



NEW PERSPECTIVES FOR THE USE OF LITHOTHAMNIUM CALCAREUM IN THE POST-TREATMENT OF DOMESTIC SEWAGE

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ABSTRACT

Objective: This study aimed to evaluate phosphorus removal in fixed-bed columns using Lithothamnium calcareum, a calcareous algae widely used in the agricultural sector, exploring its potential as a sorbent medium in wastewater treatment.

Theoretical Framework: The research was based on established kinetic and equilibrium models for describing pollutant removal. The pseudo-second-order model was employed for kinetics, while the Temkin model was used to describe equilibrium, providing consistent theoretical support for data analysis.

Methodology: Initially, kinetic parameters and equilibrium data were determined for phosphorus removal from synthetic solutions. Subsequently, continuous tests were conducted in fixed-bed columns using effluents from a wastewater treatment plant located in Rio de Janeiro, Brazil. Operational parameters, such as flow rate, bed height, and initial phosphorus concentration, were adjusted to evaluate process efficiency. The Yoon-Nelson model was applied to describe operational behavior.

Results and Discussion: Phosphorus removal was highly efficient, with rates ranging from 84% to 98%. The kinetics followed the pseudo-second-order model, while equilibrium data aligned with the Temkin model. The Yoon-Nelson model demonstrated good compatibility under varied experimental conditions.

Research Implications: The application of Lithothamnium calcareum as a sorbent represents a sustainable and effective alternative for phosphorus removal, particularly in wastewater treatment plants, promoting greater environmental sustainability.

Originality/Value: This study highlights the innovation of using Lithothamnium calcareum in continuous systems, reinforcing its feasibility as a practical solution for wastewater treatment.

Keywords: Marine Bioclastic Granulate, Adsorption, Phosphorus, Eutrophication, Fixed-bed.

NOVAS PERSPECTIVAS DO USO DO LITHOTHAMNIUM CALCAREUM NO PÓS-TRATAMENTO DE ESGOTO DOMÉSTICO

RESUMO

Objetivo: Este estudo teve como objetivo avaliar a remoção de fósforo em colunas de leito fixo utilizando Lithothamnium calcareum, uma alga calcárea amplamente utilizada no setor agrícola, explorando seu potencial como meio sorvente no tratamento de efluentes.

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Referencial Teórico: A pesquisa baseou-se em modelos cinéticos e de equilíbrio consagrados para descrever a remoção de poluentes. O modelo de pseudo-segunda ordem foi empregado para a cinética, enquanto o modelo de Temkin foi utilizado para descrever o equilíbrio, fornecendo embasamento teórico consistente para a análise dos dados.

Método: Inicialmente, foram determinados parâmetros cinéticos e de equilíbrio para a remoção de fósforo de soluções sintéticas. Posteriormente, realizaram-se ensaios contínuos em colunas de leito fixo, utilizando efluentes de uma estação de tratamento de esgoto localizada no Rio de Janeiro. Foram manipulados parâmetros operacionais, como vazão, altura do leito e concentração inicial de fósforo, para avaliar a eficiência do processo. O modelo de Yoon-Nelson foi aplicado para descrever o comportamento operacional.

Resultados e Discussão: A remoção de fósforo foi altamente eficiente, com taxas variando entre 84% e 98%. A cinética ajustou-se ao modelo de pseudo-segunda ordem, enquanto os dados de equilíbrio se alinharam ao modelo de Temkin. O modelo de Yoon-Nelson demonstrou boa adequação em condições experimentais variadas.

Implicações da Pesquisa: A aplicação do Lithothamnium calcareum como sorvente apresenta-se como alternativa sustentável e eficaz para a remoção de fósforo, especialmente em estações de tratamento de esgoto, promovendo maior sustentabilidade.

Originalidade/Valor: Este estudo destaca a inovação no uso do Lithothamnium calcareum em sistemas contínuos, reforçando sua viabilidade como solução prática para o tratamento de águas residuárias.

Palavras-chave: Granulado Bioclástico Marinho, Adsorção, Fósforo, Eutrofização, Leito Fixo.

NUEVAS PERSPECTIVAS PARA EL USO DE LITHOTHAMNIUM CALCAREUM EM EL POSTRATAMIENTO DE AGUAS RESIDUALES DOMÉSTICAS

RESUMEN

Objetivo: Este estudio tuvo como objetivo evaluar la eliminación de fósforo en columnas de lecho fijo utilizando Lithothamnium calcareum, un alga calcárea ampliamente utilizada en el sector agrícola, explorando su potencial como medio adsorbente en el tratamiento de aguas residuales.

