Process intensification and emerging contaminant management in wastewater treatment using reactive migrating carriers

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Abstract

Results of an innovative use of GAC for process intensification carbon efficient nutrient and micropollutant removal are presented. GAC is used as a reactive migrating carrier enabling SRT uncoupling and GAC bioregeneration furthering the use of migrating carriers for process intensification in existing wastewater treatment plants. Two model micropollutants were used, short and long-chain per- and polyfluoroalkyl substances (PFAS), and one synthetic estrogen, 17α-ethynylestradiol (EE2). Two sequencing batch reactors were operated in classical A2O mode, with one serving as a control (RC) and the other was supplemented with granular activated carbon, and was designated as reactive migrating carrier reactor (RAC). The nutrient removal efficacy in both RAC and RC was similar, with average ammonium nitrogen (NH_4^+-N) at 95.2 ± 4.8%, total inorganic nitrogen (TIN) at 76.4 ± 17.6%, phosphate (PO_4^{3-}-P) at 89.7 ± 10.3%, and soluble chemical oxygen demand (sCOD) at 97.1 ± 1.4% achieved in both reactors. However, the removal efficiencies of long hanin PFAS compounds and the estrogen in the RAC was mush higher than in the RC reactor in which case, both physical sorption to biomass and potential biodegadation contributed to the fate of these micropollutants. The average EE2 removal efficiencies were 72 ± 9% in RAC, attributed to high localized EE2 concentrations, and 35.2 ± 13.9% in RC. A physical selective pressure of passing the waste sludge through a 500 micron sieve promoted significant

granulation in both reactors, where the extent of granulation in the RAC reactor was higher than in the RC reactor.

Keywords

Reactive Migrating Carriers, GAC, Process Intensification, PFAS, EE2, Biofilm, Sludge Densification, Nutrient Removal, Granulation

Introduction

Much of the infrastructure associated with WWTPs was built between the 1940s and 1970s. Most Wastewater Treatment Plants (WWTPs) in the U.S. need significant upgrades in terms of the treatment of wastewater to accommodate population growth (e.g., increased flows), industrialization, and more stringent effluent regulations for nitrogen management. There is an increase in concern for managing micropollutants, especially for treatment plants discharging into sensitive waterbodies. Expanding existing WWTPs through new construction is often not feasible due to space and budget limitations related to high infrastructure costs. Additionally, more and more wastewater utilities, including those located in coastal areas (such as California, Florida, Washington, Oregon, and more), need to either add total inorganic nitrogen removal (TIN) in the treatment train or increase the removal efficiency of existing configurations. Hence, there is an urgent need to increase the capacity of existing WWTPs and achieve process intensification through densification and efficient nitrogen management. Process intensification defines the scenario where a higher contaminant removal rate is achieved in a given configuration/volume. In addition to these pressing needs, new pollutants such as per- and polyfluorinated compounds (PFAS) have necessitated innovative treatment schemes.

Migrating carrier technology is a cost-effective option to achieve process intensification by uncoupling the SRT of an existing plant enabling slow growing carbon efficient nitrogen cycle organism such as AOB, NOB, Comammox and denitrifying PAOs in a carrier biofilm with a long SRT, while fast growing CBOD removal heterotrophs thrive in a floc at low SRT. We further propose the use of granular activated carbon (GAC) as migrating reactive carriers to accomplish densification-intensification and enhancement of trace organic removal . The reactive absorptive media, granular activated carbon, add to the removal mechanisms and is less expensive and environmentally friendly compared to the use of plastic carriers. The use of absorptive migrating carriers allowed for the sorption of micropollutants to increase their localized concentrations enabling long contact times between the organisms and micropollutants for enzyme induction. Some known mechanisms as bioregeneration of the sorption potential of GAC is also expected to take place.

The objective of this research was to demonstrate the use of granular activated carbon as migrating reactive technology for process densification and micropollutant management. Because the specific growth rate (μ) is inversely proportional to SRT ($\mu = \frac{1}{SRT}$), reducing SRT will require high μ, which will be conducive for fast-growing heterotrophs but could washout slow-growing organisms such as autotrophic ammonia and nitrite oxidizers. Hence, reactive migrating carriers will provide a place for slow growers to reside and form a biofilm, in which case the SRT control in the bioreactor will primarily be based on suspended biomass consisting mainly of fast-growing heterotrophs. Emerging pollutants such as PFAS and estrogens are present in municipal wastewater at concentrations smaller than their Ks values, making it difficult for organisms to access and degrade these. The reactive/sorptive migrating carriers, in addition to providing space for slow-growing organisms, will enable higher localized concentrations of emerging micropollutants greater than their Ks values and enhance their potential biodegradation.

