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Abstract

Wastewater, especially anaerobic treatment effluent, contains high ammonia nitrogen (NH_4-N) and inorganic orthophosphate (PO_4-P), which necessitate additional treatment to meet stringent discharge regulations. Ion exchange regeneration is a process that can be adopted for not only removing but also recovering nutrients. However, recovering nutrients by ion exchange from nutrient-rich effluents that also contain micropollutants (which typically pass through anaerobic treatment as well) may result in subsequent problems, since micropollutants could end up in ion exchange effluent, regenerant, or recovered fertilizer products. Micropollutant removal by a nonselective adsorbent, such as biosolids-derived biochar, before nutrient recovery processes would mitigate potential risks. The objective of this research was to evaluate the capability of biosolids-derived biochar as a pretreatment step for separating micropollutants from nutrient-rich water before ion exchange for nutrient recovery. In the presence of ammonium and phosphate, both pristine and regenerated biosolids-derived biochar could effectively adsorb triclosan (TCS) and estradiol (E2), and to a lesser extent, sulfamethoxazole (SMX) in batch sorption experiments. On the other hand, nutrient ions were not effectively adsorbed by biosolids-derived biochar. A continuous flow-through system consisting of columns in series filled with biochar, LayneRT, and then clinoptilolite was operated to test selective removal of micropollutants and nutrients in a flow-through system. The biochar column achieved more than 80% removal of influent TCS and E2, thereby reducing the chances of micropollutants being adsorbed by ion exchangers. Sulfamethoxazole removal through the biochar column was only 50%, indicating that biosolids-derived biochar would have to be optimized in the future for hydrophilic micropollutant removal. Influent nutrients were not effectively removed by the biochar column, but were captured in their respective selective ion exchanger columns. This research revealed that biosolids-derived biochar could be employed before ion exchange resins for removal of micropollutants from nutrient-rich water.

Introduction

Water resource recovery facilities (WRRFs) have advanced beyond a sole focus on treating wastewater, and now encompasses recovery of value-added products as well (Mo and Zhang, 2013). For instance, anaerobic treatment processes such as anaerobic membrane bioreactors have been investigated for their ability to treat wastewater (i.e., remove biochemical oxygen demand [BOD_5] and suspended solids), while producing energy in the form of biogas (McCarty et al., 2011; Seib et al., 2016) and reducing sludge production (Mota et al., 2013). However, the effluent from anaerobic treatment processes contains high ammonia nitrogen (NH_4-N) and inorganic orthophosphate (PO_4-P), which may necessitate additional treatment to meet stringent discharge regulations (Wisconsin DNR, 2016). The nutrient-rich effluent from anaerobic treatment is a potential resource from which to recover nitrogen and phosphorus for subsequent reuse. Nutrient recovery from wastewater could help close anthropogenic nutrient loops by supplementing supplies of phosphate mined from depleting natural reserves and nitrogen produced by the energy-intensive Haber-Bosch process (Mayer et al., 2016).

Ion exchange-precipitation is one technique that can be used to remove and concentrate nitrogen and phosphorus from wastewater and recover the nutrients in the form of solid fertilizer products, for example, struvite ($MgNH_4PO_4$). Clinoptilolite, which is a natural zeolite, can effectively exchange ammonium (Williams et al., 2015). LayneRT (Layne Christensen, The Woodlands, TX) is a commercial hybrid anion exchange resin that provides strong ligand adsorption of orthophosphate (the most common form of phosphorus in nutrient-rich anaerobic effluent (Seib et al., 2016)) through hydrated ferric oxide nanoparticles impregnated in a strong base anion exchange polymer (Sengupta and Pandit, 2011). Regeneration of these ion exchangers is conducted using highly concentrated brines, which results in desorption of ammonium and phosphate into a concentrated brine solution that can subsequently be used for precipitation of nutrient-rich solids suitable for reuse as fertilizer.

In addition to valuable nutrients, anaerobic effluent may also contain a mixture of potentially harmful micropollutants. For instance, the extent of removal of antimicrobials such as triclosan, antibiotics such as sulfamethoxazole, and estrogens is inconsistent through anaerobic treatments, but tends to be low (de Mes *et*

al., 2008; Hruska and Franek, 2012; Samaras *et al.*, 2013; Alvarino *et al.*, 2014; Monsalvo *et al.*, 2014; Malmborg and Magnér, 2015). Recovering nutrients through ion exchange from anaerobic effluents that also contain micropollutants may result in subsequent problems. For instance, a wide range of micropollutants adsorb to polymeric ion exchangers, including estrone, ibuprofen, and sulfadiazine (Neale *et al.*, 2010; Jiang *et al.*, 2015). The tendency of micropollutants to adsorb to ion exchangers may result in elevated concentrations of micropollutants in the regeneration brines (Neale *et al.*, 2010). For the last step of solid fertilizer recovery, that is, controlled struvite precipitation, studies have revealed that synthetic fragrances, 4-nonylphenols, and tetracyclines in the feed water were present in the precipitated struvite crystals (Başakçilardan-Kabakci *et al.*, 2007; Ronteltap *et al.*, 2007). Thus, strategies to mitigate the risks of micropollutants being present in the recovered nutrient products (and finished water) are needed.

