Controlled Release of Phosphorus from Superabsorbent Phosphate-Bound Alginate-Graft-Polyacrylamide: Resistance to Soil Cations and Release Mechanism

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ABSTRACT: Two controlled-released fertilizers of phosphorylated alginate grafted with polyacrylamide (P-Alg-g-PAM) were synthesized. Monoammonium phosphate (MAP) and diammonium phosphate (DAP) were reacted with a matrix of sodium alginate (Alg) and poly(vinyl alcohol) (PVA). The phosphorylated matrix was then graft with acrylamide. The obtained fertilizer materials showed excellent water absorbance. The controlled-release behavior of phosphorylated alginate grafted with polyacrylamide (P-Alg-g-PAM) was investigated at normal pH and 25 °C. The fertilizer materials exhibited release of phosphorus up to 77% for the MAP sample and up to 57% for the DAP sample till the forty fifth day of the application at pH 7 and 25 °C. More importantly, when the release experiments were conducted in calcium chloride medium, the fertilizers were able to release phosphorus efficiently with slight decrease until the forty fifth day of the application, suggesting that the presence of Alg in the fertilizer formulation may help in extending the duration for which phosphorus is available to the plant.

INTRODUCTION

Phosphorus (P) is an essential nutrient for all plant and animal cells and is one of a group of 17 elements necessary for plant growth, being vital for normal plant development and nutrition. However, it has no suitable alternative in plant growth and cannot be manufactured. Unfortunately, plant uptake of P from soil can be limited by the capacity of phosphate binding of various types of soil, making it a significant restricting parameter in accomplishing ideal yields in agriculture. In a recent study conducted by both Cordell and White, it was shown that nearly two thirds of the agricultural soil in the world suffers from phosphorus deficiency. It has also been stated that ~30% of soil in several countries shows a high phosphate-fixing ability, for example, in northern and sub-Saharan Africa, Brazil, and southern China. The same applies to Saudi Arabian soils, which are mainly calcareous and/or coarse-textured soils. These soils are also very poor in organic matter and have high amounts of CaCO₃. Under such alkaline and calcareous soil conditions, the use of P by plants is impaired, owing to the formation of insoluble calcium phosphate minerals. As a result, the phosphorus uptake and utilization by the crops are very low, and addition of a P fertilizer is required to meet the crops’ need for this nutrient. However, addition of high levels of P in agricultural soil has led to environmental problems. Another challenge is that P resources could be depleted within 30–70 years.

Hence, several research groups conducted studies to find a solution to this problem. The slow- or controlled-release method was used by different research groups. This method is based on fixing or coating the fertilizer on a material that is in most applications a polymer, and through this material, the fertilizer is released at a slow rate. This means that the plants can take up most of the P without it being lost through leaching into ground and surface water, which would be harmful to the nearby environment. The major benefit of the controlled-release technique is avoiding adding heavy doses of fertilizers and, hence, reducing the environmental pollution caused by the excessive use of P.

For example, Sanders et al. used a formulation made from water-soluble copolymers of maleic anhydride and vinyl acetate, itaconic anhydride, or citraconic anhydride, followed by direct addition of MAP or DAP. Such a polymer formulation could mask soil cations, hence allowing improved usage of the P fertilizer. Other formulations used an inorganic matrix such as zeolite or montmorillonite mixed with MAP where the fertilizer is physically mixed with the matrix. In the last decade, new emerging materials were used in the slow-release formulation. These materials include, for example, nanoparticles and metal oxides, layered double hydroxide (LDH), graphene oxide (GO), and metal–organic frameworks (MOF). Some polysaccharide-graft formula-
Synthesis of several hydrogels for utilization in agriculture and horticulture. The latter relies on the idea of bonded to MAP and DAP. The latter relies on the idea of controlled-release techniques, in which a sufficient amount of the fertilizer is provided to the plant. Most of the previous studies are concerned with the slow-release process and did not address or report the effect of competitive cations.

Polysaccharide-graft copolymers have been used in the synthesis of several hydrogels for utilization in agriculture and horticulture. The use of polysaccharide-graft copolymers in agriculture depends on their properties, which can be tailored during preparation. Important properties for agricultural applications include the physical form, swelling behavior, surface characteristics, permeability, diffusion, chemical sensitivity and stability, and mechanical and long-term stability. Various polysaccharides have been used, including starch, cellulose, chitin/chitosan, carrageenan, agar, and alginate. Alginate, one of the polysaccharides used in agriculture, is a naturally occurring polymer generally found in and extracted from brown seaweed and comprises a linear block copolymer of (1→4)-linked β-D-mannuronic acid and α-L-guluronic acid units. In spite of its poor water solubility, alginate forms a gel with water and is able to form gels through crosslinking with divalent cations of metals such as calcium, magnesium, barium, and so forth. via carboxyl and hydroxyl groups. As a result, it can be used as a matrix for phosphate fertilizers, with the role of masking calcium ions and thus facilitating phosphate uptake by the plant. On the other hand, PVA is a water-soluble polymer that contains a large number of pendant hydroxyl groups and is nontoxic, biocompatible, and biodegradable. Because of these features, it has found many applications in pharmaceuticals, cosmetics, textiles, and the paper and food industries. The presence of the hydroxyl groups renders the PVA hydrophilic and helps in binding with heavy metals. Therefore, we propose that mixing both substances would result in a material capable of masking soil calcium ions, therefore permitting the phosphorus to be released with limited reaction with soil calcium ions.

