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Ligand-Enabled Donnan Dialysis for Phosphorus Recovery from Alum-Laden Waste Activated Sludge

Utsav Shashvatt, Fabian Amurrio, and Lee Blaney*

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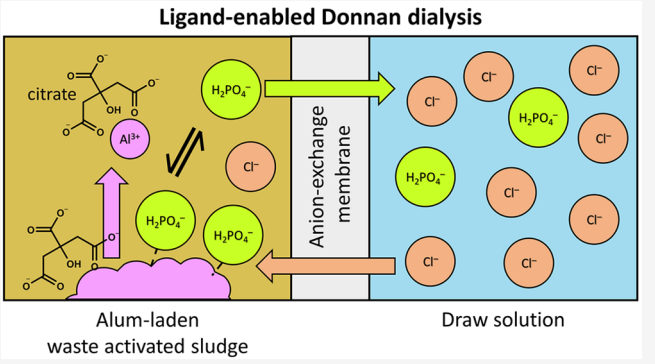
ABSTRACT: While many nutrient recovery technologies target liquid waste streams, new strategies are required for effective phosphorus recovery from solid waste. This study reports an innovative ligand-enabled Donnan dialysis process to recover orthophosphate (P(V)) from alum-laden waste activated sludge (WAS). Four ligands, namely acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate, were evaluated for P(V) release from a synthetic sludge containing 5 mM P(V) and 25 mM Al(III) and a real, alum-laden WAS with similar contents. Citrate and EDTA released more than 95% of P(V) at doses of 30 mM, outperforming acetate and oxalate. The ligand-based solubilization strategy was coupled with Donnan dialysis to recover P(V) into a clean sodium chloride draw solution. After Donnan dialysis with the synthetic sludge, the P(V) recovery's order was as follows: EDTA (54.4%) > citrate (41.7%) > oxalate (4.3%). The P(V) recovery efficiencies were slightly lower for Donnan dialysis with real, alum-laden WAS, namely 45.1% and 25.2% for EDTA and citrate addition, respectively, due to competitive effects exerted by other dissolved species. These promising results successfully demonstrated the proof-of-concept for ligand-enabled Donnan dialysis.



KEYWORDS: *Donnan dialysis, nutrients, resource recovery, phosphorus, ion exchange, circular economy*

1. INTRODUCTION

With the rapid depletion of phosphate rock reserves, alternative sources of phosphorus will play a key role in sustaining large-scale food production in the coming decades.[1−3] One potential strategy is to recover phosphorus from waste activated sludge (WAS) generated at municipal wastewater treatment plants.[4,5] In many locations, WAS contains high levels of coagulant residuals from the use of alum ($Al_2(SO_4)_3{\cdot}18H_2O$) or ferric chloride ($FeCl_3{\cdot}6H_2O$) for enhanced phosphorus removal.[6−8] Dewatered WAS is often used as a soil amendment;[9,10] however, the high aluminum or iron content lowers the agronomic value of WAS-derived products because phosphorus remains strongly bound to the metal (oxy)hydroxide solids and is, therefore, unavailable to crops.[11,12] Lime or other alkaline substances are frequently used to stabilize dewatered sludge, further reducing phosphorus availability to plants.[13] Due to risks from heavy metals, agricultural reuse of WAS is not always feasible.[14−16] For these reasons, new technologies that enable the selective recovery of phosphorus from WAS are needed to produce high-quality fertilizers and achieve a circular phosphorus economy. This study evaluated the ability of a novel ligand-enabled Donnan dialysis process for targeted recovery of orthophosphate, or P(V), from WAS.

Donnan dialysis exploits electrochemical potential gradients across ion-exchange membranes to drive ions from a waste solution, such as WAS, to a draw solution that contains a concentrated acid, base, or salt.[17] One advantage of Donnan dialysis-based P(V) recovery is that the anion-exchange membranes enable low co-recovery of heavy metals and organic matter.[18] In addition, Donnan dialysis is not pressure driven and, therefore, does not entail the high operational costs associated with other membrane processes.[19,20] Previous reports have documented the successful application of Donnan dialysis for recovery of nutrients in wastewater.[21−23] However, no prior literature has evaluated Donnan dialysis for P(V) recovery from solid wastes, such as sludge produced during enhanced phosphorus removal. In such systems, Donnan dialysis is constrained by the P(V) distribution between the aqueous and solid phases. Prakash and SenGupta overcame a similar challenge for Al^{3+} recovery from drinking water treatment residuals by using H_3O^+ as the draw cation.[24]

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Transport of H_3O^+ to the waste solution facilitated dissolution of aluminum (oxy)hydroxide solids and released Al^{3+}. A similar strategy cannot be employed for P(V) recovery from WAS because the low pH needed to dissolve aluminum (oxy)-hydroxide solids will concurrently lower the valence of P(V) anions, leading to lower recovery efficiencies for Donnan dialysis.[23] Sustainable approaches to P(V) recovery from WAS must, therefore, consider both solid−liquid and Donnan equilibrium chemistry.

The majority of P(V) in alum-laden WAS is present as aluminum phosphate solids or bound to amorphous aluminum hydroxide particles.[25] Previous efforts have explored different approaches to release P(V) from the solid phase. For example, alkaline treatment (pH 12−14) of WAS led to dissolution of aluminum-bound P(V);[26,27] however, a high pH waste solution is not ideal for Donnan dialysis due to competition from hydroxide. Pyrolysis at 575 °C followed by acid hydrolysis (sulfuric acid) at pH 2−3 effectively released P(V) from swine manure.[28] Similarly, Fang et al. reported effective P(V) recovery from sewage sludge ash at pH < 1 (sulfuric acid).[29] Unfortunately, these acidification techniques for P(V) release are not conducive to subsequent P(V) recovery by Donnan dialysis due to (i) the low valence of P(V) at acidic conditions (e.g., H_3PO_4 is dominant at pH < 2.2 and not recoverable by Donnan dialysis) and (ii) the strong competition for ion-exchange sites from the added sulfate (SO_4^{2-}). The pH swings required for these approaches also involve high operational costs. For these reasons, alternative strategies are needed to facilitate P(V) release from WAS at near-neutral pH without addition of competing anions to the Donnan dialysis system.