Micropollutant removal before nutrient recovery processes would mitigate these risks. Biochar, which has been shown to remove triclosan, bisphenol A, atrazine, sulfamethoxazole, tetracycline, and phenanthrene by adsorption (Jung *et al.*, 2013; Shimabuku *et al.*, 2016; Thompson *et al.*, 2016; Feng and Zhu, 2017; Zhou *et al.*, 2017), could offer an effective means of adsorbing micropollutants to provide removal before ion exchange nutrient recovery. Among applicable feedstocks that can be pyrolyzed to produce biochar, wastewater biosolids can provide benefits for WRRF management (Hadi *et al.*, 2015). Specifically, municipal biosolids are centrally treated, which facilitates their use as a feedstock for biosolids-derived biochar production followed by on-site utilization as an adsorbent material at WRRFs.

In this study, the use of biosolids-derived biochar as an initial step for separating micropollutants from nutrients before ion exchange for nutrient recovery was evaluated. Two hydrophobic compounds, triclosan (TCS) and 17β-estradiol (E2), and one hydrophilic compound, sulfamethoxazole (SMX), were assessed. The phosphate and ammonium concentrations mimicked those typically observed in the effluent of anaerobic membrane bioreactors. As reported in several other proof-of-concept studies (Zhang and Zhou, 2005; Jung *et al.*, 2015), the synthetic water matrix used here was simplified by controlling environmentally relevant factors. Future work should investigate the role of other water matrix characteristics such as organic matter and other ions. The research objectives were to: (1) determine the impact of ammonium and phosphate on micropollutant adsorption on biochar in batch reactors, (2) explore the feasibility of reusing spent biosolids-derived biochar for multiple cycles of adsorption following pyrolysis activation, and (3) conduct a mass balance on micropollutants and nutrients through a biochar-ion exchanger flow-through column system. It was hypothesized that (1) biochar would more readily adsorb micropollutants than ionic nutrients, (2) the functionality of spent biochar as an adsorbent can be regenerated by pyrolysis, and 3) biochar can retain the majority of micropollutants without removing nutrients when used in a flow-through column system that employs biochar adsorption to remove micropollutants and ion exchange to recover nutrients.

Materials and Methods

Biochar preparation/reactivation and batch adsorption experiments

Biochar adsorption experiments were performed to determine the adsorption of micropollutants to biochar when both micropollutants and nutrients are initially present in solution. In addition, experiments were performed to determine the suitability of reusing spent biochar following activation by pyrolysis.

Biosolids-derived biochar was prepared using a similar method to Tong *et al.* (2016). Briefly, biosolids were placed in a flask, purged with Ar gas, and pyrolyzed at 600°C for 1 h. This is a typical pyrolysis temperature, and the biochar produced at this temperature provides sufficient adsorption capacity for removing micropollutants (Tong *et al.*, 2016). The resultant biochar was treated with 1 M HCl to reduce ash content. The biochar particle size ranged from 0.9 to 1.9 mm. Surface characterization of biosolids-derived biochar (from the same source) was presented by Tong *et al.* (2016) and Kimbell *et al.*(2017). To reactivate biochar after one cycle of sorption experiments, spent biochar (i.e., biochar used in a previous sorption experiment) was dried in a desiccator for 1

week and pyrolyzed at 600°C in a furnace for 60 min. The reactivated biochar was not acid treated to evaluate the feasibility of one-time acid treatment.

Batch adsorption tests were conducted at room temperature to determine the impact of nutrients on micropollutant adsorption to biochar. The batch adsorption tests were performed in 50 mL Milli-Q water with 40 mg-N/L as NH_4Cl and 5 mg-P/L as K_2HPO_4 to mimic plausible nutrient levels in mainstream anaerobic effluents (Williams *et al.*, 2015; Seib *et al.*, 2016). The micropollutants TCS (97%; Sigma Aldrich, St. Louis, MO), E2 (98%; Sigma Aldrich), and SMX (Sigma Aldrich) were predissolved in high performance liquid chromatography (HPLC)-grade methanol and stored at 4°C for use as stock solutions. The feed water was injected with the stock solution to yield ∼350 μg/L each of TCS, E2, and SMX in 50 mL feed water. The micropollutant concentrations for batch tests were higher than in actual anaerobic effluents (Alvarino *et al.*, 2014; Monsalvo *et al.*, 2014) so that micropollutant adsorption capacities could be determined by liquid chromatography–mass spectrometry (LC-MS; detection limits were in the 10 μg/L range). Control experiments in which only micropollutants were added to the feed water (no nutrient ions) were also performed. The pH of the feed water was adjusted to 7 with NaOH, and pH was measured again at the end of the adsorption experiments. Biochar was mixed with the solutions at a dosage of 0.4 g/L. The batch reactor was mixed on an end-over-end rotator at a speed of 60 rpm. Adsorption experiments lasted 4 days to ensure equilibrium was reached for both micropollutants and nutrients, as previously determined by Williams *et al.* (2015) and Tong *et al.* (2017). Surface characterization of biosolids-derived biochar (from the same source) was previously presented by Tong *et al.* (2016) and Kimbell *et al.* (2017). Liquid samples were collected before and after experiments to quantify micropollutants and nutrients, as described previously (Tong *et al.*, 2017). All batch adsorption experiments were conducted in triplicate.

