https://doi.org/10.1590/S1413-415220230087

Scientific Paper

Biopolymers recovery from biological sludge and its use as phosphorus biosorbent

Recuperação de biopolímeros de lodo biológico e seu uso como biossorvente de fósforo

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ABSTRACT

Biopolymers can be recovered from aerobic sludge and used for environmental applications, such as phosphorus adsorbent material, instead being sent to sanitary landfills. In this resource recovery perspective, this work aimed to study the recovery of alginate-like exopolymer (ALE) from activated sludge (AS) compared to aerobic granular sludge (AGS). ALE-based biosorbent was prepared and tested to remove phosphorus from aqueous solutions, and the adsorption kinetics and isotherm models were studied. The recovery yield of ALE from a full-scale wastewater treatment plant (WWTP) AS (18.7%) was close to that obtained from a pilot-scale AGS (22%). ALE recovered from AS presented hydrogel properties and humic substances in its composition, which are important features for future applications. The equilibrium of the adsorption was reached after 10 minutes. The Langmuir isotherm model and the PFO kinetic model best fitted to the experimental data, resulting in maximum adsorption capacity of 8.164 mgP·gALE. Thus, ALE recovered from AS has the potential to be used as a phosphorus biosorbent from effluents and further used as a nutrient delivery system with hydrogel properties.

Keywords: phosphorus; biological sludge; biosorbent; resource recovery; alginate-like exopolymer.

RESUMO

Biopolímeros podem ser recuperados do lodo biológico e utilizados em aplicações ambientais, como adsorvente de fósforo. O fósforo é um nutriente abundante em efluentes, que pode ser adsorvido para posterior aplicação na agricultura. Nesta ótica, este trabalho teve por objetivo o estudo da recuperação do biopolímero alginate-like exopolymer (ALE) de lodo ativado (LA) e lodo granular aeróbio (LGA), e posterior aplicação como adsorvente de fósforo de efluente. O rendimento de recuperação de ALE do LA (18,7%) foi próximo ao obtido com o LGA (22%), ressaltando que o primeiro é um processo amplamente difundido em comparação ao último. A proporção da mistura mais adequada (ALE e alginato de sódio) foi de 2,5% de alginato (m/m). O local de coleta de LA na ETE não apresentou influência nas capacidades de adsorção ou na característica microbiológica do LA; o lodo centrifugado foi selecionado como a melhor opção. O ALE extraído de LA apresentou-se com características de hidrogel e substâncias húmicas em sua composição, que são importantes para a agricultura. O equilíbrio do processo de adsorção foi atingido após 10 minutos, o modelo de isoterma de Langmuir e o modelo cinético de pseudoprimeira ordem (PPO) foram os que apresentaram os melhores ajustes aos dados experimentais, resultando na capacidade de adsorção (qmax) de 8,164 mg/gALE. Os resultados obtidos apontam que o ALE recuperado de LA tem potencialidade para ser utilizado como biossorvente de fósforo de efluentes, para sua posterior aplicação na agricultura, tanto como fonte deste nutriente, como devido à sua composição de hidrogel.

Palavras-chave: fósforo; lodo biológico; biossorvente; recuperação de recursos; exopolímero do tipo alginato.

1. INTRODUCTION

The mineral exploitation of phosphorus for its use as a fertilizer contributes to the scarcity of its reserves which are estimated to be exhausted in the next century. In this scenario, the recovery of phosphorus from effluents becomes an alternative aligned with the concept of the circular economy (CORDELL, DRANGERT and WHITE, 2009; EGLE *et al.*, 2016). Among the main effluents with high phosphorus content, piggery wastewater stands out. According to Montalvo *et al.* (2020), the raw effluent from pig farming can contain phosphorus levels of around 2700 mgP·L, while the average concentration of phosphorus in sewage is 15 mgP·L, and it can be either particulate or soluble (CHEN *et al.*, 2020).

Some absorbent materials derived from the natural resources are known as biosorbents and are characterized by their biodegradable properties when disposed of, and they also offer a lower cost compared to synthetic adsorbents (ABBAS *et al.*, 2014). Moreover, when biosorbents are used to remove nutrients

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Conflicts of interest: the authors declare no conflicts of interest.
Funding: none.
Received on: 09/27/2023 – **Accepted on:** 02/28/2024.

from wastewater, they enhance the value-added of the adsorption process due to their reusability.