Our aim in this work was to develop a hydrogel fertilizer system capable of providing P at a prolonged rate and maintaining an adequate hydration level for the plant. Because of their abundance and variety of sources, natural polysaccharides such as sodium alginate would be good candidates as feed materials for the synthesis of modified hydrogels. In this study, we describe the synthesis of a slow- or controlled-release formulation based on a phosphorylated sodium alginate grafted with polyacrylamide (P-Alg-g-PAM), as a controlled-P release system with integration of water retention to maintain a proper level of hydration of the plant and a slow-release fertilizer. The release behavior was studied also in the presence of calcium chloride solution to check the role of alginate in the prepared hydrogel fertilizer. The swelling behavior and swelling kinetics of the hydrogel were studied at 25 °C, and the mechanisms of P release were investigated using the Korsmeyer–Peppas model. Such a formulation can be applied to solve phosphorus deficiency.

### RESULTS AND DISCUSSION

#### Synthesis of P-Alg-g-PAM

In order to examine the prepared formulation as a powerful controlled P releasing system so that it can be helpful in application to the crops and maintain the swelling behaviors of the controlled-release fertilizer system, sodium alginate was mixed with PVA to form a matrix network for attaching the fertilizer. This was then phosphorylated with MAP and DAP, separately, to provide the base fertilizers. Alginate is extensively used in industrial applications because of its ability to retain water and to form gels, in addition to its thickening and stabilizing properties. It is also able to bind easily with various divalent metal ions. PVA can form hydrogels and exhibit higher mechanical strength and durability in acidic concentrated solutions than the alginate gel; hence, mixing with alginate may result in improving the brittleness of pure calcium alginate. It is worth mentioning that PVA is biodegradable by different organisms under both aerobic and anaerobic conditions. Microorganisms capable of degrading PVA include both Gram-negative and Gram-positive bacteria and fungi. Although literature data indicate that under conditions of soil burial, the biological degradation of PVA and PVA-based materials is quite slow, it has been established that biodegradation of PVA is enhanced in water media. In addition, its blend with biodegradable polysaccharides can achieve efficient biodegradation. Therefore, mixing alginate with PVA is the main impetus for its use in this research, where we can maintain soil water retention and for masking soil cations without harming the environment.

The phosphorylation of alginate was carried out using two commercially popular phosphate fertilizers, MAP and DAP, in approximately 1:1 M ratio, in order to compare the results of the final compounds. The phosphorylated samples were further grafted with acrylamide using KPS as an initiator to obtain a high-absorbent hydrogel fertilizer. Methylene bisacrylamide was used as a crosslinking agent to prevent the final product from dissolution during the final application. The extent of crosslinking was 6.3% based on the stoichiometry of the monomers. The grafted material was highly swellable and took a long time to dry in the vacuum oven. The grafting yield, grafting efficiency, degree of swelling, and equilibrium water content (EWC) (Table 1) were calculated according to eqs 1–4:

1. \[ \text{grafting yield} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100 \]
2. \[ \text{grafting efficiency} = \left( \frac{W_2 - W_1}{W_0 - W_1} \right) \times 100 \]
3. \[ \text{degree of swelling, } DS = \left( \frac{W_s - W_d}{W_d} \right) \times 100 \]
4. \[ \text{EWC} = \left( \frac{W_e - W_d}{W_d} \right) \times 100 \]

where \( W_1 = \) weight of the alginate; \( W_2 = \) weight of the grafted material (i.e., weight of the extracted grafted product); \( W_3 = \)...
weight of the crude product before extraction; and \( W_d \): dry material and \( W_s \): wet or swollen material.

The route to the superabsorbent phosphate formulations (exemplified for MAP-Alg-g-PAM) is outlined in Scheme 1.

The obtained materials were characterized by Fourier-transform infrared spectroscopy (FTIR). As revealed in Figure 1, pure sodium alginate shows a wide peak at 3400−3500 cm\(^{-1}\) because of OH stretching vibration and another at 1617 cm\(^{-1}\) corresponding to the symmetrical stretching of COO\(^-\), in addition to the bands in the ranges at 1317 cm\(^{-1}\) because of C−O−C (ring) vibrational modes. Upon phosphorylation reaction, new bands appeared at 1247−1197 cm\(^{-1}\) for P=O and at 1440−1415 cm\(^{-1}\) for PO\(_3\)\(^2-\), in addition to the overlapping band in the region 3000−3400 cm\(^{-1}\) because of OH and NH\(_2\). The spectrum of grafted products MAP-Alg-g-PAM and DAP-Alg-g-PAM showed slight differences in the region of 1575−1480 cm\(^{-1}\), which is attributed to amide II, resulting from an overlap between the N−H bending and C−N stretching of the C−N−H group. FTIR spectra of MAP, DAP, polyacrylamide PAM, phosphorylated MAP (or DAP), and the final grafted materials are given in Figures S1 and S2.
**PXRD Patterns.** The powder X-ray diffraction (PXRD) results for pure alginate and its modified derivatives are presented in Figure S3. The PXRD pattern of alginate shows two shoulders at $2\theta = 13.8^\circ$ and at $22.7^\circ$, which have been regarded as mainly semicrystalline and have been attributed to strong hydrogen bonding. After phosphorylation, a marked change in the diffraction pattern of the alginate was observed (Figure S3); new strong peaks appeared at $2\theta = 19.24^\circ$ for the MAP-modified sample and at $19.6^\circ$ for the DAP-modified sample, owing to the introduction of the new phosphate groups. These peaks were greatly reduced after grafting with acrylamide in both the MAP and DAP samples, from which we can conclude that the original semicrystalline structure of the alginate was mostly retained after the grafting reaction. After release, little changes in the peak intensities were observed.

