



Phosphate removal from municipal wastewater by alginate-like exopolymers hydrogels recovered from aerobic granular sludge

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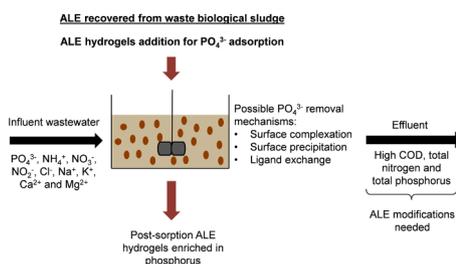
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HIGHLIGHTS

- ALE hydrogels successfully remove phosphate from real municipal wastewater.
- Acidic pH conditions reduce phosphate sorption by ALE hydrogels.
- Phosphate removal occurs even at high NH_4^+ , NO_3^- , Ca^{2+} and Cl^- concentrations.
- ALE need to be further tailored to decrease the release of structural components.
- Phosphorus-rich ALE hydrogels may be further tested for land fertilization.

GRAPHICAL ABSTRACT



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ABSTRACT

This work assessed the potential of alginate-like exopolymers (ALE) hydrogels recovered from aerobic granular sludge (AGS) in removing compounds commonly present in municipal wastewater. Batch sorption experiments were performed with ALE hydrogels at different operating conditions. Results showed that ALE hydrogels can only remove phosphate, at removal efficiencies of up to 90.8% and practical loadings of $1.22 \pm 0.07 \text{ mg PO}_4^{3-}\text{-P/g TS}_{\text{ALE}}$. Phosphate removal was observed even in the presence of competing ions. Moreover, neutral to acidic pH values strongly impaired the phosphate removal ($28.9 \pm 0.8\%$ at $\text{pH} = 6.00$), while basic pH at around 8.50 was the most favourable (up to 90.8% at $\text{pH} = 8.67$). However, ALE hydrogels contributed to the increase in COD, total nitrogen and total phosphorus in the bulk liquid, what suggests that ALE need to be further tailored. Therefore, this study demonstrates that ALE represent a relevant approach for the recovery of phosphates from municipal wastewater.

1. Introduction

The environmental sustainability of wastewater treatment plants (WWTP) can be deeply enhanced by an integrated approach based on the resource recovery from these systems (Wang et al., 2015). The main objective is the recovery and valorization of valuable materials from

wastewater. Biogas, heat, phosphorus, nitrogen, sulfur, cellulose, bioplastics and EPS (extracellular polymeric substances) can, for example, be recovered (Solon et al., 2019). In this context, the reuse of waste biological sludge is a relevant approach. The application of waste biological sludge as a raw material for manufacturing high value-added products such as adsorbents, flocculants and construction materials is

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promising (Shi et al., 2018). Given the increasing amount of wastewater treatment systems employing aerobic granular sludge (AGS) worldwide, there is an increasing interest in assessing their EPS recovery potential (Freitas et al., 2017).

Alginate-like exopolymers (ALE) recovery from waste biological sludge are an alternative route for sludge management (Nancharaiiah et al., 2018). ALE are a group of structural biopolymers that have been successfully recovered mainly from the EPS of AGS applied to the treatment of municipal wastewater (Lin et al., 2010; Schambeck et al., 2020b). ALE can form ionic hydrogels and have other similar characteristics to the commercial polysaccharide alginate (Felz et al., 2016; Lin et al., 2010; Schambeck et al., 2020b). The current market conditions are promising for ALE recovery since ALE is regarded as the most valued resource to be recovered during the treatment of municipal wastewater (Van Der Hoek et al., 2016). Recent studies suggested that ALE can be used for various industrial applications, such as coating material to provide waterproofness and flame retardancy to surfaces, or as a potential biosorbent for dyes and phosphate (Dall'Agnol et al., 2020; Kim et al., 2020; Ladnorg et al., 2019; Lin et al., 2015).

ALE are a complex group of biopolymers comprised by different constituents such as proteins, humic substances, sugars (neutral, uronic, alcoholic and amino ones), glycoconjugates and lipids (Felz et al., 2020b, 2019; Meng et al., 2019; Schambeck et al., 2020a). ALE composition is more complex than alginate, and several functional groups are suspected to be involved in formation of ALE hydrogels (Felz et al., 2020a). This complex composition can provide ALE with relevant chemical properties, such as adsorbent properties for different compounds. For instance, ALE recovered from AGS fed with municipal wastewater has been showed to have a much higher content of humic substances and proteins than neutral and uronic sugars (Schambeck et al., 2020a). Humic acids are rich in phenols and carboxylic acids, suggesting that they can be employed as chelating agents (De Melo et al., 2016). The ability of humic acids and proteins in binding with cationic metals and in turn to form complexes (De Melo et al., 2016) make them useful, in theory, for different adsorbent applications. Indeed, ALE can form ionic hydrogels by cross-linking with different cations (Felz et al., 2016, 2020a). Therefore, this complex cross-linked network of ALE hydrogels has miscellaneous polymers, which may provide sorption sites for different compounds in solutions.

Hydrogels are emerging as an efficient and low-cost technology for treating different aqueous pollutants, such as metals and dyes (Sinha and Chakma, 2019; Yazdi et al., 2020). Those water-rich and porous polymers have also been successfully employed as adsorbents for cationic elements from municipal wastewater, such as ammonium, magnesium, calcium and potassium (Cruz et al., 2018). Similarly, one interesting possibility is to test ALE hydrogels as an adsorbent for wastewater pollutants. Dall'Agnol et al. (2020) have showed that Ca^{2+} -ALE hydrogels have high affinity for phosphorus sorption with removals up to 72.5% and sorption capacity of 57.25 ± 12.18 mg P/g TS_{ALE} . Moreover, Ca^{2+} -ALE hydrogels have been able to remove up to 69% of the dye methylene blue (Ladnorg et al., 2019). However, both studies were performed using synthetic solutions. In the case of real municipal wastewaters, the presence of several ions can hinder the adsorption process and thus present different results in relation to synthetic solutions (Hu et al., 2015; Siwek et al., 2016; Yang et al., 2006a; Zheng et al., 2012). Consequently, it is imperative to evaluate the sorption process by using real wastewater to have more realistic results that ultimately may impact real applications (Kumar et al., 2019; Wu et al., 2020). Sorption experiments in literature employing real wastewaters have been scarce so far (Bacelo et al., 2020; Wu et al., 2020).

Therefore, this work aimed at assessing the potential of ALE hydrogels in removing different cationic and anionic compounds commonly present in municipal wastewater. Batch sorption experiments were performed with different dosages of ionic crosslinked ALE hydrogels recovered from AGS cultivated with real municipal wastewater. Different environmental and operating conditions were tested to assess:

(1) what wastewater soluble compounds can be removed (i.e., PO_4^{3-} , NH_4^+ , NO_3^- , NO_2^- , Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) by different dosages of ALE hydrogels; (2) the influence of the wastewater composition in terms of initial concentrations of PO_4^{3-} , NH_4^+ and NO_3^- ; and (3) the influence of the wastewater pH.