The biological sludge from wastewater treatment processes is a source of biopolymers that can be extracted and reused, aligning with the principles of circular economy, which emphasize the transformation of residual waste into value-added products of economic interest (PELLIS *et al.*, 2021; PUYOL *et al.*, 2017). Due to its similar characteristics to alginate, the biopolymer alginate-like exopolymer (ALE) also exhibits potential for various industrial applications, such as impermeable coatings and fire retardants, as well as being a potential biosorbent for dyes and phosphorus (DALL'AGNOL *et al.*, 2020; KIM *et al.*, 2020; LADNORG *et al.*, 2019; LIN *et al.*, 2015; SCHAMBECK *et al.*, 2020a). The ALE, recovered from the waste sludge of biological treatment process, has high added-value when compared to the recovery of other products in wastewater treatment plants (WWTPs) such as biogas, bioplastic, phosphorus and cellulose.

The ALE recovery from the aerobic granular sludge (AGS) has been widely reported in literature, while its recovery from activated sludge (AS) is not yet well known. The AS process accounts for 10% of the wastewater treatment processes used in Brazil, behind stabilization pounds (37%) and anaerobic reactors (35%) (CHERNICHARO *et al.*, 2018; FERREIRA *et al.*, 2021).

In addition, as an aerobic process, AS generates huge amounts of residual biomass that could be explored for resource recovery instead of being sent to sanitary landfills. According to Schambeck *et al.* (2020a), ALE extraction from AGS yielded approximately 236 ± 27 mg(ALE)·g(sludge), and the biopolymer exhibited relevant properties for industrial use. In addition, Chen *et al.* (2022) reviewed the ALE recovery yields from AS, indicating recovery efficiencies of up to 300 mg(ALE)·g(sludge).

The ALE usability as an adsorbent material was evaluated by Ladnorg *et al.* (2019), who reported a 69% removal efficiency of methylene blue using ALE beads as a biosorbent and 79% with commercial alginate beads. Dall'Agnol *et al.* (2020) obtained 49,5% removal of phosphorus from synthetic effluent using ALE beads as a biosorbent. Nevertheless, the biosorbents disintegrated during the adsorption process, which does not allow the nutrient desorption. In kinetic studies of phosphorus adsorption by ALE beads, the authors reported that modeling of experimental data was better represented by the Pseudo-First-Order (PFO) model and the Langmuir isotherm. The adsorption capacity of phosphorus was 9,12 mgP.gALE. The authors point out the direct use of the biosorbent in agriculture to utilize the adsorbed phosphorus, as well as the composition of the ALE itself. However, they indicated the need for an improvement in the biosorbent's structure to prevent it from disintegrating during the adsorption process.

This work aimed at assessing the potential of ALE as a biosorbent for phosphorus removal. The recovery yield of ALE from a full-scale AS was compared to AGS. The biosorbent composition was improved and the phosphorus removal mechanisms evaluated through adsorption kinetics and isotherm model studies.

2. METHODOLOGY

2.1. Sludge source to alginate-like exopolymer extraction

The AGS used was obtained from a pilot-scale of a sequential batch reactor (110 L). The reactor operated with a volumetric exchange ratio of 65% of the total volume per batch over a period of a hundred days. The total operational cycle was comprised of filling (60 minutes), resting (30 minutes), aeration (234 minutes), settling (30 minutes), and discharge (6 minutes). The samples were collected in the final of the aeration step and stored together to comprise a homogenous sample which represented the 100-day reactor operation.

The AS was collected on the Insular WWTP of the municipal sanitation company (CASAN), located in Florianópolis, southern Brazil. The secondary treatment system comprised a continuous flow extended aeration AS reactor, followed by secondary settlers. The residual sludge is sent to a thickener followed by a centrifuge for the final destination. The sludge samples were collected from the recirculation of the settling tank, after the thickener unit, and after the centrifugation process.

2.2. Alginate-like exopolymer extraction from activated sludge and aerobic granular sludge and biosorbents composition

The ALE extraction was performed according to Felz *et al.* (2016). Approximately 3 g of centrifuged sludge pellets (3100 g, room temperature, 25 min) were transferred to 250 mL baffled flask with 50 mL of distilled water and 0.25 g Na_2CO_3. The flask stirred in a water bath (80°C) for 35 min at 400 rpm. Afterwards, the flask's content was centrifuged (3100 g, room temperature, 25 min) to recover the soluble EPS in the supernatant fraction. The ALE fraction was precipitated from EPS by adding 1M HCl to final pH of 2 and then centrifuged again resulting in the acidic ALE. The yield for ALE extraction was calculated according to the total solids analysis (TS) and volatile solids (VS) (APHA, 2017; FELZ *et al.*, 2016).

