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Enhanced phosphorus recovery from anaerobic dairy effluent through acidification or ozonation pretreatments combined with biochar and iron chloride

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Anaerobically digested (AD) dairy effluent is rich in phosphorus (P) and nitrogen (N) and requires treatment before discharge. Effluent from the AD is often centrifuged to reduce the suspended solids, however, the supernatant liquid AD fraction (LAD) still contains high concentrations of P, N, and small diameter suspended solids. A promising approach for recovering nutrients from LAD is to use biochar as a filter aid to remove N, P, and suspended solids. The recovered biochar can be used to recycle nutrients by amending it to soil as a biochar-based fertilizer. To aid in P and suspended solid removal from the LAD, iron (Fe) can be dosed with biochar, and can be preceded by acidification or ozonation pretreatment to increase solids separation. In this study, five biochar doses (1, 2, 4, 6, and 8 g L^{-1}) and four Fe doses (2, 3, 6, and 15 mmol L^{-1}) were evaluated, with pretreatments consisting of acidification of LAD to pH 5 or 6.5, or ozone dosing applied prior to biochar and iron addition. Increasing Fe dose concentration from 2 to 15 mmol L^{-1} in the 6 g L^{-1} biochar treatment increased total-P removal from 24 to 44%. Acid pretreatments at pH 6.5 and 5 in the 6 g L^{-1} biochar treatment with Fe dose of 15 mmol L^{-1} increased TSS removal from 50 to 86%, and increased total-P removal from 64 to 85%. Ozonation also decreased TSS and increased the P concentration in the recovered solids. These results offer insights into the conditions needed to optimize production of a biochar-based fertilizer using dairy anaerobic digester effluent, which is a key step toward realizing the sustainable bioeconomy potential of dairy operations.

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Sustainability spotlight

Recovering nutrients from anaerobically digested dairy effluent is a strategic opportunity to advance sustainability and recycle phosphorus and nitrogen. This will support food security (SDG 2), reduce soil and aquatic pollution (SDG 6), and promote responsible production and resource efficiency (SDG 12). Moreover, improving the efficiency of flocculant use is crucial to prevent salt accumulation downstream from the treatment process and in agricultural soils (SDG 12). Finally, the use of biochar as a nutrient adsorbent and for soil amendment enables nutrient recovery, improves soil health, and contributes to long-term carbon sequestration, supporting climate change mitigation (SDG 13).

Introduction

Phosphorus (P) is a macronutrient fertilizer required for crop production and is mainly derived from mining of non-renewable resources, of which there are limited reserves.[1] This presents a long-term vulnerability to the global food supply.[2,3] Additionally, P mining is an energy-intensive process that contributes to greenhouse gas emissions.[4,5] While P is a limited resource, its excess in the environment from the widespread use of mineral fertilizers and the direct application of livestock manure can cause runoff into freshwater and marine ecosystems, causing eutrophication. This dual problem, of simultaneously depleting a resource while polluting with its excess, underscores the need for a circular, regenerative approach to phosphorus management,[6] necessitating the development of innovative methods for recovering and recycling P from biowastes.[7,8]

Anaerobic digestion (AD) has emerged as a sustainable waste management technology for treating dairy farm manure to produce biogas, a renewable energy source that can be used to generate electricity and heat, or upgraded to renewable natural gas (RNG).[9] Many commercial dairy farms manage manure wastewater onsite using anaerobic biological treatments combined with solid–liquid separation techniques, such as screening and centrifugation, which significantly reduces the chemical oxygen demand (COD) and suspended solids of the liquid AD (LAD).[10] Although the LAD is reduced in primary organic matter, it still contains high concentrations of valuable

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nutrients like nitrogen (N) and P, as well as significant amounts of non-digested organic suspended solids that can be used to support a circular economy.[11,12] Further, when LAD is centrifuged, the remaining solids have a very small particle size distribution,[13] and are difficult to separate, making management of the centrifuged LAD difficult.[11] The high water content of LAD limits the potential for broader application due to high transportation costs.[14,15] This highlights the need to develop strategies to reduce the water in the LAD, which would lower transportation costs[9] and enable broader application and movement of P-rich biowastes to P-deficient regions.[15]

While technologies like ammonia stripping and struvite precipitation are established for P and N recovery from dairy effluents, the reactions have limitations for dairy effluents such as LAD because the high concentrations of suspended solids pose a considerable obstacle to efficient nutrient recovery. Membrane-based technologies, such as nanofiltration and reverse osmosis, face significant challenges when treating digestates due to membrane fouling from the high concentrations of suspended solids, even with pretreatment.

One approach to remove nutrients from animal manure is the Quick Wash process,[16] which is a patented method for P recovery from manure slurries that uses acidification to solubilize P associated with manure solids followed by flocculation for solids separation and then pH increase of the liquid fraction to precipitate Ca and Mg phosphates. This approach has been successfully applied to dairy manure,[16] swine manure,[17] and poultry litter,[18] but has not been tested on LAD. Ultimately, all reviewed technologies have drawbacks, and further research is needed to develop methods that are effective and economically viable for managing solid and liquid residuals and meeting market demands for recovered products.[19]

More recently, nutrient recovery from biowastes has increasingly focused on using biochar in filtration processes.[20,21] Biochar has high porosity, carbon sequestration potential, and beneficial properties as a soil additive, which can improve soil quality and increase soil pH and water retention capacity.[22] Biochar that is enriched with nutrients is known as a biochar-based fertilizer (BBF). Studies indicate that BBFs can act as enhanced efficiency fertilizers,[23,24] increasing crop productivity by at least 10% compared to commercial fertilizer controls due to improvement of the physical properties of soils,[25] increased fertilizer use efficiency,[25,26] and increased soil microbial activity.[27,28]

While numerous laboratory studies have demonstrated the high efficiency of using biochar as an adsorbent for P recovery from effluents, the challenge of recovering the biochar on a large scale from a system with high concentrations of suspended solids, such as AD effluent, is not typically addressed.[21,29,30] Rotary belt filters (RBFs) enable the *in situ* application of biochar in a practical, large-scale system. Unlike membrane technologies that are prone to fouling, RBFs are designed to handle high-solids effluents by using a recirculating mesh belt that collects solids and forms a filter cake, which is then scraped off for subsequent processing. However, RBF efficiency for solids removal is limited by the pore size of the rotary belts (generally 350 μm to 30 μm) and must be selected to best match the solid particle sizes in the suspension. In AD effluent, the suspended solids are notoriously small (most particles are <10 μm),[13] and the RBF pore sizes may not be able to effectively remove them. However, using biochar of greater diameter than the RBF may create a filter cake effect that can trap solids from the AD effluent that are smaller than the nominal size of the RBF. Another effective way to overcome the small particle size of LADs without requiring the use of extremely fine meshes is the addition of flocculants to produce stable flocs that are bigger than the mesh pore size.[31,32] Flocculation can be further enhanced using preliminary treatments such as oxidants or acids or bases to change pH. The recovered solids that are entrained in the biochar have high N and P contents, which make a biochar-based fertilizer that has increased economic value. These enhanced filtration processes have not been tested.