We hypothesized that complexing agents could promote dissolution of aluminum solids in WAS and, thereby, release P(V) for subsequent recovery by Donnan dialysis. Organic ligands have been previously used to release P(V) bound to aluminum and iron minerals in soil.[30,31] Similarly, citrate and ethylenediaminetetraacetate (EDTA) have been added to WAS to release P(V) in anaerobic fermentation processes.[32,33] Due to their larger molecular volume, complexing agents have lower charge densities and are, therefore, expected to exhibit less competition for ion-exchange sites and slower transport across ion-exchange membranes; furthermore, the valence of metal−ligand complexes is generally less negative than the free ligands, resulting in lower competition for ion-exchange sites in the membrane. The aggregate effects are expected to facilitate the effective recovery of P(V) from solid waste by Donnan dialysis.

The main objectives of this study were to investigate the efficacy of four organic ligands to (1) release P(V) from alum-laden WAS and (2) enable the subsequent recovery of P(V) by Donnan dialysis. The four complexing agents, namely acetate, citrate, EDTA, and oxalate, were chosen for their different physicochemical properties (Table S1 in the Supporting Information (SI)) and affinities for Al^{3+} (Table S2 in the SI). A synthetic sludge composed of aluminum hydroxide and aluminum phosphate solids was employed to optimize the required ligand dose for P(V) solubilization. The optimized process chemistry was used to investigate P(V) release and recovery from a real, alum-laden WAS. The overall performance of each complexing agent was considered as a function of P(V) release efficiency, required dose, and competition to P(V) uptake by and transport across the anion-exchange membrane. The outcomes highlight a novel strategy, namely ligand-enabled Donnan dialysis, to selectively recover P(V) from metal-laden sludge.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Chemicals. All chemicals were purchased from Fisher Scientific (Waltham, USA) or Sigma-Aldrich (St. Louis, USA). A stock solution of 0.25 M aluminum sulfate decahexahydrate (alum; $Al_2(SO_4)_3{\cdot}16H_2O$) was prepared in deionized water. A 0.5 M P(V) stock solution was generated by adding monosodium hydrogen phosphate (NaH_2PO_4) to deionized water. For pH adjustment, 2 M hydrochloric acid (HCl) and 2 M sodium hydroxide (NaOH) solutions were prepared by mixing concentrated HCl (35.5%) and solid NaOH (97%), respectively, with deionized water. The 0.5 or 1.0 M stock solutions of organic ligands were created by dissolving acetic acid, citric acid, EDTA (acid form), and oxalic acid in deionized water; the purity of all complexing agents was greater than 99%. For Donnan dialysis experiments, the 0.16−1.80 M chloride-based draw solutions were generated by adding sodium chloride (NaCl) to deionized water. For compositional analysis, 30% hydrogen peroxide and 15.8 M nitric acid were used to digest the real, alum-laden WAS.

2.2. Preparation and Composition of Synthetic Sludge. Synthetic sludge containing 5 mM P(V) and 25 mM Al(III) was prepared by mixing appropriate volumes of a 100 mM NaH_2PO_4 solution, 250 mM alum suspension, and deionized water (Figure S1 in the SI). The pH was adjusted to 5.5−6.0, and the mixtures were stirred at 300 rpm for 30 min to ensure equilibrium (Figure S2 in the SI). For these conditions, aluminum phosphate ($AlPO_4{\cdot}1.5H_2O(s)$) precipitated, as confirmed by chemical equilibrium modeling (Figure S3 in the SI) and previous studies.[34,35] Over 99% of the P(V) was contained in the solid phase. However, only 20% of the Al(III) was present as $AlPO_4{\cdot}1.5H_2O(s)$, while the rest mostly precipitated as amorphous aluminum hydroxide ($Al(OH)_3(am)$).[36]

2.3. Composition of the Real, Alum-Laden WAS. A real, alum-laden WAS (or WAS, henceforth) (Figure S1 in the SI) was collected from a wastewater treatment plant in Maryland (USA) and stored at 4 °C. Prior to characterization, the WAS was dried at 50 °C for 72 h. Acid digestion was performed according to EPA Method 3050b,[37] and the chemical composition was measured using inductively coupled plasma mass spectrometry for metals (PerkinElmer NexION 300D; Waltham, USA), ion chromatography for anions (Thermo Scientific Dionex Integrion; Sunnyvale, USA), and the stannous chloride colorimetric method for P(V).[38] The suspended solids content was measured by gravimetric analysis. All measurements were made in triplicate, and the overall WAS composition is reported in Table 1. For experimentation, the WAS was used as collected, without drying or other modifications.

2.4. P(V) Release from Synthetic Sludge and WAS. Synthetic sludge (125 mL) was added to Erlenmeyer flasks and dosed with nine different concentrations (i.e., 0, 5, 10, 20, 30, 40, 50, 70, 100 mM) of the four organic ligands. The phosphorus-to-aluminum molar ratio was maintained at 1:5 to represent a typical composition of alum-laden WAS.[39] The experiments with real WAS were conducted with 10 mL volumes in centrifuge tubes. For both cases, the appropriate mass of organic ligands was added via small volumes of 1 M acetic acid, 1 M citric acid, 0.5 M EDTA (acid), or 1 M oxalic acid. The solution pH was maintained at 5.5−6.0. The

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Table 1. Chemical Composition of the Real, Alum-Laden WAS[a]

species	total concentration or value	species	total concentration
Al^{3+}	25.8 ± 1.3 mM	PO_4^{3-}-P	3.9 ± 0.5 mM
Ca^{2+}	9.7 ± 3.7 mM	CH_3COO^-	3.6 ± 0.5 mM
Fe^{3+}	6.3 ± 2.9 mM	$HCOO^-$	0.38 ± 0.02 mM
Mg^{2+}	7.8 ± 3.4 mM	Cl^-	4.1 ± 0.7 mM
K^+	1.4 ± 0.2 mM	HCO_3^-	3.2 ± 0.3 mM
Na^+	5.5 ± 0.5 mM	SO_4^{2-}	0.16 ± 0.01 mM
pH	5.84 ± 0.31	total suspended solids	11.8 ± 0.3 g L^{-1}

[a]The values are for the original slurry and reported as total concentrations of each species.