2. Materials and methods

2.1. Alginate-like exopolymers (ALE) hydrogels preparation

ALE was extracted from AGS cultivated in a sequencing batch reactor which treated municipal wastewater from the city of Dübendorf, Switzerland. Details about the reactor operation can be found in Layer et al. (2019). ALE was recovered from AGS under hot, alkaline and mixing conditions according to the protocol described by Felz et al. (2016). Briefly, a known mass of wet sludge was centrifuged (4000g, 4 °C, 20 min) prior discharging the supernatant. The pellet was then transferred to a 1 L beaker filled with demineralized water, Na_2CO_3 and equipped with a magnetic stirrer. A ratio of 3:50:0.25 (sludge mass (g), demineralized water (mL) and Na_2CO_3 (g)) was kept during the extractions. The solution was heated up to (80 °C) and stirred for 35 min at 400 rpm. The mixed liquor was then centrifuged (4000g, 4 °C, 20 min) to recover the supernatant that comprised the solubilized EPS. Acidic ALE were extracted from EPS by acidic precipitation: 1 M HCl was added to the soluble EPS solution to reach a final pH of 2.20 ± 0.05 while stirred at approximately 100 rpm. Soluble Na^+ -ALE were then obtained by the addition of 0.5 M NaOH to the precipitated acidic ALE until pH reached 8.5.

Ca^{2+} -ALE hydrogels (from now on called only as ALE hydrogels) were formed by immersing and pipetting continuously (10 mL micro-pipette tip) Na^+ -ALE into a 5% (w/v) CaCl_2 solution. ALE hydrogels strips were thus formed without control of their shape (Appendix A - Fig. S1). After 24 h, the hydrogels were washed 5 times with tap water and reserved in a 1 L beaker filled distilled water for at least 24 h before being used for the sorption tests. ALE were quantified as total solids (TS) according to Felz et al. (2016).

2.2. Wastewater characterization

Fresh primary effluent municipal wastewater from the WWTP of Eawag (Dübendorf, Switzerland) was collected and immediately frozen to avoid microbial conversion, and thus keeping a similar composition for the different adsorption tests. Prior to the experimental runs, the wastewater was brought to ambient temperatures (~ 21 °C). The same initial collected wastewater was used for every set of experiments with characterization as shown in Table 1.

Table 1

Characterization of the primary effluent municipal wastewater used in the experiments. Error estimates are standard deviation from five measurements (n = 5).

| Parameter | Value |
|---|-----------------|
| Soluble COD (sCOD) (mg/L) | 341 ± 13 |
| Total COD (tCOD) (mg/L) | 571 ± 21 |
| Temperature (°C) | 20.5 ± 1.0 |
| pH | 8.67 ± 0.20 |
| PO_4^{3-} (mg PO_4^{3-} -P/L) | 2.7 ± 0.2 |
| Total phosphorus (TP) (mg/L) | 6.2 ± 0.7 |
| NH_4^+ (mg NH_4^+ -N/L) | 21.4 ± 3.3 |
| NO_3^- (mg NO_3^- -N/L) | 1.3 ± 0.1 |
| NO_2^- (mg NO_2^- -N/L) | 0.3 ± 0.1 |
| Total nitrogen (TN) (mg/L) | 40.2 ± 4.6 |
| Cl^- (mg/L) | 129 ± 23 |
| Na^+ (mg/L) | 111 ± 2 |
| K^+ (mg/L) | 31.8 ± 21.0 |
| Ca^{2+} (mg/L) | 83 ± 6 |
| Mg^{2+} (mg/L) | 19.7 ± 0.7 |

2.3. Sorption tests

Three sets of 4-hour batch experimental runs (triplicates – three batches, ~21 °C) were conducted to: (i) assess the influence of the initial different dosages of ALE hydrogels on the sorption capability of several ions under normal wastewater conditions; (ii) to investigate separately the effect of the PO_4^{3-} , NH_4^+ and NO_3^- initial concentrations on the overall sorption capacity of ALE hydrogels; (iii) to determine the impact of the wastewater pH on the sorption performance of several ions by ALE hydrogels (Table 2).

Experiments were carried out in 600 mL beaker reactors using 300 mL of primary effluent municipal wastewater. ALE hydrogels were sieved prior being added to the adsorption tests beakers to remove the supernatant. The beakers were placed on a horizontal shaking incubator and shaken at a moderate speed to allow fully mixed conditions without excessive breaking of hydrogels. Aliquots of 5 mL were collected from the settled liquid at $t = 5, 10, 25, 60$ min and 2, 3 and 4 hrs.

The parameters measured in the experiments are shown in Table 2. NH_4^+ -N and PO_4^{3-} -P concentrations were measured at $t = 0, 5, 10, 25, 60$ min and 2, 3 and 4 hrs. The remaining parameters were analysed in the beginning ($t = 0$, corresponding to primary wastewater without hydrogel addition) and end of the experiments ($t = 4$ hrs). Since the volume of wet hydrogels added to the batches was significant in comparison to the volume of wastewater, the dilution factor must be considered for the concentrations decay at the beginning of the tests (i. e., at $t = 0$ min). Therefore, all the initial concentration values were corrected considering the dilution factor. The dilution factor was calculated considering the volume of hydrogel added to the volume of wastewater. Thus, a dilution factor of 1.19, 1.16, 1.13 and 1.10 was applied for the dosages of 3.75, 3.13, 2.50 and 1.88 g $\text{TS}_{\text{ALE}}/\text{L}$, respectively. The practical loading was calculated and regarded as the sorption capacity that will be realized in practice for a given set of conditions as the ones used in the present study (Kumar et al., 2019). The practical loading (q) and removal efficiency (R) were calculated as follows:

$$q = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Table 2
Summary of the sorption tests performed.

| | Experiment #1 - Influence of the ALE hydrogel dosage | Experiment #2 - Influence of the wastewater composition in terms of PO_4^{3-} , NH_4^+ and NO_3^- initial concentrations | Experiment #3 - Influence of the wastewater pH |
|--|---|--|---|
| ALE hydrogel dosage (g $\text{TS}_{\text{ALE}}/\text{L}$) | 3.75, 3.13, 2.5 and 1.88 | 3.75 | 3.75 |
| PO_4^{3-} , NH_4^+ and NO_3^- initial concentration | Original values from the primary effluent municipal wastewater | 7.3 mg PO_4^{3-} -P/L 82.5 mg NH_4^+ -N/L 17.5 mg NO_3^- /L (by the addition of KH_2PO_4 , NH_4Cl and NaNO_3 - ACS reagents, Sigma Aldrich USA) | Original values from the primary effluent municipal wastewater |
| pH | Original values from the primary effluent municipal wastewater | Original values from the primary effluent municipal wastewater | 6.00, 7.00 and 8.57 (by adjusting the pH of the primary effluent municipal wastewater with HCl) |
| Parameters measured | tCOD, sCOD, TN, TP, PO_4^{3-} -P, NH_4^+ -N, NO_3^- -N, NO_2^- -N, Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+} | | |

where q (mg/g) is the amount of ion sorbed per unit weight of the sorbent, V (L) is the volume of the solution, and W (g) is the weight of the ALE hydrogel. C_o and C_e (mg/L) are the initial and final concentrations of ion in the solution, respectively.