Continuous flow-through column experiments

Column adsorption experiments were conducted to determine if micropollutants and nutrients could be selectively removed by employing biochar followed by ion exchangers under continuous flow-through conditions. The nutrient composition and pH were the same as in the batch tests. Influent concentrations of TCS, E2, and SMX were ∼300, ∼330, and 450 μg/L, respectively. All glassware was silanized using a 5% by volume dichlorodimethylsilane (99.5%; Sigma Aldrich) and 95% by volume heptane (99%; Sigma Aldrich) solution to prevent chemicals from adsorbing onto the glass surface.

Down-flow fixed-bed column experiments were conducted using three 60-cm long, 11-mm inner diameter glass columns (Ace Glass Incorporated, Vineland, NJ). One column each was packed with biochar, LayneRT resin (0.3–1.2 mm in diameter; Layne Christensen, The Woodlands, TX), and clinoptilolite (0.4–1.4 mm in diameter; St. Cloud Mining, Winston, NM), which provided particle diameter/column diameter ratios of 0.08–0.17, 0.03–0.10, and 0.04–0.13, respectively. Adsorption columns were operated at room temperature and fed by a peristaltic pump (Syringe Pump NE-9000G; New Era Pump Systems, Inc., Farmingdale, NY) programmed at a constant 10 mL/min volumetric flow rate.

The columns were packed with 12.7 cm adsorbents in depth, layered between two supporting layers of glass wool and glass beads. The empty bed contact time was 1.2 min, which was selected based on being able to detect micropollutant concentrations in the biochar column effluent under these conditions. As shown in Fig. 1, column configuration consisted of three adsorption columns operated in series with the first column packed with 6 g of biosolids-derived biochar adsorbent targeting removal of the target micropollutants (E2, TCS, and SMX). The effluent from the biochar column was collected in a glass beaker, which was used as the influent for the second column. The second column was packed with ∼6 g of LayneRT resin, an anionic resin, which was used to selectively remove phosphate from solution. The third column was packed with 6 g of clinoptilolite, a cationic ion exchanger, which was used to selectively remove ammonium from solution. Influent and effluent water samples were collected in glass amber vials and analyzed for micropollutants, phosphate, and ammonium. The pH in the influent and effluent of the entire column system was monitored. A single column test was performed as Kimbell *et al.* (2017) demonstrated minor variation in replicate column tests of biochar adsorption.
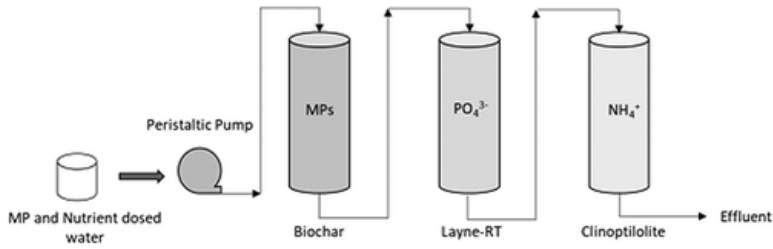
FIG. 1. Experimental setup for flow-through column removal studies. Columns were arranged to sequentially remove micropollutants (MPs, using biosolids-derived biochar), PO43− (using LayneRT ion exchange resin), and NH4+ (using clinoptilolite ion exchange media). Feed water was pumped in at 10 mL/min flow rate. Samples were taken at the influent and effluent points of each column.

Analytical methods

Micropollutants were quantified through online solid-phase extraction (SPE) with LC-MS. An online SPE cartridge (Phenomenex, Torrance, CA) was incorporated in the LC-MS system (LC-MS 2020; Shimadzu, Columbia, MD) to mitigate interference from the nutrients. All samples were filtered through 0.45 µm polytetrafluoro-ethylene (PTFE) filters. Prior to SPE, ^{13}C-TCS, estrone (E1), and ^{13}C-SMX were added as internal standards. Details of the analytical methods and quality control parameters such as method detection limit and recovery are provided by Tong *et al.* (2017). The standard phenate and ascorbic acid methods were employed to quantify NH_4-N and PO_4-P, respectively (APHA, AWWA, WEF, 1998). Each NH_4-N and PO_4-P sample was analyzed in triplicate, and the average was reported.

Data analysis

For batch experiments, the mass of nutrients or micropollutants adsorbed per mass of ion exchanger (Q_e), was calculated using Equation (1):

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \qquad (1)$$

where C_0 is the initial concentration of NH_4-N (mg/L), PO_4-P (mg/L), or micropollutant (µg/L); C_e is the concentration at equilibrium; V is the volume of feed water (L); and M is the mass of biosolids-derived biochar (g).

The molar ionic strength was calculated using Equation (2):

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \qquad (2)$$

where c_i is the molar concentration of ion i (mol/L) and z_i is the charge of the ion. The addition of NH_4 and PO_4 into water increased ionic strength.