Erlenmeyer flasks were sealed with Parafilm, and the centrifuge tubes were capped. The suspensions were mixed at 300 rpm for 24 h, and then samples were withdrawn and passed through 0.2-μm nylon syringe filters before P(V) analysis.

The impact of pH on P(V) release from the synthetic sludge was investigated to consider acid and base extraction processes as alternatives to the ligand-assisted strategy. For four specific phosphorus-to-aluminum molar ratios (i.e., 1:2, 1:5, 1:7, 1:10), 11 Erlenmeyer flasks were filled with 100 mL of synthetic sludge prepared with 5 mM P(V) and variable Al(III). The equilibrium pH values of the synthetic sludge mixtures were 2.3, 3.6, 4.1, 4.8, 5.6, 6.6, 7.6, 9.0, 10.1, 11.0, and 12.0. The suspensions were stirred at 300 rpm for 30 min to achieve equilibrium (Figure S2 in the SI), and then samples were collected and analyzed.

2.5. Chemical Equilibrium Modeling. The conditions tested in Section 2.4 were also evaluated using the Visual MINTEQ v3.1 chemical equilibrium modeling software.[40] The models were run at pH 5.5 and 25 °C, and activity coefficients were corrected based on ionic strength. Equilibrium constants from the Visual MINTEQ v3.1 database were directly used for most reactions; however, the default log K value for formation of the Al-citrate complex was updated to 20.0.[41]

2.6. Donnan Dialysis Experiments. *2.6.1. Reactor Design.* The Donnan dialysis reactor system was previously described by Shashvatt et al.[23] For the reported experiments, the membrane surface area was 4.51×10^{-3} m^2. The waste and draw solutions (380 mL, each) were separated by the AMI-7001 anion-exchange membrane from Membranes International, Inc. (Ringwood, USA). This membrane includes fabric reinforcement, maintains a wide pH tolerance (0−10), and exhibits a moderate anion-exchange capacity (1.1−1.3 meq g^{-1}).[23] For this study, the membranes were pre-exposed (conditioned) to wastewater for approximately 320 h to emulate real operational scenarios. The Donnan dialysis performance of the conditioned membranes was slightly lower than that of fresh membranes (Figure S4 in the SI). All Donnan dialysis experiments were run for 300 h with continuous mixing at 600 rpm.

2.6.2. P(V) Recovery from Synthetic Sludge. Synthetic sludge suspensions (380 mL) were prepared with a phosphorus-to-aluminum molar ratio of 1:5 in accordance with the methods described in Section 2.2. The solution pH was adjusted to 5.5−5.8, and the suspension was stirred at 300 rpm for 30 min to ensure well-mixed conditions. To remove excess SO_4^{2-} introduced via alum addition, the synthetic sludge mixtures were centrifuged, the supernatant was removed, and the residual solids were rinsed and resuspended in deionized water; this protocol was repeated three times. The rinsed solids and an appropriate volume of the organic ligand stock solution were added to deionized water to achieve a total volume of 380 mL. Donnan dialysis experiments were performed at three different ligand concentrations. For citrate and EDTA, the synthetic sludge was dosed with 5, 20, and 40 mM ligand. Due to the weaker complexation reactions, oxalate was dosed at concentrations of 20, 60, and 80 mM. Donnan dialysis experiments were not performed for synthetic sludge dosed with acetate due to low P(V) release (see Section 3.1). Control experiments were conducted with (i) P(V) + alum (no ligand added) and (ii) P(V) + ligand (no alum added). Upon addition of the ligand, the synthetic sludge was mixed for 5 min before introducing the suspension into the Donnan dialysis reactors.

The draw solution composition was designed using the $R_{d/w}$ parameter, which is the ratio of the minimum draw ion concentration in the draw solution to the maximum draw ion concentration in the waste solution for a target removal efficiency.[23] In these experiments, $R_{d/w}$ was set to 10 to achieve theoretical P(V) removal efficiencies greater than 90%. Both P(V) and ligand anions interact with the quaternary ammonium groups of the AMI-7001 membrane, and this situation must be considered when designing the draw solution composition with eq 1. For waste solutions with pH 5.5−6.0, the valences of P(V), citrate, oxalate, and EDTA were equal to 1, 2, 2, and 3, respectively. Based on these conditions, the design Cl^- concentrations in the draw solution were as follows: 0.16, 0.49, and 0.92 M for synthetic sludge dosed with 5, 20, and 40 mM citrate, respectively; 0.27, 0.79, and 1.54 M for synthetic sludge dosed with 5, 20, and 40 mM EDTA, respectively; and 0.49, 1.38, and 1.80 M for synthetic sludge dosed with 20, 60, and 80 mM oxalate, respectively. For the EDTA-dosed synthetic sludge, additional Cl^- was introduced through pH adjustment, but the draw solution composition was appropriately adjusted to account for the Cl^- content of the initial waste solution. The draw solutions (380 mL) were added to the Donnan dialysis reactors to initiate the P(V) recovery process.

$$C_{Cl^-,in}^{draw} = \sum \frac{z_i}{z_{Cl^-}}(1 + R_{d/w})\frac{(R_{d/w})^{\frac{z_i}{z_{Cl^-}}}}{[1 + (R_{d/w})^{\frac{z_i}{z_{Cl^-}}}]}C_{i,in}^{waste} \quad (1)$$

In eq 1, $C_{Cl^-,in}^{draw}$ is the initial aqueous-phase concentration of Cl^- in the draw solution, $C_{i,in}^{waste}$ is the initial aqueous-phase concentration of anion i (i.e., P(V), ligand, Cl^-) in the waste solution, z_{Cl^-} is the valence of Cl^-, and z_i is the valence of the waste ion.