2.4. Wastewater chemical analysis

Samples were analysed for total COD (tCOD), total nitrogen (TN) and total phosphorus (TP) using photochemical tests (Hach Lange, Germany, LCK 114, 314, 338, 238, 348, 349). Soluble COD (sCOD) was measured after filtration at 0.45 μm (Macherey Nagel, Nanocolor Chromafil membrane filter GF/PET 0.45 μm , Germany). NH_4^+ -N was measured using flow injection analysis (Foss, FIA star flow injection 5000 analyser, Denmark). NO_3^- -N, NO_2^- -N, PO_4^{3-} -P Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+} were measured by anion chromatography (Methrom, 881 compact IC, Switzerland). The pH was monitored using a handheld pH probe (Thermo Fisher, USA).

2.5. Inductively coupled plasma optical emission spectrometry (ICP-OES)

ALE hydrogel samples before and after the sorption tests were collected, frozen and lyophilized. Then, samples were digested in 4 mL HNO_3 and 500 μL H_2O_2 at 240 °C and 120 bar of pressure for 20 min before being analyzed via inductively coupled plasma optical emission spectrometry (ICP-OES). This analysis aimed at acquiring information about specific elements sorption by ALE hydrogels.

3. Results and discussion

3.1. Influence of ALE hydrogels dosage on different wastewater constituents sorption (experiment #1)

The effectiveness of different dosages of ALE hydrogels to sorb different soluble compounds from wastewater was investigated. ALE hydrogels were capable to efficiently remove PO_4^{3-} ions from the wastewater while no effect on other soluble compounds were observed (Appendix A - Table S1). Since ALE hydrogels were only able to efficiently remove PO_4^{3-} from the municipal wastewater, the evaluation of the effect of ALE dosage on the removal of phosphate was further investigated. Interestingly, a direct relationship between the dosage of ALE hydrogels and phosphate removal sorption capacity was not clearly observed (Table 3 and Fig. 2A). The highest removal of $90.8 \pm 0.0\%$ was obtained when the highest ALE dosage (3.75 g $\text{TS}_{\text{ALE}}/\text{L}$) was used, while the lowest removal of $52.4 \pm 2.0\%$ occurred for the second highest ALE dosage (3.13 g $\text{TS}_{\text{ALE}}/\text{L}$). In terms of mass of phosphate sorbed by ALE, the highest value of 0.85 ± 0.02 mg PO_4^{3-} -P/g TS_{ALE} was obtained for the lowest mass of 1.88 g $\text{TS}_{\text{ALE}}/\text{L}$. Moreover, the least practical loading of 0.28 ± 0.01 mg PO_4^{3-} -P/g TS_{ALE} occurred for the second highest dosage of 3.13 g $\text{TS}_{\text{ALE}}/\text{L}$. Therefore, although the highest dosage of ALE tested presented the highest phosphate removal efficiency, it did not lead to the highest practical loading of the hydrogels. On the contrary, a relatively high removal ($75.6 \pm 1.5\%$) and the highest practical loading were obtained by the lowest dosage of ALE hydrogels added to the batches (1.88 g $\text{TS}_{\text{ALE}}/\text{L}$). This can be attributed to the higher initial PO_4^{3-} concentration in the wastewater used for the 1.88 g $\text{TS}_{\text{ALE}}/\text{L}$ sorption tests

Table 3
 PO_4^{3-} -P removal and practical loading from wastewater by different initial dosages of ALE hydrogels. Conditions: initial pH 8.67 ± 0.20 , temperature 21 ± 1 °C, duration 240 min.

| ALE dosage (g $\text{TS}_{\text{ALE}}/\text{L}$) | PO_4^{3-} -P removal (%) | PO_4^{3-} -P sorption (mg/g TS_{ALE}) |
|---|-----------------------------------|---|
| 3.75 | 90.8 ± 0.0 | 0.40 ± 0.00 |
| 3.13 | 52.4 ± 2.0 | 0.28 ± 0.01 |
| 2.50 | 57.9 ± 1.8 | 0.38 ± 0.01 |
| 1.88 | 75.6 ± 1.5 | 0.85 ± 0.02 |

(2.8 mg PO_4^{3-} -P/L vs. 2.2 mg PO_4^{3-} -P/L). Sorption is a concentration-dependent mechanism, in which higher initial concentrations acts as a gradient driving-force to overcome the mass transfer resistance between the aqueous and solid phases, resulting in higher sorption/removal capacities (Hu et al., 2015; Jang and Lee, 2019; Yang et al., 2006b). Furthermore, the dosages of ALE used in the experiments may have been larger than the optimum point to enable the highest sorption/removal. In this case, the number of active and available sites for interactions between the adsorbent and ions also goes up along with the adsorbent concentration, successively reducing the adsorptive capacity of the adsorbent (Dos Reis et al., 2020; Poormand et al., 2017). Also, higher dosages of ALE hydrogels can increase the repulsion forces between phosphate and negatively charged functional groups which would be negative for adsorption (Banerjee et al., 2019).

Organic matter and nitrogen compounds were largely released from ALE hydrogels, as indicated by an increase up to $87.1 \pm 1.2\%$ of tCOD, $117.6 \pm 1.5\%$ of sCOD, and $118.0 \pm 3.4\%$ of TN when 3.13 g $\text{TS}_{\text{ALE}}/\text{L}$ was employed (Fig. 1). Even though the overall PO_4^{3-} removal up to $90.8 \pm 0.0\%$ by ALE hydrogels, TP increased up to $42.5 \pm 3.5\%$ in the experiments with 3.75 g $\text{TS}_{\text{ALE}}/\text{L}$ (Fig. 1). TP concentration lowered following the PO_4^{3-} removal only when a lower mass of ALE was used (1.88 g $\text{TS}_{\text{ALE}}/\text{L}$). The lowest dosage of ALE was also beneficial for the lower release of COD and TN (Fig. 1). Therefore, lower dosages of ALE hydrogels can be further employed which would be helpful to decrease the release of COD, TN and TP, as well as present good performance for phosphate removal.

For all ALE hydrogels dosages, Ca^{2+} and Cl^- ions concentrations significantly rose as a result of the residual solution used for cross-linkage (CaCl_2) still present on ALE hydrogels, even after the several steps of washing (Appendix A - Table S1). However, those high ions concentration presented no detrimental effects on phosphate sorption. Even so, a longer and more efficient washing step of hydrogels is recommended to avoid the generation of a highly concentrated anionic solution with Cl^- and Ca^{2+} ions that could hinder potential large-scale applications. No clear influence of ALE hydrogels could also be ascertained in relation to the concentration of the ions NO_3^- , NO_2^- , Na^+ , Mg^{2+} and K^+ , despite a considerable K^+ removal of $82.9 \pm 0.6\%$ occurred in the experiment with 1.88 g $\text{TS}_{\text{ALE}}/\text{L}$ (Appendix A - Table S1).