For column tests, the total input mass of micropollutants or nutrients ($M_{influent}$) was calculated using Equation (3):

$$M_{influent} = C_{in} \times t_{op} \times Q \qquad (3)$$

where $C_{in, ave}$ (mg/L) is the average influent mass-based concentration of NH_4-N, PO_4-P or micropollutants; t_{op} is the total column operation time; and Q is the flow rate (mL/min). The total mass in each column's effluent was estimated using Equation (4):

$$M_{influent} = \sum_{n=1}^{12} Q \times \frac{C_{eff,n}}{2} \times (t_{n+1} - t_n) \qquad (4)$$

where n indicates the nth sampling point during operation (maximum of 12); C_{eff} is the effluent concentration of NH_4-N, PO_4-P, or micropollutants for each column; t is the time when the nth sample was taken; and Q is the flow rate. Total mass removed by each column was calculated as the difference between influent and effluent masses [Eqs. (3) and (4)]. The mass of compounds in the effluent from each column was considered to be the influent into the subsequent column, assuming no loss in tubing or columns, as demonstrated in previous column tests (Kimbell, 2017). The carbon usage rate (CUR) of biosolids-derived biochar was calculated by dividing the mass of micropollutants removed in the biochar column using Equation (3) minus Equation (4) divided by the total volume of solution passed through the column, as shown in Equation (5):

$$CUR = \frac{Equation\ (3) - Equation\ (4)}{Q \times t_{12}} \qquad (5)$$

Statistical analyses (t-test, α level = 5%) were conducted to test significance of differences using GraphPad Prism 6 (Graphpad Software, Inc., La Jolla, CA).

Results and Discussion

Biochar as an adsorbent for micropollutants in the presence of nutrients

In batch tests with water containing 40 mg/L NH_4-N and 5 mg/L PO_4-P, micropollutants were successfully adsorbed onto biochar (Fig. 2). Less SMX adsorbed in comparison to TCS and E2. The average mass adsorbed was ~330 ± 73 µg TCS/g biochar, 572 ± 20 µg E2/g biochar, and 145 ± 12 µg SMX/g biochar. The extent of removal for TCS, E2, and SMX was 38% ± 7%, 65% ± 2%, and 17% ± 2%, respectively. For feed water containing micropollutants without nutrients, the average mass adsorbed for TCS, E2, and SMX was 215 ± 42, 233 ± 11, and 64 ± 34 µg/g biochar, respectively, corresponding to 25% ± 5% TCS, 27% ± 1% E2, and 7% ± 4% SMX removal (Supplementary Table S1).
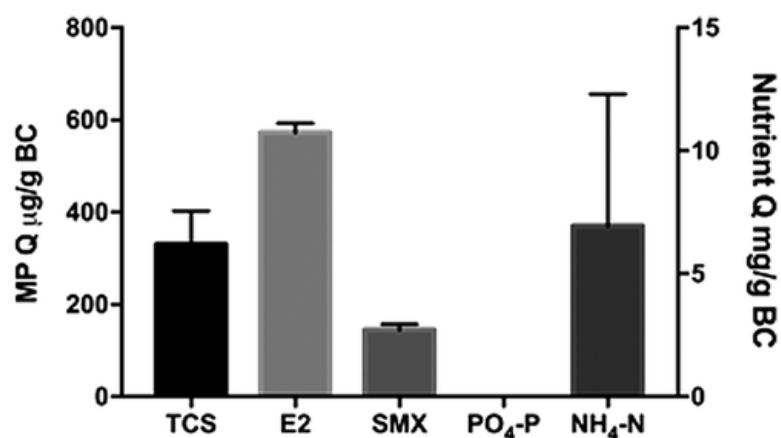

FIG. 2. Micropollutant (MP) mass adsorption per gram of biochar (BC) (primary y-axis) and nutrient mass adsorption per gram of BC (secondary y-axis). The biochar concentration was 0.4 g/L. The bars represent average results and error bars show ±1 standard deviation of triplicate experiments.

The pH of the water after adsorption dropped from 7 to 5. In accordance with their pKa values, TCS (pKa = 7.9) and E2 (pKa = 10.8) are neutral molecules at this pH range. On the other hand, SMX (pKa = 5.7) likely changed

from predominantly anionic to predominantly neutral, but is hydrophobic even in the neutral form (Tong *et al.*, 2017), which explained its low removal across the testing period. Biosolids-derived biochar, as characterized in a past study (Tong *et al.*, 2016), has a negative surface charge in neutral pH water. Repulsion between the biochar's negative surface charge and anionic SMX could lead to lower SMX uptake compared to the neutral TCS and E2 molecules. Removal of the neutral molecules may be attributed to hydrophobic interactions and intermolecular forces between compounds and biochar functional groups (Moreno-Castilla, 2004; Ni *et al.*, 2011; Lattao *et al.*, 2014; Leng *et al.*, 2015; Tong *et al.*, 2016). The adsorption capacity of biochar varies with feedstock. For example, Jung *et al.* (2013) demonstrated SMX adsorption on pine chip biochar at mg/g biochar levels. However, experimental conditions such as contaminant and biochar concentrations are also critical factors affecting adsorption capacity. In future research, it is important to study the impact of feedstock and pyrolysis under the same experimental conditions.

