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Charles D. Spellman Jr.
University of Rhode Island

Travis L. Tasker

William H.J. Strosnider

Joseph E. Goodwill
University of Rhode Island, goodwill@uri.edu

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Abatement of Circumneutral Mine Drainage by Co-treatment with Secondary Municipal Wastewater

Charles D. Spellman Jr^a, Travis L. Tasker^b, William H.J. Strosnider^c, Joseph E. Goodwill^{a*}

^a *Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, RI, 02881 USA*

^b *Department of Environmental Engineering, Saint Francis University, Loretto, PA 15940 USA*

^c *Belle W. Baruch Marine Field Laboratory, University of South Carolina, Georgetown, SC 29440 USA*

** Corresponding Author at: Fascitelli Center for Advanced Engineering, 2 East Alumni Ave, Room 260, Kingston, RI 02881 USA. E-mail address: goodwill@uri.edu*

Abstract

Acid mine drainage (AMD) is a persistent and problematic source of water pollution. Co-treatment with municipal wastewater (MWW) at existing wastewater treatment plants (WWTPs) has several advantages; however, potential impacts on downstream physicochemical and biological processes are not completely known. This bench-scale study examined the impact of co-treatment by combining a mild AMD at various ratios with MWW, followed by sludge settling and supernatant comparative analysis by a variety of effluent water quality parameters. These measurements were combined with carbonate system and adsorption isotherm modeling to elucidate the mechanisms underlying the experimental results. AMD addition decreased MWW effluent PO_4^{3-} concentrations by up to 90%, demonstrating co-treatment as a low-cost solution for MWW nutrient removal. Coagulation from metals in AMD was incomplete due to PO_4^{3-} adsorption, confirmed by comparing experimental results with Langmuir isotherm behavior. Sweep flocculation was the dominating particle aggregation mechanism, and co-treatment led to improved particle clarification outcomes. Carbonate system modeling adequately explains pH effects, and can

also be applied to varying AMD matrices. The impact of AMD addition on the MWW microbial community was also investigated which provided evidence of microbial adaptation. This study demonstrates post-aeration co-treatment enables mitigation of mild AMD without adversely affecting WWTP processes. Reported results also frame required future studies to address extant questions prior to full-scale adaptation.

Highlights

- Addition of mild AMD to a secondary wastewater treatment processes examined
- Co-treatment removed >90% of PO_4^{3-} in wastewater via adsorption
- Coagulation of iron particles incomplete, dominated by sweep flocculation
- Secondary settling improved at highest drainage dosages
- Minor impact to microbial oxygen consumption rates, with adaptation noted.

Keywords

Acid Mine Drainage; Co-treatment; Phosphate adsorption; Iron; Oxygen demand

1. Introduction

Acid mine drainage (AMD) is a legacy pollution issue in many areas with a history of mining activity (Johnson, 2003). AMD is generated when mining exposes pyrite rock (FeS_2) to water in the presence of oxygen, thus facilitating pyrite oxidation and producing waters with elevated acidity and dissolved metals (Akcil and Koldas, 2006; Evangelou and Zhang, 1995; Ziemkiewicz et al., 1997). Metals of concern vary geographically and often include iron (Fe), aluminum (Al), manganese (Mn), copper (Cu), zinc (Zn), and lead (Pb) (Jacobs et

al., 2014). Climatic change, such as decreases in seasonal snow pack, can also worsen mineral acidity (Todd et al., 2012). Methods for treating AMD include both passive and active approaches. Passive treatment utilizes calcite rock dissolution, constructed wetlands, and/or biological sulfate reduction (Hedin et al., 1994; Johnson and Hallberg, 2005; Watzlaf et al., 2004). Active AMD treatment utilizes addition of alkaline chemicals or oxidants (Goodwill et al., 2019; Singer and Stumm, 1970) and ongoing energy inputs for pumping, mixing, and/or aeration (Coulton et al., 2003; Mitsch and Wise, 1998). There are several additional options for co-treating AMD with other waste streams, including the use of organic solid waste substrates or flowback water produced from hydraulic fracturing (Chang et al., 2000; He et al., 2016). Although these co-treatment options improve water quality, disadvantages exist including the need for construction of treatment infrastructure (e.g. wetlands or limestone beds) or perpetual process inputs (e.g. active treatment). These requirements present difficulties for AMD treatment in economically and/or geographically isolated areas.

A novel approach for AMD mitigation is co-treatment with municipal wastewater (MWW) in existing wastewater treatment plants (WWTPs). Co-treatment is the combination of AMD and MWW waste streams, turning one into a resource, best utilizing extra WWTP capacity, and further leveraging existing infrastructure and energy inputs. Declining industrial activity and urban population shifts has resulted in “shrinking cities” for some North American municipalities with historical industrial centers (Rybczynski and Linneman, 1999; Schilling and Logan, 2008). This population loss, combined with water conservation efforts has decreased overall domestic sewage production and increased financial stress on utilities (Faust et al., 2016). As a result, these WWTP have extra

treatment capacity (Dominguez and Gujer, 2006). Co-treating MWW with AMD makes use of this extra capacity and may ultimately improve MWW treatment, while simultaneously mitigating the ecological impact from AMD on receiving water.