Samples (1 mL) were periodically collected from the draw and waste solutions, and the pH was recorded at each sampling event. The waste solution samples were immediately passed through a 0.2-μm nylon syringe filter before analysis of P(V) and ligand concentrations. Due to osmotic effects, the volume of the waste and draw solutions decreased and increased, respectively, by 5−20%. The recovery efficiency ($\eta_{recovery}$) was calculated in terms of P(V) mass in the draw solution after Donnan dialysis, as indicated in eq 2.

$$\eta_{recovery} = \left(\frac{C_{P(V)}^{draw} V_{300h}^{draw}}{q_{P(V),in}^{sludge} M_{in}^{sludge}}\right) \quad (2)$$

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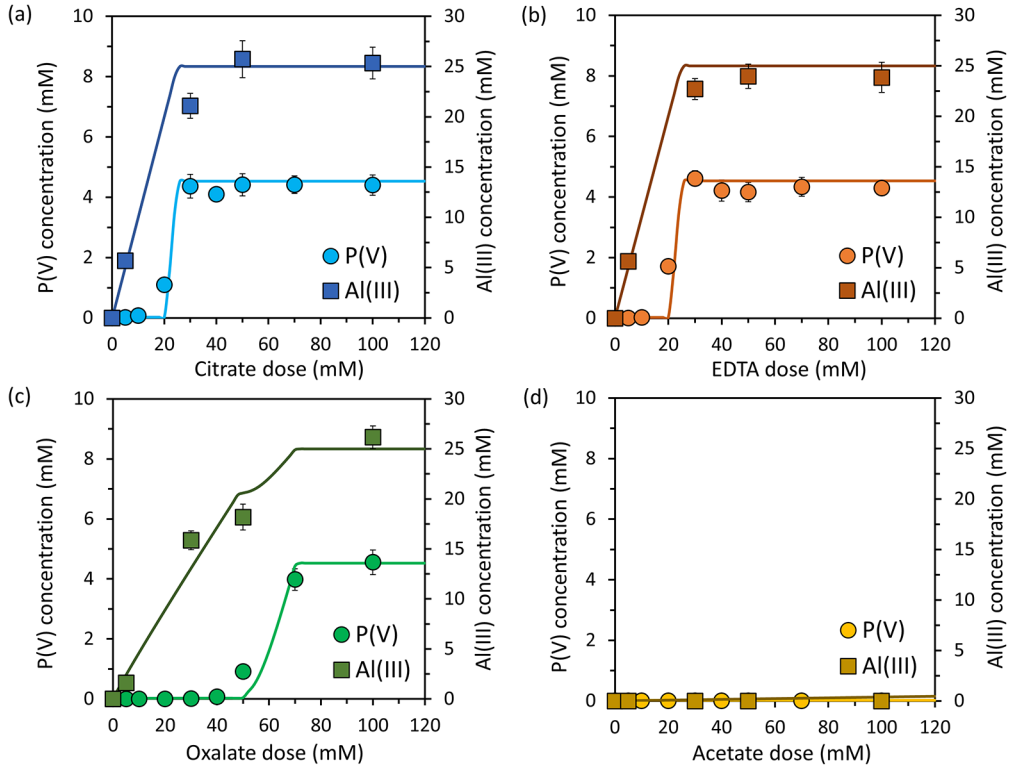

Figure 1. P(V) and Al(III) release from synthetic sludge upon addition of (a) citrate, (b) EDTA, (c) oxalate, and (d) acetate. The symbols are experimentally measured mean concentrations, the error bars are standard deviation ($n = 2$), and the curves are unfitted models generated by Visual MINTEQ v3.1. The inputs to the model were as follows: 5 mM PO_4^{3-}; 25 mM Al^{3+}; pH 5.5; and, 25 °C. The corresponding chemical reactions and associated equilibrium constants are provided in Table S2 of the SI.

In eq 2, $C_{P(V)}^{draw}$ is the P(V) concentration in the draw solution after 300 h of operation, V_{300h}^{draw} is the volume of the draw solution after 300 h, $q_{P(V),in}^{sludge}$ is the initial P(V) concentration in the sludge, and M_{in}^{sludge} is the initial mass of sludge.

2.6.3. P(V) Recovery from WAS. Before conducting Donnan dialysis experiments, real, alum-laden WAS was equilibrated to room temperature (22 °C). The WAS container was well mixed, and then 370 mL was removed and placed in the Donnan dialysis reactor. Organic ligands were dosed (10 mL) into the WAS at a concentration of 40 mM citrate or 40 mM EDTA; note, Donnan dialysis was not performed with acetate or oxalate due to the low P(V) release (Section 3.1) or recovery (Section 3.3), respectively, observed for synthetic sludge. For each condition, 0.5 and 1.0 M Cl^- draw solutions were employed. All other operational and analytical protocols were the same as described in Section 2.6.2.

3. RESULTS AND DISCUSSION

3.1. P(V) Release from Al(III) Solids by Ligand Addition. Due to the favorable complexation reactions between the citrate, EDTA, and oxalate ligands and Al^{3+} (Table S2 and Figure S5 in the SI), the $AlPO_4{\cdot}1.5H_2O(s)$ and $Al(OH)_3(am)$ solids in the synthetic sludge dissolved (Figure S6 in the SI) and, concurrently, released Al(III) and P(V), as shown in Figure 1. For the same ligand dose, the aqueous-phase P(V) concentration varied between the four complexing agents according to the magnitude of the aluminum-ligand complexation constants. P(V) release from the synthetic sludge occurred in three main regimes, namely minimal, quick, and complete release. The experimental data highlighted the similarity of P(V) solubilization upon addition of citrate and EDTA to the synthetic sludge. In both cases, P(V) release was first observed for a ligand concentration of 20 mM, and the maximum P(V) concentration occurred at 30 mM ligand. Because the total Al(III) content was 25 mM, these data suggested formation of 1:1 Al(III)-citrate and Al(III)-EDTA complexes, which were confirmed by the chemical equilibrium model predictions of $Al(citrate)^0$ and $Al(EDTA)^-$ as dominant species (Figure S5 in the SI). For oxalate, the quick-release regime started at a ligand concentration of 50 mM, with complete P(V) solubilization achieved at 70−100 mM. These results suggested that 3−4 moles of oxalate were needed for each mole of Al(III) to release P(V) in alum-laden sludges, in agreement with the predicted dominance of the $Al(oxalate)_3^{3-}$ species in Figure S5 of the SI. The addition of 100 mM acetate resulted in negligible P(V) concentrations, proving that acetate was not an effective complexing agent for Al(III). For this reason, acetate was not included in further testing.