Materials and Methodology

Perfluorinated analytical standards (>98% purity) and isotopically labeled standards (>99% purity), including both short- and long-chain perfluoroalkyl carboxylic and sulfonic acids, were obtained from Wellington Laboratories LLC (Overland Park, KS, USA). EE2 was sourced from Steraloids, USA. LC-MS grade solvents and reagents—such as acetonitrile, methanol, water, ammonium acetate, and ammonium hydroxide—were purchased from Fisher Scientific (Pittsburgh, PA, USA). Virgin coconut shell-based granular activated carbon (GAC, GC 20X50S) was supplied by General Carbon Corp. (NJ, USA); all other chemicals and sampling tubes were also obtained from Fisher Scientific (Pittsburgh, PA, USA).

Two identical lab-scale plexiglass SBRs (2H/D ratio, 3L working volume) were operated at room temperature (22±1°C) in Dr. Goel's lab. 2 g/L of GAC was added in RAC. Both RAC and RC were operated in an anaerobic-anoxic-oxic (A^2O) process. Each cycle was comprised of 6 h, involving

9 min of anaerobic synthetic wastewater feeding, 51 min of anaerobic, 50 min of anoxic (by dosing nitrate (7-8 mg/L) to mimic the internal recycling), 229 min of aerobic, 20 min of settling, and 1 min of effluent discharge. The DO levels were maintained in the 0.4 to 0.6 mg/L range in the oxic phase to achieve simultaneous nitrification and denitrification (SND) with P removal using DO sensors. The targeted feed concentrations of EE2 and each PFAS were 5 µg/L and 50 ng/L, respectively. The hydraulic retention time (HRT) was 10 h, and the solids retention time (SRT) was maintained at 10 d by wasting sludge through a 500 µm sieve. The sieve pass through biomass was wasted, while the biomass retained in the sieve was returned to the bioreactor, achieving SRT uncoupling. The overhead mixer speed was set at 60 rpm in both reactors to ensure proper biomass suspension and mixing of the feed. Dissolved oxygen (DO) levels were maintained between 0.4 and 0.6 mg/L using a DO sensor and transmitter (Mettler-Toledo, USA). At the start of each anoxic phase, 7 mg/L of NO_3^--N was added to simulate internal recycling. The synthetic influent was spiked with emerging contaminants of concern (ECEs), including EE2, two long-chain PFAS (PFOA and PFOS), and two short-chain PFAS (PFBA and PFBS).

The synthetic feed medium per liter contained: 311 mg ammonium acetate, 57.6 mg peptone, 19.2 mg beef extract, 38.4 mg glucose, 74.9 mg cellulose, 83.3 mg sodium carbonate, 76.5 mg magnesium chloride, 32±3 mg ammonium nitrogen, 7.5±0.5 mg phosphate phosphorus, 25.5 mg calcium chloride, 0.5 mg EDTA, and 0.4 mL of a trace element solution (Goel and Noguera, 2006). EE2 and PFAS were dosed into the synthetic influent from concentrated stock solutions to achieve target concentrations of 5.3 ± 0.8 µg/L EE2 (up to day 230), and increased to 10.1 ± 0.3 µg/L EE2 (after day 230), and 51.2 ± 4.3 ng/L of each PFAS compound.

Influent and effluent samples were periodically collected in 15 mL and 50 mL polypropylene (PP) centrifuge tubes following EPA Draft Method 1633 (US EPA, 2024). Nutrient and carbon samples were filtered through 0.22 µm syringe filters, while EE2 and PFAS samples were processed via solid phase extraction (SPE) without filtration. EE2 was extracted using Oasis HLB SPE cartridges (60 mg, Waters Corp., USA), conditioned with methanol and Milli-Q water. Samples were passed at 2–3 mL/min, followed by cartridge drying and elution with 2.5 mL methanol. Eluates were dried at 22 ± 1°C, reconstituted with 500 µL each of 2 mM NH_4F in water and methanol, and transferred to 1.5 mL amber vials for LC-MS analysis. Liquid PFAS samples were vortexed, spiked with 50 µL extracted internal standard (EIS), and processed using Oasis WAX cartridges (Waters Corp., USA). Cartridges were conditioned with 0.1% NH_4OH, and samples were loaded and rinsed with Milli-Q water. Elution was done with 6 mL of 6% NH_4OH in acetonitrile. Eluates were dried under N_2 at 35°C, reconstituted with 50 µL non-extracted internal standard (NIS), 200 µL of 16 mM ammonium acetate in methanol, and 250 µL water, then transferred to 0.7 mL PP vials for LC-MS. Milli-Q blanks were included in each extraction batch to check for contamination.