Interestingly, adding nutrient ions to the feed water increased micropollutant uptake by 100–250 μg/g biochar, perhaps due to increasing ionic strength (~0.0033 M ionic strength increase in this study). Previous studies revealed comparable relationships between ionic strength and adsorption of organic micropollutants to carbonaceous adsorbents (Fontecha-Cámara *et al.*, 2007; Kim *et al.*, 2016). For example, Fontecha-Cámara *et al.* (2007) tested diuron adsorption in 0.01 and 0.3 M KCl. The increase in ionic strength was ~0.3 M and the increase in diuron adsorption was ~100 mg/g. These results were attributed to compression of electrical double layers by adding salt, that is, ammonium and phosphate salts. The thickness of the double layers surrounding both biochar and micropollutants was compressed by an increase in the ionic strength of the solution (Rashid *et al.*, 1972; Kim *et al.*, 2016). This allows micropollutants to more easily diffuse toward the biochar surface.

The acid-treated biosolids-derived biochar did not efficiently adsorb phosphate or ammonium ions (Fig. 2), with no detected removal of P and <7% for N, which accounted for 0.5 mmol-N removed per gram of biochar. The surface of this biochar is negatively charged; therefore, phosphate ions are likely repulsed. Generally, phosphate adsorption capacities for biochar derived from different feedstocks are low (Hale *et al.*, 2013; Takaya *et al.*, 2016). Certain feedstocks that are modified with, or are intrinsically rich in, cationic metals such as magnesium can achieve phosphate adsorption due to ligand binding that overcomes biochar's negative charge (Yao *et al.*, 2011; Fang *et al.*, 2014). The negligible phosphate adsorption observed in this study could be due to lack of this binding mechanism. The biochar in this batch test provided limited adsorption of ammonium compared to the large amount of ammonium used in this study.

Unlike phosphate ions that need metals to form ligand bonds, SMX has an aromatic moiety in its molecular structure and is able to participate in π-stacking on the biochar surface even though SMX was primarily in anionic form under these experimental conditions (Tong *et al.*, 2017). However, the repulsive effect of the biochar's surface charge likely interferes with the approach of SMX ions, resulting in relatively low adsorption of SMX.

Impact of biochar regeneration with pyrolysis

Previous studies revealed that pyrolysis removes micropollutants from the influent biosolids, leaving a biochar product with substantially less micropollutants (Hoffman *et al.*, 2016; Ross *et al.*, 2016). In this study, spent biosolids-derived biochar from the batch adsorption test was regenerated in a furnace at 600°C to determine if adsorption capacity could be restored after pyrolysis. After each of two sequential regeneration cycles, the regenerated biochar was still capable of adsorbing micropollutants (Fig. 3). The first regeneration cycle (denoted as "1-biochar") increased biochar's adsorption capacity for TCS (*t*-test, $p = 0.04$), but there was no significant change in TCS adsorption capacities using biochar after the second regeneration (denoted as "2-biochar," Supplementary Table S2). For E2, the adsorption capacity of the pristine biochar (denoted as "0-biochar") and 2-biochar was essentially the same, whereas the 1-biochar was significantly higher. Biochar provided lower adsorption of SMX compared to the other two micropollutants. Regenerated biochar adsorption capacities were lower than 0-biochar, with no significant decrease in SMX adsorption capacity after multiple

regeneration cycles. The results imply that regeneration of spent biochar can have different extents of impact on adsorbing micropollutants for multiple cycles. In practice, pyrolysis reactors at WRRFs would be fed a blend of pristine biosolids and spent biochar to produce useable biochar adsorbents, while simultaneously removing micropollutants adsorbed in previous adsorption cycles.
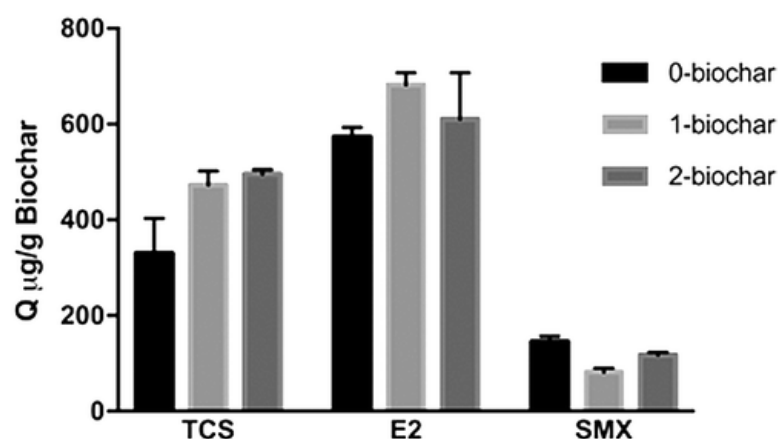

FIG. 3. Micropollutant mass adsorption per gram of biochar over multiple regeneration cycles. Pristine biochar is denoted as 0-biochar, 1-biochar refers to a single regeneration cycle, and 2-biochar refers to two cycles. The bars represent average results and error bars show ±1 standard deviation of triplicate batch experiments.