**Thermogravimetric Analysis.** The thermal stabilities of MAP-Alg-g-PAM and DAP-Alg-g-PAM were compared with those of alginate and phosphorylated alginate (Figure 2). For the MAP samples (Figure 2a), the observed thermogram for sodium alginate showed three degradation steps. The first step was observed at $\sim 42 - 115$ °C and mostly was due to moisture evaporation. After the previously mentioned stage, a major weight loss was observed at $\sim 207 - 315$ °C, probably because of decomposition of carboxylate groups and CO$_2$ evolution. A third step of weight loss appeared at $\sim 400 - 800$ °C because of
depolymerization and degradation of the C−O−C bonds of
the alginate backbone and resulted in a residue of 22%.
When the alginate was phosphorylated, the second
degradation step was slightly delayed, occurring in the range ∼237–372 °C,
and the third step occurred at ∼390–514 °C, with a residue of
about 16%. Upon grafting with acrylamide, the observed
thermogram showed a shift in the second step to ∼286−454 °C,
and less residue was obtained owing to the increased
organic content from the acrylamide. A similar trend was
observed for DAP-Alg-g-PAM (Figure 2b). It can be concluded
that both MAP-Alg-g-PAM and DAP-Alg-g-PAM are stable up
to 200 °C and can thus be applied safely.

Scanning Electron Microscopy. The Scanning electron
microscopy (SEM) images of MAP-Alg-g-PAM and DAP-Alg-
g-PAM show that the surface nature of alginate (Figure S4)
appeared to be slightly altered and showed sharper edges of
finely divided crystallites, owing to phosphorylation with either
MAP (Figure S4b) or DAP (Figure S4c) and the formation of
phosphate groups. The SEM photo of the grafted MAP-Alg-g-PAM
and DAP-Alg-g-PAM revealed smoother edges in the
surface morphology, owing to grafting and surface coverage by
polyacrylamide chains.

Swelling Studies. It is well known that reaction conditions
strongly influence the swelling performance of the super-
absorbent polymers. The swelling profiles of the fertilizer
materials MAP-Alg-g-PAM and DAP-Alg-g-PAM are presented
in Figures 3 and S5. The behavior of swelling for a hydrogel
polymer depends on crosslinking and the presence of pendant
ionic groups of the polymer network. The swelling of a
hydrogel network occurs because of the presence of charged
groups where adjacent fixed charged groups repel each other,
leading to the network expanding and the swelling. In the
present systems, there are carboxylate and phosphate groups in
the network, where electrostatic repulsion between these
charged groups will lead to additional osmotic pressure that
induces network swelling. Besides, the presence of the highly
hydrophilic grafted polyacrylamide within the hydrogel matrix
will contribute to the total osmotic force in the system, which
leads to more swelling although not participating in electro-
static interactions.

**Swelling Kinetics.** The swelling kinetics of the fertilizer
materials MAP-Alg-g-PAM and DAP-Alg-g-PAM were evaluated
by the gravimetric method as a function of time till
attainment of a fixed weight for each material. The contact of
the solvent with a polymer results in polymer swelling, until the
maximum amount of absorbed water is reached, which is
termed as equilibrium swelling. The water diffuses through the
available pores in the hydrogel matrix or those formed because of
the movement of the inner sections of the polymer matrix. Polymer swelling can be described by the model suggested
earlier by Schott (eq 5).

\[
\frac{t}{S} = \frac{1}{k_e S_{eq}^2} + \frac{1}{S_{eq}} \cdot t
\]

The mechanism of swelling is then described by the
propagation and relaxation times of the matrix. The values
for the swelling rate constant \(k_e\) and the theoretical
equilibrium swelling \(S_{eq}\) can be determined from the plot
of \(t/S\) with \(t\). A straight line will result from this plot; thus, we
can determine both \(k_e\) and \(S_{eq}\) from the slope and
intercept, respectively. The values of \( k_i \) and \( S_{eq} \) are given in Table 2.

Table 2. Swelling Parameters of Hydrogel Fertilizer Materials

| sample            | \( ^{a}n \) | \( ^{b}S_{eq} \) | \( ^{c}k_s \) | \( ^{d}K_s \) |
|-------------------|--------------|---------------|--------------|--------------|
| MAP-Alg-g-PAM     | 0.69         | 8.1           | 0.018        | 2.75 \times 10^{-4} |
| DAP-Alg-g-PAM     | 0.63         | 7.2           | 0.016        | 2.99 \times 10^{-4} |

\( ^{a} \) Diffusion exponent. \( ^{b} \) Swelling rate constant (g water/g gel)/min. \( ^{c} \) Theoretical equilibrium swelling; g water/g gel. \( ^{d} \) Initial swelling constant (g water/g gel)/min.