Results and Discussion

The average influent concentrations were 33 ± 3 mg/L for NH_4^+-N, 7.9 ± 1 mg/L for PO_4^{3-}-P, 33 ± 3 mg/L for TIN, and 350 ± 16 mg/L for sCOD. Based on these values, the corresponding average loading rates were 77.69 ± 5.74 mg/L·d (NH_4^+-N), 19.02 ± 1.95 mg/L·d (PO_4^{3-}-P), 78.51 ± 5.67 mg/L·d (TIN), and 836.69 ± 35.09 mg/L·d (sCOD). A typical complete cycle analysis representative of steady state reactor performance for nutrients and COD for both reactors is shown in Figure 1. Both reactors performed nearly identically in terms of nutrient and sCOD removals. Although complete nitrate removal was observed in both RAC and RC during the pre-anoxic phase (see complete cycle analysis; figure 1), the average effluent NO_3^--N concentrations in RAC and RC were 4.67 ± 4.44 and 4.52 ± 4.31 mg/L, respectively, due to the nitrification in the aerobic zone. Both reactors consistently delivered high removal efficiencies, with average effluent concentrations of 4.5 ± 4.5 mg/L (NH_4^+-N), 0.8 ± 0.8 mg/L (PO_4^{3-}-P), 7.9 ± 5.9 mg/L (TIN), and 9 ± 6 mg/L (sCOD). These results align with previous findings, which also reported no significant performance improvement with the addition of GAC media (Tao et al., 2017). PO_4^{3-}-P was significantly released within the first 25 minutes of the anaerobic phase at the expense of the readily biodegradable organic carbon from acetate, accounting for nearly 75 % of sCOD reduction from the synthetic feed. A significant P-uptake during the anoxic phase, potentially by denitrifying PAOs (DPAOs) was observed in both reactors. Overall, greater than 90 % TIN removal in both SBRs was consistently recorded and the dissolved ortho-P in the final effluent of both SBRS was always <0.1 mgP/L

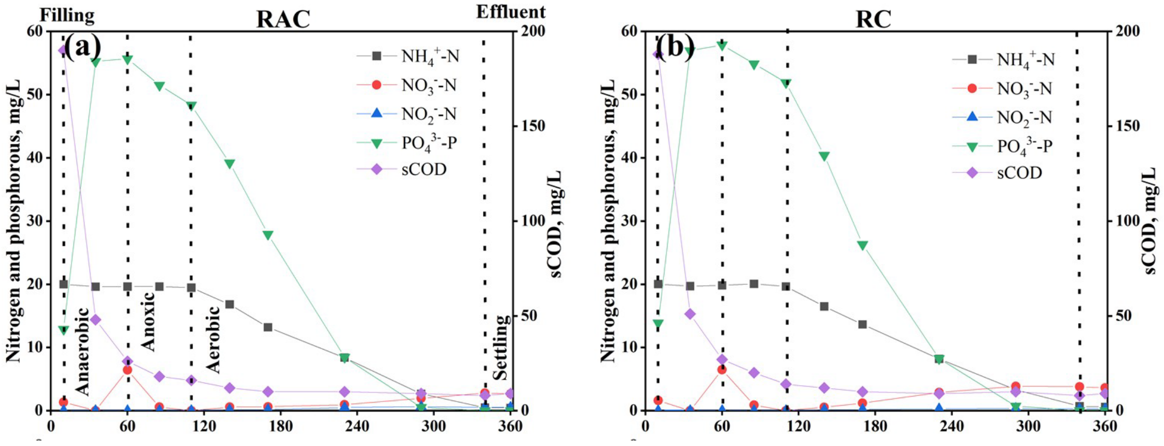

Fig. 1. Complete cycle analysis results for nutrients and sCOD in (1) RAC, and (b) RC. Biomass settling characteristics in both reactors.