Similar to pristine biochar, regenerated biochar did not effectively adsorb nutrient ions (Supplementary Fig. S1 and Supplementary Table S3). However, the phosphate in water increased 4% after application of pristine biochar ($p = 0.004$). Due to increasingly strict phosphorous discharge regulations, caution must be employed when using biosolids-derived biochar to ensure additional phosphorous is not released in the treated effluent. Therefore, having a nutrient removal process downstream of biochar treatment could also be necessary to eliminate the phosphate leaching problem. There was no significant change in the ammonium concentration in water.

Collectively, the batch studies indicated that biosolids-derived biochar could be a reusable adsorbent for selective removal of micropollutants, while leaving nutrients in water for subsequent recovery. Unit operations consisting of columns packed with biochar followed by columns packed with nutrient-selective ion exchangers, and finally struvite precipitation could be used to recover nitrogen and phosphorus, while eliminating potential risks caused by micropollutants in the water or struvite.

Continuous flow columns: Biochar and ion exchangers in series for sequential micropollutant and nutrient removal

Based on biosolids-derived biochar's higher micropollutant adsorption efficiency (17%–65%) and lower co-adsorption of phosphate and ammonium (no P and <7% N adsorption) (Fig. 2), the biosolids-derived biochar column was operated ahead of the LayneRT and clinoptilolite columns (Fig. 1). Thus, the biosolids-derived biochar column acted as a prepolishing step to remove micropollutants ahead of nutrient ion exchange. The columns were denoted as the BC-column (biochar), L-column (LayneRT), and C-column (clinoptilolite).

The TCS concentration in the BC-column effluent started at 20% of the influent concentration and gradually increased to ~30% after 200 bed volumes (Fig. 4). For the L-column effluent, TCS was less than 20% of the treatment train's influent. Approximately 20% of the system-influent TCS remained in the C-column effluent. The E2 concentration in the BC-column effluent was 10% of influent within the first 100 bed volumes treated and then increased to 20% of the influent after 100 bed volumes. In the L-column and C-column effluents, E2 concentrations were ~10% of the system's influent. SMX in the BC-column effluent rapidly increased and

remained above 60% of influent. The SMX concentration in the L-column and C-column effluents increased to 40–50% of the influent after 200 bed volumes. Overall, removal of SMX was much poorer than TCS and E2, which may be due to the hydrophilicity of SMX. At pH 7, the distribution ratio of ionic compounds, $logD_{ow}$, for TCS, E2 and SMX is 4.70, 3.94, and −0.43, respectively (Tong *et al.*, [2017]). With higher $logD_{ow}$ values, hydrophobic TCS and E2 are more easily adsorbed to solid biochar. The low $logD_{ow}$ value of SMX is indicative of the compound's tendency to remain in water.
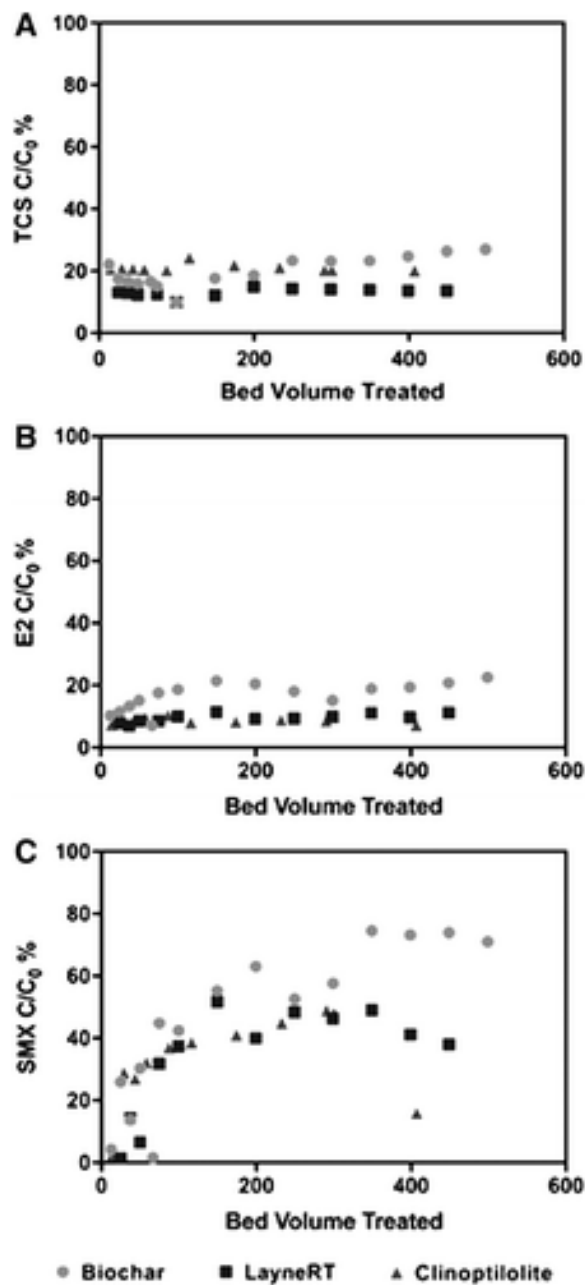

FIG. 4. (A) TCS, (B) E2, and (C) SMX effluent concentrations relative to influent concentrations (C/C0) for each column(biochar [BC-column], LayneRT [L-column], and clinoptilolite [C-column]) as a function of the number of bed volumes treated.