The values of the theoretical equilibrium swelling (\( S_{eq} \)) presented in Table 2 are almost the same as the experimentally determined values of DS presented previously in Table 1. The values of the rate of initial swelling (\( k_i \)) can be obtained by multiplying \( k_s \) and \( S_{eq} \) (Table 2). In order to describe the diffusion of the solvent in hydrogel polymers, Korsmeyer and Peppas applied the power law model (eq 6), as was first suggested by Alfrey and co-workers\(^{41,63}\)

\[
F = M_t / M_{\infty} = k^n t^n
\]

where \( F \) denotes the power of swelling of the hydrogel polymer or the fractional uptake of water at time \( t \); \( M_t \) and \( M_{\infty} \) denote the masses of absorbed water at time \( t \) and at equilibrium, respectively; and \( k \) represents a constant associated with the polymer framework. The parameter \( n \) represents the exponent of diffusion (or swelling exponent), a characteristic of the mechanism of swelling that describes the type of diffusion within the matrix. Equation 6 is applied for the initial stages, representing \( \sim 60\% \) of the water uptake. A Fickian diffusion mechanism is attained when \( n = 0.5 \). In this case, the rate of diffusion of the solvent is significantly less than the mobility of the polymer chains, while when \( 0.5 < n < 1 \), a non-Fickian or abnormal diffusion is accomplished as the rates of polymer chain relaxation and the solvent motion are comparable. The behavior of diffusion of most polymer–solvent systems may fall between these two values, regardless of the temperature and the penetrant activity.\(^{64}\) The situation when \( n = 1.0 \), which occurs when the rates of diffusion of the solvent are a lot quicker than the relaxation of polymer chains, is termed as case II transport, while for \( n > 1.0 \), the mechanism of transport is denoted as supercase II. A plot of \( \ln F \) against \( \ln t \) gives a straight line (Figure 3). When calculating values of \( n \) for all examined samples, this value ranged between 0.5 and 1. This result indicates that the diffusion is non-Fickian, where the rate of water diffusion is similar to the relaxation of the chain. The diffusion of water through the hydrogel fertilizer was determined from the following eq 7, which was derived from the power law model\(^{63,65-67}\)

\[
F = 4(Dt/\pi l^2)^{0.5}
\]

where \( D \) is the coefficient of diffusion \( D \) of water through the hydrogels and \( l \) is the radius or thickness of the cylindrical hydrogel sample. In this case, we assume the cylindrical shape of the sample under study. From the plot of \( F \) against \( t^{0.5} \) (Figure 3d), which gives a straight line, the value of the diffusion coefficient \( D \) can be calculated from the slope of the straight line.

**Kinetics of Grafting.** In order to optimize the yield of the product, we investigated some reaction parameters that affect

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03740)  
Figure 4. Effect of reaction parameters on grafting.
the grafting reaction: monomer and initiator concentration, alginate weight, and temperature (Figure 4). The MAP sample was selected for the grafting study because of its high swelling.

**Effect of Monomer Concentration.** The effect of acrylamide concentration has been examined in the range of 0.20–0.70 mol/L (Figure 4a). Upon increasing the concentration of the monomer, the yield of grafting also increases and reached its maximum value at 0.4 mol/L, after which it started to decline. The observed increase in the grafting yield in the early stages could be explained by the availability of fewer numbers of monomer molecules available for reaction with alginate to form grafted chains.

**Effect of Concentration of the Initiator.** The effect of concentration of the initiator was examined in the range of 0.05–0.40 mol/L, while the other parameters were kept constant. As shown in Figure 4b, it was observed that both %GY and %GE were increased upon increasing the concentration of the initiator from 0.05 to 0.1 mol/L. Beyond that concentration, the grafting yield began to decrease. This decrease in the grafting yield may be due to the competition resulting from the transfer of the chain to the initiator, between chain initiation and termination reactions.

**Effect of Temperature.** The grafting reaction of acrylamide with P-Alg was investigated in the temperature range of 30–60 °C. As shown in Figure 4c, at 50 °C, the grafting yield reached its maximum, and then, a reduction in the grafting yield occurred. The observed decrease could be due to chain transfer reactions, as it is predominant at higher temperatures. Moreover, the increase in temperature may lead to deactivation of the initiator system, and thus, the efficiency of the grafting process decreases. Hence, the decrease in the amount of the copolymer of the graft may be explained by the combination of less-effective chain termination and initiation factors.

**Effect of Alginate Weight.** When the weight of the starting material was increased (Figure 4d), the grafting yield increased gradually till 2.5 g and then decreased. The observed decrease could be due to more alginate chains being available for reaction, combined with insufficient amounts of both the monomer and the initiator to start the grafting reaction.

**Release Behavior.** The release behaviors of P from both MAP-Alg-g-PAM and DAP-Alg-g-PAM fertilizers were determined in distilled water at room temperature, as shown in Figure 5. The cumulative release of P on day 45 was 77 and 57% for the MAP and DAP samples, respectively. The release behavior of the MAP sample was higher than that of the DAP sample (Figure 5).