The biosorbent beads containing ALE and 1% (m·v) sodium alginate were tested for three alginate·ALE ratios (2.5, 5 and 10%). The pellet of ALE previously obtained presented pH enhanced up to 8.5 (0.5M, NaOH), mixed with alginate and dripped in a 12% $CaCl_2$ solution, to make the hydrogel beads.

2.3. Alginate-like exopolymer and sludge characterization

To determine the protein concentration (PN), the modified Lowry method was adopted (FROLUND, GRIEBE and NIELSEN, 1995), considering the interference of humic substances. The polysaccharides (PS) were determined using a modification of the classic anthrone method developed by Rondel, Marcato-Romain and Girbal-Neuhauser (2013), which allows quantifying the neutral and uronic sugar fractions in a single experiment. The samples were prepared in triplicate and the results were expressed in terms of total VS concentration.

The identification community was obtained with the DNA sequencing of sludge samples. The DNA, previously extracted (MoBio Laboratories Inc., USA), was used for the new generation sequencing of the gene 16S rRNA in the regions V3/V4, according to the analysis protocol (Neoprospecta Microbiome Technologies, Brazil). Amplification of 16rRNA V3/V4 was done using the primers 341F (CCTACGGGRSGCAGCAG) and 806R (GGACTACHVGGGTWTCTAAT). The 16S rRNA library was sequenced using the system MiSeq Sequencing System (Illumina Inc., USA) (Neoprospecta Microbiome Technologies, Brazil).

2.4. Adsorption studies

The adsorption experiments were performed on a bench scale stirred thermostatic bath (MARQ LABOR, BM/DR, Brazil), using a magnetic stirrer for continuous agitation (133 rpm), controlled temperature (25, 35 e 45°C) and a synthetic phosphorus solution (KH_2PO_4, 100 mgP·L). The adsorption batch experiment was performed according to Dall'Agnol *et al.* (2020). After adsorption, the samples were centrifuged (2.150 g, 2 min). The total phosphorus concentration (P_t) was determined using the vanadomolybdate reagent method, and the chemical oxygen demand (COD) was determined using the colorimetric method (APHA, 2017). The phosphorus removal efficiency (RE%) was determined according to Equation 1.

$$RE = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

Where:

RE = removal efficiency (%);

C_0 = initial phosphorus concentration (mgP·L)

C_f = final phosphorus concentration (mgP·L).

The adsorption capacity on the equilibrium was evaluated according to the Equation 2.

$$q_e = \frac{(C_o - C_f)V}{W} \quad (2)$$

where C_0 and C_f are the initial and final phosphorus concentration (mgP·L), W is the biosorbent concentration (mg·L) and V is the volume of the phosphorus solution (mL).

The kinetics models were performed in the Statistica® 8.0 software. The non-linear Pseudo-First Order (PFO), Pseudo-Second-Order (PSO) and Elovich models were tested using the following equations in **Table 1**.

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg·g); t is the reaction time(min); K_1 (1·min) and K_2 (g·mg.min) are the rate constants of PFO and PSO models, β (mg·g) is the desorption constant, and α (mg·g.min) is the initial adsorption rate, respectively.

The Langmuir, Freundlich, Redlich-Peterson and Sips isotherm models are presented in **Table 2** with their respective non-linear equations, which were used with the Origin® software.

Table 1 – Non-linear kinetic models applied on the experiment.

Kinetic model	Non-linear equation
PFO	$q_t = q_e(1 - e^{-K_1 t})$
PSO	$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$
Elovich	$q_t = \frac{1}{\beta} ln\ (1 + \alpha \beta t)$

PFO: Pseudo-First-Order; PSO: Pseudo-Second-Order.

Table 2 – Isotherm models in non-linear forms to be applied in the experiment.

Isotherm	Non-linear equation
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^b}$
Sips	$q_e = \frac{K_S {C_e}^{\beta_S}}{1 + a_S C_e^{\beta_S}}$

Where qm is the monolayer sorption capacity (mg·g), K_L is the Langmuir constant (L·mg), C_e is the concentration at the equilibrium (mg·L), K_F is the Freundlich constant (mg·g), and n is the adsorption intensity. K_R (L·g), a_R and b are the Redlich-Peterson constants (0 < b < 1) and K_S is the Sips constant (L·g), β*s* is the biosorbent surface heterogeneity coefficient and a_S is the affinity coefficient.

2.5. Statistical analyses

The statistical analyses (analysis of variance [ANOVA] and Tukey's test) were performed using the software Statistica (version 7.0, TIBCO Statistica™), considering a confidence level of 95% (α = 0.05).

3. RESULTS AND DISCUSSIONS

3.1. Yield of alginate-like exopolymer extraction from activated sludge and aerobic granular sludge

The yields obtained from ALE extraction and recovery from AS and AGS are presented in **Table 3**.