Optimization of solids removal from the LAD supernatant will inform new methods of handling this difficult to separate slurry and could facilitate a more efficient Quick Wash-type process on the LAD. Additionally, aiming to recover P through filtration to produce a BBF combines the potential benefits of biochar in soil amendment with nutrient recycling.[21,33] Another opportunity at dairies that use reverse osmosis (RO) to treat LAD[34] is to use the biochar-integrated RBF as a pretreatment to reduce fouling of the expensive membranes in RO systems.

To aid in filtration, flocculants are often used to aggregate suspended particles, which enhances solid recovery and nutrient densification.[35,36] Among the most used and effective inorganic flocculants are aluminum (Al) salts such as Al chloride (*e.g.*, poly-Al chloride), and Fe salts such as $FeCl_2$ and $FeCl_3$.[37,38] Although Al salts can be highly efficient, Fe salts have the advantage of lower environmental risk and better compatibility for growing plants when amended to soils because Al is toxic to plants when it is in the soil solution.[37,39,40] Thus, Fe-based flocculants have greater potential for better nutrient recycling opportunities in soil amendment.

The use of $FeCl_3$ as a flocculant has been shown to be a low-cost, effective solution under various process conditions, such as in a dairy wastewater where $FeCl_3$ has demonstrated 82% biological oxygen demand (BOD) removal.[41] In addition, the addition of Fe to the LAD and biochar slurry enhances P removal; Strawn *et al.*[42] showed that Fe-dosed biochar had Fe sorbed on the biochar surfaces as adsorbed Fe or Fe-oxide precipitates, which increased P removal capabilities of the biochar. However, a challenge in effluents such as the LAD is that high amounts of flocculant may be required to achieve effective solid–liquid separation.[29,30,43,44] This can lead to high chemical costs, a significant environmental footprint, and adverse effects on downstream treatment processes.[37,38]

To enhance the efficiency of LAD flocculation, the application of oxidizing agents as a pretreatment has been proposed.[44,45] Ma *et al.*[44] showed that pretreating dairy wastewater with calcium hypochlorite ($Ca(ClO)_2$), followed by the addition of a ferric salt (polyferric sulfate) could increase suspended solids removal by at least 10% compared to flocculation alone.[44]

An alternative to chemicals as oxidizing agents is the application of an advanced oxidation process using ozone (O_3).[46] Ozone (O_3) treatment significantly improves wastewater quality by reducing turbidity and chemical oxygen demand (COD), while effectively removing color, odor, bacteria, and viruses.[46,47] dos Santos *et al.*[48] demonstrated the effectiveness of ozonation when applied as a pretreatment step for filtration of milk-processing effluent, achieving a COD reduction of up to 57% and a turbidity reduction of 93%.[48] Ozone pretreatment can also improve flocculation.[49] Addition of a flocculant after ozonation can further remove extracellular biopolymers from suspension.[50]

To address the challenges of removing high suspended solids from liquid anaerobic digestate (LAD), this study evaluates an integrated treatment approach consisting of: (1) biochar as a filter aid and adsorbent, (2) ferric chloride ($FeCl_3$) dosing, and (3) ozonation and acidification as pretreatments. It is hypothesized that pretreatment with acid and ozone will significantly enhance the performance of $FeCl_3$ in recovering solids and nutrients from LAD. These promising treatment technologies have not previously been tested in combination on complex dairy effluents such as centrifuged LAD. Furthermore, it is hypothesized that the combined pretreatments and Fe dosing will increase the recovery of solids and nutrients, which can then be mixed with biochar and recovered using a rotary belt filter. The resulting recovered solids-biochar mixture may be used as a BBF, thereby improving the economic and environmental sustainability of dairy waste management.

Methods

Biochar sources

Two commercially available biochar types were used: Biochar Now (BN) (Biochar Now LLC, Colorado, USA), synthesized through slow pyrolysis using beetle-killed and fire-damaged trees or other woody materials as feedstocks; and Pacific Biochar (PB) (Pacific Biochar Benefit Corporation, California, USA), which was manufactured through fast pyrolysis using forest biomass collected primarily from designated high fire hazard areas in California.

The P concentration and particle size distribution of BN and PB biochars are presented in Table 1. Their complete elemental composition and physicochemical properties are provided in Tables S1 and S2 in the SI. The characteristics of the biochars listed in Table 1 correspond to the batches used in this study. Since the properties of the feedstock can change, properties of different biochar production batches may vary.

Table 1 P concentration and particle size distribution of BN and PB biochars

	BN biochar	PB biochar
P Concentration (mg kg^{-1})	196 ± 80.6	1103.4 ± 37.3
Particle size (%)		
>4	0.14	1.05
4–2 mm	29.19	24.19
2–0.1 mm	69.93	54.18
<0.1 mm	0.73	20.58

AD effluent source characteristics and handling

In this study, the experiments were conducted using an AD effluent sample collected from a centrifugation facility at a commercial dairy in Idaho. The anaerobic digester is a completely mixed system operated at 37.8–38.3 °C with a hydraulic retention time (HRT) of 20 days. After digestion, the effluent undergoes solids separation by centrifugation (model CS 26, Centrisys/CNP, LLC, Wisconsin, USA). The LAD effluent used in this study corresponds to the liquid phase (supernatant) obtained after centrifugation, and thus the suspended solids have very small particle size distribution and are inherently difficult to separate.

For the laboratory experiments, the LAD material was collected and stored in a refrigerator at 4 °C. The characteristics of the effluent can vary among different batches. The range of concentrations of total-P, orthophosphate, TSS and pH of the LAD used in the experiments is summarized in Table 2.

Biochar dosing

The biochar dosing experiments were conducted using a four place portable jar test apparatus (Tintometer Inc., Florida, USA). 30 mL of LAD effluent was mixed for 20 minutes at 200 rpm with either BN or PB biochar that were added at dosing rates of 1, 2, 4, 6, and 8 g L^{-1}. After mixing, the samples were vacuum filtered on a 50 mm Buchner ceramic funnel using a filter mesh that is similar to the mesh used in the filter belts on the RBF. The mesh pore size is 139 μm (#112 mesh). A vacuum pressure of 6.666 kPa was maintained on the filter. All experiments were done in triplicate.

AD effluent pretreatment

For the $FeCl_3$ dosing experiments, one control (LAD, no pretreament) and three different pretreatments were tested before the addition of biochar and $FeCl_3$ – one consisting of ozonation, and two consisting of acidification to two different pH levels.