To characterize the mechanism of release, the Korsmeyer–Peppas model in the “ln” form was used for data fitting, as shown in eq 8

\[ \ln F = \ln t + \ln k \quad (8) \]

where \( F \) was given before in eq 6 (\( F = M_t/M_\infty = k t^n \))

A plot of \( \ln F \) against \( \ln t \) resulted in a straight line, from which the exponent of release \( n \), coefficient of correlation \( R^2 \), and release factor \( k \) could be obtained. Equation 8 is applied for the initial stages, representing \( \sim 60\% \) of the release data. The values of \( n \) and \( k \) for the examined hydrogel fertilizers are listed in Table 3. The calculated values of \( n \) for the MAP and DAP samples were 0.81 and 0.98, respectively. Both values were higher than 0.5, indicating that the release of P from the MAP and DAP fertilizer samples follows a non-
phosphorous release into soil from MAP-Alg-g-PAM and DAP-Alg in comparison with that from commercial MAP and DAP, an incubation experiment was performed. The results of the study showed that the ratio of available P in soils having various calcium carbonate contents at the onset of the incubation period was slightly lower in MAP-Alg-g-PAM and DAP-Alg-g-PAM than that from commercial MAP and DAP. However, over time, the available soil-P ratio released from MAP-Alg-g-PAM and DAP-Alg-g-PAM was higher than that released from commercial MAP and DAP. Sequential P fractionation indicated that the concentration of soluble-P, exchangeable-P, Al- and Fe-bound-P, Ca-bound-P, and residual-P was higher for commercial MAP and DAP compared with that for MAP-Alg-g-PAM and DAP-Alg-g-PAM.71

**Conclusions.** According to the results, we can conclude that the prepared fertilizer formulations based on P-Alg-g-PAM were successfully able to extend the release of phosphorus at a controlled rate over 45 days. Hence, this formulation may help extend the duration for which phosphorus is available to the plant. The importance of such formulations is their ability to resist the presence of calcium cations and other soil cations such as iron and aluminum due to the presence of the alginate in the formulation. Therefore, this combination will be very helpful to the plant and will reduce the environmental damage resulting from the excessive addition of phosphorus fertilizers and reduce the cost of excessive quantities of the fertilizer. Besides, the presence of polyacrylamide leads to excellent swelling ability and high water holding capacity, which are other advantages of the formulation especially when applied in arid and semiarid regions.

**MATERIALS AND METHODS**

**Materials.** Sodium alginate and acrylamide 98% were supplied from Techno Pharmchem, India. Potassium persulfate (KPS) was provided from S.D. Fine Chemical, India. Methanol, acetone, N,N-dimethylformamide, and chloroform (laboratory reagent grade) were supplied by Fisher Chemicals, UK. Monoammonium phosphate (MAP; 98%), diammonium phosphate (DAP; 97%), and calcium chloride were provided from Loba Chemicals, India. Ammonium molybdate, potassium antimony tartrate, and stannous chloride were received from LobaChem, Mumbai, India. Poly(vinyl alcohol) (PVA; Mw = 100,000–500,000) was received from Sigma-Aldrich. The rest of the solvents and reagents were of analytical grade and were used as supplied.

**Characterization.** FTIR Spectroscopy. FTIR spectra were recorded on a TENSOR 27 Bruker spectrometer using KBr pellets without any matrix.
pellets. The dry sample is mixed with NaBr and compressed to produce a transparent disc and scanned from 4000 to 400 cm\(^{-1}\).

**Scanning Electron Microscopy.** The morphology of the surface of the dry sample was examined using a JEOL (JSM-6380) instrument. The specimens were coated with a layer of gold for enhanced SEM imaging and examined at their fracture surface.

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) was conducted on a TA-Q500 instrument (TA, USA). Samples that weighed 5–10 mg were heated from 30–800 °C at 10 °C/min in a platinum pan under an atmosphere of nitrogen, with a flow rate of 25 mL/min.

**Ultraviolet (UV) Spectral Measurements.** Determinations were conducted using a PerkinElmer UV/vis spectrophotometer (Lambda-35) on solution samples at 400 nm.

**Powder X-ray Diffraction.** Measurements of X-ray diffraction were conducted on a Rigaku Miniflex 600 X-ray diffractometer operated at Cu Kα radiation (40 kV, 15 mA), over an angular range of 2θ from 10 to 90° and at a scan rate of 5°/min.

**Synthesis of Phosphorylated Alginate.** Two commercially popular phosphate fertilizers were used, MAP and DAP, using a modified procedure described elsewhere.\(^4\)

**MAP Sample.** The preparation of the MAP-modified sample is typical: sodium alginate (2.0 g) (11.36 mmol) was dissolved in 40 mL of water at 60 °C in a 250 mL round-bottomed three-necked flask outfitted with a mechanical stirrer, nitrogen opening, and addition funnel. In another flask, a mixture was prepared consisting of PVA (6 g in 80 mL of H\(_2\)O), sodium bicarbonate (0.5 g in 5 mL of H\(_2\)O\(_2\)), and MAP [1.15 g (10 mmol) in 5 mL of H\(_2\)O\(_2\)]. This mixture was added gradually through the dropping funnel to the alginate solution. The resulting contents were stirred at 60 °C for 2 h, and the product was precipitated by addition of methanol. The product was filtered and dried under vacuum at 40 °C for 12 h. The dry product was then baked in an oven at 120 °C for 3 h. The product was washed with excess water for 8 h and precipitated with methanol. The precipitate was then dried under vacuum at 40 °C to give a yield of 3.59 g. The total phosphorus content was 235 mg/g.