The average yields of ALE extraction from AGS and AS obtained in this study were similar to those reported by other authors, according to **Table 3**.

Although the ALE recovery yield from AS is still lower than that obtained from AGS (**Table 3**), the ubiquitous usage of AS technology in WWTP worldwide may overlap this limitation in a technical and economic way. Also, the improvement of operational aspects and recovery techniques may overcome this limitation. In full-scale AS systems, it is challenging to set the operational conditions to result in more ALE without disturbing the wastewater treatment performance, which is the first WWTP goal.

It is worthwhile that each reported study used a different operational condition and influent composition. Li *et al.* (2022), *apud* Chen *et al.* (2022), reported ALE recovery rates up to 300 $mgVS_{ALE}·mgVS_{sludge}$, which were achieved using synthetic effluent containing starch with adjustments to temperature and the C:N ratio, while in this study real wastewater without temperature control was used. Some key factors influencing ALE production are the SBR cycle steps, organic loading rate, sludge discharge, shear stress, temperature, microbial diversity, influent C:N ratio, salinity and cations (CHEN *et al.*, 2022).

Table 3 – Yield of alginate-like exopolymer extraction from activated sludge and aerobic granular sludge compared to the literature. Number of replicates (n) = 3.

Yield of ALE extraction $(mg \frac{VS_{ALE}}{gVS_{sludge}})$		Reference
AGS	AS	-
220 ± 20	187 ± 13	This study
-	120 - 300	Chen *et al.* (2022) and Li *et al.* (2022)
-	92.9 - 187.9	Li *et al.* (2021)
236 ± 27	187 ± 94	Schambeck *et al.* (2020a)
213 ± 16	-	Dall'Agnol *et al.* (2020)
-	72 ± 6	Lin, Sharma and van Loosdrecht (2013)
160 ± 4	-	Lin *et al.* (2010)

ALE: alginate-like exopolymer; AS: activated sludge; AGS: aerobic granular sludge.

3.2. Definition of the alginate and biosorbent proportion

To enhance the resistance of ALE beads as a biosorbent, sodium alginate solution was added to their composition. **Table 4** shows the alginate proportions and their corresponding COD and residual Pt results from preliminary adsorption experiments.

Considering the COD after adsorption, the ANOVA performed at a confidence level of 95% (α = 0.05) suggested a difference among the alginate proportions evaluated (p_{value} = 0.0031). However, Tukey's test (α = 0.05) revealed that that difference is only between 5% and the other alginate proportions, indicating that there is no significant difference in COD values after adsorption when applying either 2.5 or 10% of alginate. Thus, it is preferable to work with 2.5% of alginate since it has a lower COD value than 5%. Regarding phosphorus, the Pt post-adsorption concentration in the aqueous solution was similar for all tested proportions according to ANOVA (p_{value} = 0.5585), indicating that their addition to the bead composition does not influence the adsorption efficiency.

Figure 1 presents the ALE beads before and after adsorption, in which it is possible to observe that the addition of sodium alginate to the ALE maintains the integrity of the biosorbent.

3.3. Evaluation of the influence of activated sludge type on Pt adsorption

The activated sludge was collected at three different stages of the WWTP to assess whether its composition could influence the integrity of the biosorbent beads as well as the phosphorus adsorption process. Samples from the recirculated sludge from the secondary settler to the aerobic reactor (recirculated), the sludge after passing through the settling process (settled), and the sludge after the centrifugation process (centrifuged) were used (**Table 5**).

Table 4 – Results of preliminary adsorption experiment varying alginate-like exopolymer and alginate proportion. Number of replicates (n) = 3.

Sample	***COD post-adsorption (mg·L)	COD Increase (%)	**Pt post-adsorption (mg P·L)	Pt removal efficiency (%)
Alginate	20 ± 2	*	66 ± 5	50
ALE	243 ± 8	619	56 ± 5	57
2.5%	40 ± 1^a	19	61 ± 3^a	53
5%	50 ± 3^b	49	63 ± 2^a	52
10%	39 ± 3^a	17	62 ± 1^a	53

COD: chemical oxygen demand; *COD decreased in this sample; **initial phosphate concentration: 131 ± 11 mg·L; ***initial COD concentration: 34 ± 4 mg·L; different superscript letters in the values indicate that they are statistically different according to Tukey's test.