3.2. Influence of wastewater composition in terms of initial concentrations of PO_4^{3-} , NH_4^+ and NO_3^- (experiment #2)

Since sorption is also a concentration-dependent phenomenon, the effect of high initial concentrations of the ions PO_4^{3-} , NH_4^+ and NO_3^- separately on ALE hydrogels sorption behaviour was also evaluated. Even when the adsorption tests were performed at high concentrations of PO_4^{3-} , NH_4^+ or NO_3^- , ALE hydrogels only removed PO_4^{3-} (Fig. 2B, C and D and Appendix A - Table S2). The higher PO_4^{3-} initial concentration of 7.3 mg PO_4^{3-} -P/L considerably increased the practical loading by more than three times when compared to concentration at 2.2 mg PO_4^{3-} -P/L (from 0.40 ± 0.00 mg PO_4^{3-} -P/g TS_{ALE} to 1.22 ± 0.07 mg PO_4^{3-} -P/g TS_{ALE}), although the removal efficiency was slightly reduced (from $90.8 \pm 0.00\%$ to $83.6 \pm 4.7\%$) (Table 4). Furthermore, a sharp drop on PO_4^{3-} concentration from 7.3 mg PO_4^{3-} -P/L to 4.6 mg PO_4^{3-} -P/L was observed during the first 5 min of experiment for the higher initial PO_4^{3-} concentration (Fig. 2B). The lower concentration of organic phosphorus in relation to phosphates due to KH_2PO_4 addition also led to an overall TP removal of $34.7 \pm 2.7\%$ (15.45 ± 0.63 mg TP/L) (Fig. 3).

Higher initial NH_4^+ -N and NO_3^- -N concentrations did not result in the removal of these ions by ALE hydrogels (Fig. 2C and D). Besides, PO_4^{3-} -P removal and sorption occurred even at higher initial NH_4^+ -N and NO_3^- -N concentrations. At initial concentration of 82.5 mg NH_4^+ -N/L, $85.2 \pm 3.9\%$ of PO_4^{3-} -P was removed and the practical loading was 0.40 ± 0.00 mg PO_4^{3-} -P/g TS_{ALE} (Table 4). Also, no release of TP occurred (Fig. 3). For the initial concentration of 17.5 mg NO_3^- -N/L, there was both lower removal of $66.2 \pm 6.6\%$ of PO_4^{3-} -P and practical loading of 0.22 ± 0.02 mg PO_4^{3-} -P/g TS_{ALE} apart from an increase of $39.9 \pm 2.3\%$ of TP. The lower removal efficiency and sorption is probably because of the lower initial PO_4^{3-} concentration (1.7 mg PO_4^{3-} -P/L), but with no clear influence of the high NO_3^- concentration. Initial concentrations act as a driving-force that can result in higher or lower sorption capacities (Hu et al., 2015; Jang and Lee, 2019; Yang et al., 2006b). Besides, nitrate has been demonstrated to present negligible effects on phosphate adsorption by hydrogels in synthetic solutions (Zheng and Wang, 2010).

As observed for the previous experiments, a high release of COD and TN also occurred for all the tests with higher PO_4^{3-} -P, NH_4^+ -N and NO_3^- -N concentrations and no clear effect on Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+} concentrations was ascertained (Fig. 3 and Appendix A - Table S2).

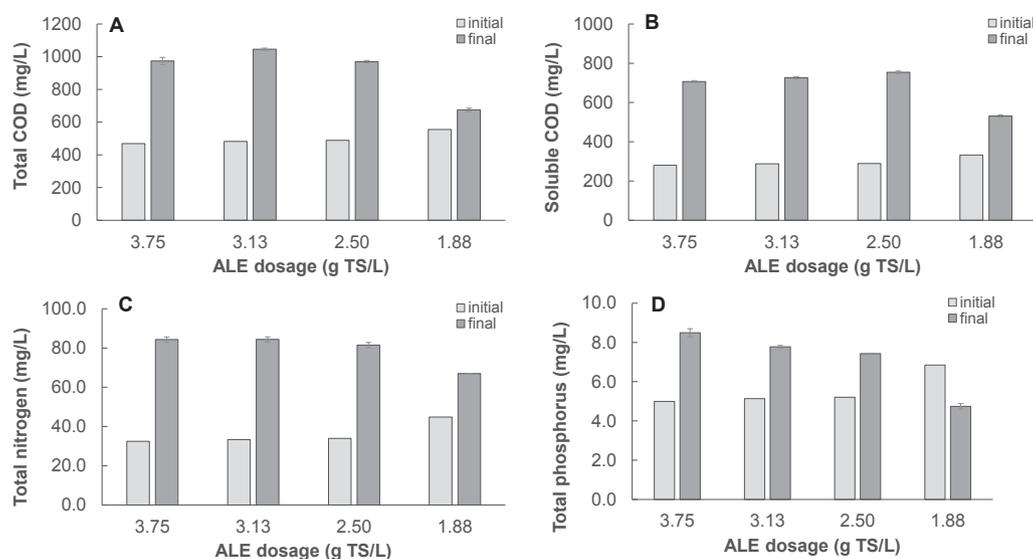


Fig. 1. Wastewater parameters measured during the sorption tests with different dosages of ALE hydrogels (experiment #1). (A) tCOD (B) sCOD, (C) TN and (D) TP measured in the wastewater at the beginning (initial, $t = 0$ min, light gray) and end (final, $t = 240$ min, dark gray) of the sorption tests. Conditions: initial pH 8.67 ± 0.20 , temperature 21 ± 1 °C, duration 240 min.

