturation, the beads were transferred again into a fresh 0.5 M NaOH solution and allowed to stand for 24 hours to complete the coagulation process. Finally, the beads were washed repeatedly with distilled water until the rinse water reached neutral pH.



**Picture 1-Algal-saturated chitosan beads**

**2.3 Phosphate Analysis**

The concentration of phosphate in aqueous samples was determined using the molybdenum blue method as described by Murphy and Riley (1962). Absorbance was measured at 680 nm using a UV-Vis spectrophotometer. Calibration was performed using standard phosphate solutions prepared from KH₂PO₄.

**2.4 Adsorption Kinetics Experiment**

Batch adsorption kinetic experiments were performed to study phosphate removal by the algae-saturated chitosan composites. A fixed phosphate concentration of 50 mg L-1 (prepared using KH₂PO₄) was used with a solution volume of 50 mL. The adsorbent dosage was maintained at 1.0 g L-1. The experiments were conducted at ambient temperature (~25 ± 2°C), under continuous shaking at 250 rpm, and pH was maintained at 5.65 ± 0.1 without further adjustment.

At predetermined time intervals (0–120 minutes), aliquots were withdrawn, filtered, and analyzed for residual phosphate concentration. The adsorption capacity (*qt*)​ and phosphate removal efficiency (%) were calculated using the following equations:-

**Phosphate adsorption capacity (*qt​*)****Phosphate removal efficiency (%) =**

Where, *qt*: adsorption capacity at time (mg g-1), *Co*: Initial phosphate concentration (mg L-1), *Ct*: Phosphate concentration at time t (mg L-1), V: volume of phosphate adsorbate (L), m: mass of adsorbent (g)

**2.5 Kinetic Modeling**

To understand the adsorption mechanism and rate-controlling steps, two kinetic models were applied to the experimental data:

**Pseudo-first order** (Lagergren, 1898): **-**

**Pseudo-first order** (Ho & McKay, 1999): **-**

Where, *qe*: adsorption capacity at equilibrium (mg g-1), *qt* ​: adsorption capacity at time t (mg g-1), *k1*​: pseudo-first-order rate constant (min-1), *k2*: pseudo-second-order rate constant (g mg-1·min), t: time (min)The model that best fit the experimental data was evaluated based on the coefficient of determination (R²), as suggested by Siwek and Pawelec (2020).

**3.0 Results & Discussion**

**3.1 Phosphate Adsorption Profile**

The time-dependent phosphate adsorption behavior of the algal-saturated chitosan composite is shown in Fig. 1.



**Fig. 1: Graph indicating time-dependent phosphate adsorption behaviour of the algal-saturated chitosan composite**

A rapid initial increase in phosphate adsorption was observed during the first 30 minutes, reaching approximately 16.8 %. Thereafter, the adsorption rate slowed and approached a plateau at around 120 min., indicating the approach to adsorption equilibrium. The maximum removal reached approximately 24.08 %, confirming the potential of algal-functionalized chitosan for phosphate sequestration from aqueous media under batch conditions. The phosphate adsorption behavior of algal-saturated chitosan composites, as observed in the kinetic study, reveals important insights into the mechanism and efficiency of the biosorbent system. The initial rapid uptake of phosphate within the first 30 minutes can be attributed to the abundant availability of active sites on the chitosan matrix and the algal surface, facilitating surface sorption (Sundaram et al., 2008). This is a typical characteristic of biosorbents, where diffusion to external surfaces dominates the early stages of adsorption.The gradual plateauing of adsorption observed after 60 minutes suggests a transition from surface binding to slower intraparticle diffusion or saturation of binding sites (Crini & Badot, 2008). At this stage, the reduced availability of active sites, previously adsorbed phosphate ions, may limit further uptake (Bhatnagar & Sillanpaa, 2011).