Average MLSS and MLVSS concentrations in RAC were 4.2 ± 0.5 and 3.2 ± 0.2 g/L, and in RC, they were 4.2 ± 0.5 and 3.1 ± 0.1 g/L. At the beginning of GAC addition, GAC particles broke down to smaller particles <500 µm due to attrition and perhaps lost in the final effluent or wasted biomass. This demonstrates that a periodic addition of fresh GAC particles would be needed to maintain a consistent mass of GAC in the bioreactor. Sludge settleability in both RAC and RC was continuously improved, ultimately >0.7 SVI30/SVI5 values in RAC and RC were recorded after 190 and 215 operational days, respectively, showcasing the physical characteristics of the rapid settling biomass in both reactors. Granulation was observed in both reactors. However, the RAC had much higher granulation (nearly 87 % >500µm granules as compared to 52 % in the control based on volatile suspended solids) in the RC, perhaps because the smaller pieces of GAC could have served as the nucleation site for granulation RAC. The observed SRT for flocs and granules-biofilm was 8~10 days and >40 days.

A complete cycle analyses of EE2 fate in both reactors are shown in Figure 2. The average EE2 feed concentration was 5.3 ± 0.6 µg/L. Until day 190, the RAC reactor achieved an EE2 removal efficiency of 72 ± 9%. The RC reactor maintained an average EE2 removal efficiency of 35.2 ± 13.9%. As shown in figure 2 for complete cycle of EE2 fate in both reactors, the EE2 concentrations in the mixed liquor of both reactors remained nearly unchanged during the anaerobic and anoxic phases of reactor run cycles. However, an immediate decrease in EE2 concentration was recorded in the mixed liquor of both reactors as soon as soon as both reactors entered into the aerobic cycle. The EE2 concentration became nearly stable and remained unchanged after 60~70 minutes into the aerobic cycle. The removal of EE2 likely involved both biotic degradation—potentially by ammonium monooxygenase (AMO) enzymes and contributions from autotrophic and heterotrophic organisms (T. Yi & Harper, 2007)—and abiotic sorption, given EE2's high octanol-water partition coefficient (Log Kow > 4), which favors adsorption onto solids (Tang et al., 2021). Notably, batch tests ruled out volatilization as a significant removal mechanism. Previous studies have also indicated no clear correlation between EE2 removal and sludge retention time (SRT) (Clara et al., 2005; Kreuzinger et al., 2004). However, it remains elusive why further degradation of EE2 after 60~70 minutes into the aerobic phase did not take place in both reactors, and is an object of further research.

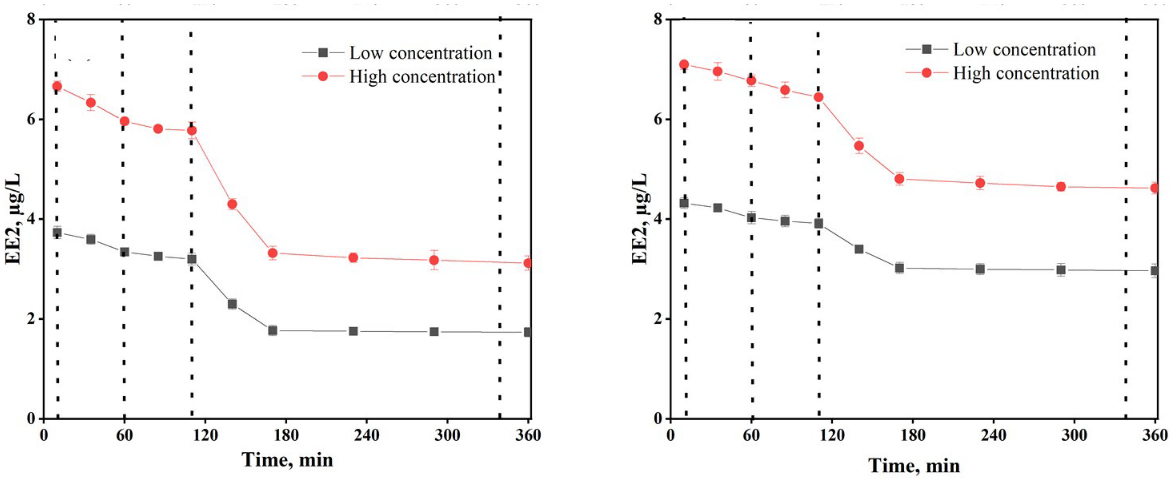

Fig. 2. Complete cycle profile for EE2 in (Left) RAC, and (Right) RC.

