Nutrient Capture from Aqueous Waste and Photocontrolled Fertilizer Delivery to Tomato Plants Using Fe(III)–Polysaccharide Hydrogels

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ABSTRACT: Inexpensive and sustainable methods are needed to reclaim nutrients from agricultural waste solutions for use as a fertilizer while decreasing nutrient runoff. Fe(III)–polysaccharide hydrogels are able to flocculate solids and absorb nutrients in liquid animal waste from Confined Animal Feeding Operations (CAFOs). Fe(III)–alginate beads absorbed 0.05 mg g⁻¹ NH₄⁺ and NO₃⁻ from 100 ppm solutions at pH = 7, with > 80% phosphate uptake and ~30% uptake of ammonium and nitrate. Ammonium uptake from a raw manure solution (1420 ppm NH₄⁺) showed a significant 0.7 mg g⁻¹ uptake. Tomato plant trials carried out with Fe(III)–alginate hydrogel beads in greenhouse conditions showed controlled nutrient delivery for the plants compared to fertilizer solution with the same nutrient content. Plants showed an uptake of Fe from the gel beads, and Fe(III)–alginate hydrogel beads promoted root growth of the plants. The plants treated with nutrient-loaded Fe(III)–alginate hydrogels yielded comparable tomato harvest to plants treated with the conventional fertilizer solution.

INTRODUCTION

Every summer since the mid-1990s, Lake Erie, the smallest and shallowest of the Laurentian Great Lakes, experiences blooms of cyanobacteria. These blooms are driven by the nutrient-rich environments that are created when phosphorus and nitrogen flow from the watershed into the lake.1,2 These events are called cyanobacterial harmful algal blooms (CHABs) that can cause both adverse environmental and public health impacts. The most direct threat to human health is when drinking water supplies become polluted with microcystin, a toxic natural product produced by many CHAB-forming cyanobacteria.2 The phosphorus and nitrogen that feed the CHABs come primarily from the runoff of fertilizers applied to agricultural fields, including animal waste.1 Applying animal manure on fields is a common practice around the world to utilize the nutrient-rich manure as a fertilizer for farmlands.3,4 While levels vary with the type of animals, feed, and treatment methods, manure usually contains valuable amounts of nitrogen and phosphorus for crop fertilization.5–7 Utilizing the manure as fertilizer is an effective method of agricultural nutrient recycling and potentially an environmentally sustainable practice. However, Confined Animal Feeding Operations (CAFOs) typically generate more manure than they can utilize, and transporting the animal waste that is typically 95–98% water is costly relative to its fertilizer value. Furthermore, if the amount of nutrients applied to agricultural fields exceeds the amount that crops absorb during the growing season, the excess nutrients can be transported by rainfall into watersheds where they promote eutrophication. Indeed, as climate change increases local heavy rain events, even larger amounts of fertilizers and applied manure are transported since the amount transported increases with the rate of precipitation.8 Low-cost manure treatment that separates nutrients from water and binds nutrients in an insoluble matrix that reduces hydrological mobility, while slowly releasing nutrients during the growing season, can reduce this problem and improve the environmental sustainability of the use of this otherwise valuable commodity.

Capturing nitrogen and phosphorus from waste solutions to use as plant fertilizer can address certain waste management issues as well as the increasing fertilizer demand.9 A number of processes have been developed for this purpose but none are
currently in widespread use because of cost and complexity. Inorganic salts can be used to precipitate phosphorus as salt solids such as struvite. This is energy-intensive since nutrients must be first captured from the waste before application as fertilizer and typically requires the critical adjustment of parameters to achieve sufficient yield and efficiency. These systems usually do not capture ammonia, which is the predominant form of nitrogen in manure, and are too complex to likely be conducted over the long term, efficiently by a typical agricultural producer. In addition, dissolved organic compounds such as humic acid that are present in the waste interfere with nutrient capture. A promising alternative is to flocculate and capture the solids and nutrients using petroleum-based polymers like polyacrylamide or biopolymers like chitosan. Acrylamide polymers have been shown to be quite effective at flocculating the solids but lack the ability to effectively capture ammonia. Chitosan-based absorbents show good flocculation and nutrient capture but are not yet cost-effective due to the higher cost of chitosan and large amounts of chitosan necessary to flocculate the solids. Chitosan is also not very soluble and is not good for flocculation or nutrient capture except at a specific pH. The challenge then is to create a natural polymer material with better flocculation and more efficient nutrient capture in a variety of conditions while ensuring low cost and biodegradability.

Municipal, industrial, and agricultural wastewaters are also rich in nitrogen and phosphorus. Treatment of these waste solutions before releasing back to the environment or reusing is expensive. At the same time, improper management of these wastes results in many adverse environmental effects including greenhouse gas emissions, eutrophication, and soil pollution. Even though these byproducts are considered waste, the reclamation of important nutrients can be economically beneficial and environmentally friendly.

In addition to the direct effects of applying fertilizers or any waste-based materials to agricultural fields, there is also the potential for indirect effects via edaphic factors. Previous work has suggested that the type of fertilizer used (organic versus chemical) affects the composition of microbial communities in the soil. Soil microbes are estimated to be responsible for up to 50% of plant productivity via the cycling of carbon and nutrients, and soil biodiversity plays an important role in ecosystem function. It will be important then to ensure that any applied nutrient fertilizer or material does not negatively affect soil microbial communities.