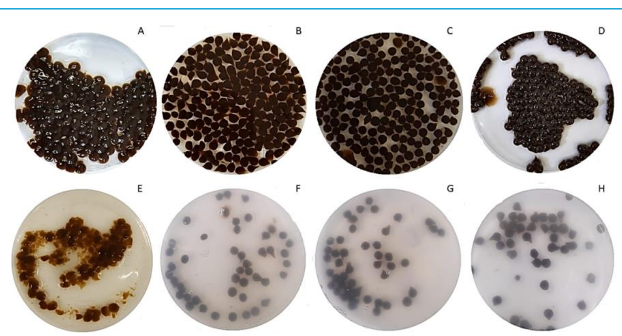

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Figure 1 – Morphological features of the beads prior to adsorption composed of alginate-like exopolymer — ALE (A), ALE + 2.5% alginate (B), ALE + 5% alginate (C), ALE + 10% alginate (D). Biosorbents after adsorption composed of ALE (E), ALE + 2.5% alginate (F), ALE + 5% alginate (G), ALE + 10% alginate (H).

The ALE extraction yields were consistent, even though they originated from different locations of the WWTP, ranging from 175 ± 23 to 203 ± 7 mg $\frac{VS_{ALE}}{gVS_{sludge}}$. As shown by the ANOVA performed at a confidence level of 95% (α = 0.05), the extraction yield was not influenced by the type of sludge (p_{value} = 0.1589). Considering no statistical difference between the analyzed results and that the centrifugation process is already a unit operation commonly employed in WWTPs, it emerges as the most suitable sludge for ALE extraction. From a technological perspective, the centrifuged sludge is suitable for ALE recovery and valorization, instead of being sent to landfills. The phosphorus removal efficiency ranged from 68 to 70%, and COD removal from 4 to 21%.

Figure 2 presents the microbial community profiles at the phylum level found in the samples of recirculated sludge, settled sludge, and centrifuged sludge, collected for ALE extraction.

According to **Figure 2**, the dominant phyla for recirculated, settled, and centrifuged sludge were Bacteroidetes (73.2, 59.25, 64.0%), Proteobacteria (14.2, 20.1, 21.6%), Firmicutes (4.7, 10.7, 6.8%), and Actinobacteria (4, 7.7, 5.4%), respectively. According to Li *et al.* (2021), the phyla Proteobacteria, Chloroflexi, and Bacteroidetes were dominant in biomass samples from conventional activated sludge systems sampled at eight WWTPs in China. The authors found high correlation coefficients between Firmicutes (R^2 = 0.76), Bacteroidetes (R^2 = 0.58), and Proteobacteria (R^2 = 0.41) and biopolymer production. Proteobacteria was the most abundant bacterial phylum found by Frutuoso *et al.* (2023) during the operation of a sequential batch reactor focused on the development of aerobic granular sludge.

The microbial diversity result indicates similarity between the tested sludge samples for ALE extraction. The thickening and the centrifugation process do not affect the sludge composition.

3.4. Evaluation of the polysaccharide and protein concentration in the alginate-like exopolymer

The ALE extracted from the recovered sludge after the centrifugation step WWTP was analyzed for its protein and polysaccharide content, as presented in **Figure 3**, expressed in terms of proteins, humic substances, neutral sugars, and glucuronic acid. The ALE samples showed a significant amount of humic substances (663.6 ± 51.7 mg $_{\text{humic substances}}$·$gVS_{ALE}$) and glucuronic acid (482.3 ± 97.2 mg $_{\text{glucuronic acid}}$·$gVS_{ALE}$), with lower quantities of proteins and neutral sugars (69.2 ± 31.3 mg $_{\text{proteins}}$·gVS_{ALE} and 69.3 ± 6.8 mg $_{\text{neutral sugars}}$·gVS_{ALE}), respectively. The significant presence of glucuronic acid and a lower concentration of neutral sugars were also observed by Schambeck *et al.* (202b0), who obtained 254 ± 32 mg $_{\text{glucuronic acid}}$·$gVS_{ALE}$ and neutral sugars varying depending on the sludge type from 34 ± 5 mg $_{\text{neutral sugars}}$·gVS_{ALE} to 53 ± 1 mg $_{\text{neutral sugars}}$·gVS_{ALE}. The results obtained in the analysis corroborate those found in the literature, where ALE presents a complex composition of polysaccharides, proteins, and humic acids (LIN *et al.*, 2010; SAM and DULEKGURGEN, 2015; SCHAMBECK *et al.*, 2020b)

The presence of glucuronic acid imparts hydrogel characteristics to ALE, which is a substance with high water absorption capacity, making it suitable for water retention in agriculture (ABEDI-KOUPAI, SOHRAB and SWARBRICK, 2008; AZEVEDO *et al.*, 2002; PREVEDELLO and LOYOLA, 2007). Furthermore, concerning the application of ALE in agriculture, humic substances aid in seed

Table 5 – Adsorption using biosorbents prepared with different sludge samples. Number of replicates (n) = 3.