Both AMD and MWW pose serious risks to the environment if inadequately treated. Eutrophication is a problem in surface waters, globally (Dodds and Smith, 2016; Smith, 2003). Nitrogen and phosphorus present in MWW can cause eutrophication in downstream receiving waters (Harper, 1992). Co-treatment offers WWTPs a low-cost nutrient management approach utilizing another waste stream. The addition of Fe-based coagulants is a relatively common approach to nutrient removal in these situations, and AMD co-treatment presents a primary beneficial use of this otherwise problematic waste (deBashan and Bashan, 2004). AMD discharges to surface waters also degrade water quality by acidification and increased metal loadings which pose risks to aquatic ecosystems (Azapagic, 2004; Gray, 1998). The co-treatment of AMD and MWW can remove metals from low pH AMD while also decreasing effluent biochemical oxygen demand (BOD) and Phosphorous (P) in higher pH MWW (Hughes and Gray, 2013a; Strosnider et al., 2013, 2011). AMD can also decrease fecal bacteria counts from a MWW discharge when mixed *in situ* (i.e. within a stream) under low-flow conditions (Kruse et al., 2019).

The effectiveness of passive MWW and AMD co-treatment utilizing specific, additional infrastructure has been quantified across several scales. Bench-scale treatment wetlands with clarification, biofilm media, and limestone beds have also effectively co-treated AMD and MWW by removing BOD and dissolved metals from the combined wastewaters (Strosnider and Nairn, 2010; Winfrey et al., 2010). In other bench-scale studies, sludge from an active AMD treatment plant was mixed with synthetic and raw

MWW effluent at several ratios to determine the potential for enhanced P removal, yielding over 90% P removal and residual P levels below 0.5 mg/L (Ruihua et al., 2011; Wei et al., 2008). Field-scale research has included the addition of AMD to an evaporation pond for MWW, which increased solution pH and removed metal and sulfate concentrations from the wastewaters during 18 months of monitoring (McCullough et al., 2008). A large pilot-scale aerobic wetland, one of the first attempts to treat an AMD discharge with poorly treated secondary MWW, removed Fe (> 60%) and BOD (> 30%) well beyond system design expectations (Johnson and Younger, 2006). The first full-scale co-treatment wetland provided evidence that water quality improved with co-treatment increasing BOD, $\text{NH}_3\text{-N}$, Fe, and total P removal during a four-year monitoring period (Younger and Henderson, 2014). Although successful, these examples of co-treatment still require establishment of new treatment infrastructure and do not adequately inform the feasibility of direct co-treatment within an existing WWTP.

The addition of AMD to any portion of a conventional activated sludge treatment system poses risks to the biological treatment phase, however, data quantifying these potential impacts is limited. An influx of AMD constituents (e.g. metals, trace organics) could impact microbial community survival, taxonomy, and/or oxygen utilization rates (Ong et al., 2010; Ren and Frymier, 2005; Yuan et al., 2015). Although Fe is a crucial element for growth in nearly all biological organisms, large fluxes of Fe can be detrimental to microorganisms (De Freitas and Meneghini, 2001). The use of Fe-based coagulants in activated sludge systems can impact microbial metabolism, decrease nitrification, and degrade floc formation due to elevated Fe(III) content (Clark et al., 2000). This decreased suspended solids removal is a function of excessive filamentous bacteria growth, a problem

that frequently plagues conventional MWW treatment facilities (Sezgin et al., 1978). Similarly, Fe(III) concentrations of ~100 mg Fe/L in activated sludge can inhibit overall microbial activity and nitrification (Philips et al., 2003). However, at lower Fe additions (25 mg Fe/L), microbial activity and nitrification were not inhibited but less stable flocs were observed (Oikonomidis et al., 2010). In a simultaneous nitrification, denitrification, and P removal process, high Fe(III) concentrations can decrease N removal, but this inhibition can be adapted to and recovered after four, 270-minute cycles (Jia et al., 2016). Furthermore, Deng and Lin (2013) demonstrated co-treating prior to an anaerobic biological treatment step can maintain system performance, completely remove PO_4^{3-} under certain conditions, increase alkalinity, and consistently decreasing COD by >60%.