Marco Teórico: La investigación se basó en modelos cinéticos y de equilibrio establecidos para describir la eliminación de contaminantes. Se empleó el modelo de pseudo-segunda orden para la cinética, mientras que el modelo de Temkin se utilizó para describir el equilibrio, proporcionando un soporte teórico consistente para el análisis de los datos.

Metodología: Inicialmente, se determinaron los parámetros cinéticos y los datos de equilibrio para la eliminación de fósforo en soluciones sintéticas. Posteriormente, se realizaron ensayos continuos en columnas de lecho fijo utilizando efluentes de una planta de tratamiento de aguas residuales ubicada en Río de Janeiro, Brasil. Se ajustaron parámetros operativos, como el caudal, la altura del lecho y la concentración inicial de fósforo, para evaluar la eficiencia del proceso. Se aplicó el modelo de Yoon-Nelson para describir el comportamiento operativo.

Resultados y Discusión: La eliminación de fósforo fue altamente eficiente, con tasas que oscilaron entre el 84 % y el 98 %. La cinética se ajustó al modelo de pseudo-segunda orden, mientras que los datos de equilibrio se alinearon con el modelo de Temkin. El modelo de Yoon-Nelson demostró una buena compatibilidad en condiciones experimentales variadas.

Implicaciones de la Investigación: La aplicación de Lithothamnium calcareum como adsorbente representa una alternativa sostenible y eficaz para la eliminación de fósforo, especialmente en plantas de tratamiento de aguas residuales, promoviendo una mayor sostenibilidad ambiental.

Originalidad/Valor: Este estudio destaca la innovación en el uso de Lithothamnium calcareum en sistemas continuos, reforzando su viabilidad como una solución práctica para el tratamiento de aguas residuales.

Palabras clave: Granulado Bioclástico Marino, Adsorción, Fósforo, Eutrofización, Lecho Fijo.

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1 INTRODUCTION

The accumulation of phosphorus in water bodies is the main cause of eutrophication, being one of the biggest global problems when it comes to water quality. In wastewater, phosphorus is incorporated into biological solids or can be removed through physical-chemical treatments (Hauda et al., 2020). In recent years, much work has been developed to improve the removal and recovery of this nutrient (Lee et al., 2022; Zahed et al., 2022).

Adsorption systems using fixed bed columns consist of a column filled with particles of the adsorbent material, where contact with the solution to be treated will occur. Compared to batch systems, continuous fixed bed systems are the most viable option (Patel, 2020). Several studies report promising results with the use of continuous systems for the most diverse applications (Coelho & Do Rozário, 2019; El Mouhri et al., 2020; Nishikawa et al., 2020). Among the materials used in adsorption processes, several types of algae and marine sediments have shown very satisfactory results in the removal of heavy metals such as nickel, chromium and cadmium (Nishikawa et al., 2020; Van et al., 2019; Vu et al., 2019), phosphorus (Jensen et al., 2022; Lee et al., 2022; Pap et al., 2020), among others.

The Brazilian Continental Shelf is covered by carbonate sediments that can be exploited. One of the main forms of calcareous marine algae found in the country and in the world belongs to the Corallinacea family, *Lithothamnium calcareum*. Its use in agricultural and rural areas is not recent (Campos et al., 2022; Zafar et al., 2022), being used both in the correction and maintenance of soil quality for various crops and in food supplementation for animals (Almeida et al., 2021). In the last decade, this material has aroused interest for its use as an adsorbent in effluent treatment (Campos et al., 2022; Da Silva et al., 2021; Veneu et al., 2019, 2023).

This study evaluated the use of *Lithothamnium calcareum* as packing in fixed bed columns as an alternative for phosphorus removal in the post-treatment of sanitary sewage. The phosphorus sorption parameters by the bioclastic granulate were investigated. To predict the theoretical breakthrough curves, the Thomas, Adams-Bohart and Yoon-Nelson models were applied to the experimental adsorption processes conducted under different operating conditions.



2 THEORETICAL FRAMEWORK

2.1 KINETIC MODELS

Kinetic models analyze experimental data in order to guide which mechanisms control the adsorption process, such as mass transfer, diffusion within pores and chemical reaction (Anastopoulos & Kyzas , 2016).

pseudo-first- order kinetics , the rate is based on the adsorption capacity of the solid in a solid-liquid system and can be determined from an expression given by Lagergren . To this end, Lagergren assumed that the rate of adsorbate removal in relation to time is directly proportional to the difference in saturation concentration and the number of active sites of the solid (Lagergren , 1898).