Type of sludge	Sludge to solids ratio $\left(\frac{g_{VS}}{g_{sludge}}\right)$	ALE extraction yield $\left(mg \frac{VS_{ALE}}{gVS_{lodo}}\right)$	Pt post- adsorption (mg P·L)	Pt removal (%)	COD post- adsorption (mg·L)	COD removal (%)
Recirculated	0.051	203 ± 7	32 ± 1	70	28 ± 1	18.4
Settled	0.055	183 ± 10	32 ± 1	70	27 ± 2	21.5
Centrifuged	0.124	175 ± 23	33 ± 2	68	33 ± 3	4.1

ALE: alginate-like exopolymer; COD: chemical oxygen demand; **initial phosphate concentration: 131 ± 11 mg·L; ***initial COD concentration: 34 ± 4 mg·L

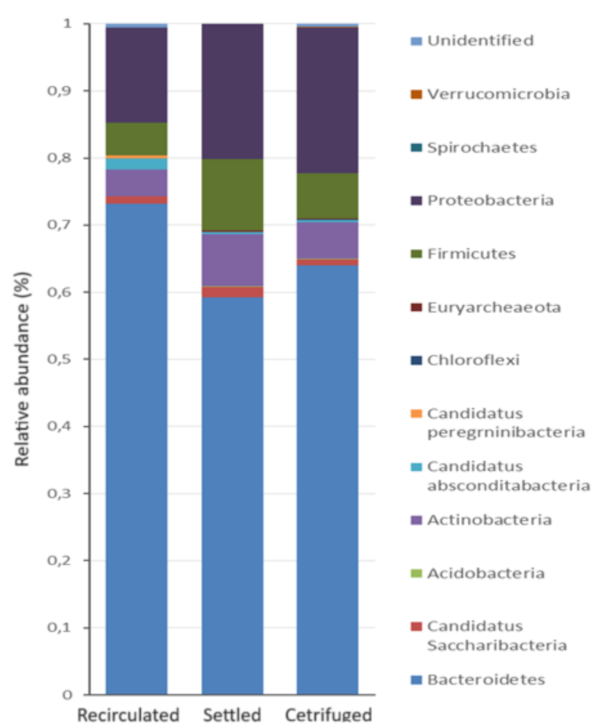

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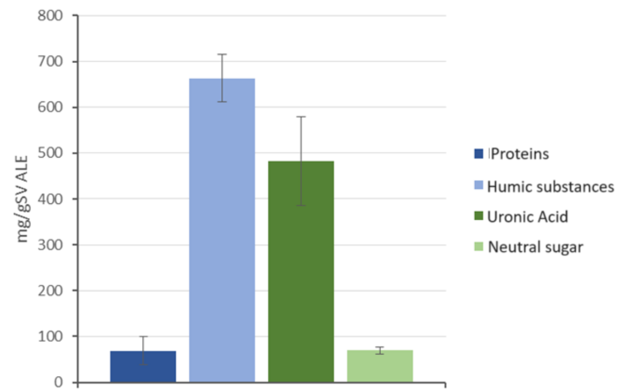
Figure 2 – Microbial diversity at the phylum level for the sludge samples collected at the wastewater treatment plant.



ALE: alginate-like exopolymer.
Source: the author.

Figure 3 – Characterization of alginate-like exopolymer based on proteins, humic substances, neutral sugars, and glucuronic acid.

germination and root development in plants, as they contribute to heat retention due to their coloration and also assist in soil water retention by facilitating water infiltration, acting like a sponge owing to their extensive surface area and charge presence (NOVOTNY, 2002; OLIVEIRA, 2011). Thus, the properties of the substances present in ALE can find application in various fields, including agriculture, as a delivery matrix for various substances, including fertilizers in the soil (PEÑA-MÉNDEZ, HAVEL and PATOCKA, 2005; SCHAMBECK *et al.*, 2020b).

3.5. Evaluation of equilibrium time and adsorption kinetics

The evaluation of the adsorption process equilibrium time was performed using an initial Pt concentration of 100 mg·L, pH 8.0, 25°C, and a biosorbent concentration of 0.39 g·L. Equilibrium in the adsorption process was achieved within 60 minutes. After 10 minutes, no significant difference in adsorption capacity values was observed, considering the standard deviations.