The P(V) and Al(III) solubilization trends predicted by Visual MINTEQ v3.1 closely matched the experimental data for the four organic ligands (Figure 1). The model confirmed that addition of ligands to the synthetic sludge caused dissolution of $Al(OH)_3(am)$ in the minimal-release regime. Since 99% of the P(V) was contained in $AlPO_4{\cdot}1.5H_2O(s)$, dissolution of $Al(OH)_3(am)$ had no direct benefit for P(V) release. After complete dissolution of $Al(OH)_3(am)$, the system transitioned into the quick-release regime for P(V), wherein ligands complexed with Al(III) from $AlPO_4{\cdot}1.5H_2O(s)$. These reactions resulted in complete dissolution of the Al(III) solids for citrate, EDTA, and oxalate addition. The ligand doses needed for complete P(V) release were

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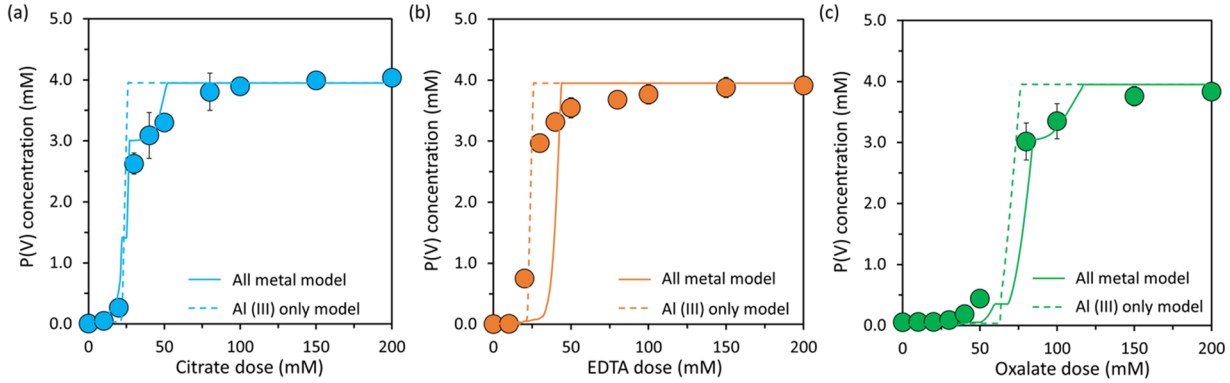

Figure 2. Effect of (a) citrate, (b) EDTA, and (c) oxalate addition on P(V) release from real WAS. The symbols represent experimentally measured concentrations, and errors bars are standard deviation (n = 3). The curves are unfitted models generated by Visual MINTEQ v3.1 for systems with the (i) full WAS composition and (ii) only the Al(III) content from Table 1 at pH 5.5 and 25 °C.

determined from the chemical equilibrium models (Figure S7 in the SI): 26 mM for citrate; 28 mM for EDTA; and 76 mM for oxalate.

3.2. P(V) Release from Real, Alum-Laden WAS. The synthetic sludge experiments demonstrated the potential for citrate, EDTA, and oxalate to release P(V) from aluminum-based solids. Similar tests were conducted to evaluate the performance of these ligands for P(V) release from real, alum-laden WAS, which also contained the additional metals reported in Table 1. The data in Figure 2 confirmed the presence of three P(V) release regimes and highlighted the effective performance of the citrate and EDTA ligands for real wastes. For citrate and EDTA, negligible P(V) release occurred for ligand doses of less than 10 mM, but approximately 95% of the P(V) was released after addition of 70 mM ligand. As with the synthetic sludge, higher doses of oxalate were required to achieve the same P(V) concentrations.

Similar ligand doses were required to reach the quick-release regimes for the synthetic sludge and real WAS, namely 20 mM citrate, 20 mM EDTA, and 70 mM oxalate. This finding can be attributed to the almost identical Al(III) content of the WAS (25.8 mM) and synthetic sludge (25 mM). However, the maximum P(V) release from WAS was achieved at higher ligand doses compared to the synthetic sludge due to the presence of other cations, which also react with the ligands. Figure 3 shows that addition of 100 mM citrate, 100 mM EDTA, and 100 mM oxalate resulted in the release of 33−52% Al(III), 3−27% iron, 20−75% magnesium, and 21−62% calcium from WAS. These metals were all fairly stable in the unmodified WAS.

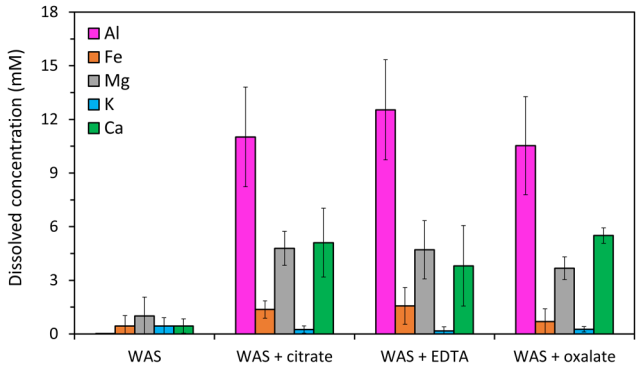

Figure 3. Aqueous-phase concentrations of Al(III) and other metals in the unmodified WAS and WAS treated with 100 mM citrate, EDTA, or oxalate ligands. The pH was maintained at 5.5−6.0 for all solutions. The error bars denote standard deviation (n = 2).