Equation 1 represents the pseudo-first order kinetic model :

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

pseudo-second order model describes a system that exhibits nonlinear driving force performance. It also indicates that chemical adsorption controls the process and this is based on the adsorptive capacity of the material (Ho & Mckay, 1999) . The model is described by Equation 2.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where k_2 is the pseudo-second- order adsorption rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$) and q_e and q_t are, respectively, the quantities adsorbed per gram of adsorbent (mg.g^{-1}) at equilibrium and at time t .

In cases where the limiting stage of the process is diffusion within the adsorbent particle, that is, this is considered the slow stage, then the model that will best describe the adsorption process is the intraparticle diffusion model. (Weber & Morris, 1963) . The diffusion constant within the solid is calculated from Equation 3.

$$q = k_{di}t^{\frac{1}{2}} \quad (3)$$



where k_{di} is the model constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{1/2}$) and the graph of q versus $t^{1/2}$ showing linear behavior with angular coefficient k_{di} .

2.2 EQUILIBRIUM MODELS

Several theoretical and empirical models are found in the literature that can be used to describe adsorption equilibrium data. In this work, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were chosen.

The Langmuir model is based on the hypothesis that adsorption occurs in a monolayer, through a chemical bond by a fixed number of well-defined active sites. Each site is energetically equivalent and can retain only one adsorbate molecule, with no lateral bonds of any nature or steric hindrance between the adsorbed molecules (Langmuir, 1918).

Equation 4 presents the commonly used linearized form of the Langmuir model.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max} C_e} \quad (4)$$

where q is the amount of adsorbate adsorbed at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), q_{max} is the maximum adsorption capacity related to the coverage of a monolayer ($\text{mg} \cdot \text{g}^{-1}$), K_L is the Langmuir affinity constant and C is the concentration of adsorbate in the liquid phase at equilibrium ($\text{mg} \cdot \text{L}^{-1}$).

Freundlich model assumes that adsorption occurs with the formation of multilayers. This behavior is commonly assumed for heterogeneous systems (Freundlich, 1906). Equation 5 represents the linearized form of the model.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (5)$$

where K_F and n are the Freundlich parameters, which indicate the relative capacity ($\text{mg} \cdot \text{g}^{-1} \cdot (\text{L} \cdot \text{g}^{-1})^n$) and adsorption intensity, respectively.

Unlike the Langmuir and Freundlich models, the Temkin model considers that the adsorption energy decreases linearly as the surface coverage of the material occurs, considering the electrostatic interaction. It is the model that best describes the chemical adsorption process (Temkin; Pyzhev, 1940). Equation 6 describes the linear form of the model.



$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (6)$$

where K_T (L.mg⁻¹) is the equilibrium binding constant related to the maximum binding energy; b_T is the Temkin constant, related to the heat of adsorption; R is the universal gas constant (8.314 J.mol⁻¹.K⁻¹) and T is the temperature (K).

More comprehensive than the Langmuir model, the Dubinin-Radushkevich (DR) model does not assume a homogeneous surface and a maximum adsorption constant. This model has been used to distinguish processes in which chemical adsorption occurs from physical adsorption (Dubinin; Radushkevich, 1947). Equation 7 represents the linearized form of the model.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

Where q_m is the maximum amount of adsorbate that can be adsorbed per unit mass of adsorbent (mg.g⁻¹), β is the constant related to the adsorption energy, R is the universal gas constant (8.314 J.mol⁻¹.K⁻¹), T is the temperature (K) and C is the equilibrium concentration (mg.L⁻¹).

2.3 THEORETICAL MODELS IN THE STUDY OF FIXED BED COLUMNS

The Thomas model is the most widely used. Through it, it is possible to obtain the maximum concentration of adsorbate present in the solid phase (adsorbent) and the rate constant (k_{th}). This model was proposed assuming adsorption-desorption kinetics following the Langmuir model (Patel, 2020). Equation 8 describes this model:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left(k_{TH} q_{máx} \frac{x}{v} - k_{TH} C_0 t \right)} \quad (8)$$

where k_{TH} is the Thomas rate constant (mL.min⁻¹.mg⁻¹), $q_{máx}$ is the maximum adsorption capacity (mg.g⁻¹), v is the flow rate (mL.min⁻¹), x is the mass of adsorbent used in the column (g) and t is the breakthrough time (min).

Using a gas-coal adsorption system, scientists Adams and Bohart proposed a model in which the adsorption rate depends on the concentration of the sorbent species and the residual



adsorption capacity. The Adams- Bohart model can be represented by Equation 9:

$$\frac{C_t}{C_0} = \exp \exp \left(k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \right) \quad (9)$$

where k_{AB} is the Adams- Bohart rate ($\text{mL} \cdot \text{min}^{-1} \cdot \text{mg}^{-1}$), N_0 is the column saturation concentration ($\text{mg} \cdot \text{L}^{-1}$), Z is the column height (cm) and U_0 the superficial velocity ($\text{cm} \cdot \text{min}^{-1}$).