Dall'Agnol *et al.* (2021) reported that equilibrium was reached after 20 minutes for phosphorus adsorption using ALE beads, while Ladnorg *et al.* (2019) stated that the equilibrium time for methylene blue dye adsorption using ALE beads was 60 minutes, although shorter times have demonstrated process equilibrium. Similarly, Fortebraccio (2020) employed a 60-minute standard time for textile effluent adsorption assays using biosorbent beads (AGS + ALE and AGS + sodium alginate). Therefore, kinetic experiments were conducted over 30 minutes to ensure equilibrium was achieved during all experiments.

Adsorption kinetic models elucidate the interaction between the biosorbent and adsorbate at equilibrium, as well as the speed of the adsorption reaction (MOUSSOUT *et al.*, 2018). Model verification was conducted using the Statistica® 8.0 program. The non-linear pseudo-first order (PFO), pseudo-second order (PSO), and Elovich kinetic models were applied.

The application of PFO and PSO models resulted in a good representation of the sample points, based on the correlation coefficient analysis, resulting in 0.93 and 0.92, respectively, while the Elovich kinetic model exhibited a coefficient of 0.89 (**Table 6**). The PFO model achieved equilibrium at approximately 30 minutes (**Figure 4**), after which increasing the contact time had little significant effect on the adsorption amount. This model also yielded an equilibrium adsorption capacity (qe_{mod} of 3.29 ± 0.15 mg·g) similar to the experimentally obtained adsorption capacity (qe_{exp} of 3.22 mg·g), indicating the predominance of the adsorption process.

This demonstrates that the PFO kinetic model better explains the system, where adsorption occurs primarily through the initial surface contact between the adsorbent (ALE beads with alginate) and adsorbate (phosphorus in the solution), a mechanism represented by the pseudo-first order adsorption rate constant (K_1), which is more representative than the second-order constant (K_2), corroborating the results obtained in the studies by Dall'Agnol *et al.* (2020) and Kumar *et al.* (2019).

For the study of adsorption isotherms, four models were tested at three different temperatures, 25, 35, and 45°C, with an initial Pt concentration of 100 mgP·L and a pH of 8, to replicate the conditions previously tested (**Table 7**). Only at a temperature of 25°C did all models converge to the applied data.

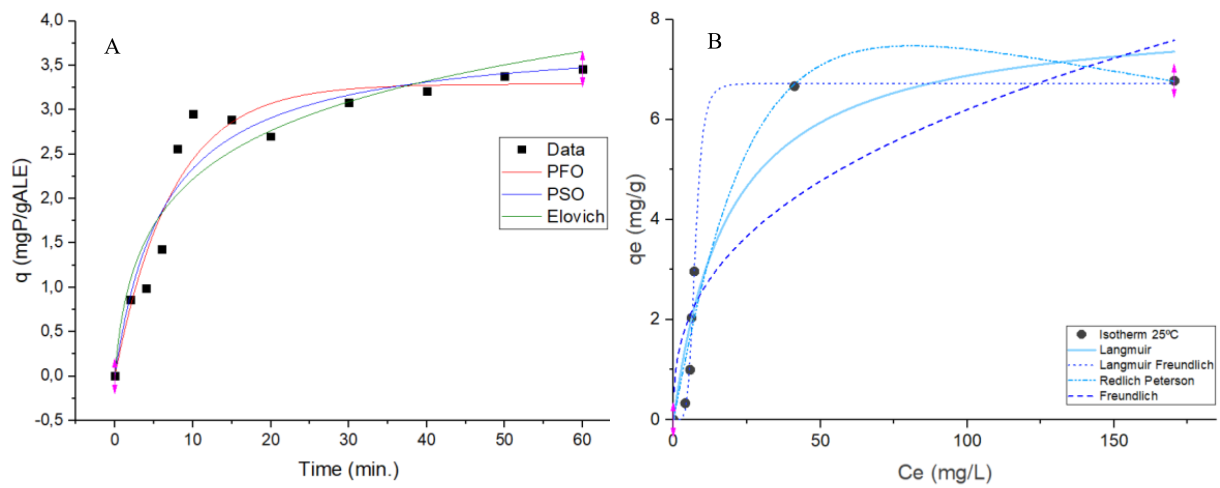
Table 6 – Parameters obtained by the kinetic models. Number of replicates (n) = 3.

Models	Parameters				
PFO	qe_{exp}(mg·g) 3.22	qe_{mod}(mg·g) 3.29 ± 0.15	K_1(min^{-1}) 0.13 ± 0.02	-	R^2 0.93
PSO	qe_{exp}(mg·g) 3.16	qe_{mod}(mg·g) 3.85 ± 0.27	K_2(g mg^{-1} min^{-1}) 0.04 ± 0.01	h (mg·g min^{-1}) 0,59	0.92
Elovich	qe_{exp}(mg·g) 3.79	β (mg·g) 0.83 ± 0.23	α (mg·g min^{-1}) 0.89 ± 0.52	-	0.89

Source: the author.