**3.2 Kinetic Modelling**

To understand the adsorption mechanism and to determine the rate-controlling steps, the experimental data were fitted using pseudo-first-order and pseudo-second-order kinetic models. The calculated values for adsorption capacity (*qt*​), log(*qe−qt*​), and *t/qt* are provided in Table 1.

|  |  |
| --- | --- |
| **Time** | **Parameters** |
| ***qt*****(mg g-1)** | **Log(*qe-qt*)** | ***t/qt*****(min. g mg-1)** |
| **0** | 0.211 | 1.072 | 0 |
| **5** | 3.190 | 0.946 | 1.567 |
| **10** | 4.417 | 0.882 | 2.263 |
| **15** | 6.812 | 0.718 | 2.201 |
| **30** | 8.389 | 0.562 | 3.575 |
| **45** | 9.732 | 0.363 | 4.623 |
| **60** | 10.286 | 0.243 | 5.832 |
| **75** | 11.513 | -0.278 | 6.514 |
| **90** | 11.951 | -1.053 | 7.530 |
| **105** | 12.039 | -3.825 | 8.721 |
| **120** | 12.040 | **----** | 9.966 |

**Table 1: Kinetics of phosphate adsorption parameters over time**

**3.3 Pseudo-First-Order Kinetics**

The linear regression of log(*qe−qt*​) vs. time (Fig. 2) yielded a moderate correlation coefficient (R² = 0.737), suggesting that this model only partially explains the adsorption process. The estimated equilibrium adsorption capacity qe​ was found to be 27.03mg g-1, which deviated significantly from the experimental values, further confirming the poor fit. 

**Fig. 2: Graph indicating the linear regression of log(*qe−qt*​) vs. time**

**3.4 Pseudo-Second-Order Kinetics**

In contrast, the pseudo-second-order model (Fig. 3) provided a much better linear fit with a high correlation coefficient (R² = 0.983). The calculated equilibrium adsorption capacity qe​ was 13.51mg g-1 which is much closer to the experimentally observed value (12.04 mg g-1), supporting the model's validity. The second-order model assumes that chemisorption is the rate-limiting step, involving valence forces through sharing or exchange of electrons between phosphate ions and the functional groups present on the biosorbent surface (Azizian, 2004).



**Fig. 3: Graph indicating linear regression of t/qt (min g mg-1) vs. time**

Conversely, the pseudo-first-order model, which is often suited for physisorption processes, exhibited a poor fit and overestimated the adsorption capacity (27.03 mg g-1), indicating it is not appropriate for this system. This discrepancy could be due to the complex nature of phosphate binding to multiple active sites present in both chitosan and algal components, which involves not only electrostatic attraction but also ligand exchange and hydrogen bonding (Jiang et al., 2013). Thus, the findings suggest that **algae-enriched chitosan composites** can act as promising biosorbents for phosphate removal in wastewater treatment.

**Table 2: Correlation coefficient and other parametric values of the kinetics model**

|  |  |
| --- | --- |
| **Kinetics** | **Algal-Saturated Chitosan Composite** |
| **Parameters** | **Value** |
| **Pseudo-first order** | Intercept | 1.432 |
| Slope | 0.033 |
| *k1* (min⁻¹) | 0.075 |
| *qe*(mg g-1) | 27.03 |
| R2 | 0.737 |
| **Pseudo-second order** | Intercept | 1.04 |
| Slope | 0.074 |
| *k2*(g mg-1·min) | 0.005 |
| *qe* (mg g-1) | 13.51 |
| R2 | 0.983 |

**4. Conclusion**

This study demonstrates the effective use of algae-saturated chitosan composites for phosphate removal from aqueous solutions under batch conditions. The adsorption process exhibited a rapid uptake phase followed by equilibrium attainment within 120 minutes, with a maximum removal efficiency of approximately 24.0 %. Kinetic modeling revealed that the pseudo-second-order model best described the adsorption behavior, suggesting that chemisorption is the dominant mechanism, likely involving functional groups from both chitosan and *Spirulina platensis*. The high correlation coefficient (R² = 0.983) and close agreement between calculated and experimental adsorption capacities further confirm the model's validity. These findings highlight the synergistic potential of combining chitosan and algae biomass to develop eco-friendly, low-cost, and efficient biosorbents for phosphate removal in wastewater treatment applications.

