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FEASIBILITY ASSESSMENT OF ACID MINE DRAINAGE AND MUNICIPAL WASTEWATER CO-TREATMENT

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FEASIBILITY ASSESSMENT OF ACID MINE DRAINAGE AND MUNICIPAL WASTEWATER CO-TREATMENT

BY

CHARLES D. SPELLMAN JR.

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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UNIVERSITY OF RHODE ISLAND

2020

MASTER OF SCIENCE THESIS

OF

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2020

ABSTRACT

Acid mine drainage (AMD) and municipal wastewater (MWW) are two constituents that pose major environmental risks to surface waters if left untreated. Modern MWW treatment facilities are capable of removing organics and pathogens from wastewater before being discharged into surface waters. Although proven methods also exist for treating AMD, it is commonly untreated. Over the past few years, researchers have illuminated new approaches to simultaneously co-treat AMD and MWW. However, there is little research on combining the two waste streams within a conventional wastewater treatment plant for co-treatment. Co-treatment could facilitate metal removal from AMD while also improving MWW treatment processes. The city of Johnstown, PA hosts a unique opportunity for co-treatment with an urban AMD discharge in relative proximity to the city's MWW treatment facility.

AMD often possess a high iron (Fe) content, which has the potential to benefit or disrupt MWW treatment processes. One potential risk of adding AMD is the amount of Fe that could end up in the facility's solids (sludge) handling processes. Adding AMD to Johnstown's MWW treatment facility at a 20% mixing ratio (the maximum AMD:MWW ratio predicted from the recorded data) could result in as much as 10 grams of Fe per kilogram of dry, dewatered sludge. This amount of Fe would fall in the low end of the EPA reported range for Fe content in dry solids. In addition, the published literature suggests the addition of Fe could be beneficial. The additional Fe content could help increase the sludge dewatering efficiency, improve the stabilization process, reduce odors produced from MWW solids, and raise the quality and marketability of the resulting biosolids currently used for land application.

Adding AMD after the biological treatment process and before the final clarification step will likely have little to no impact on MWW treatment. AMD addition likely offers improved final clarification of effluent and holds the lowest risk of disruption of the biological treatment phase. Our laboratory study examined the impact of co-treatment using raw Johnstown AMD and MWW samples at three mixing ratios with increasing amounts of AMD (1:25, 1:15, and 1:5 AMD to MWW). Results showed that co-treatment increased sludge settling at high ratios and significantly reduced effluent phosphate concentrations without impacting effluent pH, biochemical oxygen demand, or total solids. However, the effluent Fe and sulfate ($SO_4^{2-)}$ content did increase.

Co-treating AMD and MWW does have the potential to influence microbial activity in MWW treatment facilities. At the start of respiration rate trials, microbial respiration rates were lower than treatments without AMD, which suggests that AMD additions could influence biological processes in conventional wastewater treatment plants. However, as these trials progressed, the respiration rates eventually converged, suggesting that microorganisms in conventional wastewater treatment plants ought to be able to adapt to conditions with AMD.

ACKNOWLEDGMENTS

I want to first thank my major professor Joseph Goodwill for his endless support, assistance and relentlessness to push this research to be the best it could be. This work would not be possible without all the support from members of the URI Water for the World environmental engineering research lab. Furthermore, I would like to thank Dr. William Strosnider of the University of South Carolina (previously at Saint Francis University) for providing me the opportunity to work on this project and his support during the development of this thesis from project initiation through research defense. Additionally, I want to thank Dr. Travis Tasker of Saint Francis University for all of his support on this project. This thesis would not have been possible without the endless support and guidance from Dr. Goodwill, Dr. Strosnider, and Dr. Tasker. I want to extend gratitude to the entire Saint Francis University Environmental Engineering Department for the use of their facilities and the assistance received from numerous faculty and undergraduate students during this project. I would also like to thank Dr. Vinka Oyanedel-Craver for her support joining Dr. Goodwill and Dr. Strosnider on my thesis committee, as well as Dr. Thomas Boving for chairing my defense. Lastly, I want to thank the Johnstown Dornick Point Wastewater Treatment Plant, the Mattabassett District Water Pollution Control facility for supplying access to necessary samples for this project.

PREFACE

This thesis is written and organized in manuscript format in accordance with the University of Rhode Island Graduate School guidelines. The thesis is divided into two distinct chapters, each an independent manuscript. Chapter 1 is a manuscript that has been submitted to *Environmental Pollution* entitled *Abatement of Circumneutral Mine Drainage by Co-treatment with Secondary Municipal Wastewaters* with authors Charles Spellman Jr, Travis L. Tasker, William H.J. Strosnider, Joseph E. Goodwill. Chapter 2 is also a manuscript, in preparation for submission to *IWA Water Science & Technology*, entitled *Implications of Mine Drainage Metals Addition on Waste Activated Sludge Processing & Disposal: A Brief Review* with the same aforementioned authors.