In our previous work, we developed an Fe(III)–polysaccharide-based hydrogel material capable of reclaiming phosphate ions from aqueous waste solutions, including manure. These hydrogels are photosensitive and release the captured phosphate when irradiated with light (Figure S1). The hydrogels are stable in a variety of aqueous solutions, under a broad pH range. This system uses the polysaccharides, alginate and pectin, that can come from algae and plant waste, which decreases cost. In this paper, we build on these findings and show how the Fe(III)–polysaccharide hydrogel beads can uptake and release not only phosphate but also ammonium and nitrate ions. We also show that this system can act as an effective slow-release fertilizer for tomatoes and compare the Fe(III)–polysaccharide gels to a standard fertilizer solution to benchmark performance. Our Fe(III)–polysaccharide hydrogel-based controlled-release fertilizer system showed comparable results to a conventional fertilizer solution for various parameters including plant growth, chlorophyll production, and fruit formation, for the short-season crop, tomato. This study shows that our Fe(III)–polysaccharide hydrogel-based fertilizer system can be as effective as a conventional fertilizer solution and tomatoes can uptake and translocate nutrients, including Fe, into the plant with minimal effects on soil microbial communities. In addition, the slower release of nutrients from the hydrogels can help reduce nutrient runoff. These hydrogels can also be an on-site animal waste treatment method for dewatering manure and reclaiming nutrients, eliminating problems with the overflow of holding lagoons, and reducing lagoon storage costs for animal waste.

**RESULTS AND DISCUSSION**

Polysaccharide-based hydrogels were recently shown to absorb phosphate ions from wastewater solutions, and we wanted to investigate this further for use in reclamation of other nutrients from wastewater, such as ammonia and nitrate. An additional aim of this project was to determine how Fe(III)–polysaccharide hydrogel beads perform as a fertilizer compared to a conventional chemical fertilizer. Different polysaccharides were chosen since the overall electrostatic charge on the polymer could change depending on the structure of the polysaccharide. For example, pectin has additional ester groups that are not present in alginate. Pectin could also be sourced from food waste like fruit peels, making this a more sustainable choice. Polysaccharide–0.1 M Fe(III) hydrogel beads showed ammonium uptake of approximately 0.05 mg g\(^{-1}\) for all three types of gel beads studied (Figure 1A). This is an uptake of about 27% of ammonium ions from the initial 100 ppm solution. Similarly, all three types of hydrogels had a nitrate ion uptake of approximately 0.05 mg g\(^{-1}\), which corresponded to about 32% of nitrate ions from the initial 100 ppm solution (Figure 1B).

Nitrate and ammonium uptakes were similar to nutrient solutions that also contained phosphate ions (Figure 1C). Phosphate uptake from the mixed solution was around 0.18 mg g\(^{-1}\) for all three types of beads (more than 90% uptake), three times higher than the nitrate uptake. This suggests that trivalent phosphate ions bind more strongly to the hydrogels than the monovalent nitrate ions, possibly coordinating via bridging to a dinuclear Fe(III) carbonate-bridged site that is expected in these hydrogels.

In our previous work, we demonstrated that these polysaccharide–Fe(III) hydrogels can uptake more than 1 mg g\(^{-1}\) phosphate from 800 ppm phosphate solutions at pH = 7.0, including from liquid manure, representing more than 80% phosphate uptake. With more dilute 100 ppm phosphate solutions, the phosphate uptake was around 0.2 mg g\(^{-1}\) corresponding to about 99% uptake. With the increased phosphate concentration in solution, the phosphate uptake value exceeded 1 mg g\(^{-1}\), while the percent phosphate uptake declined, showing a saturation of phosphate binding in the gels. In this study, the ammonium uptake from more dilute 100 ppm waste solutions was 0.05 mg g\(^{-1}\), which is a 27% uptake of ammonium. Notably, the ammonium uptake from the raw manure solution (initial ammonium concentration of 1420 ppm, pH = 7.6 ± 0.1) was as high as 0.7 mg g\(^{-1}\) corresponding to a 26% ammonium ion absorption (Figure 2A). The similar percentage absorption in the 14-fold higher concentration ammonium solution shows that the hydrogels were not saturated at the higher concentration, as was observed with...
FeCl₃ beads from a solution with a 100 ppm concentration of each ion

Ammonium, nitrate, and phosphate ion uptakes for alginate from a 100 ppm solution at pH = 7. (B) Nitrate uptake of different alginate−Fe beads from orange (Figure 2B) to brown (Figure 2C) after incubation with hydrogels. This was visualized by the change in color of the Fe(III)−polysaccharide hydrogels.

This was expected since the hydrogels do degrade over time in the soil, even in the dark. Some nutrient release was still apparent, even in the dark. This was due to the release of ammonia during heating. Gels soaked in the nitrate solution also had a different thermal stability from control, and the final weight percent was again lower than blank hydrogels due to the loss of nitrate ions. Hydrogel samples soaked in phosphate solutions and mixed nutrient solutions were also different from the blank hydrogel samples. Interestingly, their final weight percent was higher than the blank hydrogel sample, showing the coordinated phosphate ions were left even after the heat treatment.