A more comprehensive chemical equilibrium model was employed to include all of the relevant species in WAS. The composition followed Table 1, but the stored WAS was assumed to contain a 1:1 mixture of Fe(II) to Fe(III), in accordance with previous literature.[42] The model predicted the formation of vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O(s)$), which caused the noticeable changes in the P(V) concentration profiles at the onset of the complete-release regime for citrate (25−50 mM) and oxalate (75−100 mM) in Figure 2. While the maximum P(V) release from synthetic sludge occurred at 1:1 molar ratios for the Al(III)-citrate and Al(III)-EDTA systems, higher ligand doses were needed for the real WAS due to scavenging from $Fe_3(PO_4)_2{\cdot}8H_2O(s)$. Nevertheless, greater than 95%, 95%, and 87% P(V) extraction was achieved for addition of citrate, EDTA, and oxalate, respectively, even though these conditions only resulted in 33−52% Al(III) dissolution. The same ligand doses caused an 80% Al(III) release in the synthetic sludge. The discrepancy may have stemmed from conversion of $Al(OH)_3(am)$ into more stable forms, such as gibbsite ($Al(OH)_3(s)$), during WAS storage.[43,44] This result was favorable as an equivalent P(V) release was achieved without excessive solubilization of $Al(OH)_3(s)$.

3.3. Selective P(V) Recovery from Alum-Based Sludge by Ligand-Enabled Donnan Dialysis. To selectively recover P(V) from alum-laden wastes, Donnan dialysis was conducted with synthetic sludge slurries dosed with citrate, EDTA, or oxalate. For each ligand, three doses were investigated to evaluate performance in the minimal, quick, and complete P(V) release domains. As shown in Figure 4, the P(V) levels in the waste solutions varied for each ligand dosing scheme, but the results were in good agreement with the data in Figure 1. The maximum P(V) concentrations in the ligand-dosed waste solutions were as follows: 0.04, 1.96, and 4.15 mM P(V) for 5, 20, and 40 mM citrate, respectively; 0.02, 2.47, and 3.75 mM P(V) for 5, 20, and 40 mM EDTA, respectively; and 0.27, 2.83, and 3.82 mM P(V) for 10, 60, and 80 mM oxalate, respectively. The initial P(V) content in the waste suspension was 4.58 mM; therefore, the P(V) release efficiencies in waste solutions dosed with 40 mM citrate, 40 mM EDTA, and 80 mM oxalate were at least 91.8%, 82.2%, and 83.7%,

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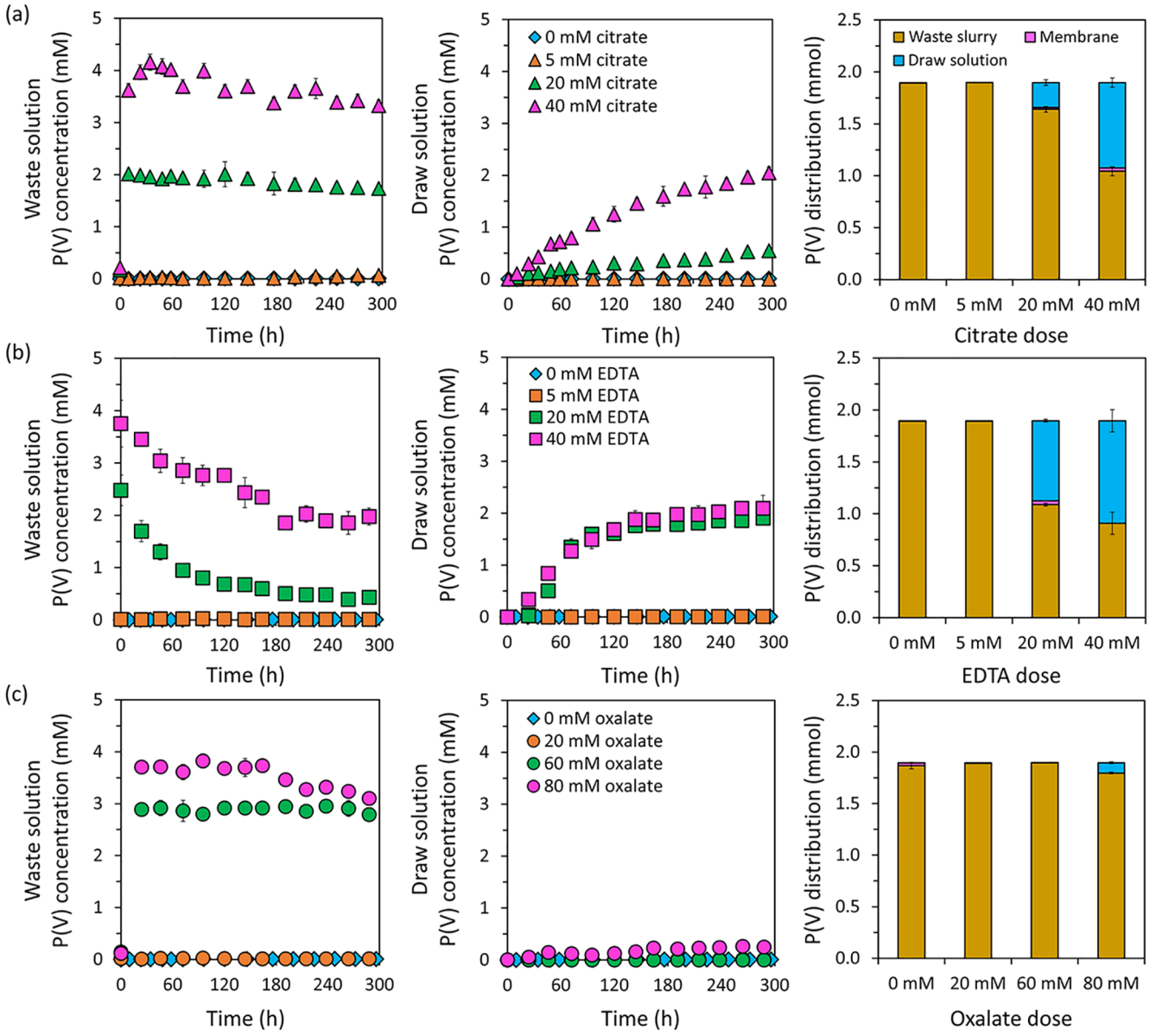

Figure 4. P(V) concentrations in the (left) waste and (center) draw solutions and (right) P(V) mass distribution for Donnan dialysis of synthetic sludge dosed with (a) citrate, (b) EDTA, or (c) oxalate. The legends in the draw solution plots also apply to the corresponding waste solutions. The (a,b) symbols and (c) columns report mean values, and the error bars are standard deviation (n = 2).

respectively. These values are conservative because P(V) solubilization continues during Donnan dialysis.