The ozonation pretreatment was done in 50 mL amber bottles with septum caps (Environmental Express, Inc., South Carolina, USA). Stainless steel 18-gauge needles were used for the ozone purging and gas outflow. The ozone generator (Azco Industries Ltd, Vancouver, Canada) was set up with a gas flow rate of 1 mL min^{-1}. The ozone was purged into vials containing 30 mL of sample for 10 minutes. The ozone concentration in DI water (Table S3) was used as a reference for the amount of ozone

Table 2 LAD effluent characteristics

Parameters	LAD
Total phosphorus (mg L^{-1})	230–267
Soluble *ortho*-P (mg L^{-1})	18–34
Total suspended solids (mg L^{-1})	21 000–26 000
pH	7.9–8.2

purged in the AD effluent (the ozone concentration in the effluent was not directly measured because of the turbidity that interferes with the ozone measurement methods). After 10 min of ozonation, the DI water ozone concentration was 11 mg L^{-1}. The ozonation was carried out in triplicate for each dose of $FeCl_3$ tested.

The acidification pretreatment used a 5 M HCl solution to acidify 500 mL of the AD dairy effluent to the desired pH levels of 5.0 and 6.5. The amount of acid used was recorded (SI Table S4).

Fe dosing

Different doses of $FeCl_3$ flocculant were tested with various pretreatments to enhance the suspended solids separation in the BN biochar LAD suspensions. 6 g L^{-1} of biochar was mixed with 30 mL of the LAD effluent (control or pre-treated) for 20 min at 200 rpm using the jar test mixer, followed by the addition of $FeCl_3$ to achieve final concentrations of 2, 3, 6, and 15 mmol L^{-1}. The Fe-biochar mixtures were then stirred for 1 min at 200 rpm and subsequently for 20 min at 40 rpm. After mixing, the samples were vacuum filtered using the same procedure described above for biochar dosing experiments.

Biochar and AD effluent characterization

The solids retained on the mesh were collected, air-dried overnight, and analyzed for total P using a modified dry ash method followed by acid digestion.[51] A portion of the filtrate was used for TSS analysis, while another portion was digested using the acid digestion method for sediments, sludges, and soils (Method 3050B, EPA, 1996).[52] The digestates were filtered through a 0.45 μm PES syringe filter and analyzed for elemental composition (P, Al, Ca, Fe, K, Mg, Mn, Na, and Zn) using an ICP-OES (Agilent 5110, California, USA). LAD was centrifuged at 4000 RCF for 30 min and the supernatant was collected to measure the soluble *ortho*-P by the ascorbic acid method (UV-vis absorbance 880 nm).[53]

TSS analysis was performed using an adapted method from Queenan *et al.*;[54] a 10 mL aliquot of the sample was mixed with 10 mL of ultrapure water in a centrifuge tube (50 mL conical polypropylene tube). The mixture was centrifuged at 4000 RCF for 30 min at 25 °C. The supernatant was removed, and 10 mL of ultrapure water was added to the remaining solids, followed by a second centrifugation under the same conditions. This washing and centrifugation step was repeated a total of three times. After the final centrifugation, the supernatant was discarded, and the tubes containing the precipitates were dried in an oven at 105 °C for 24 h. The dried solids were then weighed, and the final mass was considered the TSS content of the 10 mL sample.

Quantities of carbon and nitrogen present in the solid samples were measured using a combustion analyzer (samples sent to the University of Idaho Analytical Science Laboratory, Idaho, USA). Plant-available P in the biochar was estimated using the 2% formic acid extraction method, which is the recommended method to assess P bioavailability in biochar.[55] Briefly, 0.10 g of biochar was mixed with 10 mL of 2% formic acid solution and dispersed using ultrasonification for 10 min followed by mixing on an end-over-end shaker for 30 min at room temperature (20 °C ± 2). The samples were filtered through a 0.45 μm PES syringe filter followed by P analysis on an ICP-OES. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) of biochar samples were carried out using a Zeiss Supra 35 FEG-SEM. Biochar samples were mounted on a metal stub and carbon coated and analyzed at an accelerating voltage of 15 kV.

Statistics

Data analysis was conducted in RStudio (R version 4.4.2). Both one-way and two-way ANOVA models were used, with statistical significance assessed using *F*-tests and a significance threshold of $p < 0.05$. All references to significant differences correspond to *p*-values below this threshold. Post hoc analyses were performed using estimated marginal means calculated with the emmeans package, and pairwise comparisons were adjusted using Tukey's method to control the family-wise error rate. One-way ANOVA was used to evaluate the effect of biochar dose on TSS, P concentration in LAD, and P concentration in solids. Two-way ANOVA was used to evaluate the effects of Fe dose and pretreatment on TSS concentration, P concentration in LAD, and P concentration in solids.

Results and discussion

Effect of biochar dose on LAD filtration

The effects of biochar dosing on P recovery from the LAD are presented in Fig. 1. The initial total P concentration in the LAD ranged between 240 and 262 mg L^{-1} (Fig. S1). The TSS concentrations of the LAD also varied between different batches (Fig. S2). The LAD batch used to conduct the experiments with BN biochar had higher TSS concentration (mean 25 750 mg L^{-1}) than the batch used with the PB biochar (mean 22 673 mg L^{-1}). The filtration using BN biochar removed up to 19% (50 mg L^{-1}) of total P and 22% of TSS (Fig. S3) for the 4 and 6 g L^{-1} biochar doses. For the PB biochar, maximum total P removal was 18% (44 mg L^{-1}) for the 8 g L^{-1} biochar dose, and TSS removal was

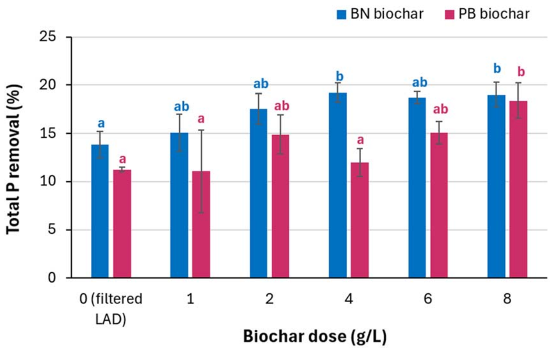

Fig. 1 Total P removal (%) from LAD (P recovery) after treatment with increasing doses of BN or PB biochars. Initial total P concentrations for BN and PB treatments were 262 and 240 mg L^{-1}, respectively. Different letters indicate significant differences between biochar doses within each biochar type ($p < 0.05$).