The Yoon -Nelson model of simple theoretical conjunction does not take into account the properties of the adsorbent, the characteristics of the bed, nor the characteristics of the adsorbate . It considers that the decreasing rate of adsorption is directly proportional to the adsorption and diffusion of the adsorbate in the adsorbent (Patel , 2020). The following is Equation 10 that characterizes the YN model:

$$\frac{C_t}{C_0} = \frac{\exp \exp (k_{YN} t - \tau k_{YN})}{1 + \exp \exp (k_{YN} t - \tau k_{YN})} \quad (10)$$

where k_{YN} is the Yoon -Nelson constant ($\text{mL} \cdot \text{min}^{-1} \cdot \text{mg}^{-1}$), τ is the time required to retain 50% of the initial adsorbate concentration (min) and t is the breakthrough time (min).

3 METHODOLOGY

3.1 EFFLUENT SAMPLES USED IN THE STUDY

The effluent used in this study was collected at the Piráí I Sewage Treatment Plant (STP), located upstream of the Vigário Reservoir, in the municipality of Piráí, in the state of Rio de Janeiro (latitude $22^{\circ}37'58''$ S and longitude $43^{\circ}54'03''$ W). With a population of 6,168 inhabitants and an influent flow rate of 11.6 L s^{-1} , the treatment technology used is an upflow anaerobic reactor and sludge blanket (UASB reactor).

The WWTP effluent was collected in two 10 L samples at the station outlet between April and May/22. Color, turbidity, conductivity, pH, COD and phosphorus analyses were previously performed and these samples were then subjected to column tests as well as batch tests.



3.2 GRINDING AND PREPARATION OF BIOCLASTIC GRANULATE

The bioclastic granulate was donated by the company PrimaSea®, located in the Candeias Industrial District, in the state of Bahia.

The material was crushed in a knife mill in order to reduce its particle size. The material was separated into particles using an electromagnetic stirrer and a set of sieves, with the aim of obtaining the material in the particle size range of 0.3-0.6 mm, as described and used in the tests by Caletti (2017). The material obtained was then washed with deionized water, dried in an oven at 90-95°C and stored in glass bottles for later use.

3.3 PREPARATION OF SYNTHETIC SOLUTIONS AND ANALYSIS OF CONCENTRATIONS

To perform the tests, both in batch and in column, synthetic solutions were prepared from a standard supplied by the company Alfakit (Phosphorus 1000 mg.L⁻¹ traceable). The solutions were prepared at the time of use, by diluting the standard for each concentration tested.

To determine the phosphorus concentration, colorimetric methodologies were used following the recommendations and methodologies defined by the Standard Methods for the Examination of Water and Wastewater (APHA, 2018).

3.4 BATCH TESTS

The batch tests aimed to obtain data that described the adsorption behavior of the different adsorbates analyzed. Synthetic phosphorus solutions (1, 8, 15, 25 and 50 mg.L⁻¹) were used and all tests were performed in triplicate at an average temperature of 25°C.

The calculation of the adsorbed quantity of phosphorus per mass of the adsorbent material was calculated from Equations 11 and 12 representing the quantity adsorbed at time *t* and at equilibrium, respectively. The percentage of removal indicates the efficiency of the adsorbent studied in removing a certain pollutant from a solution and was calculated by Equation 13 for each of the concentrations evaluated in the preliminary tests.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (11)$$



$$q_e = \frac{(C_0 - C_e)V}{m} \quad (12)$$

$$\%R = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (13)$$

Where C_0 (mg.L⁻¹) is the initial concentration of the solution, C_t (mg.L⁻¹) is the concentration at time t , C_e (mg.L⁻¹) is the concentration when equilibrium is reached, V is the volume of solution used in liters and the mass of adsorbent in grams.

3.5 TESTS TO OBTAIN KINETIC DATA

The experiments consisted of promoting the contact of 250 mL of synthetic solutions at different initial concentrations with 10 g of bioclastic granulate. This contact was maintained in 400 mL beakers using a magnetic stirrer. Each test was conducted for time intervals ranging from 5 to 1500 minutes. After each test time, the sample was filtered using a vacuum suction pump and a 0.45 µm glass fiber filter, and then the remaining phosphorus concentration in solution was quantified. Each test time was performed in triplicate. The experimental data were fitted to pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

3.6 TESTS TO OBTAIN EQUILIBRIUM DATA

Solutions with different initial phosphorus concentrations were kept under agitation with Lithothamnium calcareum for long time intervals, varying from one hour to one hour. In this case, 500 mL of solution was kept in contact with 20 g of bioclastic material under agitation using a Jar test equipment, rotating at 180 rpm. Similar to the previous experiments, after the contact time the sample was filtered and then the remaining phosphorus concentration was quantified. These tests were conducted, gradually increasing the contact times, until the phosphorus concentration in solution remained constant. Triplicate tests were performed for each contact time tested. The data obtained were adjusted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models.