Only one study has focused on AMD and MWW co-treatment in a conventional activated sludge system (Hughes and Gray, 2013b). Hughes and Gray (2013) examined several different options for co-treatment including (1) the addition of untreated AMD to aeration tanks, (2) the pretreatment of AMD by mixing with digested sewage sludge followed by sedimentation and then mixing in the aeration tank, and (3) the pre-treatment of AMD by mixing with screened MWW prior to treatment in the aeration tank. In all of these experiments, a synthetic AMD was made to simulate the chemistry from copper mines in Ireland (pH 3.6, Fe = 130 mg/L, Al=150 mg/L, and SO_4^{2-} = 1670 mg/L). Systems co-treating with MWW remained effective at removing metals and COD by precipitation and adsorption mechanisms in the activated sludge reactors. In the co-treatment experiments, the synthetic AMD was mixed with synthetic MWW at a 1:2 AMD:MWW volumetric ratio. Metal removal by adsorption was relatively high in all experimental configurations, averaging 52-84% for Al and 74-86% for Fe. Final effluent COD

concentrations were generally less than 50 mg/L for all treatment configurations but increased on the last sampling event in experiments where AMD was pretreated before addition to aeration reactors. This project concluded that co-treatment did not cause a significant decrease in, nor improve, system performance for the removal of COD, total organic carbon (TOC), or BOD compared to controls, but did improve P and metals removal. Additional work by Hughes and Gray (2012) used Activated Sludge Respiration Inhibition Tests (Organization for Economic Cooperation and Development Method 209) to show that activated sludge systems could adapt to and function with AMD additions as high as 50% by volume.

The strength of the AMD utilized in co-treatment systems may have major process implications. Many of the aforementioned studies examined co-treatment utilizing a narrow range of strong AMD (pH range 2-4.5), neglecting potential impacts when utilizing milder (pH >4.5) Class I AMD (as defined by Watzlaf et al., 2004). Class I AMD may make up >50% of discharges in the eastern United States (Herlihy et al., 1990), with the vast majority in Northern Appalachia (Watzlaf et al., 2004). Mild or circumneutral discharges are not a localized phenomenon and may also be found in the mid-western United States (Labrenz and Banfield, 2004), Southern Africa (Madzivire et al., 2011), the United Kingdom (Warrender et al., 2011), and certain regions of China (Feng et al., 2014). These mild AMD discharges may be more conducive for co-treatment having bulk water qualities (e.g., pH, alkalinity, etc.) more similar to MWW.

The small quantity of data on co-treatment with mild AMD in WWTPs leaves many unanswered questions regarding the physicochemical and biological processes within an existing WWTP. Also, the variability of AMD water quality leaves the opportunity for novel

co-treatment developments utilizing AMD of various water chemistry. The overarching objectives of this study were to quantify the water quality impacts of co-treating circumneutral AMD with secondary MWW MLSS and elucidate the underlying mechanisms. There are many locations within a WWTP where AMD could be added, however the presented study addresses mixing AMD post aeration basin and prior to secondary settling (Figure S1). Laboratory work included bench-scale experimentation with robust water quality analysis, in conjunction with water quality modeling. In order to fill known research gaps, specific project aims included: (1) assessing changes in overall water quality, (2) evaluating coagulation potential from AMD-sourced Fe, (3) demonstrating enhanced PO_4^{3-} removal, and (4) characterizing the impact on MWW microbial metabolism. Results of this study advance co-treatment towards potential full-scale adaptation within existing WWTPs.

2. Materials & methods

A graphical representation of the overall analytical procedure is shown in Figure S2.

2.1. Water quality and sampling

AMD was collected from an abandoned mining site near the core of a city with declining population and industrial activity (Johnstown, PA; see Figure S3). Historic water quality for the mild AMD includes a slightly acidic pH (average pH=6.1) and averages 85 mg/L of alkalinity, >1,000 mg/L of SO_4^{2-} , 206 mg/L of total Fe, 0.3 mg/L of total Al, and 1.9 mg/L of total Mn. The mild AMD has relatively low acidity, which is typical of AMD found in coal mining regions in eastern North America (Hedin et al., 1994). AMD samples were

collected immediately downstream from the AMD discharge pipe. This low-pH, high-Fe AMD source was selected due to its proximity to a situationally-relevant (i.e. shrinking cities) WWTP. MWW were collected from a conventional WWTP (average flow = 10 MGD) at the same time of AMD collection. Mixed liquor suspended solids (MLSS) was collected from the WWTP aeration tank effluent, prior to the secondary clarifiers and used to represent “MWW” samples. The MLSS samples were mixed to prevent the sludge from becoming anoxic. Raw AMD and MLSS (MWW) samples were collected headspace free in collapsible five-gallon polyethylene containers. Methods for examining the impacts on a microbial community are presented in Section 2.4.

2.2. Experimental design

All experiments were performed in mixed, square 2-L batch reactors (Phipps & Bird). Eight different sample matrices were tested. MWW MLSS was mixed with either AMD or deionized water (DI) at ratios of 1:25, 1:15, and 1:5 (AMD:MWW; DI:MWW) in addition to 100% AMD-only and 100% MWW-only as controls. Ratios were chosen based on practical estimates of extra treatment capacity. All experiments were performed in triplicate. Quality control experiments utilized DI water in place of AMD to address potential dilutive effects from AMD. Samples were mixed for five minutes at $G \sim 120 \text{ sec}^{-1}$ to simulate the two waste streams rapidly mixing in a pipe. They were subsequently allowed to settle for 30 min, representing final clarification (Standard Method 2710D, APHA, 2012). After settling, the top $\sim 1 \text{ L}$ of supernatant, representing a secondary settling effluent, was decanted into a borosilicate glass beaker. The supernatant beakers were placed on stir plates and mixed while sub-samples for further analysis were collected.