17%. There was no effect of biochar addition on TSS removal for either biochar type (Fig. S3). The PB biochar has a greater number of particles that are less than 0.1 mm (21% by mass) than the BN biochar (1% for the BN biochar) (Table 1). Thus, PB biochar is more likely to pass through the filter mesh and contribute to the TSS.

The total P concentration on the solids recovered from the biochar dosing experiments is shown in Fig. 2. The initial total P content on BN biochar was ~200 mg $\mathrm{kg^{-1}}$ (Table 1). The PB biochar had an initial total P concentration of 1100 mg $\mathrm{kg^{-1}}$. Without biochar addition, the LAD solids retained on the filter mesh had 6000 to 7000 mg $\mathrm{kg^{-1}}$ P, corresponding to 11 to 14% recovery of total P in the LAD suspension (Fig. 1). The addition of 1 g $\mathrm{L^{-1}}$ BN biochar increased total P recovery to 15%, and addition of 4 g $\mathrm{L^{-1}}$ BN biochar increased recovery to 19%. However, increasing BN biochar dose beyond 4 g $\mathrm{L^{-1}}$ did not further increase P removal (Fig. 1). The decrease in P concentration on solids with increasing biochar addition (Fig. 2) is caused by a dilution effect due to increasing biochar addition and recovery.

Previous studies have reported that differences in pyrolysis temperature and biochar feedstock strongly affect biochar characteristics and adsorption capacity.[56–58] BN biochar and PB biochar, which are very different types of biochar (Tables S1 and S2), did not significantly affect the relative amount of P and TSS removed from the LAD ($p > 0.05$). Unmodified biochar often has limited direct phosphate adsorption capacity because its surface is mostly negatively charged and thus repels phosphate anions.[56,57] Zhang *et al.*[57] compared P sorption by different types of biochar and showed that only woody biochar exhibited favorable P adsorption, and, in fact, they also observed that some biochars release P into the solution.[57] In addition to the limited P sorption capacity of unmodified biochar, the LAD used in this study contained a relatively high concentration of P associated with the suspended solids; only about 10% of the total P (25 mg $\mathrm{L^{-1}}$) was present as soluble *ortho*-phosphate (Table 2). Thus, part of the P removed from the LAD was associated with the suspended solids.

The P concentration in the recovered biochar was much greater than that of raw, untreated biochar (Fig. 2), indicating that despite the relatively low recovery rates of P from the LAD, the LAD-treated biochar has more P, which makes it a better BBF. It has been observed that biochar can increase soil microbial activity,[28] accelerating soil organic matter (SOM) decomposition, which reduces the C sequestration balance of biochar amendment to soil. However, by recovering carbon-rich suspended solids from the LAD with the biochar, this effect can be mitigated, further enhancing the benefits of LAD-treated biochar for use as a BBF to improve soil quality.[27,59]

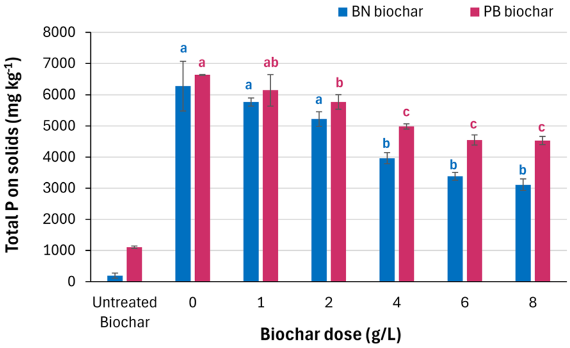

Fig. 2 Total P concentration on solids recovered through filtration after LAD was treated with increasing doses of BN or PB biochars. Different letters indicate significant differences between biochar doses within each biochar type ($p < 0.05$).

The 139 μm mesh used in the filtration system removed 15% of TSS when no biochar was added and 17% to 22% with the different BN biochar doses. In RBFs, not only is the pore size of the mesh important, but the formation of a cake on the mesh is also beneficial for achieving high removal efficiencies. For filter cake formation, particles larger than the pore size of the mesh accumulate on the filter forming a cake that can act to retain particles smaller than the mesh pore size, yet remains permeable to solutions.[31,32] In most of the biochar dosing experiments, the filtration rate slowed before a thicker cake could develop, indicating clogging of the filter mesh by small particles. Preliminary experiments were conducted under higher vacuum pressures to solve the clogging issue; however, the amount of solids retained on the mesh decreased proportionally as the applied vacuum pressure increased, which is not representative of the RBF filtration dynamics.

Rusten *et al.*[32] reported TSS removals of 25–60% during RBF treatment of municipal wastewater due to filter cake formation. In contrast, in the present study, substantially lower removal was observed for LAD using a finer 139 μm mesh (Fig. S3), indicating that most of the LAD particles are smaller than the effective pore size of the filter, and further, the filter cake is not optimized for enhanced filtration in the experimental system. The relatively low solids recovery from the LAD is attributed to its properties, the treatments applied, and the experimental system simulating the RBF system. Anaerobic digestion breaks down organic material into smaller particles,[31] and the LAD was centrifuged prior to collection, which removed larger fibers. Consequently, the centrifuged LAD contains a much higher proportion of fine particles than municipal wastewater, resulting in fewer suspended solids being removed by the RBF as compared to Rusten *et al.*[32]

The BN biochar was selected for experiments testing the effect of Fe dosing and pretreatments because it has a lower initial P concentration than the PB biochar. Additionally, the BN biochar had a larger particle size distribution, which results in less loss during filtration. Biochar dose results indicate that between 4 and 6 g $\mathrm{L^{-1}}$ the P recovery and the TSS removal reached a plateau. Therefore, 6 g $\mathrm{L^{-1}}$ was chosen as a representative, feasible dose for subsequent experiments involving Fe dosing and LAD pretreatment with either acid or ozone.

Effect of $FeCl_3$ dose on LAD filtration

Fig. 3 shows the total P removal from LAD for the 6 g $\mathrm{L^{-1}}$ biochar treatment with increasing Fe doses. At 2 mmol $\mathrm{L^{-1}}$ Fe, 60 mg $\mathrm{L^{-1}}$ (23%) of total P was removed, compared with 36 mg $\mathrm{L^{-1}}$ (14%) for biochar only treatment. At 3 and 6 mmol $\mathrm{L^{-1}}$ Fe addition, P removal was 27%, which was not significantly different from that at 2 mmol L^{-1} Fe. P removal at 15 mmol L^{-1} Fe treated sample was significantly higher than the lower doses, with 114 mg L^{-1} (43%) removed.

The TSS removal for these treatments (Fig. S4) increased from 20% at 2 mmol L^{-1} Fe addition to 26% at 15 mmol L^{-1} Fe. However, none of these treatments were significantly different from the biochar only treated sample. Fe solution is acidic, however, none of the Fe doses significantly changed the pH of the LAD from the original pH 8 (SI Table S7), and thus pH change was not a factor in the filtration efficiency.