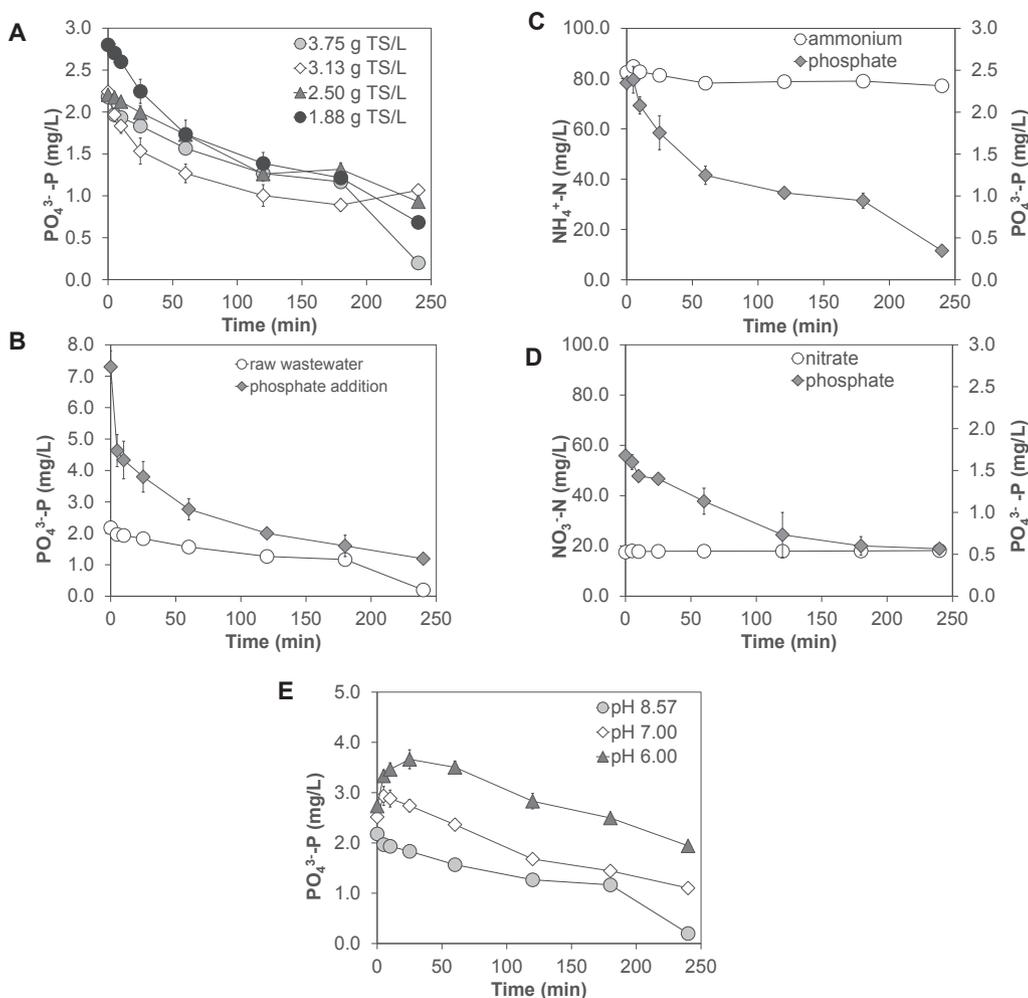


Fig. 2. Kinetics of sorption. (A) $\text{PO}_4^{3-}\text{-P}$ concentration in the wastewater as a function of time after the addition of different initial masses of ALE hydrogels. (B) $\text{PO}_4^{3-}\text{-P}$, (C) $\text{NH}_4^+\text{-N}$ and (D) $\text{NO}_3^-\text{-N}$ concentration in the wastewater as a function of time after the addition of 3.75 g TS_{ALE} g/L and KH_2PO_4 , NH_4Cl and NaNO_3 , respectively. (E) $\text{PO}_4^{3-}\text{-P}$ concentration in the wastewater as a function of time at different pH values after the addition of 3.75 g TS_{ALE} g/L. pH 8.57 corresponds to raw wastewater (without amendments). Error bars in all graphs show the standard deviation from triplicate tests.

Table 4

$\text{PO}_4^{3-}\text{-P}$ removal and practical loading from wastewater by ALE hydrogels at different initial ions concentrations. Conditions: initial pH 8.68 ± 0.23 , dosage 3.75 g $\text{TS}_{\text{ALE}}/\text{L}$, temperature 21 ± 1 °C, duration 240 min.

| Initial ion concentration in wastewater | $\text{PO}_4^{3-}\text{-P}$ removal (%) | $\text{PO}_4^{3-}\text{-P}$ sorption (mg/g TS_{ALE}) |
|---|---|---|
| 2.2 mg $\text{PO}_4^{3-}\text{-P}/\text{L}^*$ | 90.8 ± 0.0 | 0.40 ± 0.00 |
| 7.3 mg $\text{PO}_4^{3-}\text{-P}/\text{L}$ | 83.6 ± 4.7 | 1.22 ± 0.07 |
| 82.5 mg $\text{NH}_4^+\text{-N}/\text{L}$ | 85.2 ± 3.9 | 0.40 ± 0.02 |
| 17.5 mg $\text{NO}_3^-\text{-N}/\text{L}$ | 66.2 ± 6.6 | 0.22 ± 0.02 |

* Raw wastewater (without amendments)

3.3. Influence of pH on the PO_4^{3-} removal by ALE hydrogels (experiment #3)

During the sorption tests, pH considerably affected the phosphate concentration dynamics by ALE hydrogels for the three pH values tested of 6.00, 7.00 and 8.57 (Fig. 2E, Fig. 4 and Table 5). Interestingly, according to the kinetics (Fig. 2E), an initial increase in PO_4^{3-} concentration occurred at pH 7.00 and even more pronounced at pH 6.00, which is a tendency not observed at pH 8.57. For pH 7.00, the PO_4^{3-} concentration rose until $t = 5$ min and then declined. On the contrary, at pH 6.00 the increase in PO_4^{3-} concentration lasted at least until $t = 25$ min. Decreasing pH also tended to reduce both the removal efficiency and practical loading of PO_4^{3-} by ALE during the timeframe of the experiments (Table 5). pH 6.00 significantly decreased the PO_4^{3-} removal efficiency down to $28.9 \pm 0.8\%$ and the practical loading to 0.16 ± 0.00

mg $\text{PO}_4^{3-}\text{-P}/\text{g}$ TS_{ALE} compared to the other pH values tested. Moreover, the pH in the end of all the experiments tended to rise (Table 5). The lower the initial pH, the higher was the increasing in the final pH. For instance, for the initial pH 6.00, the solution pH was 8.06 at $t = 240$ min. For all the values of pH tested occurred a high release of COD and TN with no clear influence of pH (Fig. 4). There was no release of TP only at pH 7 and 6, while for pH 8.57 there was a raise of $42.5 \pm 3.5\%$ (Fig. 4). Finally, no clear pH influence was observed for the other parameters analyzed (Appendix A - Table S3).

Results showed that pH has a great impact on phosphate removal, what can help elucidating mechanisms of phosphate sorption by ALE hydrogels. At initial pH value of 7.00 and especially of 6.00, an initial increase of PO_4^{3-} concentration followed by a further decrease occurred along sorption, while the pH rose to final values of 8.40 ± 0.02 and 8.06 ± 0.00 respectively (Fig. 2E and Table 5). The increase of pH is an evidence of the release of OH^- from ALE and/or consumption of H^+ cations from the solution. Initially, the lower pH values may have weakened the ALE hydrogels matrix which in turn increases the release of ions such as OH^- and phosphates, since ALE composition also include phosphates (Kim et al., 2020). Besides, the pH dependence for phosphate adsorption has been associated to the ligand exchange between phosphate and OH^- (Xue et al., 2009; Yang et al., 2006b). At low pH, OH^- is released from alum sludge, which in turn provides active sites for phosphorus adsorption and increases pH (Liu et al., 2016). The same mechanism may have occurred with ALE along the experiment by PO_4^{3-} replacing OH^- on the surface of the hydrogel and thus increasing the pH. When the pH reached values over 7, ALE structure may be more stable and PO_4^{3-} sorption exceeds the rate of PO_4^{3-} release. At these conditions, a lower