The column system removed 90% of total influent TCS and E2 and 70% of total influent SMX ([Fig. 5]). The majority of TCS and E2 was removed by the BC-column. Of the three columns, SMX removal was also greatest in the BC-column. The biochar's CUR for TCS, E2, and SMX was 236, 275, and 127 µg/L, respectively, the relative

order of which is the same as that observed for biochar adsorption capacities in batch tests. The L-column retained 9% of influent TCS, 6% of E2, and 20% of SMX, indicating that LayneRT was able to adsorb substantial amounts of micropollutants. This supports the need for a prepolishing step to prevent micropollutants from flowing into the ion exchange process. Clinoptilolite did not remove TCS or E2, but removed 2% of influent SMX.
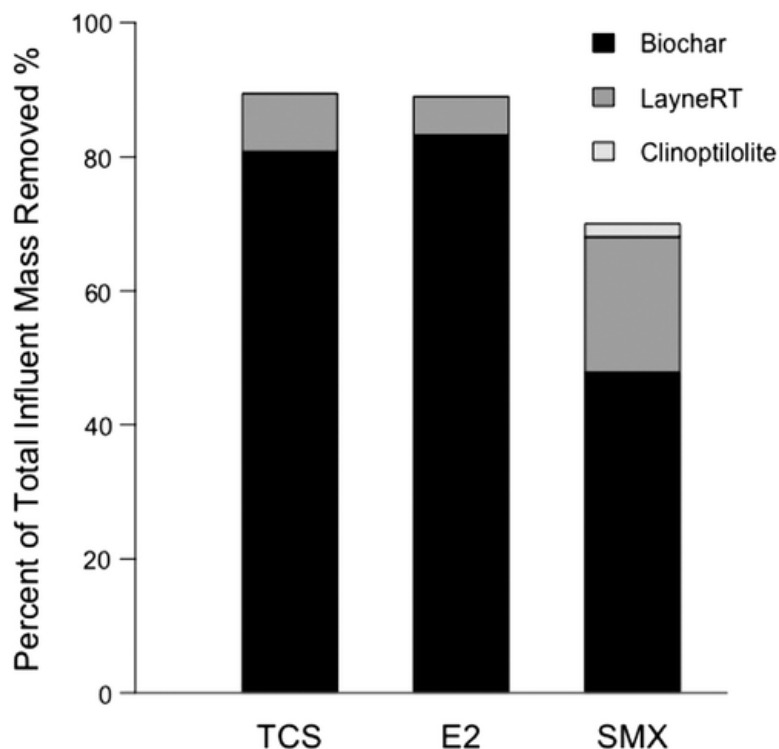

FIG. 5. Percent of total influent TCS, E2, and SMX mass removed by each media (biochar, LayneRT, and clinoptilolite) in the sequential flow-through system in single-column run.

Use of biochar in the sequential column operation enabled removal of the majority of TCS, E2, and SMX before the nutrient exchange columns. However, since removal of the more hydrophilic SMX was relatively low, improving removal of hydrophilic compounds such as SMX by improving the BC-column performance would be an important future step.