Fig. 4 shows total P concentration on solids recovered from LAD with no pretreatment using 6 g L^{-1} of biochar with increasing Fe doses. As Fe dose increased from 2 to 15 mmol L^{-1}, the concentration of P on the recovered solids increased from 3256 to 5126 mg kg^{-1}.

Considering that the centrifuged supernatant LAD used in the current study has about 250 mg L^{-1} of total P but only 25 mg L^{-1} as soluble *ortho*-P, part of the recovered P must have come from the removal of suspended solids. Similar trends have been reported using flocculant in anaerobic wastewater systems, in which high doses of $FeCl_3$ (up to 28 mmol L^{-1}) were used to achieve nearly complete recovery of soluble *ortho*-P and a fraction of particulate P.[43] In this study, given the high suspended solids content of LAD, results suggest that P recovery is partly associated with suspended solids removal through flocculation.

LAD is a complex matrix, with high concentration of TSS, and Fe addition can promote both flocculation of the particulate material and formation of Fe–P phases. There are multiple P retention pathways that can concurrently occur in the iron and biochar treated LAD, including (i) particulate P physically retained with captured solids, (ii) Fe-associated P formed *via* precipitation or co-precipitation, and (iii) P adsorption on biochar surfaces. SEM images of solids recovered from 6 g L^{-1} biochar only and the 6 g L^{-1} of biochar combined with 15 mmol L^{-1} of Fe are shown in Fig. S8–S14, along with their respective EDS spectra. SEM-EDS shows the presence of LAD-solids coating the recovered biochar particles, and further indicates that P is primarily associated with these coatings. Comprehensive P speciation is beyond the scope of this process-optimization study and warrants future investigation.

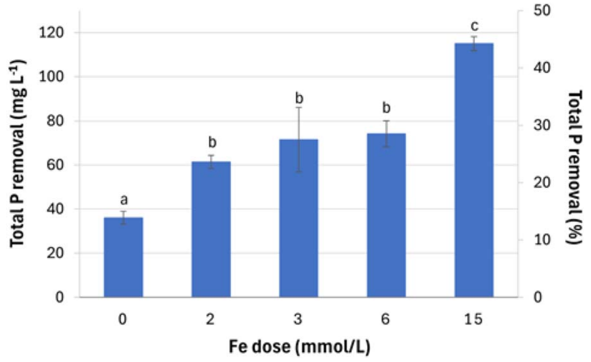

Fig. 3 Total P removal for the 6 g per L BN biochar treatment at different Fe doses. The initial total P concentration of LAD was 262 mg L^{-1}. Different letters indicate significant differences in P recovery between Fe doses ($p < 0.05$).

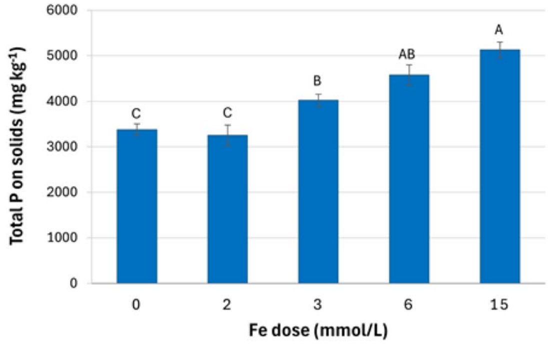

Fig. 4 Total P concentration on solids recovered from LAD with no pretreatment using 6 g L^{-1} of biochar at different Fe doses. Different letters indicate significant differences in P concentration between Fe doses ($p < 0.05$).

Effect of pretreatments on LAD filtration using $FeCl_3$

Fig. 5 shows the TSS removal for the different pretreatments with increasing Fe doses. ANOVA effect sizes ($\eta^2 > 0.14$; Table S6) for iron dose, pretreatment, and their interaction across all response variables revealed a strong interaction effect, indicating that iron dose effectiveness depends on pretreatment. Consequently, the effects of iron dose cannot be interpreted independently of pretreatment conditions. Acidification and ozonation pretreatments enhanced the TSS removal compared to the LAD with no pretreatment samples that had the same Fe dose (Fig. 5). Ozonation pretreatment and the addition of 2 or 3 mmol L^{-1} of Fe removed more TSS than acidification; TSS removal in the ozonated LAD with 2 mmol L^{-1} Fe increased to

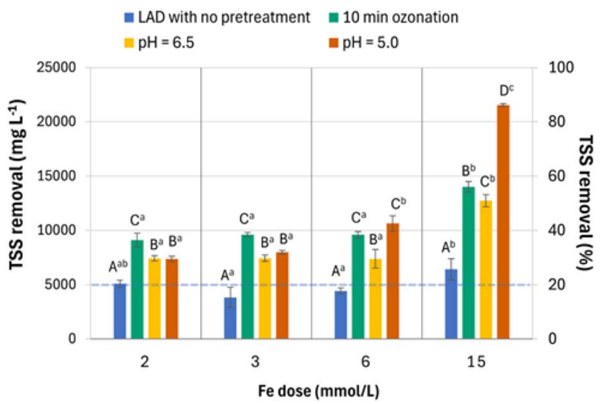

Fig. 5 TSS removal from LAD using either no pretreatment, 10 min of ozonation, acidification to pH 6.5, or acidification to pH 5.0. Pretreatments were applied before the addition of Fe and biochar. Initial TSS concentration was 25 750 mg L^{-1}. Dashed line indicates the TSS concentration for 6 g L^{-1} of biochar with no Fe addition. Different uppercase letters indicate significant differences between treatments within the same Fe dose ($p < 0.05$). Different superscript letters indicate significant differences between Fe doses within the same treatment ($p < 0.05$).

36%, whereas the TSS removal for the acidified samples was 29%. Increasing the Fe dose to 6 mmol L^{-1} of Fe did not significantly affect the TSS removal. The TSS removal at 6 mmol L^{-1} Fe with both the ozonation pretreatment and the pH 6.5 pretreatment was similar to the ozone treated samples with the lower doses of Fe. But the TSS removal in the pH 5 pretreatment at 6 mmol L^{-1} Fe was significantly higher than the same pretreatment at the lower Fe doses.

Iron addition at a rate of 15 mmol L^{-1} removed more of the suspended solids in all pretreatments than the samples treated with the lower Fe concentrations (Fig. 5). In the 15 mmol L^{-1} Fe-treated sample, the TSS removal in the ozone pretreated sample was 56% and in the pH 5 pretreated sample the TSS removal was 86% (4.4 times more suspended solids removal than the biochar only treated LAD).