Although the initial P(V) concentrations in the waste solutions were similar in magnitude, the subsequent P(V) removal trends varied for the citrate, EDTA, and oxalate treatments (Figure 4). The P(V) concentrations in the waste solution slowly decreased for the citrate- and oxalate-dosed slurries, whereas faster P(V) removal was observed when EDTA was introduced. These differences may be attributed to ligand competition for quaternary amine sites in the anion-exchange membrane. Similar competitive effects have been reported between P(V) and citrate in electrodialysis applications.[45] Based on its smaller size (i.e., greater charge density), oxalate was expected to exert more competitive effects than citrate and EDTA. This hypothesis was confirmed by performing Donnan dialysis with P(V) + ligand (no alum) for the 40 mM citrate, 40 mM EDTA, and 80 mM oxalate conditions. Figure S8 in the SI shows that oxalate was preferentially removed compared to P(V), in contrast to the experiments with citrate and EDTA. Due to its high valence, the dominant Al-oxalate complex, $Al(oxalate)_3^{3-}$, likely exerted strong competition for quaternary amine sites in the membrane. Alternatively, the $Al(citrate)^0$ and $Al(EDTA)^-$ complexes have lower charge densities than the corresponding free ligands, highlighting their beneficial use in ligand-enabled Donnan dialysis systems.

According to Figure 4, the P(V) concentrations in the draw solutions increased over time due to Donnan dialysis. Given the minimal P(V) release for the low ligand doses, negligible P(V) recovery efficiencies were expected and confirmed, for the 5 mM citrate, 5 mM EDTA, and 20 mM oxalate operating conditions. When 40 mM citrate, 40 mM EDTA, and 80 mM oxalate were applied to the sludge, the P(V) fluxes into the draw solutions were $(1.78 \pm 0.12) \times 10^{-3}$, $(1.84 \pm 0.18) \times$

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10^{-3}, and (2.18 ± 0.20) × 10^{-4} mol h^{-1} m^{-2}, respectively, and the corresponding P(V) concentrations reached 1.89, 2.18, and 0.21 mM, respectively; P(V) fluxes into the draw solutions for other conditions are available in Table S3 of the SI. The 40 mM citrate dose improved P(V) recovery by about 285% compared to the 20 mM citrate scenario due to greater solubilization, which increased the P(V) concentration gradient in the membrane and improved the rate of recovery. A minor improvement in P(V) recovery was recorded when the EDTA dose was changed from 20 mM (44.3%) to 40 mM (54.3%). Less than 5.0% P(V) recovery was observed for the 60 mM and 80 mM oxalate conditions despite the high P(V) concentrations in the waste solution, reinforcing the aforementioned competitive effects. Overall, the P(V) recovery efficiencies were as follows: 40 mM EDTA (54.4%) > 40 mM citrate (41.7%) > 80 mM oxalate (4.3%). These findings confirmed that oxalate exerted the strongest effects on P(V) transport, followed by citrate, and then EDTA for the tested conditions.

The competitive effects of the ligands were considered with respect to speciation, charge, size, and charge density (Table S4 in the SI). For example, citrate was primarily present in the synthetic waste solution as H_2Cit^-, Cit^{3-}, $HCit^{2-}$, and $Al(Cit)^0$ at concentrations of 1.5, 2.4, 11.1, and 25.0 mM, respectively; therefore, the average charge of citrate-containing species was −0.77 eq mol^{-1}. Following the same approach, the average charges of EDTA and oxalate were calculated to be −1.56 and −2.78 eq mol^{-1}, respectively. The molar volumes[46] of citric acid (109.0 cm^3 mol^{-1}), EDTA (186.6 cm^3 mol^{-1}), and oxalic acid (50.8 cm^3 mol^{-1}) were used to calculate the average charge density for each ligand (eq cm^{-3}): citrate, −7.06 × 10^{-3}; EDTA, −8.36 × 10^{-3}; oxalate, −54.7 × 10^{-3}. Figure S9 in the SI suggests that charge density was more important than ligand size or charge. This result can be explained by the greater affinity of anion-exchange membranes for species with higher charge density, which results in competitive effects on P(V) uptake. Ligands with lower charge density and larger size were, therefore, preferred for P(V) recovery by the ligand-enabled Donnan dialysis process.

3.4. Ligand-Enabled Donnan Dialysis for P(V) Recovery from Real WAS. Based on the aforementioned results, Donnan dialysis was conducted with real, alum-laden WAS dosed with 40 mM citrate or 40 mM EDTA. The overall performance was evaluated according to the P(V) mass balance analysis for WAS, WAS + citrate, and WAS + EDTA. Figure 5 shows the P(V) mass distribution in the waste solids, waste solution, anion-exchange membrane, and draw solution after 300 h of Donnan dialysis; note, the P(V) concentration profiles are available as a function of time in Figure S10 of the SI. The percentage of P(V) in the waste solids for the WAS, WAS + citrate, and WAS + EDTA scenarios was 95.4 ± 9.9%, 44.9 ± 4.8%, and 19.5 ± 3.2%, respectively. The effective release of P(V) from the WAS solids by citrate and EDTA enabled P(V) recovery by Donnan dialysis. The P(V) recovery efficiencies from the WAS, WAS + citrate, and WAS + EDTA treatments were 4.5 ± 0.8%, 25.2 ± 5.1%, and 45.1 ± 6.0%, respectively. Compared to the synthetic sludge, the P(V) flux into the draw solution decreased 5.70× for citrate and 1.70× for EDTA addition to the real WAS (Table S3 in the SI). These effects were attributed to the high concentrations of dissolved organic matter and other inorganic ions in the real WAS. Previous studies have shown that competing ions affect recovery of target ions by Donnan dialysis when other conditions are equal.[47,48] The WAS treated with citrate and EDTA still contained dissolved P(V), suggesting that further recovery was possible. In a real facility, the residual wastewater would be sent back to the head of the plant during dewatering.