To assess nutrient release from the Fe(III)−polysaccharide hydrogels and benchmark the performance, plant trials were carried out with tomato (Solanum lycopersicum) plants, comparing treatment with nutrient-loaded hydrogel beads and a standard fertilizer solution (with the appropriate control conditions described in Materials and Methods section). Tomatoes were chosen for this assessment based on several factors including the ease of growth, fruit formation, ability to grow in a compact area, and shorter lifetime of the plant. The plant growth (average plant height) under each condition was monitored weekly after germination (Figure 3A and Table S1). Plants treated with the fertilizer solution were generally taller than all of the other conditions during the first 9 weeks of the experiment. Plants treated with fertilizer gel beads had similar heights to the other plants during the first few weeks. At week 10, however, the fertilizer gel-treated plants started showing a significantly greater growth, and by the date of the final measurement (day 109), the average height was 140 ± 21 cm, which was 30 cm taller than the plants treated with the fertilizer solution. Control plants and the plants treated with fertilizer beads in darkness showed similar heights at the end of the experiment. This showed that ammonium and nitrate nutrients in the fertilizer solution were readily available for the plants to absorb and the plants treated with the fertilizer solution initially grew faster. At the same time, these nutrients have high hydrological mobility and are easily moved from soil into the watershed by precipitation, causing adverse environmental effects such as CHABs. It is likely more beneficial to have a slower-release profile, as was observed with the beads. Differences in plant growth rates suggest that the fertilizer beads were releasing the nutrients more slowly. The pot bases covered with aluminum foil to keep the beads in darkness had an average height of 103 ± 35 cm, which was 37 cm shorter than those that were exposed to sunlight (Table S1). This implies that exposure to light accelerated nutrient release due to the Fe(III)−carboxylate photochemical reaction; however, some nutrient release was still apparent, even in the dark. This was expected since the hydrogels do degrade over time in the soil, even in the dark.

In addition to plant height, fruit formation was affected by treatment with the fertilizer solution and fertilizer gels. Tomato plants started forming fruits in the 8th week of the experiment.
Plants treated with the fertilizer solution produced more fruits than the other conditions throughout the experiment (Figure 3B). This was attributed to the readily available phosphate ions from the fertilizer solution. Similar to the plant height data, both treatments with fertilizer gel beads (light and dark) were second and third in terms of the total number of tomatoes, with hydrogel beads exposed to light showing better results due to photodegradation and thus more nutrient release. Plants treated with the fertilizer bead light condition produced more fruit during the latter part of the experiment. If the experiment had continued, it is possible that the fertilizer bead light condition would yield a higher number of fruits than the fertilizer solution treatment.

This is similar to that observed in tomato plant height data such that the fertilizer gel bead light condition took longer to surpass the fertilizer solution treatment. Comparing these differences in fruit formation and plant height suggested that the release of phosphate (a major contributor for fruit development) was slower than the release of ammonium and nitrates (major contributors for plant growth) from the fertilizer beads. This can be explained by the strong binding of phosphates to Fe species within the hydrogel, where the more strongly coordinated phosphate (bridged) would be expected to be released more slowly compared to bound ammonium and nitrate (electrostatics and other weaker binding forces).

Figure 2. (A) Ammonium ion uptake of different Fe(III)−polysaccharide beads from the raw manure solution with an ammonium concentration of 1420 ppm, pH = 7.6 ± 0.1. Photograph of alginate−0.1 M Fe gel beads (B) before and (C) after nutrient uptake from the manure solution. (D) Manure solution before (left) and after (right) treatment with Fe(III)−alginate beads.
In addition to quantitative measurements of plant growth, we qualitatively observed the plant appearance. Plants treated with the fertilizer solution produced the bushiest plants with the highest number of branches and leaves. Even the length of the leaves was highest for this condition due to the readily abundant nitrogen. Fertilizer bead light and dark conditions were next and showed better growth over the other controls. The growth of the plants from the fertilizer solution was excessive compared to other conditions, and it can be hypothesized that it made the fruits compete with the other parts of the plant for nutrients and water. High ammonium activity in soil, inconsistent soil moisture conditions, and calcium deficiency (due to the competition between fruits and other parts of the plant) are the known contributing factors for blossom end rot of tomatoes. Indeed, some of the fruits from fertilizer solution-treated plants suffered blossom end rot (Figure 4A and S2). Blossom end rot turned the bottom of the tomato a dark color and eventually that area of the fruit became dehydrated and reduced the weight of the fruit making them not consumable. We suspect this was due to excessive ammonium availability from the fertilizer solution (Figures 4A and S2). Even though we used the same nutrient content for plants with fertilizer beads, blossom end rot was not observed with the fertilizer beads. We suggest that this is due to the slower release of ammonium, which prevented this problem. It is difficult to completely determine how water absorption by the beads ultimately contributed to the differences between the fertilizer solution and the hydrogel beads. However, comparison between control beads (no nutrients) and those with fertilizer showed similar results to that of control, indicating that it was the nutrients, not water absorption, that contributed most to the differences between the fertilizer solution and fertilizer beads.