3.7 TESTS ON FIXED BED COLUMNS

Continuous experiments were performed in acrylic columns measuring 25 cm in height



and 34 mm in internal diameter. Three columns could be operated simultaneously, each individually fed by three peristaltic pumps.

To prevent the bioclastic material from being dragged, glass beads were used at the bottom of the columns, followed by a piece of cotton fiber blanket that served as support for the bed of bioclastic granulate. The columns were fed individually from 10 L drums containing the sample to be used.

Initially, tests were performed using samples collected from the treated effluent of the WWTP as feed. The removal of the phosphorus parameter was evaluated, operating the columns under conditions of bed height of 2 cm and operating flow rate of $46.3 \text{ mL} \cdot \text{min}^{-1}$. Samples were collected at predetermined time intervals and the experiment was conducted until the column was completely saturated, i.e., when the inlet and outlet concentrations were equal.

4 RESULTS AND DISCUSSIONS

4.1 SAMPLE CHARACTERIZATION

The WWTP effluent samples used in this study were characterized for the parameters described below in Table 1. The high conductivity values characterize samples with a significant presence of ions in solution. The phosphorus values obtained in all analyses ranged on average from 3.81 to $9.7 \text{ mg} \cdot \text{L}^{-1}$, being considered high since the legislation of the State of Rio de Janeiro imposes the limit of $1 \text{ mg} \cdot \text{L}^{-1}$ and $4 \text{ mg} \cdot \text{L}^{-1}$ for release in lentic and lotic environments, respectively (INEA, 2021).

Table 1

Parameters analyzed for the WWTP effluent and lake sample.

Parameter	ETE	
	Collection 1	Collection 2
pH	6.95	7.12
Conductivity ($\mu\text{S} \cdot \text{cm}^{-1}$)	472.70	632.30
Turbidity (uT)	18.85	70.00
Color (uH)	12.00	19.00
Phosphorus ($\text{mg} \cdot \text{L}^{-1}$)	4.90	9.70
COD ($\text{mg} \cdot \text{L}^{-1}$)	237.33	334.00



4.2 BATCH TESTS

4.2.1 Effluent from WWTP

The experimental data obtained for phosphorus removal were fitted to the kinetic models for each of the WWTP effluent samples analyzed. Table 2 shows all the parameters calculated for each of the kinetic models used.

Table 2

Parameters calculated for the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models in the tests using WWTP effluent.

Model	Parameters	Concentration	
		4.9 mg.L ⁻¹	9.7 mg.L ⁻¹
Pseudo first order	$q_{\text{and exp}} (\text{mg.g}^{-1})$	0.1006	0.2158
	$q_e (\text{mg.g}^{-1})$	0.0722	0.1958
	$k_1 (\text{min}^{-1})$	0.1166	0.0687
	R^2	0.9174	0.9541
Pseudo second order	$q_e (\text{mg.g}^{-1})$	0.1067	0.2564
	$k_2 (\text{g.mg}^{-1}.\text{min}^{-1})$	2,5185	0.2865
	R^2	0.9982	0.9876
Intraparticle diffusion	$K_{\text{of}} (\text{g.mg}^{-1}.\text{min}^{-1/2})$	0.0555	0.0422
	c	0.0061	0.0213
	R^2	0.7948	0.8172

pseudo-first order and pseudo-second order models were the ones that best described the experimental results for the two samples of the WWTP effluent when analyzing the values of the coefficients of determination (R^2) (0.9174/0.9541 and 0.9982/0.9876, for first and second order, respectively). However, when analyzing the calculated values of the amount adsorbed at equilibrium, the pseudo -second order model was the one that came closest to the result obtained experimentally for the sample with the lowest concentration and the pseudo-first order model for the sample with the highest concentration analyzed. And these results are confirmed by the values obtained from the coefficient of determination.

The fit to the pseudo-second- order model suggests the chemical interaction step as the limiting factor of the process. Similar results were obtained for manganese removal from marine sediments (Mahmoud et al., 2020), for mercury ion and methyl violet dye adsorption by eggshell nanoparticles (Foroutan et al., 2019), for phosphorus adsorption by calcite-based adsorbent and for nickel (Veneu et al., 2019) and phosphorus (Veneu et al., 2023) ion capture using *Lithothamnium calcareum* .