Figure 3 presents the PFAS removal performance in RAC and RC over a complete cycle of each reactor under steady state conditions. Each PFAS compound was introduced at an average feed concentration of 51.2 ± 4 ng/L, resulting in a total influent PFAS loading rate of 491.6 ± 38.7 ng/L·d for both reactors. Short-chain PFAS compounds (PFBA and PFBS) were not removed in either reactor, likely due to their high solubility and low affinity for solid-phase adsorption. In contrast, the RAC reactor demonstrated notable removal of long-chain PFAS: PFOA and PFOS were removed at average efficiencies of 32.8 ± 21.8% and 36.7 ± 16.3%, respectively. In the RC reactor, these removal efficiencies were substantially lower—only 2.3 ± 0.3% for PFOA and 3.6 ± 1.1% for PFOS.

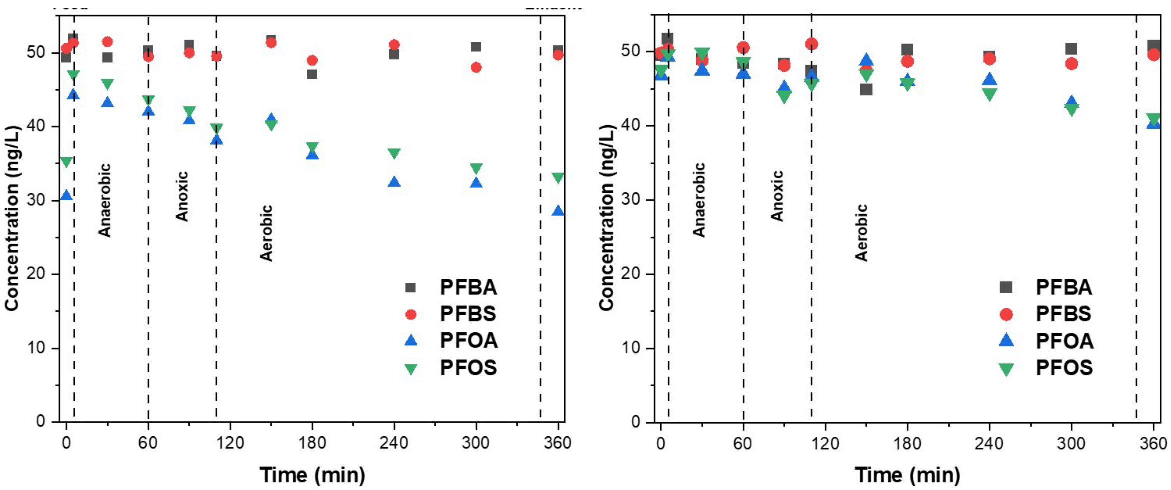

Fig. 3. Complete cycle profile for PFAS compounds in (Left) RAC, and (Right) RC.

Further confirmation of long-chain PFAS retention was obtained through analysis of biosolid samples. In RAC biosolids, PFOA and PFOS concentrations reached 18.72 ± 2.61 and 19.48 ± 2.08 µg/g dry weight (DW) of total solids (TS), respectively. In contrast, PFOA was not detected in RC biosolids, reflecting the low removal observed in RC, while PFOS was present at 74.07 ± 7.16 ng/g DW-TS. The substantially higher accumulation of long-chain PFAS in RAC is attributed to adsorption onto the granular activated carbon (GAC) media.

Conclusions

Granular activated carbon (GAC) used as a migrating carrier serves as an effective reactive bio-carrier, enhancing EE2 removal by adsorbing and concentrating the contaminant for microbial degradation, while also promoting biofilm formation, granulation, and improved sludge settleability and enabling SRT uncoupling. In the GAC-amended reactor (RAC), EE2 and long-chain PFAS (PFOA and PFOS) removal was significantly higher than in the control, with elevated PFAS levels detected in RAC biosolids. These findings highlight GAC's potential for process intensification, and carbon efficient nutrient removal , applicable to existing wastewater treatment plants. This study also highlights the potential of GAC-augmented biofilm reactor (RAC) to intensify biological wastewater treatment processes for the concurrent removal of nutrients and both biodegradable and difficult-to-biodegradable ECs. The innovative integration of GAC offers a practical pathway for upgrading existing WWTPs and designing future systems to address the challenges of complex influent loads and stricter regulatory requirements.

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