Even though the fertilizer solution produced the most number of fruits, the average ripened fruit weight from this condition was low. Dehydration of the bottom of some tomatoes due to blossom end rot was part of the reason for this. Other than that, some fruits from the fertilizer solution ripened prematurely, when the fruits were small in size (Figure 4B). There are reports of higher nitrogen and phosphorus nutrient availabilities increasing the production of lycopene, the natural pigment that gives the red color for tomatoes. These small ripened fruits were not seen in any other condition and these smaller sizes lowered the overall average ripened fruit weight for this treatment. Again, this showed that the fertilizer gel beads (both light and dark conditions) released the nutrients in a slower manner, avoiding the excessive lycopene formation for young immature fruits. Regardless, the
predicted ripened tomato harvest calculated by multiplying the average ripened tomato weight by the total number of fruits with a minimum diameter of 1 cm at the end of the experiment was highest for the fertilizer solution (Figure 4C). The fertilizer gel bead conditions were next, however, showing improved tomato harvest over the control conditions.

Significant changes were observed in the green color of the tomato leaves from different conditions (Figure S4). To gain quantitative data for these observations, chlorophyll was extracted from the leaves. After the extraction, clear differences were visible in the green color of the extracts from several treatments (Figure S5). A colorimetric analysis for the total chlorophyll content was performed for leaf samples. The total chlorophyll content for fertilizer solution-treated plants was a lot higher than all of the others, and the fertilizer beads light condition was clearly second (Figure S6). The plants treated with control beads (no nutrients, both dark and light) had a lower total chlorophyll content compared to the control plants, suggesting that control gel beads might have some effect on chlorophyll formation in the plant.

After the end of the experiment, plants were destructively harvested, and all plant materials were dried to compare the biomass of plants. Above-ground biomass (Figure S7) and below-ground biomass (Figure S8) were calculated separately, and the total biomass for each condition was calculated (Figure 5). Similar to our previous observations, the total biomass was highest for fertilizer solution plants, and plants treated with fertilizer beads were next. Above-ground biomass and below-ground biomass followed the same trend as the total biomass.

The biomass data suggested that fertilizer gel beads promoted root growth more than it increased the growth of the plant shoot system. The above-ground (shoot) to below-ground (root) mass ratio (SR ratio) clearly showed that the hydrogel beads promoted greater root growth (Figure S9). Plants treated with fertilizer gel beads had the lowest SR ratio and plants treated with control beads had the second lowest. Control plants had the highest SR ratio due to low nutrient and Fe content to promote root growth.

To assess the transport of nutrients from soil into the plants, elemental analysis of Fe and P contents (inductively coupled plasma-mass spectrometry (ICP-MS)) was performed on leaf samples from control, fertilizer solution, and fertilizer bead dark and fertilizer bead light conditions. All three analyzed fertilizer conditions had higher phosphorus content than the control (Figure S10). The high phosphorus content suggests that the fertilizer beads released the phosphate ions so that the plant could uptake this nutrient. The Fe analysis data showed that the leaf samples from control plants and fertilizer solution treatment had very low Fe content (Figure S11). This Fe would come exclusively from the soil as well as possible contaminating Fe present in the chemicals used for the fertilizer solution. The high Fe content in leaf samples from conditions 5 and 6 is likely due to the Fe(III) that we used for fertilizer gel bead preparation. This suggests that the gel beads degraded, and the plants were able to absorb the Fe that was released.

Elemental analysis (ICP-OES) for tomato fruits from all plants treated with hydrogel beads (control beads and fertilizer beads in both dark and light) did not show significant differences in K, P, Fe, and Ca contents. Therefore, the elemental analysis data for these four conditions was combined and represented as Fe—alginate hydrogel bead treatments and was compared with control and fertilizer solution conditions (Figure 6). Tomato fruit samples showed no significant differences in the potassium (K) content even though K was included in the solution used for the fertilizer solution and for fertilizer gel bead preparation (Figure 6A). Comparisons of the P content clearly showed that fruits from the control had a lower P content compared to those of both the fertilizer solution and Fe—alginate hydrogel bead treatments (Figure 6B). This limited P in the control fruits was expected due to the low phosphate content of the soil. Unlike the observations for the P content in leaves, the P analysis in fruits had a different trend where the fertilizer solution had the highest P content (Figure 6B). This suggested that abundant phosphate in soil from the fertilizer solution increased the P content in fruits in addition to yielding the highest total number of fruits.

Similar to leaf sample elemental analysis, the Fe content was much higher in the Fe—alginate hydrogel treatments compared to that of the control and fertilizer solution, showing that the plant was taking Fe from the Fe—alginate hydrogels and translocating within the plant (Figure 6C) to the fruits. Tomato plants translocating Fe in their fruits were previously demonstrated, where the soil was contaminated with Fe nanoparticles compared to their controls. The Fe content in fruits varied a lot, resulting in a high standard deviation, suggesting that the Fe content in fruits varied depending on the location of fruit formation. In this study, fruits were randomly chosen for analysis and they were not picked from the same part of the plant such as fruits formed on the top or in the middle of the plant. Regardless, this showed that the use of this fertilizer system on crops will increase the Fe content in plant materials, which is also beneficial for preventing iron-deficiency anemia.