The total P removal from the LAD after the different pretreatments is shown in Fig. 6 (total P concentration in the LAD for these treatments is shown in Fig. S5). As the Fe dose increased, the amount of P removal from the LAD also increased, especially in the 6 and 15 mmol L^{-1} Fe dose samples.

For Fe doses of 2 and 3 mmol L^{-1}, the different pretreatments showed distinct effects on P removal as compared to the biochar only LAD treatment (dashed line in Fig. 6). At 2 mmol L^{-1} Fe, ozonation was the only treatment that had a significant difference in LAD P recovery. At 3 mmol L^{-1} Fe, effluent P recoveries were not significantly different from the 2 mmol per L Fe treatment, regardless of the pretreatment. At 6 mmol L^{-1} of Fe, the P removal from the LAD increased significantly when the pH 6.5 and pH 5 pretreatments were used. At 15 mmol L^{-1} of Fe, all the pretreatments showed significant increases in effluent P removal as compared to the lower Fe doses; the order of total P removal at this Fe dose is LAD < ozonated < pH 6.5 < pH 5.

Compared with the non-pretreated samples, the addition of the Fe at the pH 6.5 and pH 5 pretreatments slightly decreases the suspension pH because the system is not buffered at these pHs (SI Table S7). At pH 5, dosing 15 mmol L^{-1} Fe resulted in a pronounced decrease in pH. An advantage of this is that the lower pH promotes flocculation;[60] however, the filtered water will require lime addition to increase the pH prior to release of the treated water back into surface waters.

The concentration of total P on the solids recovered from each treatment is shown in Fig. 7. For most of the treatments, the higher the dose of $FeCl_3$ resulted in greater concentration of P on the recovered solids, which agrees with the results obtained for P removal from the LAD (Fig. 6).

The treatment with the highest P concentration on solids was the ozonated sample with the addition of 15 mmol L^{-1} Fe, reaching 5338 mg kg^{-1} P, although it was not significantly different from the other treatments with the same Fe dose. At the lowest dose of Fe (2 mmol L^{-1}), ozonation had the highest P concentration on the solids, while the other treatments had equivalent P concentrations. For Fe doses of 3 and 6 mmol L^{-1}, ozonation and acidification to pH 6.5 had the highest P concentrations on the solids.

The pH 5 pretreatment with 15 mmol L^{-1} of Fe had significantly more total P removed from the LAD effluent than the other treatments (Fig. 6); however, the solid P concentration was not greater (Fig. 7). This discrepancy may be attributed to a dilution effect because the large amount of solids removed in the pH 5 treatment decreases the P concentration per unit mass of recovered solid. Similar results were reported by Yadav *et al.*,[29] where 95–98% total P recovery from swine manure at pH 4.5 using high $FeCl_3$ doses (~80 mmol L^{-1}) was achieved. P recovery in their experiments was primarily driven by flocculation and the removal of suspended solids and slightly enhanced by the addition of biochar.[30]

After ozone pretreatment, TSS removal increased significantly when Fe dose was increased from 6 mmol L^{-1} to 15 mmol L^{-1}, suggesting that at higher flocculant doses, the oxidation of LAD promoted more flocculation. At 15 mmol L^{-1} Fe dosing,

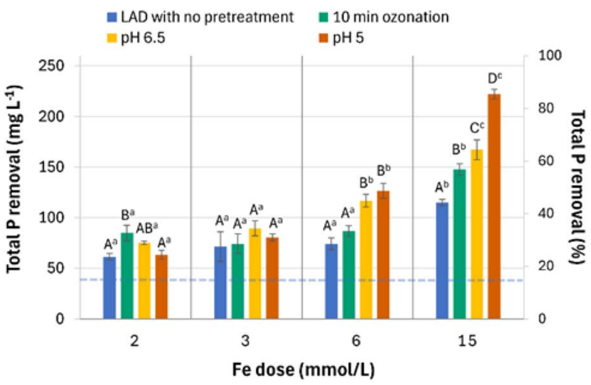

Fig. 6 Total-P removal from LAD using either no pretreatment, 10 min of ozonation, acidification to pH 6.5, or acidification to pH 5.0. Pretreatments were applied before the addition of Fe and biochar. Dashed line indicates the total P concentration on LAD when 6 g L^{-1} of biochar was used with no Fe addition. Different uppercase letters indicate significant differences between treatments within the same Fe dose ($p < 0.05$). Different superscript letters indicate significant differences between Fe doses within the same treatment ($p < 0.05$).

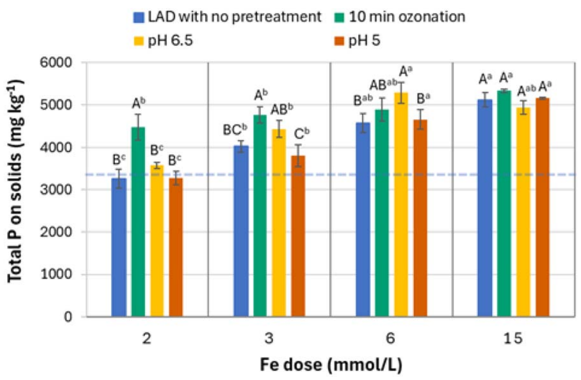

Fig. 7 Total P concentration on solids recovered from LAD with either no pretreatment, 10 min of ozonation, acidification to pH 6.5, or acidification to pH 5.0; pretreatments were applied before the addition of Fe and biochar. Dashed line indicates total P concentration for the 6 g L^{-1} of biochar with no Fe addition. Different uppercase letters indicate significant differences between treatments within the same Fe dose (Tukey, $p < 0.05$). Different superscript letters indicate significant differences between Fe doses within the same treatment ($p < 0.05$).

ozone pretreatment had higher total P removal (148 mg L^{-1}) than the LAD with no pretreatment (115 mg L^{-1}).

Ma *et al.*[44] used polyferric sulfate (PFS) as a flocculant to treat LAD from dairy wastewater and observed enhanced TSS removal, increasing from 40 to 60%, when $Ca(ClO)_2$ was applied as an oxidizing pretreatment.[44] This is similar to the results in this study that used ozone as an oxidant and 15 mmol L^{-1} Fe to promote flocculation.