2.3. Supernatant analysis

The settled sludge blanket height was recorded prior to the supernatant being decanted. Supernatant pH values were determined immediately (Mettler-Toledo LE438 ATC probe/FiveEasy Plus FP20 meter). Sample turbidity was determined using a portable turbidimeter (Hach, 2100Q) following EPA method 180.1 (via Hach method 8195). Streaming current (a method for quantifying suspended particle surface charge *in situ*; (Dentel et al., 1989)) was determined using a laboratory charge analyzer (Chemtrac LCA-01).

COD was determined for each sample by the reactor digestion method using Hach low range COD vials according to Hach Method 8000. Vials were digested in a digital reactor block (Hach, DRB200) and analyzed using a UV-Vis spectrophotometer (Hach, DR6000). BOD was determined by the 5-day BOD test performed at 20 °C (Standard Methods 5210B). Three BOD bottles were collected per beaker at varying dilutions. Dissolved oxygen concentrations were collected using an optical BOD probe (YSI Pro Series) with a multiparameter meter (YSI Pro Plus).

Anion samples for NO_3^- , SO_4^{2-} and PO_4^{3-} were collected in amber glass vials, filtered through 0.45- μm nylon filters, and analyzed within 24 hours on an ion chromatograph (Dionex ICS-1100) with an AS18 column following EPA method 300.

Samples for solids content were collected in 1000 mL HDPE bottles and stored at ~4 °C for later analysis. Total solids (TS) were determined by evaporating 100 mL overnight for 10-12 hours in pre-dried and pre-weighed 150 mL Erlenmeyer culture media flasks at 103 °C (Standard Methods 2540). Total dissolved solids (TDS) were determined in a similar

manner with the exception that a 50 mL sample volume was filtered through 0.45- μ m nylon filters (Fisher).

Samples for Fe, Al and Mn were collected in metals-free Nalgene LPDE bottles and preserved to 2% with trace metal grade HNO₃. Fe, Al, and Mn were selected due to their relative geographic abundance in AMD discharges. For each beaker, metals concentrations were fractionated with various filter pore sizes to quantify the relative size distribution of resulting particles under each condition (Carlson et al., 1997; Goodwill et al., 2015). Fractionated particles were operationally defined as total, colloidal or dissolved. The total particulate metals were unfiltered and colloidal metals were filtered 0.20- μ m nylon filters, and each sample was collected in triplicate. Two samples per experimental water matrices (i.e. two for each tested ratio & control) were also filtered through 30 kDa ultrafiltration (UF) membranes inside a 200 mL nitrogen pressurized stirred UF cell (Amicon). Total metal samples were digested in a digestion/extraction microwave system (CEM, Mars 6) according to EPA method 3015A. Metals concentrations were then quantified using an inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific X-Series 2) measuring isotopes Fe-57, Al-27 and Mn-55. While Fe speciation was not quantified, thermodynamics at equilibrium under test conditions suggest the primary species to be Fe(III).

2.4. Cellular respiration

Cellular respirometric oxygen demand (i.e. respirometry) was used to assess the impact of AMD on the microbial community within an activated sludge system (Scaglione et al., 2008). Respirometer experiments compared the microbial oxygen uptake between a

control aeration mixed liquor sample to a co-treated sample containing synthetic AMD at a ratio of 1:15. Aeration tank mixed liquor samples (MLSS = 4,670 mg/L, data obtained from WWTP operations report at time of collection) were collected at the Mattabassett District Water Pollution Control Facility (Cromwell, CT), a conventional aeration MWW treatment facility. Synthetic AMD was generated in the lab to replicate the batch study AMD using ultrapure deionized water and dosed to an Fe content of 200 mg/L using a 1000 mg/L Fe standard solution (in 3% HCl) and initial pH adjusted to ~6 with NaOH and H₂SO₄ (Karapanagioti and Atalay, 1996).

Trials were performed in specialized, air tight 250mL sample bottles (Xylem WTW, MF45). Each bottle was equipped with a CO₂ absorbent quiver, filled with NaOH pellets (98%, Fisher Chemical) to absorb CO₂ gas during experimentation, and sealed with a calibrated WTW OxiTop-C measuring head. Each sample was run in triplicate. The samples were continuously mixed for 4 hours to simulate the hydraulic retention time of typical aeration tanks (Ten State Standards, 2014). Results were gathered using the OxiTop OC100 controller and data was reported in mg/L of BOD (Spanjers and Vanrolleghem, 1995).