As Ca deficiency is a known factor contributing to blossom end rot, we analyzed the Ca content in the fruit samples. Interestingly, compared to control and Fe—alginate hydrogel treatments, the Ca content in fruits of plants treated with the fertilizer solution was much lower (Figure 6D). This suggests that Ca deficiency also contributed to the development of blossom end rot in fruits of plants treated with the fertilizer solution, along with other conditions mentioned above. This Ca deficiency could be due to soluble phosphate ions in the fertilizer solution coordinating Ca2+ ions in soil to form the sparingly soluble Ca3(PO4)2. This was not observed in the fertilizer hydrogel treatments due to the slower release of phosphates and the coordination of the phosphates to the Fe(III)—polysaccharides instead of being available for binding.

Figure 5. Average total biomass (above-ground and below-ground biomasses combined) for tomato plants from different conditions. *p < 0.05, **p < 0.01, ***p < 0.001, ns = p > 0.05.
by soil calcium. Furthermore, water-rich hydrogels maintaining a consistently moist soil could possibly mitigate the potential for fluctuating moisture levels that led to blossom end rot, as seen in fertilizer solution treatment.

Amplicon sequencing analysis of the 16S V3−V4 rRNA gene region was performed to identify how fertilizer hydrogel beads may influence the composition of bacterial assemblages at the soil surface. Over the 3 month period, the weighted phylogenetic distances (weighted-UniFrac) between the three fertilized soil samples (fertilizer solution and fertilizer gel bead dark and light) increased (Figure 7). However, of the three samples, bacterial assemblages from the pots with fertilizer beads exposed to light changed the least through time. Further, surface soil assemblages from pots with fertilizer beads exposed to light maintained higher levels of taxonomic richness (Chao1) and diversity (Shannon’s $H'$) during the experiment (Figure S12). Given the limited sampling scale (surface only) and lack of replication ($n = 1$), further exploration of the responses of soil microbial communities to fertilizer beads is warranted. Future studies should include fungi to better quantify community composition as well as utilize metagenomic and metatranscriptomic approaches to explore the functional genes present within the soil microbial communities.

These results indicate, however, that the light-controlled release of nutrients from the hydrogel beads overall showed minimal changes in the bacterial communities in the soil throughout the duration of the tomato growth. This shows that the Fe(III)−polysaccharide hydrogel system remains a promising method to treat liquid waste solutions and capture the nutrients. In addition, the slower, light-controlled, release from the Fe(III)−polysaccharide can be beneficial to the plant growth and help increase the overall fruit formation. The more controlled release of nutrients from the hydrogel beads would also help eliminate problems of fast nutrient release and nutrient runoff compared to that of conventional fertilizer. Further exploration of changes in the microbial community associated with Fe(III)−polysaccharide hydrogel beads is planned.
CONCLUSIONS

Fe(III)−polysaccharide hydrogel beads were tested for their nutrient uptake capability from wastewater using model waste solutions and natural raw manure solutions. These gel beads showed an uptake of 0.05 mg g⁻¹ for nitrate and ammonium ions and an uptake of 0.18 mg g⁻¹ phosphate from a pH = 7 model wastewater solution with 100 ppm of each type of ion. This uptake accounted for ~32%, 27%, and 90% of nitrate, ammonium, and phosphate ions from the original solution, respectively. Studies with the raw manure solution showed that lower ammonium uptake by these gels is due to the weaker binding forces between the ammonium ions and the hydrogel network, whereas high phosphate uptake by these gels is due to the strong phosphate binding to the iron nanoclusters of the hydrogels. Tomato plant trials under greenhouse conditions suggested that these Fe(III)−polysaccharide hydrogels can release nutrients that promote the growth of plants. Different observations made with gel beads placed in dark vs light suggest that nutrient release was primarily due to the degradation of the hydrogels caused by the Fe(III)−carboxylate photochemical reaction. Plants treated with fertilizer gel beads showed an enhanced plant growth as well as fruit formation compared to the controls showing the ability of the hydrogel beads to use these Fe(III)−polysaccharide hydrogels as a slow-release fertilizer system that can contribute to the mitigation of CHABs and other environmental issues associated with the agricultural use of animal manure and conventional chemical fertilizers.