High concentrations of suspended solids that bind PO_4^{3-} limit $FeCl_3$ phosphorus removal efficiency.[61] However, ozonation breaks molecular bonds, and can promote P release from the solids (SI Table S5), making it more available to react with the Fe from the Fe-based flocculants, and subsequently be removed from solution by either Fe–P mineral precipitation, adsorption on the iron oxide mineral surfaces, or as ternary complexes on Fe-biochar surfaces.[44] The QuickWash process also relies on acidification, which has been shown to promote the release of bound P from manure.[16] If poly-P and organic P are present and released as soluble *ortho*-P after acid or ozone pretreatment, the smaller ionic radius and higher negative charge per P atom make it more easily removed by the Fe flocculant, even in the presence of high concentrations of suspended solids.[43,62]

According to Liang *et al.*,[45] the pretreatment of sludge with $Ca(ClO)_2$ before $FeCl_3$ flocculation involves two steps. The $Ca(ClO)_2$ oxidation first breaks apart the sludge flocs and extracellular polymeric substances (EPS), allowing for the release of bound water. The subsequent addition of the ferric coagulant then re-flocculates the sludge into new, porous structures *via* electrostatic neutralization of the solid surfaces.[45] The flocculation process is most effective when the net surface charge of colloidal particles is close to zero, minimizing electrostatic repulsion and promoting aggregation.[63] Due to the high adsorption capacity of the suspended solids in the LAD, even the highest Fe dose tested was insufficient to balance the negatively charged colloids, resulting in low TSS removal. High salt concentrations interfere with the flocculation process by reducing the chemical activity of the flocculant, thereby diminishing their ability to adsorb and bridge particles.[49] At the natural pH of LAD (~8), particles are more negatively charged, and Fe is likely to precipitate, reducing charge-neutralization and bridging, and thus hindering flocculation.[63,64]

Even after pretreatments, the flocculation was most effective when high $FeCl_3$ doses were applied; the highest suspended solid removal occurred in the pH 5 pretreatment with 15 mmol L^{-1} Fe added. Sukenik *et al.*[49] observed that the greatest flocculation of microalgae grown in saline environments occurred at pH 5.[49] Lowering the pH reduces surface charge of the organic matter, allowing better Fe^{3+} neutralization efficiency of the particle charge, which promotes the formation of flocs that can be easily retained on the mesh.[41,63]

Studies have shown that ozonation degrades suspended particulate matter in wastewater, leading to declines in turbidity, chemical oxygen demand, and total organic carbon.[48,65,66] Dissolved ozone can reduce the flocculant dose requirements by changing the surface characteristics of suspended solids, thereby enabling formation of stable flocs.[49,67,68] Li *et al.*[68] showed that ozonation does not cause surface charge reduction of organic matter; in fact, it can slightly increase particle–particle repulsion. However, ozone can still destabilize the solution by oxidizing high-molecular-weight compounds into lower-molecular-weight molecules, increasing the concentration of oxygen-containing functional groups, and promoting the aggregation of small particles into larger ones.[67,68]

The ability of ozone oxidation to break down larger particles and aggregate smaller ones likely enhanced TSS removal in the ozonated samples in this study. At the lowest Fe doses used (2, 3, and 6 mmol L^{-1}), TSS removal was higher with ozonation than with the other treatments. In LAD, the Fe doses up to 15 mmol L^{-1} were insufficient to induce complete flocculation, yet ozonation still promoted greater TSS removal. Moreover, previous studies have reported that ozone pretreatment produces larger and denser flocs than those formed without ozonation, resulting in improved settling efficiency.[67,68] This could also have enhanced performance in the filtration system by facilitating filter cake formation.

Although flocculation after ozonation was not as effective at removing suspended solids and P as the pH 5 pretreatment and 15 mmol L^{-1} of Fe, the results indicate that the ozonation pretreatment causes the organic matter to be more susceptible to flocculation compared to LAD. Given that high doses of $FeCl_3$ are typically required for effective flocculation of suspended solids in wastewater,[41,43,61] optimization of the flocculant dosage is crucial.

Therefore, ozonation pretreatment can be considered an alternative or addition to acidification, as it improves the susceptibility of organic matter to flocculation. Minimizing acid addition and eliminating subsequent alkalinity adjustment simplifies operational processes, reduces addition of salts to the LAD, and reduces overall treatment costs by decreasing chemical consumption. An advantage of this with respect to nutrient recycling by producing a BBF is that the lower acid dose with ozone pretreatment can potentially reduce salt loading when the recovered solids are applied to soils.

P availability from LAD treated biochar

P availability from biochar can be estimated as the amount of solid P on the treated biochar that is extracted with 2% formic acid. This value is important to understand to accurately predict the value of the recovered P in the biochar as a BBF. The addition of Fe reduced P availability proportionally to the applied doses (Fig. 8), indicating that higher Fe concentrations reduce P availability (the Fe concentration on solids is shown in Fig. S6). In the LAD sample with 2 mmol L^{-1} of Fe added, 100% of the P was extracted with formic acid, whereas increasing the dose to 3 mmol L^{-1} reduced P availability to only 54% of the total P on the biochar.

The samples that were pretreated at pH 6.5 and 5 had the lowest P availability, indicating that the low pH favored the formation of less extractable P species. Even in the lowest Fe dosed sample that was pretreated to pH 6.5 the P availability was only 42% of the total P. For higher Fe doses, both low pH pretreatments had similar percent P availability, which was

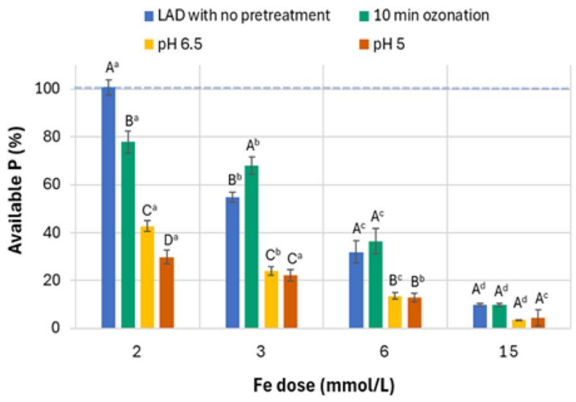

Fig. 8 Percentage of available P on recovered biochar extracted using formic acid after either no pretreatment, 10 min of ozonation, acidification to pH 6.5, or acidification to pH 5.0; pretreatments were applied before the addition of Fe and biochar. Dashed line indicates the percent of available P for 6 g L^{-1} of biochar added to LAD with no Fe addition. Different uppercase letters indicate significant differences between treatments within the same Fe dose (p < 0.05). Different superscript letters indicate significant differences between Fe doses within the same treatment (p < 0.05).

reduced to less than 25%, 15%, and 5% for the 3, 6, and 15 mmol L^{-1} Fe doses, respectively. At 15 mmol L^{-1} Fe dose, P availability decreased significantly across all treatments, reaching values below 10% and showing no significant differences among pretreatments.

In the ozonated samples, the P availability differed from that observed in the other pretreatments. At the 2 mmol L^{-1} Fe dose, P availability was lower than in the non-pretreated LAD, but higher than in the acidified samples. At 3 mmol L^{-1}, the ozonated samples had higher P availability than all other treatments. At 6 mmol L^{-1} Fe, P availability of the ozonated treatment was not significantly different from the non-pretreated LAD.