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CHAPTER 1

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

by

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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 simultaneous 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 (de-Bashan 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; William H. J. Strosnider et al., 2011; Strosnider et al., 2013). 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, NH_3-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 $G \sim 120\ sec^{-1}$ 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 ~1 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-µm 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 HNO_3. 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-µm 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 H_2SO_4 (Karapanagioti and Atalay, 1996).

Trials were performed in specialized, air tight 250mL sample bottles (Xylem WTW, MF45). Each bottle was equipped with a CO_2 absorbent quiver, filled with NaOH pellets (98%, Fisher Chemical) to absorb CO_2 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 1.1 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 relatively low acidity and high pH of the AMD. Measured results closely follow the modeled pH (Figure S4).

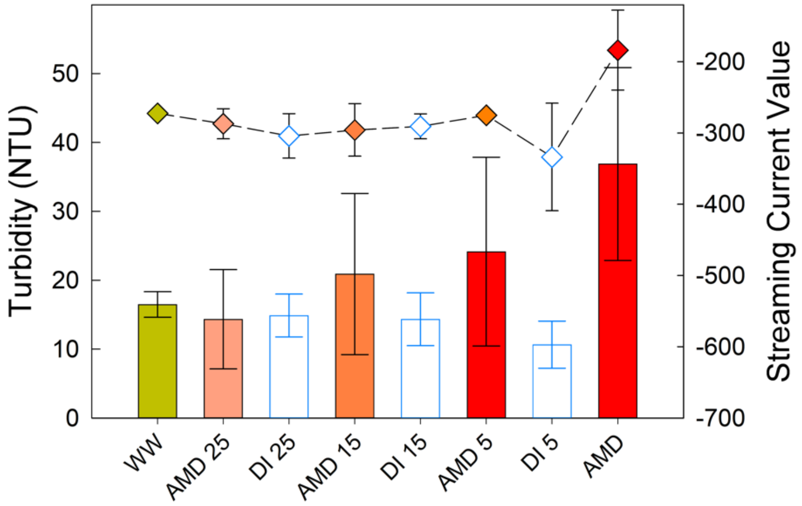

Figure 1.1: Sample turbidity (bars) and streaming current surface charge (points). Dashed line represents trend between experimental data points.

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

No significant difference in AMD nor DI supernatant turbidity relative to the MWW-only (MLSS) control was noted (Figure 1.1). Although all co-treated turbidity values were statistically similar to each other (within 2 σ, 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 1.1) 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 1.2A). 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).

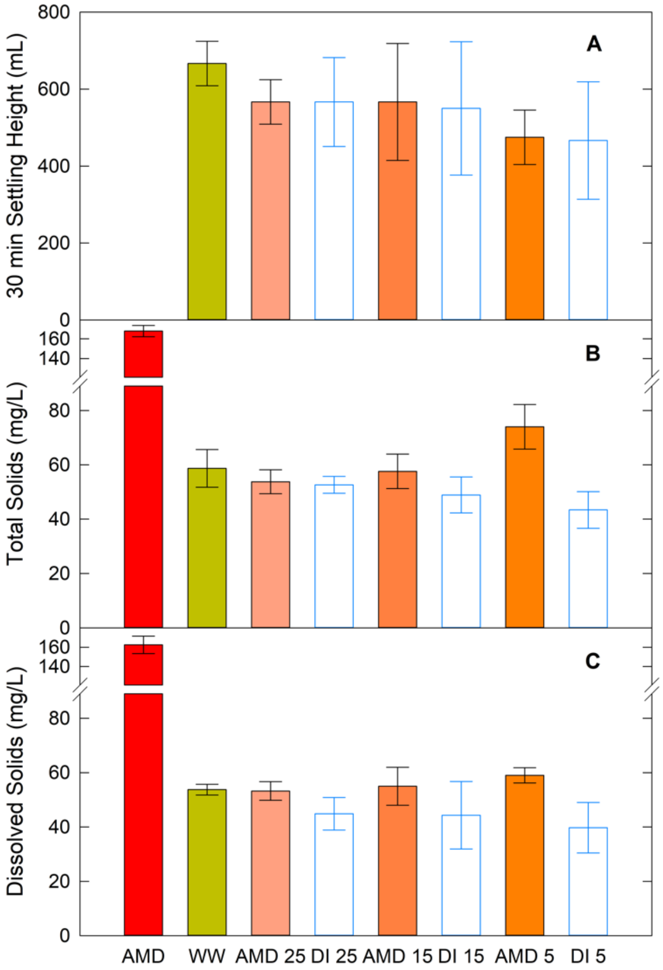

Figure 1.2: (A) Recorded sludge height in mL after 30 min of settling; (B) Experimentally determined total solids remaining in supernatant; (C) Experimentally determined dissolved solids remaining in supernatant

Co-treatment also had little influence on TS and TDS content (Figure 1.2B,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 S2 & S3). 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 1.2A). 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 ($G > 100$ 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 1.3). The COD remained relatively constant under all conditions. However, the average COD in all AMD experiments was lower than theoretically determined values (Table S4, 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 1.3). 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.