MATERIALS AND METHODS

Materials. Sodium alginate 35% mannuronate, \( M_w \approx 97,000 \) Da (Alginate) was received from Kimica Corporation. Anhydrous disodium hydrogen phosphate (Na₂HPO₄) and anhydrous sodium dihydrogen phosphate (NaH₂PO₄) were purchased from Fischer Scientific. Iron(III) chloride (reagent grade 97%), ammonium nitrate (ACS reagent 98%), and pectin from the citrus peel with 74% galacturonic acid (Lot 323016) was purchased from Sigma-Aldrich. Ammonium chloride (NH₄Cl) min. 99.5% pure and nitric acid (HNO₃ 68%) were purchased from Acros. Nitrate (KNO₃) 99% pure was purchased from Acros. Chloride (NH₄Cl) min. 99.5% pure and nitric acid (HNO₃ 68%) were purchased from EMD Chemicals Inc. Potassium chloride (KCl) min. 99.5% was purchased from Acros. Anhydrous disodium hydrogen phosphate (Na₂HPO₄) and anhydrous sodium dihydrogen phosphate (NaH₂PO₄) were purchased from Fischer Scientific. Ammonium solution was prepared by dissolving NH₄Cl in DI water so that the final ammonium concentration is 100 ppm. Nitrate solution was prepared by dissolving KNO₃ in DI water to achieve a solution with a 100 ppm nitrate concentration. A mixed nutrient solution was prepared by dissolving KNO₃, NH₄Cl, and Na₂HPO₄ in DI water so that the concentration of nitrate, ammonium, and phosphate ions is 100 ppm. The pH of these solutions was adjusted to 7.0 (using minimum volumes of 0.05–1.0 M HCl and NaOH solutions), and 20 mL of this solution was placed in 50 mL glass beakers with 10.0 g of polysaccharide–0.1 M FeCl₃ hydrogel beads and covered with parafils. These beakers were placed on top of a Daigger 22407A mechanical shaker (high shaking speed) under dark conditions for 24 h. Then, hydrogel beads were removed by filtration and the nutrient solutions were diluted to an appropriate concentration for determining the remaining nutrient content using automated colorimetric analysis with a SEAL Analytical AQ2+ Discrete Chemical Analyzer (AQ2+) having a detection range of 0.005–1.0 mg P/L for orthophosphate using U.S. Environmental Protection Agency (EPA) test method 118A Rev. 4, which is a modification of U.S. EPA 365.1, a detection range of 0.01–15 mg N/L for nitrate + nitrite using U.S. EPA test method 114A Rev. 7, which is a modification of U.S. EPA 353.2, and a detection range of 0.02–2.0 mg N/L for ammonia using U.S. EPA test method 103A Rev 6, which is a modification of U.S. EPA method 530.1 Rev. 2.

Nutrient Uptake from Raw Manure Solutions. Hydrogel bead samples of 10.0 g were placed in plastic cups along with 20 mL of the raw manure solution and were allowed to stand for 24 h. The hydrogel beads were then filtered, and the filtrate was diluted 50 times before analyzing for the remaining nutrient content using the Seal Analytical AQ2+ Discrete Chemical Analyzer as above.

Thermogravimetric Analysis (TGA). Hydrogel bead samples were allowed to air-dry on Petri dishes under dark for 3 days (at a room temperature of 22 °C). These dry gel samples were ground using a pestle and mortar. TG curves were collected using a TA Instruments TGAQ50 with a heating rate of 10 °C per min from room temperature to 1000 °C. A minimum of 7 mg of sample was used for each experiment.

Tomato Plant Trials. Tomato seeds were allowed to germinate in a tray with Sungrow professional growing mix 510. After 17 days, the plants were transplanted in plastic pots with the dimensions of 17 cm diameter and 18 cm height with ~1.7 kg of growing mix on each pot (60% soil, 20% peat moss, 10% vermiculite, and 10% perlite by volume). A nutrient

Hydrogel Bead Preparation. A 1% by weight alginate solution was prepared by dissolving sodium alginate (150 mg) in 15 mL of deionized (DI) water. This solution was then dropped into a 0.1 M FeCl₃ solution using an 18-gauge needle. Care was taken to drop the solutions at a height of ~6 in. to ensure an average bead diameter of 3.5 mm. For mixed polysaccharide gels, 0.5% by weight alginate and 0.5% by weight other polysaccharides (chitosan or pectin) were mixed in DI water (75 mg of each polysaccharide in 15 mL of DI water). For alginate–chitosan solutions, a 20-gauge needle was used to drop the polysaccharide solution to the 0.1 M FeCl₃ solution due to the higher viscosity of the solution from some incomplete dissolution of chitosan particles. Drop height was maintained ~6 in. to get gel beads with 3–4 mm in diameter.

Nutrient Uptake from Artificial Waste Solutions. Ammonium solution was prepared by dissolving NH₄Cl in DI water so that the final ammonium concentration is 100 ppm. Nitrate solution was prepared by dissolving KNO₃ in DI water to achieve a solution with a 100 ppm nitrate concentration. A mixed nutrient solution was prepared by dissolving KNO₃, NH₄Cl, and Na₂HPO₄ in DI water so that the concentration of nitrate, ammonium, and phosphate ions is 100 ppm. The pH of these solutions was adjusted to 7.0 (using minimum volumes of 0.05–1.0 M HCl and NaOH solutions), and 20 mL of this solution was placed in 50 mL glass beakers with 10.0 g of polysaccharide–0.1 M FeCl₃ hydrogel beads and covered with parafils. These beakers were placed on top of a Daigger 22407A mechanical shaker (high shaking speed) under dark conditions for 24 h. Then, hydrogel beads were removed by filtration and the nutrient solutions were diluted to an appropriate concentration for determining the remaining nutrient content using automated colorimetric analysis with a SEAL Analytical AQ2+ Discrete Chemical Analyzer (AQ2+) having a detection range of 0.005–1.0 mg P/L for orthophosphate using U.S. Environmental Protection Agency (EPA) test method 118A Rev. 4, which is a modification of U.S. EPA 365.1, a detection range of 0.01–15 mg N/L for nitrate + nitrite using U.S. EPA test method 114A Rev. 7, which is a modification of U.S. EPA 353.2, and a detection range of 0.02–2.0 mg N/L for ammonia using U.S. EPA test method 103A Rev 6, which is a modification of U.S. EPA method 350.1 Rev. 2.
solution was prepared by dissolving 27.9 g of K$_2$HPO$_4$, 29 g of NaH$_2$PO$_4$, and 35.7 g of NH$_4$NO$_3$ in 1 L of DI water, and the pH was adjusted to 7.0 with a 6 M NaOH solution (12,500 ppm N, P, and K solutions). This solution was used as the fertilizer solution. This concentration was chosen based on nutrient requirements for tomatoes and considering the soil was collected from a field that was not fertilized. Fertilizer hydrogel beads were prepared by dissolving 1% alginate by water weight in the above fertilizer solution and dropping into a 0.1 M FeCl$_3$ solution. Control hydrogel beads were prepared by dissolving 1% by weight sodium alginate in DI water and dropping into a 0.1 M FeCl$_3$ solution. NCAP-X3, an automated bead maker, was used to make gel beads in large quantities.