4.3 SYNTHETIC SOLUTIONS

The data obtained through experiments using synthetic phosphate solutions at concentrations of 1, 8, 15, 25 and 50 mg.L⁻¹ were also adjusted to the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models . Table 3 describes all the calculated parameters of each of the models.

Table 3

Parameters calculated for each of the kinetic models in tests with synthetic phosphate solutions at concentrations of 1, 8, 15, 25 and 50 mg.L⁻¹ at T = 25°C.

Model	Concentration					
	Parameters	1 mg.L ⁻¹	8mg.L ⁻¹	15 mg.L ⁻¹	25 mg.L ⁻¹	50 mg.L ⁻¹
Pseudo primeira ordem	q _e exp (mg.g ⁻¹)	0,0213	0,1955	0,3544	0,5437	0,9947
	q _e (mg.g ⁻¹)	0,0191	0,1138	0,2160	0,1679	0,4044
	k ₁ (min ⁻¹)	0,0487	0,0226	0,0128	0,0055	0,0008
	R ²	0,9532	0,9537	0,9385	0,9028	0,5238
Pseudo segunda ordem	q _e (mg.g ⁻¹)	0,0237	0,2052	0,3658	0,5460	1,0002
	k ₂ (g.mg ⁻¹ .min ⁻¹)	2,5131	0.3872	0.1564	0.1624	0.1175
	R ²	0.9738	0.9995	0.9975	0.9998	0.9999
Intraparticular diffusion	K _{of} (g.mg ⁻¹ .min ^{-1/2})	0.0050	0.0786	0.1628	0.3712	0.0587
	C	0.0015	0.0084	0.0105	0.0059	0.0098
	R ²	0.5666	0.7866	0.9343	0.7067	0.7081

When synthetic solutions containing dissolved phosphorus in different concentrations were used, a behavior similar to that obtained for the WWTP effluent was observed in the analysis of the kinetic models. In this case, the pseudo-second- order model was also the one that best described the experimental results for all the concentrations evaluated.

The data also obtained a reasonable fit to the pseudo-first -order model, especially when analyzing the first minutes of the process. Many authors describe this behavior for several types of calcareous materials, including Lithothamnium calcareum , when studying the removal of pollutants such as heavy metals, dyes, etc. (Almeida et al., 2021; Foroutan et al., 2019; Mahmoud et al., 2020; Veneu et al., 2019, 2023) .

The equilibrium data obtained experimentally for each of the analyzed phosphorus concentrations were adjusted to the models and the calculated values for their parameters and the statistical parameters are found in Table 4. Figure 1 illustrates the adjustment of the models to the experimentally obtained data.

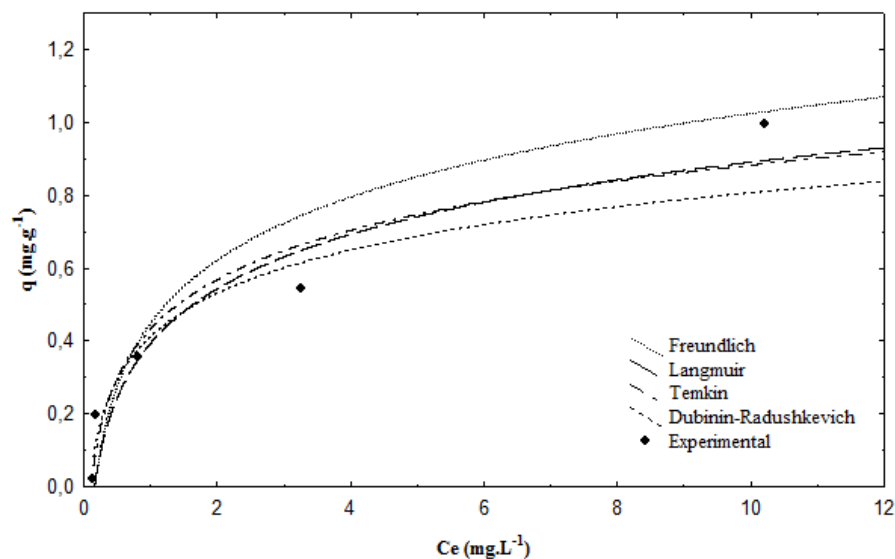
**Table 4**

Freundlich , Langmuir, Temkin and Dubinin-Radushkevich isotherm models in tests with synthetic phosphate solutions at initial concentrations of 1, 8, 15, 25 and 50 mg.L⁻¹ at T=25°C.