The phosphate concentration increased from an average of 4.85 mg PO_4-P/L to 5.22 mg PO_4-P/L across the BC-column (Fig. 6), signifying that the biochar released phosphate. With increasingly lower phosphorous discharge regulations in wastewater, leaching phosphorus from the adsorption media could be a limitation of employing biosolids-derived biochar. However, as shown in this study, situating an ion exchange column after the biochar can mitigate the phosphorous leaching from biochar column, because almost no phosphorus left the ion exchange columns (Fig. 7). The C-column had the exact same PO_4-P concentration profile as the L-column because it provided negligible PO_4-P removal. The system successfully removed 89.5% of influent PO_4-P (Fig. 7), all of which was attributed to the L-column.
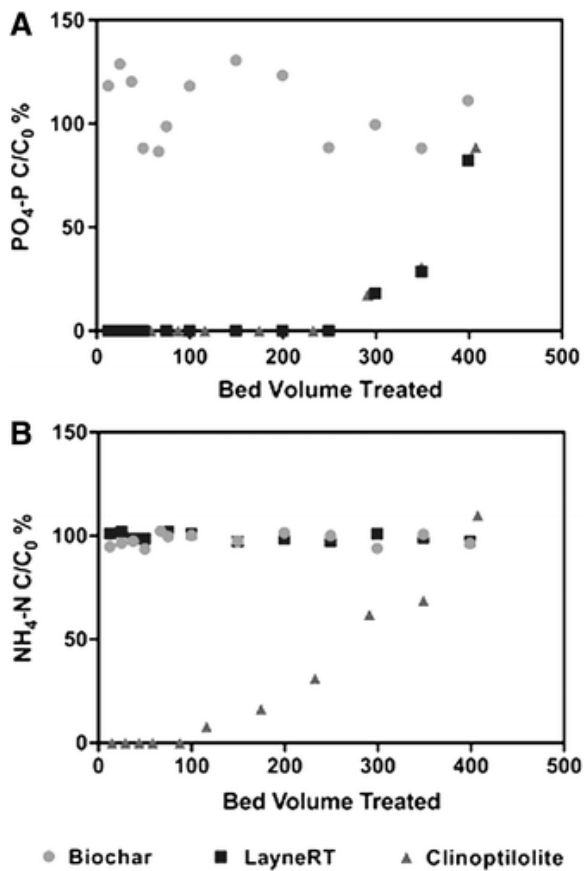
FIG. 6. (A) PO4-P and (B) NH4-N effluent concentration relative to influent concentration (C/C0) for each media (biochar, LayneRT, and clinoptilolite) as a function of the number of bed volumes treated in single-column run.
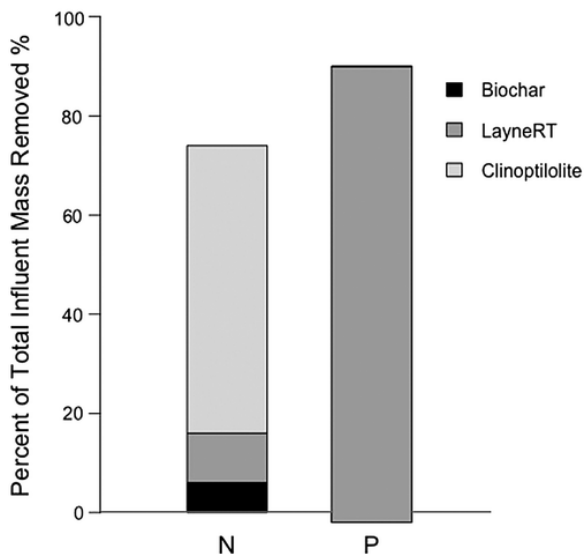

FIG. 7. Percent of total influent mass of N and P removed by each media (biochar, LayneRT, and clinoptilolite) from the sequential flow-through system in a single-column run.

As shown in Fig. 6, ~8% of input NH_4-N was removed in the BC-column, and 10% was removed in the L-column, but the majority passed through the BC- and L-columns and was mainly removed in the C-column. The C-column

achieved an average of 60% of the total influent NH4-N in the effluent ([Fig. 7](#)), and was exhausted after 400 bed volumes.

Conclusions

Biosolids-derived biochar effectively adsorbed TCS and E2, and to a lesser extent, SMX. The presence of nutrient ions in the water significantly increased micropollutant adsorption. Micropollutants adsorbed more readily to biosolids-derived biochar in comparison to nutrient adsorption on the biochar. Therefore, under the conditions studied, biosolids-derived biochar has the potential to selectively remove micropollutants from water containing nutrients, while leaving the nutrients in the water for subsequent recovery of micropollutant-free nutrient-rich fertilizer products through ion exchange followed by precipitation.

Following adsorption, spent biochar was repyrolyzed to remove micropollutants. The regenerated biochar was reused for two additional cycles, and the adsorption capacities of TCS, E2, and SMX changed to different extents. WRRFs that are equipped with pyrolysis reactors could potentially repyrolyze the biochar to remove micropollutants (Ross *et al.*, [2016](#)) and then reuse the adsorbent biochar without needing an additional acid wash. To further establish feasibility of biochar regeneration, a greater number of regeneration cycles performed using a pilot-scale pyrolyzer would be of value for future research.

The sequential flow-through column system achieved 90% removal of influent TCS and E2, in addition to 70% removal of SMX. The biochar column removed the majority of micropollutants, thereby reducing the chances of micropollutants being adsorbed by ion exchangers. The other benefit of operating the biochar column before ion exchange was that influent nutrients were not efficiently retained by the biochar column, which left a considerable amount of ammonium and phosphate for subsequent recovery. Notably, unlike other types of biochar, such as those derived from cacao shell and corn cob (Hale *et al.*, [2013](#)), which demonstrated phosphate adsorption, the biosolids-derived biochar in this study leached phosphate, which would be a major problem as WRRFs aggressively work to reduce effluent P concentrations. Placing ion exchange columns after biochar mitigates the concern of biochar leaching P. By leveraging micropollutant removal in the biochar column, nutrients can be concentrated in the subsequent ion exchange regenerant for precipitation of recovered struvite with less chance of inclusion of micropollutants in the fertilizer product. Since the biochar is from sewage sludge, the release of dissolved components such as heavy metal ions is important to address in subsequent research to better understand impacts on the removal of pharmaceuticals and the sequential ion exchange step, as well as feasibility of implementation. Given the simplified water matrix used in this research, future research utilizing more complex water matrices, for example, anaerobic treatment nutrient-rich effluent, is needed.

Author Disclosure Statement

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