Previous studies have observed that Fe-modified biochar has less P availability compared to unmodified biochar.[30,31,69,70] Recent studies have observed that the nature of P retained on biochar strongly influences its potential availability when the biochar is recycled for soil amendment.[23,42] Strawn *et al.*[42] showed that biochar derived from coniferous biomass released more than 35% of its total P during continuous leaching with DI water, whereas in iron-modified biochar samples only 3% of the P was leached. These findings imply that while Fe-modified biochars have enhanced P sorption capacity, the strong Fe–P associations may limit P availability in soils. This behavior may be advantageous for a slow-release fertilizer.

The recovered solids in this study constitute a nutrient enriched biochar-solids composite, in which P is largely associated with retained LAD solids and/or Fe–P phases. The reduced extractable P suggests lower short-term P availability, supporting potential fertilizer value. However, further work is needed to quantify release kinetics under soil conditions. Such controlled release characteristics are important when considering biochar incorporated into agricultural soils where gradual P availability can support plant uptake while minimizing rapid leaching losses.[42]

Effect of $FeCl_3$ dose and pretreatment on N recovery from LAD

The total N concentration on the solids recovered from each treatment (Fig. 9) shows that biochar has a significant potential for recovering N from the LAD (the total N concentration removed from LAD for each treatment is shown in Fig. S7). Except for the pH 5 pretreatment, raising the Fe dose from 2 to 6 mmol L^{-1} had little effect on the total N concentration in the recovered solids, which remained approximately 19 500 mg kg^{-1} for LAD at the pH 6.5 treatment, and 21 500 mg kg^{-1} for the ozonated samples. However, the 15 mmol L^{-1} Fe dose ozonated pretreatment had an increase in total N of approximately 37% compared to the LAD-biochar with no Fe treatment, and the pH 6.5 pretreatment had 56% more total N. Pretreatment by acidification to a pH of 5 had consistently higher total N concentrations than the other pretreatments, and the N concentration significantly increased with Fe dose. Nitrogen recovery from the LAD at the lowest pH pretreatment increased from 26 000 to 35 333 mg kg^{-1} N on solids as the Fe dose increased from 2 to 15 mmol L^{-1} Fe, respectively. The 35 333 mg kg^{-1} N corresponds to approximately twice the total N concentration observed in LAD-biochar without Fe treatment. Previous studies have shown that Fe-modified biochar has increased N adsorption capacity as compared to unmodified biochar.[69–71]

Anaerobic digestion produces high concentrations of ammonium (NH_4^+) through the decomposition of nitrogen-rich substrates such as proteins, making ammonium and organic N the main forms of nitrogen found in LAD.[72–76] Increasing the iron solids in the suspension makes more adsorption sites for ammonium.[77] Although low pH can decrease NH_4^+ adsorption by Fe compounds,[77] in this study the low pH enhanced the flocculation and suspended solids removed from the LAD, which increased the removal of organic-bound N. Increased N

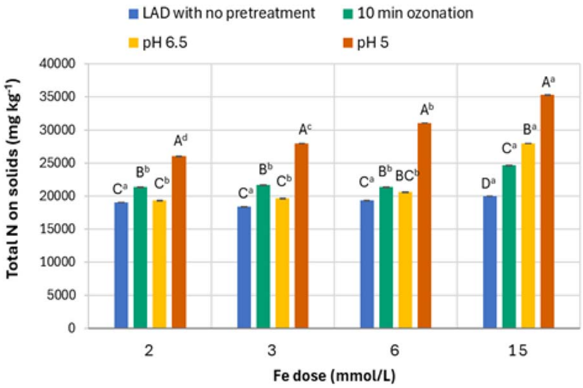

Fig. 9 Total N concentration on recovered biochar after either no pretreatment, 10 min of ozonation, or acidification to pH 6.5, and acidification to pH 5.0; pretreatments were applied before the addition of Fe and biochar. Dashed line indicates the N concentration on solids of 6 g L^{-1} of biochar added to LAD with no Fe addition. Different uppercase letters indicate significant differences between treatments within the same Fe dose (<0.05). Different superscript letters indicate significant differences between Fe doses within the same treatment (p < 0.05).

recovery on solids following acidification has also been reported in the Quick Wash process.[16] Low pH has also been shown to help reduce nitrogen losses by limiting ammonia volatilization during mixing.[70,78] Thus, the increased N recovery on the biochar filtrate can be attributed to reduced N stripping and increased removal of suspended organic matter at low pH.

Conclusions

This study demonstrated that using $FeCl_3$ and biochar to recover P from dairy LAD containing high concentrations of suspended solids requires high doses of the flocculant to be most effective. Pretreatments such as ozonation or acidification can decrease the amount of Fe flocculant required per mass of recovered P. Additionally, this study showed that high recovery of N is possible, greatly increasing the value of the recovered biochar as a BBF.

The use of a laboratory filtration system equipped with a filter mesh that is used in RBFs provides valuable insight into the feasibility of pilot-scale RBF trials applying biochar as a filter aid for LAD treatment. However, because LAD composition is highly variable and filtration performance depends strongly on the LAD properties, its variability needs to be considered in pretreatment and filtration performance. In this context, pilot-scale trials using an RBF system need to be done so that challenges and costs associated with scaling up the process can be investigated. As with any emerging treatment technology, a comprehensive techno-economic analysis is required to fully assess the feasibility and cost–benefit of large-scale implementation, and pilot-scale trials can provide more realistic operational data. The data from this study provides critical information needed to design a pilot scale process on difficult to filter LAD such as the centrifuged effluent for an anaerobic digestor.

To increase the amount of solids recovered onto biochar, future research should test the strategic placement of the filtration system before the centrifuge instead of post-centrifuge. This will likely enhance nutrient recovery and reduce the overall energy footprint of dairy manure-management systems by reducing energy consumption from the centrifuge.

The production of a BBF can play a significant role in promoting a circular economy for dairy farmers by generating a value-added product from waste streams. As increasingly stringent regulations are being applied to dairy farm effluents, costly treatment processes such as reverse osmosis and microfiltration are being considered. In this context, the development of technologies that can be implemented at significantly lower costs while also generating economic value from dairy-manure streams are highly desirable. Moreover, when applied as a pretreatment step, such technologies may reduce downstream membrane fouling and associated operational costs, particularly given the high suspended solids content of LAD.

Author contributions

Mariana C. Santoro: conceptualization, data curation, investigation, methodology, validation, writing. Daniel G. Strawn: conceptualization, funding acquisition, investigation, methodology, supervision, validation and writing. Gregory Möller: conceptualization, investigation, review and editing, and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study will be made available by the corresponding author upon reasonable request.

Supplementary information (SI) is available. See DOI: https://doi.org/10.1039/d6su00071a.

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