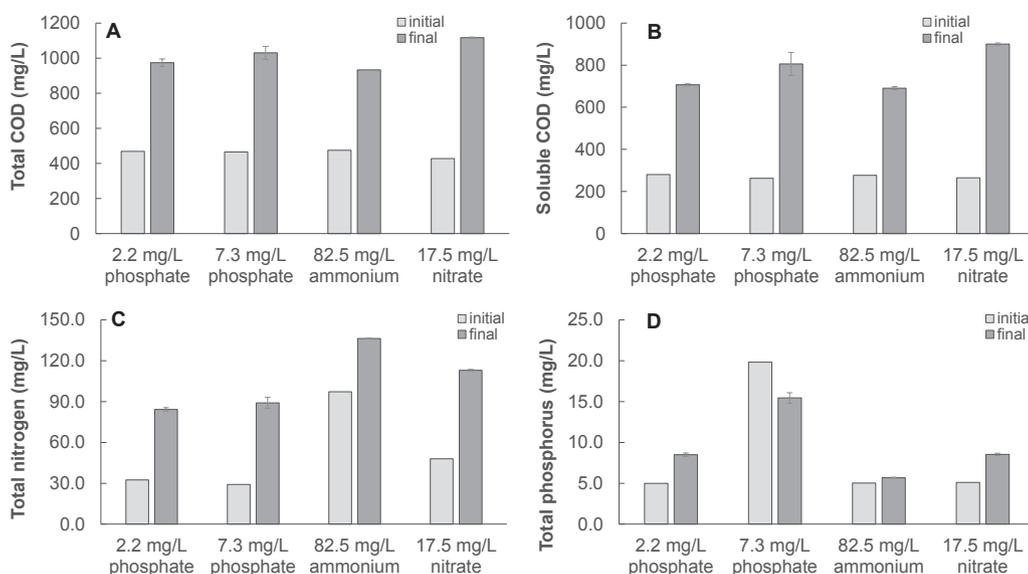


Fig. 3. Wastewater parameters measured during the sorption tests with different initial concentrations of PO_4^{3-} , NH_4^+ and NO_3^- in wastewater (experiment #2). (A) tCOD (B) sCOD, (C) TN and (D) TP measured in the wastewater at the beginning (initial, $t = 0$ min, light gray) and end (final, $t = 240$ min, dark gray) of the sorption tests. Conditions: dosage 3.75 g $\text{TS}_{\text{ALE}}/\text{L}$, temperature 21 ± 1 °C, duration 240 min. Phosphate concentration at 2.2 mg/L $\text{PO}_4^{3-}\text{-P}$ corresponds to raw wastewater (without amendments).

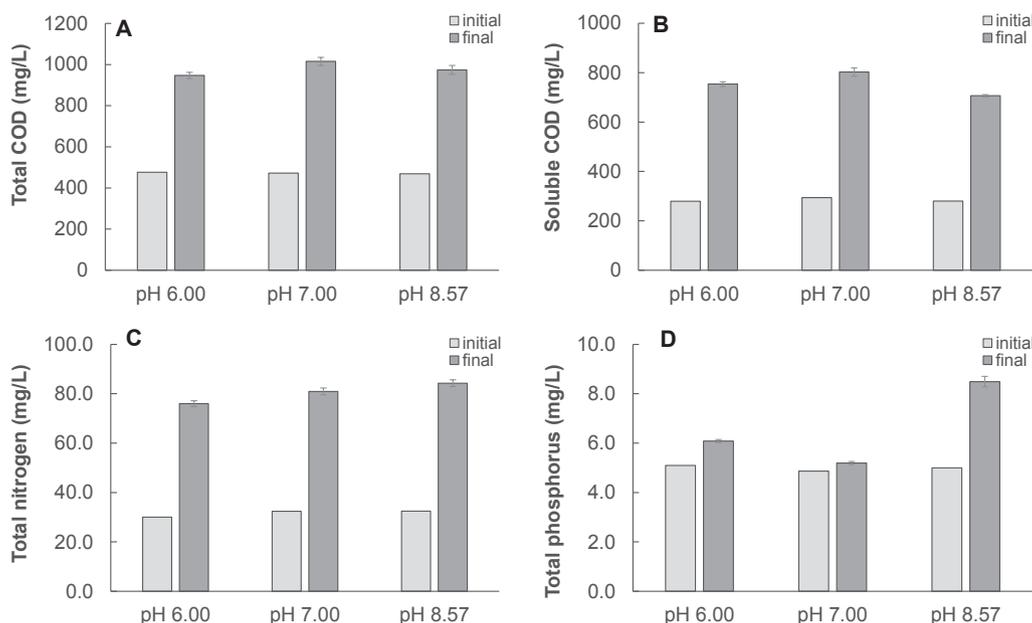


Fig. 4. Wastewater parameters measured during the sorption tests at different initial pH values (experiment #3). (A) $\text{PO}_4^{3-}\text{-P}$, (B) tCOD (C) sCOD, (D) TN and (E) TP measured in the wastewater at the beginning (initial, $t = 0$ min, light gray) and end (final, $t = 240$ min, dark gray) of the sorption tests. Conditions: dosage 3.75 g $\text{TS}_{\text{ALE}}/\text{L}$, temperature 21 ± 1 °C, duration 240 min. pH 8.57 corresponds to raw wastewater (without amendments).

Table 5

Final pH, $\text{PO}_4^{3-}\text{-P}$ removal and practical loading from wastewater by ALE hydrogels at different initial pH. Conditions: dosage 3.75 g $\text{TS}_{\text{ALE}}/\text{L}$, temperature 21 ± 1 °C, duration 240 min.

| Initial pH | Final pH | $\text{PO}_4^{3-}\text{-P}$ removal (%) | $\text{PO}_4^{3-}\text{-P}$ sorption (mg/g TS_{ALE}) |
|------------|-----------------|---|---|
| 8.57* | 8.76 ± 0.01 | 90.8 ± 0.0 | 0.40 ± 0.00 |
| 7.00 | 8.40 ± 0.02 | 56.1 ± 2.0 | 0.28 ± 0.01 |
| 6.00 | 8.06 ± 0.00 | 28.9 ± 0.8 | 0.16 ± 0.00 |

* Raw wastewater (without amendments)

rate of OH^- release may have enabled a ligand exchange reaction with organic matter from ALE which favoured PO_4^{3-} sorption. During phosphate adsorption by alum sludge, the alkaline media (pH ~ 9) induces more organic matter and humic substances release which also accelerate

the ligand exchange process (Liu et al., 2016; Yang et al., 2006a). Higher phosphate adsorption has been correlated to the release of organic matter (Liu et al., 2016). Considering the high increase of COD, TP and TN along the adsorption tests, part of ALE organic matter components may have been displaced by phosphate ions in solution (i.e., ligand exchange), which in turn favored phosphate sorption. Besides, the concentration of phosphate species in wastewater in the form of HPO_4^{2-} are higher at pH 7.00 and predominant at pH 8.57 (Jenkins et al., 1971), what in turn can facilitate the bound to Ca^{2+} ions present at the ALE hydrogel surface.