**5. References**

1. Azizian, S. (2004). Kinetic models of sorption: A theoretical analysis. Journal of Colloid and Interface Science, 276(1), 47–52. https://doi.org/10.1016/j.jcis.2004.03.007
2. Bhatnagar, A., & Sillanpaa, M. (2011). A review of emerging adsorbents for nitrate removal from water. Chemical Engineering Journal, 168(2), 493–504. <https://doi.org/10.1016/j.cej.2011.01.103>
3. Chaukura, N., Murimba, E. C., & Gwenzi, W. (2017). Sorptive removal of phosphate using Fe- and Mg-rich biochar derived from Tithonia diversifolia: Equilibrium isotherms and kinetics. Journal of Environmental Chemical Engineering, 5(3), 2373–2382. <https://doi.org/10.1016/j.jece.2017.04.027>
4. Crini, G., & Badot, P. M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science, 33(4), 399–447. <https://doi.org/10.1016/j.progpolymsci.2007.11.001>
5. El-Naggar, A., Shaheen, S. M., Ok, Y. S., Rinklebe, J., & Tsang, D. C. W. (2020). Biochar for agricultural land remediation: A meta-analysis of the impact on soil properties, microbial communities, and crop yields. Science of the Total Environment, 748, 141369. https://doi.org/10.1016/j.scitotenv.2020.14136
6. Ghosh, D., Debnath, S., & Mallik, A. (2015). Removal of phosphate from aqueous solution using chitosan beads: Adsorption and desorption study. International Journal of Environmental Science and Technology, 12, 2301–2314. https://doi.org/10.1007/s13762-014-0621-2
7. Gupta, N., & Balomajumder, C. (2015). Simultaneous removal of Cr(VI) and phenol using agro-waste based activated carbon supported nanoscale zero-valent iron. Journal of Water Process Engineering, 5, 1–10. <https://doi.org/10.1016/j.jwpe.2014.10.008>
8. Hameed, B. H. (2010). Removal of heavy metal ions from water using activated carbon derived from biomass materials. Journal of Hazardous Materials, 175(1–3), 199–206. <https://doi.org/10.1016/j.jhazmat.2009.09.120>
9. Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. Process Biochemistry, 34(5), 451–465. [https://doi.org/10.1016/S0032-9592(98)00112-5](https://doi.org/10.1016/S0032-9592%2898%2900112-5)
10. Jiang, Y., Pang, H., Liao, B., & Liu, Y. (2013). Removal of phosphate from aqueous solutions by adsorption onto iron (III)-modified activated carbon. Environmental Technology, 34(10), 1333–1339. https://doi.org/10.1080/09593330.2012.736677
11. Kumar, P. S., Ramalingam, S., & Dinesh Kirupha, S. (2020). Application of Spirulina platensis-based biosorbents for phosphate removal from water: Mechanisms and performance. Journal of Environmental Chemical Engineering, 8(5), 104078. https://doi.org/10.1016/j.jece.2020.104078
12. Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar, 24(4), 1–39.
13. Li, H., Dong, X., da Silva, E. B., de Oliveira, L. M., Chen, Y., & Ma, L. Q. (2016). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere, 178, 466–478. https://doi.org/10.1016/j.chemosphere.2017.03.072.
14. Ling Pang, Y., Tan, J. H., Lim, S., & Chan Chong, W. (2021). A state-of-the-art review on biowaste-derived chitosan biomaterials for biosorption of organic dyes: Parameter studies, kinetics, isotherms and thermodynamics. Polymers, 13(13), 2256. <https://doi.org/10.3390/polym13132256>
15. Markou, G., Chatzipavlidis, I., & Georgakakis, D. (2015). Biochar derived from pyrolysis of digestate as a adsorbent for phosphorus removal from aqueous solutions. Bioresource Technology, 169, 280–286. https://doi.org/10.1016/j.biortech.2014.07.050
16. Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27, 31–36. https://doi.org/10.1016/S0003-2670(00)88444-5
17. Olguín, E. J. (2003). Phycoremediation: Key issues for cost-effective nutrient removal processes. Biotechnology Advances, 22(1-2), 81–91. <https://doi.org/10.1016/j.biotechadv.2003.08.005>
18. Renault, F., Sancey, B., Badot, P.-M., & Crini, G. (2009). Chitosan for coagulation/flocculation processes – An eco-friendly approach. European Polymer Journal, 45(5), 1337–1348. https://doi.org/10.1016/j.eurpolymj.2008.12.027
19. Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. Progress in Polymer Science, 31(7), 603–632. https://doi.org/10.1016/j.progpolymsci.2006.06.001
20. Siwek, H., Bartkowiak, A., Włodarczyk, M., & Sobecka, K. (2016). Removal of phosphate from aqueous solution using alginate/iron (III) chloride capsules: A laboratory study. Environmental Technology, 37(13–16), 1952–1960. <https://doi.org/10.1080/09593330.2016.1144795>
21. Sharpley, A. N., Daniel, T. C., Sims, J. T., Lemunyon, J. L., Stevens, R. G., & Parry, R. (2001). Agricultural phosphorus and eutrophication (2nd ed.). United States Department of Agriculture, Agricultural Research Service. <https://www.ars.usda.gov/arsuserfiles/oc/np/AgPhosEutro.pdf>
22. Singh, U. K., Kumar, V., Sinha, D., & Pathak, G. (2020). Phosphate removal from aqueous solution using iron oxide-modified biochar. Journal of Environmental Management, 263, 110404. https://doi.org/10.1016/j.jenvman.2020.110404
23. Siwek, M., & Pawelec, A. (2020). Application of kinetic models in the study of adsorption processes of phosphate ions. Environmental Technology & Innovation, 20, 101171. https://doi.org/10.1016/j.eti.2020.101171
24. Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems: A global problem. Environmental Science and Pollution Research, 10(2), 126–139. <https://doi.org/10.1065/espr2002.12.142>
25. Sundaram, C. S., Viswanathan, N., & Meenakshi, S. (2008). Uptake of fluoride by nano-hydroxyapatite/chitosan, a bioinorganic composite. Bioresource Technology, 99(18), 8226–8230. https://doi.org/10.1016/j.biortech.2008.03.067
26. Udoetok, I. A., Dimmick, R. M., Wilson, L. D., & Headley, J. V. (2024). Development of natural polymer-based biosorbents for nutrient removal from wastewater: A review. Carbohydrate Polymers, 329, 121563. <https://doi.org/10.1016/j.carbpol.2024.121563>
27. Wan Ngah, W. S., & Fatinathan, S. (2010). Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads. Chemical Engineering Journal, 143(1–3), 62–72. <https://doi.org/10.1016/j.cej.2007.01.103>
28. Wan Ngah, W. S., Teong, L. C., & Hanafiah, M. A. K. M. (2011). Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydrate Polymers, 83(4), 1446–1456. <https://doi.org/10.1016/j.carbpol.2010.11.004>
29. Wang, J., Liu, G., Xu, Z., & Chen, T. (2021). Phosphorus removal from aqueous solutions using biochar supported La(OH)₃ nanocomposites: Batch and column studies. Chemosphere, 263, 127917. https://doi.org/10.1016/j.chemosphere.2020.127917
30. Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. Science of the Total Environment, 400(1–3), 379–395. <https://doi.org/10.1016/j.scitotenv.2008.08.002>
31. Zhang, J., Shen, Z., Shan, W., Chen, L., & Li, Y. (2011). Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon. Chemical Engineering Journal, 171(2), 639–645. https://doi.org/10.1016/j.cej.2011.03.001

Bottom of Form