2.5. Statistical presentation of data

All reported values represent the mean of triplicate experimental replicates. All error bars represent the 95% confidence interval (2 standard deviations (σ)), unless otherwise noted. Within each triplicate, any individual value that was more than 3 σ , or outside the 99.7% confidence interval (Pukelsheim, 1994) from the mean was considered an outlier.

2.6. Water quality modeling

Iron speciation, pH, PO_4^{3-} were modeled to further understand the impacts of co-treatment, and elucidate mechanisms underlying laboratory measurements. The influence of varying AMD acidity on pH was examined by calculating the alkalinity and total H^+ that would result from mixing AMD of several pH's with pH 6.7 MWW, under open-system carbonate buffering conditions (Stumm and Morgan, 1996), using Equation S5. Changes in PO_4^{3-} concentration were used to create an adsorption isotherm, in a manner similar to Yang et al. (2006). Experimental data was fitted to the Langmuir isotherm (see SI S5, Equation S7) where a high (>0.95) linear coefficient of determination would indicate adsorption as the primary mechanism. The resulting regression also allowed for the determination of the maximum adsorption capacity under tested conditions. It was assumed experimental mixing and settling was sufficient for the adsorption reaction to reach equilibrium. Fe speciation resulting from co-treatment was determined by combining applicable pK_s values (Stumm and Morgan, 1996) with empirical models for Fe stability and coagulation (Johnson and Amirtharajah, 1983). This allowed further assessment of dominate coagulation mechanisms.

3. Results & Discussions

3.1. Supernatant water quality

Figure 1 reports impacts of AMD's on general supernatant water quality characteristics. Co-treating had little influence on pH (Figure S4). All pH values were above 6.0, a typical Environmental Protection Agency (EPA) National Pollutant Discharge Elimination System (NPDES) permit limit for MWW facilities (Environmental Protection Agency, 2019; EPA Region 3, 2016). The negligible pH change in this study is attributed to

302 relatively low acidity and high pH of the AMD. Measured results closely follow the modeled
 303 pH (Figure S4).

304
 305 Figure 1: Sample turbidity (bars) and streaming current surface charge (points). Dashed
 306 line represents trend between experimental data points.

307 Higher strength AMD than the matrix used in this work could still be feasible in co-
 308 treatment. Alkalinity and pH modeling results show that co-treating at 1:25 with AMD of a
 309 pH as low as 2.7 would still leave MWW (with a similar pH and alkalinity to experimental
 310 MWW) effluent above discharge minimums of pH 6.0 (Figure S4). Mild AMD with a pH
 311 similar to that of AMD used in this study could theoretically be used up to AMD:MWW
 312 ratios beyond 1:1 whereas co-treatment with stronger AMD of pH 3.0 could likely not
 313 exceed 1:25. Moderate strength AMD at a pH of 4.0 could still be feasible for co-treatment
 314 at ratios up to 1:3 where the mixed pH would remain above the target minimum, pH 6.0.
 315 These modeled results are in agreement with co-treatment performed with lower pH AMD
 316 (Deng and Lin, 2013).

No significant difference in AMD nor DI supernatant turbidity relative to the MWW-only (MLSS) control was noted (Figure 1). Although all co-treated turbidity values were statistically similar to each other (within 2σ , see section 2.5), the averages appear to trend upwards with higher values of AMD resulting from the relatively high turbidity of the AMD-only control. The turbidity trends of the co-treated trials agree with predictions from a simple mass balance on TSS (turbidity of AMD added with turbidity of MWW at each ratio, Equation S7). The similarity of settled turbidity values across all experiments indicates a stable colloidal suspension.

The addition of positively charged hydrolyzed Fe (and Al) species from AMD could serve as a coagulant and destabilize particles in the co-treated mixture via charge neutralization and or “sweep-flocculation” mechanisms (Davis and Edwards, 2014). However, co-treatment had no influence on particulate surface charge (Figure 1) which indicates that charge neutralization was not significant. No change of particulate surface charges can be explained by several factors. The experimental water chemistry (pH and Fe concentration) was not favorable for adsorption-destabilization (charge neutralization) mechanisms, as shown in Figure S5 (Johnson and Amirtharajah, 1983). Rather, experimental conditions were more likely to have encouraged sweep flocculation, where the kinetic energy of larger falling particles is adequate to overcome electrostatic surface repulsive forces of suspended particles (Gregory and O’Melia, 1989). Additionally, NOM in MWW exhibits coagulant demand, which likely dominates surface charge neutralization, making destabilization even less favorable (Stumm and O’Melia, 1968). These elevated concentrations of organic matter require increased coagulant doses compared with what would typically be required to achieve destabilization (Fettig and Ratnaweera, 1993).