Therefore, **Table 7** presents the models that converged to represent the adsorption behavior. Values of R^2 close to 1 were observed in the applied models, except for the Freundlich model, which, at temperatures of 25 and 35°C, exhibited R^2 values of 0.755 and 0.886, indicating lower accuracy in representing the adsorption phenomenon. Models were also discarded when the parameter K was close to zero, indicating a weak affinity between the adsorbent and adsorbate (Langmuir-Freundlich at 25 and 45°C), or when this parameter showed a high deviation from its absolute value, as in the case of Freundlich at 45°C, implying greater errors associated with the model. The highest q_{max} value was 8.164 mg·g at 25°C, in the Langmuir model, with a K_L of 0.053 L·mg. The suitability to this model indicates that there is a monolayer of adsorbate covering the surface of the adsorbent.

Besides the kinetic models which represent the adsorption mechanism, it is worthwhile to consider the selectivity between phosphorus and cations such



Source: the author.

Figure 4 – (A) Kinetic adsorption models; (B) fit of models applied to isotherms in experimental data applied at 25°C.

Table 7 – Parameters resulting from the applied isotherm models. Number of replicates (n) = 3.

Models	Parameters	Temperature °C		
		25	35	45
Langmuir	q_{max}(mg·g)	8.164 ± 1.116	0.928 ± 0.024	-
	K_L(L·mg)	0.053 ± 0.021	0.434 ± 0.064	-
	R^2	0.917	0,996	-
Freundlich	K_F(mg1-(1-n)L-1n ·g)	1.083 ± 0.584	0.461 ± 0.074	0.00149 ± 0.003
	n	0.379 ± 0.122	0.178 ± 0.050	1.856 ± 0.489
	R^2	0.755	0.886	0.917
Langmuir-Freundlich	q_{max}(mg·g)	6.720 ± 0.135	0.930 ± 0.076	4.620 ± 1.106
	K_S(L·g)	0.000014 ± 0.000023	0.438 ± 0.146	0
	n	5.576 ± 0.868	0.986 ± 0.382	6.988 ± 21.800
	R^2	0.997	0.996	0.963
Redlich-Peterson	K_{RP}(L·g)	0.307 ± 0.082	-	-
	α_{RP}(L·mg)	0.004 ± 0.007	-	-
	b	1.428 ± 0.291	-	-
	R^2	0.957	-	-

Source: the author.

as zinc, calcium, magnesium, nickel, and copper. Calcium and magnesium are related to the precipitation when combined to phosphate on the adsorbent surface (BACELO *et al*., 2020). Calcium was used to prepare the ALE-alginate beads and one may consider that it may result in some precipitation effect over the phosphorus in the aqueous solution. However, the addition of alginate to the ALE beads resulted in an adsorbent with better integrity, refuting the hypothesis of calcium leakage to the aqueous solution which would result in phosphate precipitation. Also, the possible effect of competing ions in phosphorus adsorption was presented in a study performed by Schambeck Da Costa and Derlon (2021). The authors found that ALE hydrogels presented selectivity for phosphate even in the presence of NH_4, Cl^-, Na^+, Ca^{2+} and Mg^{2+}.

4. CONCLUSIONS

The recovery yields of ALE from AS and AGS were similar, around 220 mg VS_{ALE}·(gVS_{sludge}), corresponding to an extraction efficiency of 22%. It is worth noting that the recovery of AS-ALE holds greater application potential, as AS systems are widely used in sewage treatment plants in Brazil, when compared to AGS. The centrifuged residual AS exhibited desirable characteristics for the ALE extraction process. Additionally, centrifugation is a commonly used unit process for sludge dewatering and may be advantageous for implementing a pilot ALE extraction process at WWTP. The extracted ALE from this sludge exhibited a complex mixture of polysaccharides, proteins, and humic acids in its composition. To provide greater structural stability to the adsorbent spheres during the adsorption process, the addition of alginate to the ALE (2.5%) provided efficient phosphorus removal and maintenance of structural integrity. In the adsorption experiments, it was possible to achieve 70% Pt removal efficiency from an initial concentration of 100 mgP·L. The biosorbent exhibited an adsorption capacity of 8.164 mg·g_{ALE}. Equilibrium in the adsorption process was reached after 10 minutes, and both the Langmuir isotherm and the PFO kinetic model were suitable for the system. Therefore, residual AS process sludge holds potential for ALE recovery and subsequent use as a phosphorus adsorbent and a source of this nutrient and other compounds.

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