Results also showed that ALE hydrogels behaved as a buffer agent by heading pH to over 8 along most of the sorption tests performed at different initial pH (Table 5). Other hydrogels adsorbents have also been reported to act as a buffer agent at wide ranges of pH along ions adsorption, such as mixtures of drinking water treatment residuals and

alginate (Shen et al., 2018), chitosan-Fe³⁺ complex (Hu et al., 2015) and alum sludge (Liu et al., 2016). At alkaline conditions, the existence of OH⁻ in the bulk liquid can reduce the release rate of OH⁻ from ALE. Furthermore, in the presence of phosphate, organic matter is released for PO₄³⁻ and OH⁻ exchange (Liu et al., 2016). In this case, phosphate adsorption can be also followed by H⁺ release which ultimately controls the pH variation (Yang et al., 2006b). Those mechanisms may act as stabilizers to keep the pH balanced at the values between 8 and 9 as herein observed.

3.4. Phosphorus content determination in ALE hydrogels

The sorption of phosphorus by ALE hydrogels was confirmed by the mass balance derived from ICP-OES measurements of hydrogels before and after sorption. The significant sorption of PO₄³⁻ was especially demonstrated for the experiment at initial high PO₄³⁻ concentration. ALE hydrogels before sorption had up to 8120 mg P/kg ALE and the content of phosphorus clearly increased more than three times to 26102 mg P/kg ALE after the sorption experiment with PO₄³⁻ amendment (experiment #3).

3.5. Possible mechanisms acting on phosphate removal by ALE hydrogels

An important point to be discussed is about the possible mechanisms acting on phosphate removal by ALE hydrogels. Phosphate adsorption experiments using adsorbents with calcium have showed that precipitation in the bulk may contribute to phosphorus removal (Siwek et al., 2016; Xu et al., 2019). At high calcium concentration and pH values, phosphate ions react with calcium ions to form calcium phosphates (Joko, 1985). Herein, although ALE hydrogels went through several washing steps to remove the excess of Ca²⁺, an increase of calcium ions in solution may have occurred slowly along the adsorption tests due to hydrolysis and deterioration of the crosslinked network (Appendix A - Tables S1, S2 and S3). However, at Ca²⁺ concentrations of 50–350 mg/L and pH values of 8.00–9.00 at the beginning of the adsorption experiments, phosphate might not have initially been precipitated (Joko, 1985). A study which assessed phosphate adsorption by calcite have reported that at pH 8.3 there is no phosphate precipitation when the initial phosphate concentration is below 7.5 mg/L (Li et al., 2017), i.e., conditions similar to ours. In addition to that, at pH 9.1–10.1 and PO₄³⁻ concentrations below 10 mg/L, phosphate adsorption was the main mechanism for phosphate removal (Li et al., 2017). Furthermore, ICP-OES measurements (see section 3.4) indicated an enrichment of phosphorus in ALE, what demonstrates the entrapment of phosphate into ALE hydrogels. Hence, precipitation in the bulk may not have played a major role on the phosphate removal by ALE hydrogels.

Cross-linkage of calcium ions with ALE may have played a relevant role in bridging phosphate ions through surface complexation providing positive sites (Jang and Lee, 2019). Cross-linking via the diffusion method as the one herein used produces hydrogels with a higher Ca²⁺ content on the surface (Pawar and Edgar, 2012), which in turn would favor surface complexation with phosphate. Previous studies using synthetic phosphate solutions have also reported phosphate removal by Ca²⁺-ALE hydrogels via the formation of calcium phosphates crystals on the surface of ALE (Dall'Agnol et al., 2020). Besides surface complexation and surface precipitation, ligand exchange has effect on phosphate adsorption simultaneously as exposed in Section 3.3. Thus, possibly either phosphate was directly bound to a counter ion as Ca²⁺ on ALE surface or an ion/compound was released to enable phosphate bind.

3.6. ALE hydrogels help phosphate recovery

ALE hydrogels presented a selectivity for phosphate sorption even in the presence of competing ions normally presented in municipal wastewater (i.e., NH₄⁺, NO₃⁻, Cl⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺). Phosphate removals of up to 90.8% ± 0.0 and practical loadings up to 1.22 ± 0.07

mg PO₄³⁻-P/g TS_{ALE} (Fig. 2, Tables 3 and 4) were measured. Those values need to be carefully evaluated considering the experimental conditions of the sorption tests. In a study using ALE hydrogels beads and synthetic phosphate solutions, Dall'Agnol et al. (2020) obtained much higher practical loading (57.25 ± 12.18 mg P/g TS_{ALE}), but at temperature of 45 °C, pH = 8, initial phosphate concentration of 100 mg P/L and ALE dosage of 0.39 g TS_{ALE}/L. The same authors obtained a phosphorus removal efficiency of 72.50 ± 2.79% in similar conditions than the previously reported but with a dosage of 3.95 g TS_{ALE}/L. Although the removals obtained herein are similar to the one obtained by Dall'Agnol et al. (2020), the lower practical loading may be attributed to the different conditions in each work as type of adsorbate (synthetic vs. real), temperature, shape of ALE hydrogels (beads vs. stripes), adsorbent dosage and mainly initial phosphorus concentration. Adsorption capacity of phosphate by several different adsorbents ranges widely from 0.13 to 133.3 mg/g (Dall'Agnol et al., 2020; Dos Reis et al., 2020; Jang and Lee, 2019). Hence, the comparison of values of sorption capacity/removals must be carefully done due to the high variability of results according to the experimental conditions.

It was not overlooked that the batch sorption tests had a duration of 4 limited hours in which equilibrium was not reached. Thus, even lower phosphate concentrations can be achieved by ALE hydrogels. Besides, initial phosphate concentrations were overall low compared to most of adsorption experiments in literature (C₀ usually exceeding 100 mg PO₄³⁻/L) (Bacelo et al., 2020). Those features make the use of kinetic models less suitable for the present work. Considering the use of adsorbent for municipal wastewater polishing, the focus should be on the adsorption capacity and affinity at the realistic phosphate concentrations (i.e., the practical loading) rather than the maximum adsorption capacity (Kumar et al., 2019). This work was a proof-of-concept approach to test the adsorption capacity of various wastewater compounds by ALE hydrogels under more realistic conditions. Even so, adsorption equilibrium kinetics and isotherms as well as compositional analysis are encouraged to be performed in future experiments to acquire more information about the sorption dynamics of ALE hydrogels, removal mechanisms and influencing factors.