Furthermore, the presence of PO_4^{3-} likely impacted charge neutralization potential. Fe(III), and other metals, have a strong affinity for available PO_4^{3-} , and the majority of PO_4^{3-} would need to be adsorbed and precipitated before Fe(III) would begin to destabilize suspended MWW colloids (Tenney and Stumm, 1965). Higher AMD:MWW ratios would theoretically provide increased particle destabilization, however these ratios were not studied experimentally due to the perceived practical limits on WWTP capacity. pH modeling demonstrates the addition of higher strength AMD will further suppress pH (SI S4), shifting water chemistry into regions favorable for charge neutralization (Figure S5).

3.2. Supernatant solids characterization

Sludge settling was not significantly impacted by AMD co-treatment, with the exception of the highest AMD addition ratio (Figure 2A). The highest AMD dose improved settling by 20% over MWW-only, while other co-treatment conditions showed negligible improvement. No settling is reported for the AMD as the discharge contained only small and dissolved solids. The significant settling improvement noted at the highest AMD ratio was not seen with the same significance in DI water at that same ratio, suggesting improvement was not a function of dilution. Improved settling with increasing AMD ratio, despite little change in surface charge, demonstrates sweep flocculation as the controlling particle destabilization mechanism, in agreement with coagulation modeling (Figure S5).

Figure 2: (A) Recorded sludge height in mL after 30 min of settling; (B) Experimentally determined total solids remaining in supernatant; (C) Experimentally determined dissolved solids remaining in supernatant

Co-treatment also had little influence on TS and TDS content (Figure 2B,C). The AMD-only control contained nearly triple the amount of TS found in the MWW-only control. Yet even in the AMD 1:5 samples the TS was only slightly higher (74 compared to 59 mg/L in the MWW-only control) and the TDS were nearly identical (59 vs 54 mg/L). Although TDS generally represents a minimal threat to aquatic organisms (when TDS < 1,000 mg/L, per Chapman et al., 2000), TDS concentration remains a significant water

quality consideration. A relatively constant TDS concentration suggests AMD addition does not significantly increase the effluent ionic strength, which is proportional to TDS (Kemp, 1971; Langelier, 1936). If the TDS and subsequent ionic strength were to have increased, this could have decreased adsorption of PO_4^{3-} onto Fe(III) and promote destabilization (break up) of aggregates (Zhang et al., 2010; Zita and Hermansson, 1994). MWW can be co-treated with high volumes of AMD without TDS being of concern.

Although some changes in solids concentration were experienced, both the TS and TDS concentrations in all co-treatment trials were lower than what was predicted by mass balance (Tables S1 & S2). AMD 1:25 and 1:15 trials had 15% fewer TS while the AMD 1:5 had just ~10% less. A decrease in supernatant solids was likely a function of improved coagulation by sweep flocculation, as discussed in section 3.1. An increased concentration of settling solids would result in increased resultant sludge, in agreement with the minimal changes seen in sludge blanket height (Figure 2A). TDS were proportional to the amount of AMD added. As the AMD ratio increased, the amount of post-settling TDS was 9% to 24% less than predicted by mass balance calculations (e.g. 10-15 mg/L TDS). The majority of this apparent loss in TDS corresponds to the mass of PO_4^{3-} removed via adsorption onto Fe particles (see Section 3.4).

The TSS values were not directly measured in this study, but approximated by calculating the difference between the TDS and TS values. The WWTP influent TSS, obtained from the facilities DEP/EPA reports, generally contains 166 mg/L. All calculated experimental TSS concentrations were below 15 mg/L, within a typical NPDES permit weekly TSS discharge limits of 40-50 mg/L (Environmental Protection Agency, 2019; EPA Region 3, 2016). These results demonstrate co-treatment positively impacted MWW

effluent solids and retained TSS removals (compared to influent) of over 90%. It is important to note TSS removal may have been influenced by experimental mixing conditions. The velocity gradients generated during rapid mixing ($G > 100 \text{ sec}^{-1}$) could have caused orthokinetic flocculation (i.e. fluid shear), an increase in collision frequency between suspended particles, resulting in larger flocs (Han and Lawler, 1992; Teh et al., 2016). The noted improvement in TSS removal was likely a function of both orthokinetic flocculation and differential sedimentation (i.e., sweep flocculation).

3.3. Co-treatment impacts on oxygen demand

Co-treatment had minimal impact on both BOD and COD of the MWW (Figure 3). The COD remained relatively constant under all conditions. However, the average COD in all AMD experiments was lower than theoretically determined values (Table S3, Equation S3) by ~10%. The slight loss of COD suggests that there was some removal during the co-treatment process. COD removal is likely a mechanism of either microbial-mediated aggregation of organics resulting in bioflocculation, or through adsorption of biomaterial onto Fe (Choo and Kang, 2003; Jimenez et al., 2007). BOD results were similar (Figure 3). The BOD between all samples was similar relative to the MWW-only control, meaning co-treatment did not further increase oxygen demand. This is an important operational consideration as BOD is one of the most critical effluent water-quality parameters.