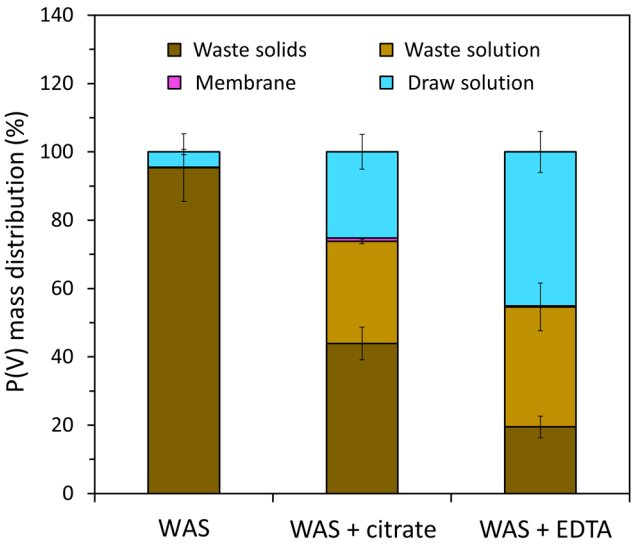

Figure 5. P(V) mass distribution for the WAS, WAS + 40 mM citrate, and WAS + 40 mM EDTA treatments after 300 h of Donnan dialysis. The pH was maintained at 5.6−7.1. Error bars represent the standard deviation of Donnan dialysis experiments conducted with 0.5 and 1.0 M NaCl draw solutions.

The novel, ligand-assisted Donnan dialysis strategy for recovering P(V) from alum-laden sludge has ancillary benefits, including waste management and minimization. For example, the P(V) content of the waste solids was reduced from 8.7 mg g^{-1} to 4.1 mg g^{-1} and 1.7 mg g^{-1} for the citrate and EDTA treatments, respectively, potentially enabling new waste management approaches based on regional nutrient regulations. The mass of waste solids decreased in the following order: WAS, 4.2 ± 0.1 g > WAS + citrate, 2.6 ± 0.1 g > WAS + EDTA, 1.7 ± 0.2 g. Overall, the P(V) content and mass of waste solids decreased 53−80% and 38−60%, respectively. The better performance of EDTA with respect to P(V) recovery aligned with the greater degree of solids dissolution. Similar phenomena were observed for the synthetic sludges dosed with citrate and EDTA, as indicated by the photographs in Figure S6 of the SI, which show dissolution of Al(III) solids at ligand doses greater than 30 mM.

The data in Figure 5 and the photographs in Figure S9 of the SI confirm the ability of Donnan dialysis to not only generate P(V)-enriched draw solutions that can be processed into value-added fertilizers[23] but also reject particulates and organic matter in real waste solids. The P(V) concentration in the 1 M NaCl draw solution reached 1.4 mM. Under similar conditions, Kumar et al. demonstrated >99% P(V) precipitation efficiency (as struvite) from a solution after dosing $MgCl_2$ and NH_4Cl and adjusting the pH to 9.0.[49] Chemical equilibrium modeling indicated that 93% of the P(V) present in draw solutions from the ligand-enabled Donnan dialysis system can be similarly recovered as struvite. Due to Donnan exclusion, cations like Al^{3+} are prevented from crossing the membrane and contaminating the recovered struvite, but future efforts are needed to evaluate the potential co-recovery of anionic metals. Most of the dosed ligand interacts with Al^{3+} in the waste

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solution, but some can be transported to the draw solution. Because EDTA and citrate are larger than P(V), these species undergo slower diffusion. The presence of ligands in the draw solution is not a major concern, because previous studies employed ligands to complex calcium and precipitate high-purity struvite from animal manure slurries.[3,50]

While the P(V) recovery efficiencies from the real, alum-laden WAS were moderate and the operational times were long, the current work demonstrated the proof-of-concept for ligand-enabled Donnan dialysis. Text S1 in the SI shows that ligand-enabled P(V) release was more cost-effective than acid or base extraction; however, technoeconomic analyses with pilot-scale reactors operated in continuous-flow or sequencing batch mode are recommended to account for all capital and operating costs. Recent literature has suggested that Donnan dialysis can be economically competitive with existing technologies. For example, Donnan dialysis achieved higher ammonia recovery and lower energy consumption than electrodialysis in a 150-L pilot-scale system for treatment of anaerobic digester centrate.[51] The performance of the ligand-enabled Donnan dialysis can also be improved through optimization of several parameters in future efforts.[23] According to eqs 1 and 2, a higher draw solution concentration would increase the overall P(V) recovery. Faster P(V) recovery can be achieved by selecting thinner membranes with higher ion-exchange capacity, greater hydration, and better P(V) selectivity. Donnan dialysis reactors with larger ratios of membrane surface area to reactor volume will improve throughput. Importantly, the ligand-enabled Donnan dialysis process can likely be applied for recovery of other resources bound to solids.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02153.

Chemical properties of ligands; anion concentrations in WAS slurries; complexation and dissolution reactions; photographs of synthetic sludge and real WAS; P(V) distribution in synthetic sludge; Donnan dialysis performance of fresh and conditioned membranes; chemical equilibrium models; P(V) flux into draw solution; competitive effects analysis; control experiments in absence of solids; and cost analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Lee Blaney − *Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States;* orcid.org/0000-0003-0181-1326; Phone: +1-410-455-8608; Email: blaney@umbc.edu; Fax: +1-410-455-1049

Authors

Utsav Shashvatt − *Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States*

Fabian Amurrio − *Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.2c02153

Notes

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