Model	Parameters	
friendly	N	1,4618
	$K_F (mg.g^{-1})(L.mg^{-1})^{-1/n}$	0,2513
	R^2	0,7203
Langmuir	$q_{max} (g.mg^{-1})$	1,4445
	$K_L (L.mg^{-1})$	0,2134
	R^2	0,6283
Temkin	b_T	12,6876
	$K_T (L.mg^{-1})$	9,1641
	R^2	0.9314
Dubinin-Radushkevich	$\beta (mol^2.J^{-2})$	0.1054
	$q_M (mg.g^{-1})$	0.7215
	R^2	0.7920

Figure 1

Adjustment of the data obtained to the Freundlich , Langmuir, Temkin and Dubinin-Radushkevich models for tests using synthetic phosphate solutions at T=25°C.



Temkin 's model best fitted the experimental data.

Caletti (2017) when analyzing the capacity of phosphorus removal from landfill leachate by Lithothamnium calcareum concluded that the process was well described by the Freundlich isotherm , indicating that adsorption occurs in multiple layers on the surface of the material. When analyzing the capture of nickel by the same material, Veneu et al. (2019) arrived at results that better fitted the Langmuir model. Still studying the same algae, Veneu et al. (2023) evaluated the removal of phosphorus from synthetic solutions by fitting the experimental results



to the Langmuir and Dubinin-Radushkevich models , finding coefficients of determination above 0.94.

4.4 TESTS ON FIXED BED COLUMNS

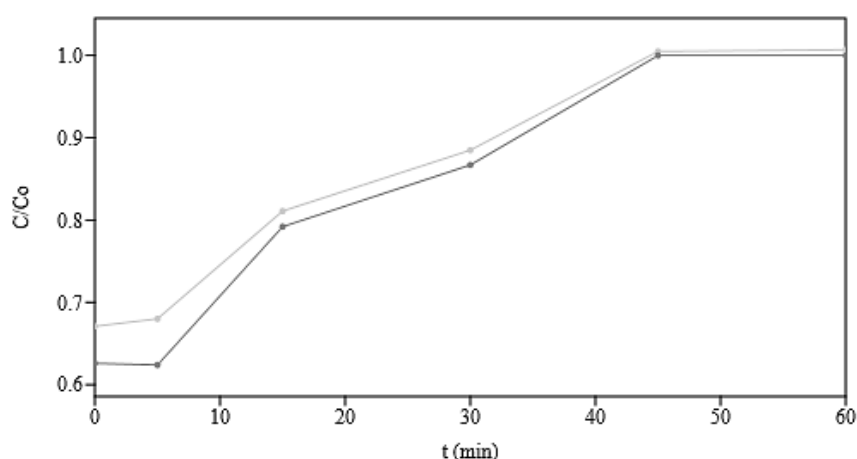
The parameter chosen as the response variable was the time for complete saturation of the bed. The choice of this parameter aimed to optimize the operating conditions in order to extend the column's useful life.

In order to identify the influence of other contaminants on the adsorption process in the columns, two test sequences were performed using as feed: 1) sample of the WWTP effluent and 2) synthetic solutions with different initial phosphorus concentrations. In the first sequence, the columns were operated according to the following conditions: bed height: 2 cm; feed flow rate: $46.3 \text{ mL} \cdot \text{min}^{-1}$. In the second sequence, the columns operated varying the parameters: bed height (1, 2 and 3 cm), feed flow rate (27.3 , 46.3 and $74.6 \text{ mL} \cdot \text{min}^{-1}$) and initial phosphorus concentration (1 , 8 and $15 \text{ mg} \cdot \text{L}^{-1}$).

4.4.1 WWTP samples

Figure 2

Breakdown curves obtained in columns fed with WWTP effluent (bed height: 2 cm; feed flow rate: $46.3 \text{ mL} \cdot \text{min}^{-1}$; initial phosphorus concentration: $9.7 \text{ mg} \cdot \text{L}^{-1}$).



Two columns were operated using the second sample collected at the sewage treatment plant as feed. The initial concentration considered for this test was the phosphorus concentration of the sample ($9.7 \text{ mg} \cdot \text{L}^{-1}$). Figure 2 shows the behavior of the two rupture curves obtained in



these tests. The average standard deviation calculated between the two curves was $\pm 1.77\%$. The maximum removal achieved, i.e., at the beginning of the operation, was 37.44%.

4.4.2 Synthetic solutions

In the second sequence, the experiments were conducted by varying the parameters of feed flow, initial concentration and bed height. It was observed that the saturation time is reduced with the increase in flow rate and initial phosphorus concentration. In operation at high flow rates, the residence time in the column is not sufficient for adsorption to occur efficiently and this becomes even more evident when the initial phosphorus concentrations are high.