Figure 3: Oxygen demand remaining for each sample after treatment

3.4. Influence on ion concentrations

Co-treated SO_4^{2-} concentrations are reported in Figure S8. The SO_4^{2-} concentrations in the supernatant increased by 75% in the 1:25 treatment, 127% in the 1:15 treatment, and 370% in the 1:5 treatment exceeding 260 mg/L. However, this increase is not problematic as SO_4^{2-} concentrations are only slightly over the 250 mg/L allowable limit for drinking water (40 CFR 143.3) and significantly below the >2,000 mg/L value determined necessary to be toxic to several freshwater fish (Soucek and Kennedy, 2005). If the AMD is added prior to the biological treatment phase it is possible that increased SO_4^{2-} reduction would take place and produce lower SO_4^{2-} effluent concentrations (Lens et al., 1995). SO_4^{2-} reducing bacteria have been shown to survive and adapt to high oxygen environments such as in activated sludge systems and enable SO_4^{2-} reduction (Kjeldsen et al., 2004). However, this does not apply to all MWW microbe populations as not all activated sludge

environments are conducive for sulfate reduction (Schramm et al., 1999). One potential issue that could arise from increased SO_4^{2-} reduction is the resultant sulfide (S) concentrations that can disrupt floc formations and Fe-based coagulation processes by the formation of FeS (Nielsen and Keiding, 1998).

Results from PO_4^{3-} analysis demonstrate the potential of co-treatment to significantly decrease PO_4^{3-} (and total P) concentrations in MWW (Figure 4A). Although PO_4^{3-} exists as inorganic and organic forms in MWW, the non-speciated total PO_4^{3-} was deemed sufficient for this study as typical MWW effluent discharge limits are set in terms of total P. All three AMD ratios exhibited PO_4^{3-} removal, with the 1:15 condition averaging ~84% decrease and the 1:5 trials averaging >97% decrease, significantly improved over the MWW control. DI trials showed no improvement over dilution alone. These results support the use of AMD co-treatment as a lower cost alternative for tertiary treatment focused on P-removal, especially in shrinking cities or other economically and geographically disadvantaged areas. Decreasing P discharges into water where it is a limiting nutrient is of increasing concern, globally, as a strategy to control harmful algal blooms and eutrophication (Alexander et al., 2008; Anderson et al., 2008).

Figure 4: A) Total P concentrations remaining in each sample supernatants, measured as mg/L PO_4 on IC. Dashed line represents trend between experimental data points B) Langmuir isotherm behavior of experimental data, demonstrating adsorption mechanism of P removal. Further explanation in SI S5.

PO_4^{3-} removal closely follows Langmuir isotherm behavior. The relative linearity ($R^2 = 0.979$) confirms that PO_4^{3-} adsorption unto *in situ* AMD-generated Fe oxides is the mechanism for nutrient removal in co-treatment (de-Bashan and Bashan, 2004; Kavanaugh et al., 1978). PO_4^{3-} removal via adsorption further explain the streaming current and settling results discussed in section 3.1, as PO_4^{3-} adsorption unto Fe(III) drastically impedes coagulation (Tenney and Stumm, 1965). Furthermore, the Langmuir relationship quantified the maximum adsorption capacity of the co-treatment system as 0.15 mg P per mg Fe added (0.46 mg PO_4^{3-} /mg Fe; see SI S5).

3.5. Supernatant metals concentrations

Total Mn and Al in both the AMD and secondary MWW were low, making AMD Fe the primary constituent of concern. Total Fe in AMD was 147 mg/L while there was little Fe in the raw MWW (< 2 mg/L). Settled, total Fe increased with increasing ratio to a maximum of 21 mg/L (Figure 5). The majority of Fe was operationally defined as dissolved, comprising 57% and 73% of the total Fe content in the AMD 1:15 and AMD 1:5, respectively. This is similar to the raw AMD in which over 80% of Fe passed through the UF membrane.

Figure 5: Fractionated iron content showing operationally defined particulate, colloidal and dissolved Fe. Bars represent the mean value for each of the three fractions

The amount of dissolved Fe is orders of magnitude higher than what would be thermodynamically expected from an Fe(III) solubility diagram at pH ~6.5 (Figure S5), suggesting that operationally defined “dissolved” Fe is actually amorphous nanoscale

Fe(III). This is supported by the stable colloidal conditions demonstrated by the streaming current results (Figure 1, surface charge), where aggregation is expected to be quite limited. The presence of PO_4^{3-} during Fe precipitation can result in particles operationally defined as dissolved despite thermodynamic predictions to the contrary (Jiang et al., 2015).