3.7. Practical implications

3.7.1. ALE hydrogels structure along sorption

ALE hydrogels greatly contributed for the increase of COD, TN and TP concentrations along the sorption tests. We hypothesize that the increased concentrations in COD, TN and TP can be attributed to the low cohesion of ALE hydrogels. Breakage of ALE hydrogels during adsorption tests could lead to the release of small debris, ultimately increasing carbon and organic nitrogen/phosphorus concentrations. The release of constitution compounds from ALE hydrogels was previously observed for pH values between 6.5 and 8.5 (Felz et al., 2020a). ALE is mainly composed by proteins, polysaccharides, humic acids and others phosphated compounds (Felz et al., 2019; Kim et al., 2020; Schambeck et al., 2020a), which consequently acted as a source of carbon, nitrogen and phosphorus to the media. Besides, ligand exchange reactions during the sorption process can destabilize cross-linked hydrogels backbone which in turn results in the release of components (Lee and Mooney, 2012). To tackle those drawbacks, ALE structure can be improved by different ways to tailor its mechanical properties and in turn to limit the debris detachment and release of ions/soluble organic constituents to the liquid. Sodium alginate alone or in mixture with other adsorbents can hinder or decrease the release of compounds to the bulk liquid (Rocher et al., 2008; Siwek et al., 2016). Thus, ALE can be mixed with other polymers (such as commercial alginate) before cross-linkage or else can be crosslinked with other cations as copper or zinc which have been demonstrated to form stronger ALE hydrogels (Felz et al., 2020a).

3.7.2. ALE as a potential agent for mainstream phosphorus recovery

Results showed that ALE hydrogels are able to recover phosphorus

from municipal wastewater. Biological nutrient removal efficiency is sometimes reported as an issue in some real wastewater treatment systems exhibiting poor stability (Milferstedt et al., 2017; Nancharaiah et al., 2018; Xu et al., 2020). Thus, sorption has recently been regarded as a promising technology to simultaneously remove and recover nutrients from municipal wastewater (Cruz et al., 2019). Domestic sewage is a promising source of phosphorus since the direct application of the sludge in the agriculture has laws restrictions in addition to the sanitation risks related to organic micropollutants and pathogens (Egle et al., 2016).

The choice of an adsorbent should be based not only on the satisfactory adsorption capacity, but also on an evaluation of several benefits and characteristics (Kumar et al., 2019). In this context, ALE hydrogels show advantages and potential as a biosorbent such as recovery from a cheap and easy available raw material (i.e., waste biological sludge), and ALE hydrogels enriched in phosphorus can be used as post-sorption biomaterial. Those two features dispense the need for reusability of ALE hydrogels, which would save the cost for regeneration processes.

ALE hydrogels have a high content of organic matter, nitrogen and especially phosphorus after adsorption. Besides, ALE are recovered under harsh conditions (i.e., high pH and temperature) which have the potential to eliminate/decrease pathogens. Those characteristics make post-sorption PO_4^{3-} -enriched ALE hydrogels potential agents for a direct application in the agronomic field as fertilizers/soil enhancers (Dos Reis et al., 2020). Or else, the heat generated by the energy use of biogas at

WWTP that implement anaerobic digestion can be directed to thermally degrade ALE to obtain by-products such as calcium phosphates ashes which can be further used as fertilizers. In Fig. 5, a new conceptual pathway is proposed that allows for continuous mainstream phosphate recovery from municipal wastewater based on ALE hydrogels adsorption coupled with further side-stream application. Nevertheless, further studies are needed to mainly address the required structural improvements discussed in Section 3.7.1, as well as to assess the potential agronomic use (e.g., phosphorus release in soil), the economic impacts of this application, and to perform a life cycle assessment.

4. Conclusions

Phosphate removal from municipal wastewater was successfully achieved using ALE hydrogels. ALE hydrogels presented high sorption selectivity for phosphate (up to 90.8% of removal) even in the presence of competing ions normally presented in municipal wastewater. pH strongly affected phosphate removal. Neutral to acidic pH values (6.00 – 7.00) decreased PO_4^{3-} removal up to 28.9%, what suggests that the use of ALE hydrogels is more suitable for basic wastewaters (pH \approx 8.50). This study demonstrates that a recovered bioresource (ALE) has a promising potential for bioresource recovery (phosphorus). Nevertheless, further studies are needed mainly to improve ALE hydrogels structure along adsorption.

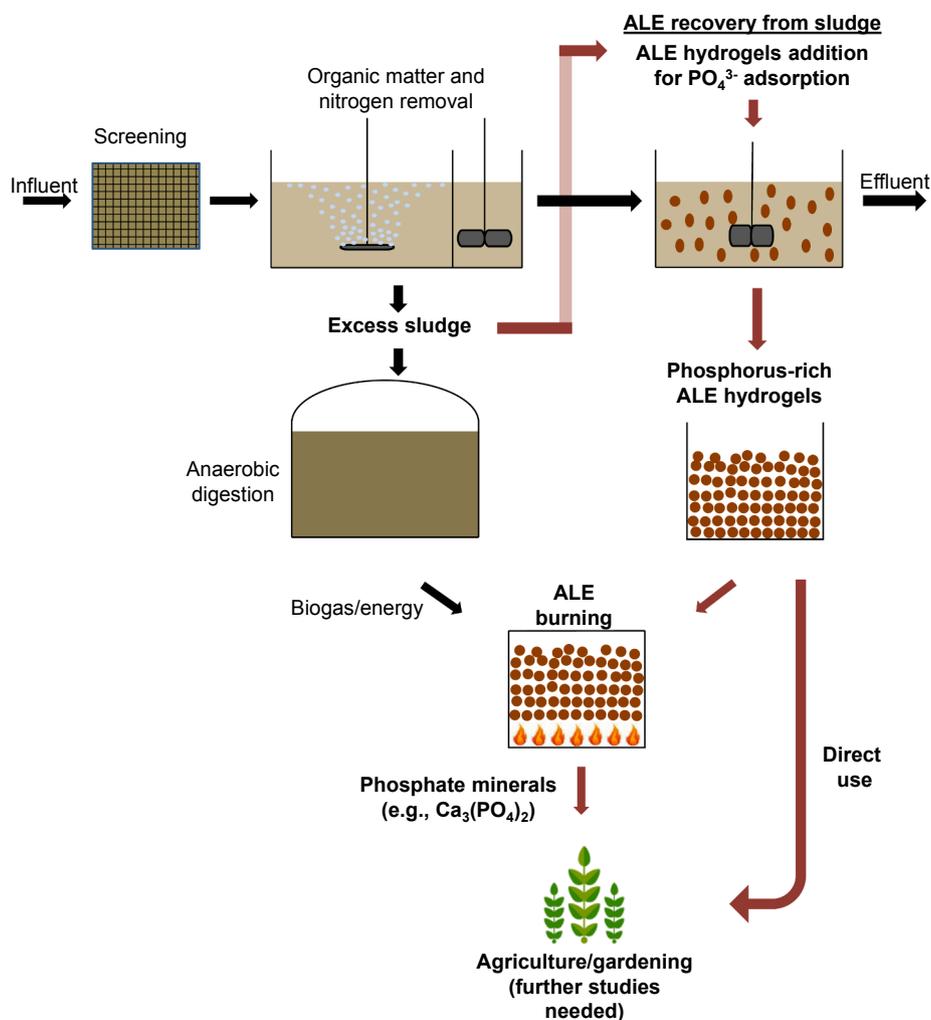


Fig. 5. Schematic conceptual diagram for mainstream continuous phosphate sorption by ALE hydrogels followed by side-stream ALE use as input in the agronomic field. This scheme depicts an implementation example of the concept of wastewater resource recovery facility in a wastewater treatment plant.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2021.125167>.

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