**DAP Sample.** DAP was used to prepare the DAP alginate sample as mentioned above, using 3.09 g of DAP, which gave a yield of 4.11 g. The total phosphorus content was 173 mg/g.

**Determination of P Content.** The total content of phosphorus has been determined using the method of molybdovanado phosphate (method # 958.01) mentioned in AOAC Official Methods of Analysis.\(^2\)

**Grafting of Acrylamide onto Crosslinked Phosphorylated Carbohydrates.** In a 250 mL three-necked flask outfitted with a mechanical stirrer, a suspension of phosphorylated alginate (0.1 g in 80 mL of distilled water) was magnetically stirred at 50 °C. Next, a solution of acrylamide (1.42 g in 5 mL of distilled water) was added to the phosphorylated alginate under stirring. \(N,\text{N}'-\text{methylene bis acrylamide solution (0.195 g in 5 mL of distilled water) was then added to the previous mixture, followed by a further addition of KPS solution (5 mL of 0.1 M) to initiate the grafting reaction. The contents of the reaction were kept under stirring for 4 h at 50 °C. The grafted alginate polyacrylamide was obtained after precipitation by adding a copious amount of methanol. Unreacted traces of the homopolymers found in the graft copolymers were removed by extraction using a mixture made from acetic acid and formamide (1:1 by volume), as described previously.** The final product was dried at 40 °C. Another sample was phosphorylated with DAP (Table 1).

**Kinetics of Grafting.** Factors that had an influence on the grafting reaction, such as temperature, period of reaction, amount of concentration of the monomer, and the initiator, were examined using the highly swollen Alg-g-PAM sample. The grafting parameters were estimated according to eqs 1 and 2 described earlier in the Results and Discussion section.

**Swelling Studies.** Absorption of water was determined by the gravimetric method as a function of time for P-Alg-g-PAM fertilizer gels. The results are the average of three runs. The swelling degree (DS) was determined from eq 3 described earlier in the Results and Discussion section. The equilibrium water content was estimated using eq 4 described earlier in the Results and Discussion section.

**Phosphorous Release in Calcium Chloride.** A parallel release study was conducted in 0.1 M calcium chloride solution as a competitive cation for phosphate, maintaining other conditions as mentioned above.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03740.

Characterization details: FTIR spectroscopy, UV spectra. FTIR spectra of MAP, sodium alginate (Alg), and MAP-phosphorylated Alg (P-Alg). FTIR spectra of phosphorylated Alg(P-Alg), polyacrylamide (PAM), final grafted material MAP-Alg-g-PAM, and final grafted material MAP-Alg-g-PAM after release. FTIR spectra of DAP, sodium alginate (Alg), and DAP-phosphorylated Alg (P-Alg). FTIR spectra of phosphorylated Alg(P-Alg), polyacrylamide (PAM), final grafted material DAP-Alg-g-PAM, and final grafted material DAP-Alg-g-PAM after release. PXRD patterns: XRD of P-Alg-P M. MAP-modified Alg-g-PAM and DAP-modified Alg-g-PAM. XRD pattern of MAP and DAP. SEM of alginate and P-Alg- and P-Alg-g-PAM, sodium alginate, DAP-modified Alg-g-PAM, and DAP-modified Alg-g-PAM. Swelling profile of the phosphorylated grafted material P-Alg-g-PAM. Swelling of fertilizer samples. Kinetic models of phosphorus release (PDF)