Mass balance calculations showed a significant portion of the Fe gravimetrically separated with the sludge (see SI S7, Table S4). The fraction of total Fe removed from the bulk solution ranged from ~50% (AMD 1:25) down to ~30% in the AMD 1:5. The AMD 1:15 ratio settled out approximately 38% of Fe added. Although AMD could have contributed insoluble Fe(II) to the system (Watzlaf et al., 2004), this was unlikely under experimental conditions. Since the solutions were open to the atmosphere, rapid mixed for several minutes, and under circumneutral pH, the oxygenation of Fe(II) to Fe(III) would have quickly proceeded to equilibrium ($k = 1.5\text{--}3.0 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$) (Davison and Seed, 1983; Moses and Herman, 1989; Stumm and Lee, 1961). Under equilibrium conditions at experimental pH, both Fe(II) solubility (O'Melia, 1973) and Fe redox potential (pE) indicate high percentages of Fe(II) were unlikely. This low percentage of Fe settling with MWW sludge was more likely a result of suspended, nanoscale Fe particles. The approximate Stoke's law terminal settling velocities of these small ($< 0.2 \text{ }\mu\text{m}$) particles are no faster than 0.6 cm/day (assuming $T = 15 \text{ }^\circ\text{C}$, $\rho_{\text{particle}} = 4250 \text{ kg/m}^3$) meaning an operationally longer settling time would not significantly improve Fe concentrations in effluent. Although it is uncommon for WWTPs to have Fe discharge limits, removal of Fe is important to maintain high effluent quality and decrease the total Fe load on the receiving water body; however, the hypothetical co-treatment effluent Fe loading from supernatant

produced in this study represents an order of magnitude improvement over an unabated AMD discharge.

3.6. Co-treatment impact on microbial activity

Co-treating MWW with AMD can impact the metabolism of activated sludge microbes. In respirometric experiments where AMD was mixed with MWW (MLSS), BOD consumption rates were impeded compared to trials where no AMD was added (Figure 6). The respirometer reactors with no AMD added achieved a higher realized-BOD consumption over the 4-hr period and consumed oxygen at a faster average rate than those with AMD. There is also a much larger variance in the co-treatment reactors relative to the narrow variation in the MLSS-only controls. Reactors with AMD consumed oxygen at a slower rate initially, likely due to the stress induced by a perturbation in water quality. Over the four hours, the MWW samples consumed oxygen (O_2) at an average rate of 3.5 mg/L of O_2 per hour [$(O_2)/hr$] while the co-treated reactors consumed at only 1.9 (O_2)/hr. In the first hour, oxygen consumption was nearly three times faster in reactors with only MWW (i.e., 3.7 (O_2)/hr in MWW reactors vs 1.2 (O_2)/hr in AMD:MWW reactors). However, the difference between the two sample rates began to decrease over time. During the last hour the co-treated samples consumed O_2 at a rate similar to the MWW samples, 5.5 vs 4.9 (O_2)/hr. The 5.5 (O_2)/hr is also the highest average hourly rate exhibited by any sample. This suggests that the bacteria in co-treated samples had begun to acclimate. Acclimation time at full-scale would be impacted by hydraulic residence time (4-8 hours), solids retention time (3-15 days (Metcalf & Eddy et al., 2013)), and sludge recycle rates.

Figure 6: Respirometric BOD results, markers represent the mean value for each sample type, and dashed line represent the corresponding highest and lowest measured value at each point

Respirometric results also inform full-scale adaptation. Co-treating with AMD at WWTPs with longer mean cell residence times would better accommodate cellular acclimation upon initiation of AMD addition. The increased O_2 consumption after 200 minutes in Figure 6 suggest microbial community adaptation to the addition of AMD, without long-term negative impacts. Gradual increases in AMD:MWW ratio may improve microbial adaptation. Although the reaction times (days compared to hours) and AMD differed (Fe dominant versus various metals in excess), MWW bacteria in experiments by Hughes and Gray (2012) behaved similarly, requiring an initial acclimation period after addition of AMD with very different quality. Further assessment of microbial community adaptation to AMD inputs over longer time scales should be a focus of future research.

4. Conclusions

This work addressed primary knowledge gaps related to co-treatment of AMD in existing WWTPs. Co-treatment resulted in a stable colloidal suspension, and conditions where differential settling is the primary mechanism for particle aggregation. Co-treatment led to improved settling when the highest ratio was evaluated, despite extant repulsive surface charges. However, this condition also yielded the highest effluent Fe loading. Resulting supernatant Fe was nanoscale. Over 90% removal of phosphate was demonstrated, and described by Langmuir adsorption isotherm unto iron oxides. AMD co-treatment represents a novel form of nutrient removal from wastewater effluents. Impact on other studied wastewater quality parameters (TS, BOD, COD) broadly indicated insignificant impact. In this way, co-treatment also represents a novel form of AMD disposal. Introduction of AMD into activated sludge communities caused a short-term decrease in oxygen consumption rate, with recovery noted after several hours, suggesting adaptation. Further research on microbial community impacts is required. Ultimately, the understanding of physio-chemical processes and other water quality results in this work support the feasibility of full-scale co-treatment, which may be especially advantageous to communities with declining MWW production.

Declaration of Interests

None.

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