Six different growth conditions were provided to the plants, namely, control plants (condition 1), treatments with fertilizer solution (condition 2), control hydrogel bead dark (condition 3), control hydrogel bead light (condition 4), fertilizer hydrogel bead dark (condition 5), and fertilizer hydrogel bead light (condition 6) with eight plants per condition. Fertilizer hydrogel beads (10 g) were placed on top of the soil in each condition where they were used. For dark conditions, the pot was covered with aluminum foil leaving a small cut in the middle for the plant to grow out (Figure S13). Plants were placed in a greenhouse and watered three times per week with 200 mL per pot from the day of transplanting. Unprocessed municipal water was used. Starting from day 37, plants were watered every morning with 200 mL of water. Starting from day 71, plants were watered with 200 mL of water both in the morning and in the evening. This increase in watering frequency was to account for the increased need for plant growth. Plants received an average of 14 h of sunlight daily, and the daily average greenhouse temperature during the trial was approximately 27.6°C. A 20 mL aliquot of fertilizer solution per plant was used for fertilizer solution treatment, and fertilizer hydrogel beads obtained from 20 mL of fertilizer solution were added for each plant in fertilizer gel dark and light conditions so that the same amount of nutrients was provided for all three fertilized conditions, so differences in nutrient uptake were accounted for. Fertilizer solution and beads were added every 2 weeks since transplanting in pots and six times during the experiment. Since differences in plants were observed under different conditions, starting from the 8th week, the plant height, number of flowers, and number of fruits in each plant were recorded every week. Ripened fruits were harvested and weighed for comparison. The trial was continued for a total of 111 days from the day that seeds were first allowed to germinate.

Chlorophyll Content Analysis in Tomato Leaves. The chlorophyll content of tomato leaves was determined according to a method reported before with appropriate modifications. In brief, tomato leaf disks with a diameter of 16 mm were punched out from a matured leaf of each plant (48 in total). Each disk was then placed in a 20 mL glass vial with 10 mL of 200 proof ethanol. These vials were stored under dark for 24 h, and the alcohol solutions were collected into 48 separate 50 mL volumetric flasks. Each vial was rinsed with 5 mL ethanol, and the washing was added to each respective volumetric flask. The same procedure was continued for 2 more days, and the solutions were added to the respective 50 mL volumetric flasks. After combining the 3 days’ worth of extracts, ethanol was added to dilute solutions in each flask up to the mark and the absorbance of these solutions was measured at 649 and 665 nm wavelengths using a Shimadzu UV-2600 UV–vis spectrophotometer. The chlorophyll a and b contents for each leaf sample were calculated using the following equations, where $A_{649}$ is the absorbance at a particular nanometer wavelength (e.g., $A_{649}$ is absorbance at 649 nm).

\[
\frac{\mu g \text{ of Chlorophyll a}}{mL \text{ of solution}} = (13.7)(A_{665 \text{ nm}}) - (5.76)(A_{649 \text{ nm}}) \tag{1}
\]

\[
\frac{\mu g \text{ of Chlorophyll b}}{mL \text{ of solution}} = (25.80)(A_{649 \text{ nm}}) - (7.60)(A_{665 \text{ nm}}) \tag{2}
\]

The total chlorophyll content was obtained by adding chlorophyll a and b weights, and the total chlorophyll per unit area of the leaf was calculated.

Biomass Analysis of Tomato Plants. On the 111th day of the experiment, tomato plants were destructively harvested, and root and shoot systems were separated, and the biomass was calculated according to a previously reported method. In brief, plant materials were cut into small pieces, placed in Petri dishes, and dried at 80°C for at least 48 h, and the dry weights of the root and above-ground biomass were recorded.