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REFERENCES
(1) Johnston, A. E. Soil and Plant Phosphate; International Fertilizer Industry Association (IFA): Paris, 2000.
(2) Syers, J. K.; Johnston, A. E.; Curtin, D. Efficiency of Soil and Fertilizer Phosphorus Use: Reconciling Changing Concepts of Soil Phosphorus Behaviour with Agronomic Information; Food and Agriculture Organization of the United Nations (FAO): Rome, 2008; Vol. 18.
(3) Kochian, L. V. Rooting for more phosphorus. Nature 2012, 488, 466–467.
(4) Cordell, D.; Drangert, J.-O.; White, S. The story of phosphorus: Global food security and food for thought. Global Environ. Change 2009, 19, 292–305.
(5) Smit, A. L.; Bindraban, P. S.; Schröder, J. J.; Conijn, J. G.; van der Meer, H. G. Phosphorus in agriculture: global resources, trends and developments: to report the steering committee technology assessment of the ministry of agriculture, nature and food quality, The Netherlands. Plant Research International B. V.: Wageningen, The Netherlands, 2009; Plant Research International Report 282; pp 1–36.
(6) Cordell, D.; White, S. Sustainable Phosphorus Measures: Strategies and Technologies for Achieving Phosphorus Security. Agronomy 2013, 3, 86–116.
(7) Al-Rohily, K. M.; Ghoneim, A. M.; Modaihsh, A. S.; Mahjoub, M. O. Phosphorus Availability in Calcareous Soil Amend with Chemical P Fertilizer, Cattle Manure Compost and Sludge Manure. Int. J. Soil Sci. 2013, 8, 17–24.
(8) Al Harbi, S. F.; Ghoneim, A. M.; Modaihsh, A. S.; Mahjoub, M. O. Effect of Foliar and soil Application of Phosphorus on Phosphorus Uptake, use Efficiency and Wheat Grain Yield in Calcareous Soil. J. Appl. Sci. 2013, 13, 188–192.
(9) Sattari, S. Z.; Bouwman, A. F.; Gilker, K. E.; van Ittersum, M. K. Residual soil phosphorus as the missing piece in the global phosphorus crisis puzzle. Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 6348–6353.
(10) Vaccari, D. A. Phosphorus: a looming crisis. Sci. Am. 2009, 300, 54–59.
(11) Akelah, A. Functionalized Polymeric Materials in Agriculture and the Food Industry; Springer: New York, 2013.
(12) Jarosiewicz, A.; Tomasewksa, M. Controlled-release NPK fertilizer encapsulated by polymeric membranes. J. Agric. Food Chem. 2003, 51, 413–417.
(13) Trenkler, M. E. Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Efficiency in Agriculture, 2nd ed.; International Fertilizer Industry Association (IFA): Paris, 2010.
(14) Sanders, J. L.; Kummerly, J. M.; Mazo, G. Anionic vinyl/dicarboxylic acid polymers and uses thereof. U.S. Patent 6,525,155 B2, 2003.
(15) Sanders, J. L.; Murphy, L. S.; Noble, A.; Melgar, R. J.; Perkins, J. Improving Phosphorus Use Efficiency with Polymer Technology. Procedia Eng. 2012, 46, 178–184.
(16) Sanders, J. L.; Mazo, J.; Mazo, G. Polyionan Polymer. WO 2015031521 A1, 2015.
(17) Liao, Z.; Bo, S.; Mao, X.; Guan, P.-O. Methods for Making Controlled-Release Ammonium Phosphate Fertilizer. U.S. Patent 7,252,697 B2, 2007.
(18) Montalvo, D.; McLaughlin, M. J.; Deggyze, F. Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in Andisols and Oxisols. Soil Sci. Soc. Am. J. 2015, 79, 551–558.
(19) Zahra, Z.; Waseem, N.; Zahra, R.; Lee, H.; Badshah, M. A.; Mehmoond, A.; Choi, H.-K.; Arshad, M. Growth and Metabolic Responses of Rice (Oryza sativa L.) Cultivated in Phosphorus-Deficient Soil Amended with TiO2 Nanoparticles. J. Agric. Food Chem. 2017, 65, 5598–5606.
(20) Kong, L.; Tian, Y.; Wang, Y.; Li, N.; Liu, Y.; Pan, Z.; Huang, X.; Li, M.; Zhang, J.; Zuo, W. Periclase-induced generation of flowerlike clay-based layered double hydroxides: A highly efficient phosphate scavenger and solid-phase fertilizer. Chem. Eng. J. 2019, 359, 902–913.
(21) Bernard, M. P.; Guimaraes, G. G. F.; Majaron, V. F.; Ribeiro, C. Controlled release of phosphate from layered double hydroxide structures: Dynamics in soil and application as smart fertilizer. ACS Sustainable Chem. Eng. 2018, 6, 5152–5161.
(22) Everaert, M.; Warrinnier, R.; Baken, S.; Gustafsson, J.-P.; De Vos, D.; Smolders, E. Phosphate-Exchanged Mg–Al Layered Double Hydroxides: A New Slow Release Phosphate Fertilizer. ACS Sustainable Chem. Eng. 2016, 4, 4280–4287.
(23) Andelkovic, I. B.; Kabiri, S.; Tavakkoli, E.; Kirby, J. K.; McLaughlin, M. J.; Losic, D. Graphene oxide-Fe(III) composite containing controlling phosphate – A novel slow release fertilizer for improved agriculture management. J. Clean. Prod. 2018, 185, 97–104.
(24) Usman, K. A. S.; Buenvijae, S. C. J.; Conato, M. T.; Payawan, L. M., Jr.; Payawan, J. L. M. Facile fabrication of a potential slow-release fertilizer based on oxalatephosphate-amine metal-organic frameworks (OPA-MOFs). Mater. Sci. Forum 2018, 936, 14–19.
(25) Anstoetz, M.; Sharma, N.; Clark, M.; Yee, L. H. Characterization of an oxalate-phosphate-amine metal-organic framework (OPA-MOF) exhibiting properties suited for innovative applications in agriculture. J. Mater. Sci. 2016, 51, 9239–9252.
(26) Bortolin, A.; Aouda, F. A.; de Moura, M. R.; Longo, E.; Mattoso, L. H. C.; Mattoso, L. H. C. Application of Polysaccharide Hydrogels in Adsorptionand Controlled-Extended Release of Fertilizers Processes. J. Appl. Polym. Sci. 2012, 123, 2291–2298.
(27) Al Harbi, K.; Ghoneim, A.; Ebid, A.; El-Hamshary, H.; El-Newehy, M. H. Controlled release of phosphorus fertilizer bound to carboxymethyl starch-g-polyacrylamide and maintaining a hydration level for the plant. Int. J. Biol. Macromol. 2018, 116, 244–231.
(28) Yu, C.; Yun-Fei, L.; Hui-Min, T. Hydroxyethyl chitosan-g-poly(acrylic acid-co-sodium acrylate) superabsorbent polymers. J. Appl. Polym. Sci. 2010, 117, 2233–2240.
(29) Zhong, K.; Lin, Z.-T.; Zheng, X.-L.; Jiang, G.-B.; Fang, Y.-S.; Mao, X.-Y.; Liao, Z.-W. Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers. Carbohydr. Polym. 2013, 92, 1367–1376.
potential solutions to environmental issues: A brief review. *J. Environ. Manage.* 2018, 228, 213–222.