The results obtained from monitoring the variation in phosphorus concentration at the column outlet were adjusted to the Thomas, Adams- Bohart and Yoon -Nelson models. The respective calculated parameters and the conditions of each experiment are described in Table 5. In general, the Yoon -Nelson model presented the best correlation coefficients ($R^2 = 0.852-0.973$), indicating that it could describe the results reasonably. However, the Adams- Bohart model fitted better to the experiments conducted with a higher bed height studied (3 cm) and lower initial phosphorus concentration (1 mg.L^{-1}), regardless of the feed flow rate used.

Van et al. (2019) describe, for the removal of Cadmium (II) by marine calcareous material in fixed bed columns, that when the bed height is increased, the saturation time of the system also increases. Likewise, when the initial concentration of the solution studied is increased, the useful life of the column is reduced. In a study conducted by Jang & Lee (2019) evaluating phosphorus removal using a hybrid material composed of organically modified chitosan /Ca -montmorillonite , the Yoon -Nelson model was also able to describe the performance of tests in fixed bed columns. Nishikawa et al. (2020) reported the influence of flow rate and initial concentration on increasing the efficiency of Cadmium (II) removal in columns packed with *Sargassum* seaweed residue. *filipendula* . Jensen et al. (2022) studied phosphorus removal using calcareous materials in fixed bed columns, evaluating the best operating conditions to increase the system's useful life and confirming that increasing the initial concentration negatively affects the variable of interest.

Table 5

Parameters of the models (a) Thomas, (b) Adams- Bohart and (c) Yoon -Nelson under different conditions.

V *1	(a) Thomas	(b) Adams- Bohart	(c) Yoon -Nelson
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	C_0 *2	H *3	K_t *4	q_{max} *5	R^2	K_b *6	N *7	R^2	K_{yn} *8	t *9	R^2
27,3	1	1	0,143	0,784	0,852	0,026	6,558	0,786	0,143	0,343	0,852
27,3	1	3	0,027	16,636	0,879	0,007	2,683	0,960	0,027	22,545	0,879
27,3	15	3	0,003	109,881	0,884	0,001	2,349	0,749	0,051	9,931	0,884
74,6	1	3	0,085	17,143	0,891	0,014	6,599	0,957	0,085	8,500	0,891
74,6	15	3	0,006	8,202	0,891	0,001	4,646	0,902	0,088	0,271	0,973
46,3	8	2	0,011	3,499	0,971	0,002	4,240	0,912	0,090	0,216	0,971

*1: V (mL.min⁻¹); *2: C₀ (mg.L⁻¹); *3: H (cm); *4: K_{th} (mL.min⁻¹.mg⁻¹); *5: q_{max} (mg.g⁻¹); *6: K_{ba} (L.mg⁻¹.min⁻¹); *7: N₀ (mg.L⁻¹); *8: K_{yn} (mL.mg⁻¹.min⁻¹); *9: τ (min).

Table 6 summarizes all the operating conditions of all the experiments performed in the column, receiving different feeds and the respective parameters and calculated results (%R and saturation time).

Table 6

Summary of the operating conditions of each column test and their respective removal percentage (%R) and saturation time (min) parameters obtained.

Feed Flow Rate (mL.min ⁻¹)	Initial Concentration (mg.L ⁻¹)	Bed Height (cm)	%R	Saturation time (min)
46,3	9,7	2	32,89	45
46,3	9,7	2	37,45	45
27,3	1	1	51,44	15
27,3	1	3	54,84	120
27,3	15	1	18,89	15
27,3	15	3	58,39	90
74,6	1	1	25,98	95
74,6	1	3	51,44	50
74,6	15	1	52,96	10
74,6	15	3	44,02	35
46,3	8	2	46,39	30
46,3	8	2	40,66	35
46,3	8	2	37,48	35

5 CONCLUSION

The *Lithothamnium calcareum* was able to remove phosphorus in preliminary batch tests, especially for synthetic solutions at initial concentrations of 1 mg.L⁻¹ (84%), 8 mg.L⁻¹ (98%) and 15 mg.L⁻¹ (94%). In tests with WWTP effluent, maximum phosphorus removal was 89%. The Temkin model was the one that best described the equilibrium data obtained from the study of the removal of this pollutant, which, in addition, presented kinetics compatible with the pseudo-second order model.

Continuous experiments in columns using this same material as packing showed maximum phosphorus removal efficiency of 33% for the treated effluent from the WWTP. When the columns were fed with synthetic phosphate solutions, the maximum operating time



observed until the complete exhaustion of the column's adsorptive capacity was 120 minutes, under conditions of lower flow rate and initial phosphorus concentration, and higher bed height. The Yoon -Nelson model was the one that best described most of the experiments performed.

Thus, it was found that the bioclastic granulate subject of this study is efficient in removing phosphorus when used as packing in fixed bed columns.

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