Fe and P Contents in Tomato Leaves Using ICP-MS. Dry tomato leaf samples from control, fertilizer solution, fertilizer bead dark, and fertilizer bead light conditions were analyzed for Fe and P contents. In brief, the samples were prepared by weighing out approximately 250 mg of plant material and adding it to a 75 mL PTFE microwave vessel in which 5 mL of water, 5 mL of concentrated HNO$_3$, and 3 mL of 30% hydrogen peroxide were added. The samples were digested using a Mars 230/60. After digestion, the samples were allowed to cool and were diluted with 50 mL DI water. All ICP-MS measurements were performed on an Agilent 7700x ICP-MS (Santa Clara, CA) in general purpose mode. After the instrument warm-up was complete, the instrument was tuned with a tuning solution for ICP-MS 7500cs (Agilent, part number 5185-5959) using the Online ICP-MS Mass Hunter Software in Helium (He), High Energy Helium (HEHe), and Hydrogen (H$_2$) gas modes. Calibration standards were made using the IV-ICP-MS-71A standard from Inorganic Ventures and diluted in a 2% HNO$_3$/0.5% HCl solution, and Fe and P were selected for this experiment. During sample analysis, a blank and a check standard (prepared separately from the calibration standards) were analyzed every seven samples. A method blank, method spike, sample duplicate, and spiked sample were also analyzed.

P and Metal Ion Contents of Tomato Fruits Using ICP-OES. Freeze-dried tomato fruit samples from each condition were powdered, and 250 mg samples were added to 50 mL Erlenmeyer flasks. A volume of 25 mL from concentrated HNO$_3$ was added to each flask and placed on a hot plate at 200°C. The samples were digested for 30 min with occasional swirling and allowed to cool down to room temperature. The acid-digested samples were added to 50 mL volumetric flasks and diluted up to mark with DI water. Each solution was diluted 10× before analysis, and sample analysis was carried out using a Thermo iCAP 6000 series ICP emission spectrometer. K, P, Fe, and Ca contents in the samples were measured using calibration curves for each element with emissions measured at 766.4, 178.2, 259.9, and 422.6 nm, respectively.
**Soil Bacterial DNA Sampling and Extraction.** Soil samples from one replicate of each condition were used. The samples were collected from the first 2 cm off the surface on days 51, 84, and 107 of the experiment. All DNA soil extractions were performed according to specifications of the Qiagen DNeasy PowerSoil Pro Kit. Briefly, 250 mg of soil was added to a PowerBeadPro tube with CD1 solution and vortexed horizontally for 10 min to lyse the cells. The tube was then centrifuged at 15 000 g for 1 min, and the supernatant was transferred to a sterile microcentrifuge tube. Two hundred microliters of CD2 solution was added, vortexed for 5 seconds, and centrifuged at 15 000 g for 1 min to removed particles. The supernatant was transferred to a sterile microcentrifuge tube, and 600 µl of CD3 solution was added and vortexed for 5 seconds. Six hundred and fifty microliters of the lysate was loaded on the MB spin column and centrifuged at 15 000 g for 1 min to bind the DNA. Five hundred microliters of EA solution was added to the column and centrifuged at 15 000 g for 1 min to wash the DNA, and the flow-through was discarded. Five hundred microliters of C5 solution was added to the column and centrifuged at 15 000 g for 1 min, and the flow-through was discarded. Hundred microliters of C6 solution was added to the column and centrifuged at 15 000 g for 1 min to elute the DNA.

**Amplicon Sequencing and Bioinformatic Processing.** Taxonomic composition of the extracted DNA was assessed via amplicon sequencing of the V3–V4 hypervariable regions (341 F and 805R primers) of the 16S rRNA gene using the Illumina MiSeq v3 600 cycle kit and sequencing platform (Illumina) to generate 351 bp amplicons at the Delaware Biotechnology Institute (Newark, DE). Demultiplexed Illumina amplicon data were processed to remove residual primers using cutadapt and error correction and taxonomic assignment using the DADA2 pipeline. Read filters were trimmed (280 and 180 bp for Reads 1 and 2, respectively), filtered (maxEE = c(2, 5), truncQ = 2), and denoised using the DADA algorithm. The DADA error model was parameterized using at least 1 × 108 bases. Following error correction, paired reads were merged and chimeras were removed from the data set using the consensus method. Taxonomic assignment was performed using the IDTAXA algorithm with the SILVA SSU reference database (v132) training set (www2.dechipher.c-odes/Downloads.html). Reads assigned by SILVA to eukaryote chloroplasts (bacteria, cyanobacteria, oxyphotobacteria, chloroplast) and mitochondria (bacteria, proteobacteria, alphaproteobacteria, rickettsiales, mitochondria) were discarded. Amplicon sequence variant (ASV) abundances were normalized by subsampling to the lowest common sequencing depth; no ASVs were lost due to normalization. Data reduction filtering for representative taxa based on abundance (>0.01%) was conducted using Phyloseq. A phylogenetic tree based on ASVs was constructed de novo by fitting a GTR + G + I maximum likelihood tree from a neighbor-joining tree, which was used to estimate weighted-UniFrac distances between samples in Phyloseq. Graphical visualizations were created using ggplot2, and all bioinformatic analyses were conducted using the R Computing Framework version 3.6.1 (R Core Team 2019).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02694. Supporting information including TGA curves, photos of tomato leaves and chlorophyll extracts, total chlorophyll in leaves, above- and below-ground biomass analyses, shoot-to-root ratio for tomato plant trial, and amplicon sequencing data is available (PDF).

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### ABBREVIATIONS

Alginane, sodium alginate 35% manuronate; EPA, Environmental Protection Agency; TGA, thermogravimetric analysis; ICP-MS, inductively coupled plasma-mass spectrometry; PTFE, polytetrafluroethyene; ICP-OES, inductively coupled plasma-optical emission spectroscopy

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