(51) Yang, G.; Zhang, L.; Peng, T.; Zhong, W. Effects of Ca2+ bridge cross-linking on structure and pervaporation of cellulose/alginate blend membranes. *J. Membr. Sci.* 2000, 175, 53–60.

(52) Laurienzo, P.; Malinconico, M.; Motta, A.; Vicinanza, A. Synthesis and characterization of a novel alginate-poly(ethylene glycol) graft copolymer. *Carbohydr. Polym.* 2005, 62, 274–282.

(53) Rani, P.; Mishra, S.; Sen, G. Microwave based synthesis of polymethyl methacrylate grafted sodium alginate: its application as flocculant. *Carbohydr. Polym.* 2013, 91, 686–692.

(54) Işıklan, N.; Kursan, F.; Inal, M. Graft Copolymerization of Itaconic Acid onto Sodium Alginate Using Ceric Ammonium Nitrate as Initiator. *J. Appl. Polym. Sci.* 2009, 114, 40–48.

(55) Melekaslan, D.; Okay, O. Swelling of strong polyelectrolyte hydrogels in polymer solutions: effect of ion pair formation on the polymer collapse. *Polym. 2000*, 21, 557–564.

(56) Bromberg, L.; Grosberg, A. Y.; Matsu, E. S.; Suzuki, Y.; Tanaka, T. Dependency of swelling on the length of subchain in poly(N,N-dimethylacrylamide)-based gels. *J. Chem. Phys.* 1997, 106, 2906–2910.

(57) Askadskii, A. A. Influence of crosslinking density on the properties of polymer networks. *Polym. Sci. U.S.S.R.* 1990, 32, 2061–2069.

(58) El-Hamshary, H. Synthesis and water sorption studies of pH sensitive poly (acrylamide-co-itaconic acid) hydrogels. *Eur. Polym. J.* 2007, 43, 4830–4838.

(59) El-Hamshary, H.; Assabaia, F. N. Synthesis of cationic and ampholytic starch graft acrylamide and their aqueous salt absorption. *J. Macromol. Sci., Part A: Pure Appl. Chem.* 2011, 48, 454–461.

(60) Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.

(61) Naylor, T. Permeation Properties. In *Comprehensive Polymer Science and Supp*; Booth, C., Price, C., Eds.; Pergamon Press: New York, 1989; Vol. 2, pp 643–668.

(62) El-Hamshary, H.; Fouda, M. M. G.; Morydeen, M.; Al-Deyab, S. S. Removal of heavy metal using poly (N-vinylimidazole)-grafted-carboxymethylated starch. *Int. J. Biol. Macromol.* 2014, 66, 289–294.

(63) Alfrey, J. T.; Gurnee, E. F.; Lloyd, W. G. Diffusion in glassy polymers. *J. Polym. Sci. Part C: Polym. Symp.* 1966, 12, 249–261.

(64) Masaro, L.; Zha, X. P. Physical models of diffusion for polymer solutions, gels and solids. *Prog. Polym. Sci.* 1999, 24, 731–775.

(65) Cranck, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: USA, 1980.

(66) Ritger, P. L.; Peppas, N. A. A simple equation for description of solute release II. fickian and anomalous release from swellable devices. *J. Controlled Release* 1987, 5, 37–42.

(67) Ritger, P. L.; Peppas, N. A. Transport of penetrants in the macromolecular structure of coals. *Feul 1987*, 66, 815–826.

(68) Siepmann, J.; Siegel, R. A.; Siepmann, F. Diffusion in glassy polymers. *J. Polym. Sci., Part C: Polym. Symp.* 1966, 12, 249–261.

(69) Siepmann, J.; Siegel, R. A.; Siepmann, J.; Siegel, R.; Rathbone, M.; Eds.; Springer: Boston, MA, 2012.

(70) Costa, P.; Sousa Lobo, J. M. Modeling and comparison of dissolution profiles. *Eur. J. Pharm. Sci.* 2001, 13, 123–133.

(71) Rohily, K. A.; Ghoneim, A.; El-Hamshary, H.; Modaihsh, A. Development and Evaluation of Slow Release Phosphorus Fertilizer Using Mono-ammonium Phosphate and Di-ammonium Phosphate. *Int. Res. J. Pure Appl. Chem.* 2019, 19, 1–15.

(72) Helrich, K. A. *AOAC: Official Methods of Analysis*, 15th ed.; Association of Official Analytical Chemists: Arlington, VA, USA, 1990; Vol. 1, p 12.

(73) Fanta, G. Synthesis of graft and block copolymers of starch. In *Block and Graft Copolymerization*; Ceresca, R. J., Ed.; Wiley: New York, 1973; Vol. 1.