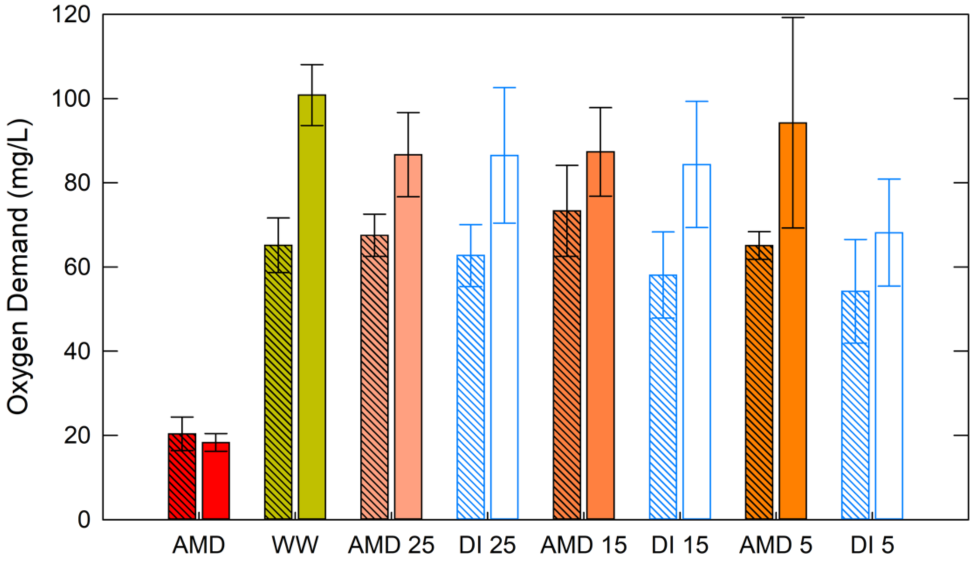

Figure 1.3: Oxygen demand remaining for each sample after treatment

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 1.4A). 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).

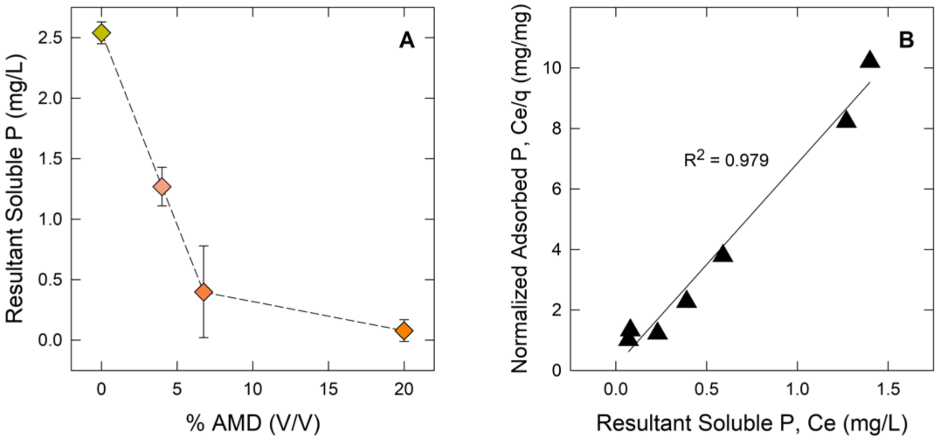

Figure 1.4: A) Total P concentrations remaining in each sample supernatants, measured as mg/L PO_4 on IC. Dashed line represents trend between experimental data points B) Langmuir isotherm behavior of experimental data, demonstrating adsorption mechanism of P removal. Further explanation in SI S5.

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). However, it is important to note that the presented data generally does not fit Freundlich isotherm behavior. This is likely due to the relatively-low initial mass and complete removal of PO_4^{3-}, suggesting there may be further PO_4^{3-} adsorptive capacity available and only the linear portion of a Freundlich curve was examined in this study.

Future research with significantly increased initial PO_4^{3-} is needed to determine the true fit of co-treatment adsorption to Freundlich behavior.

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 1.5). 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.

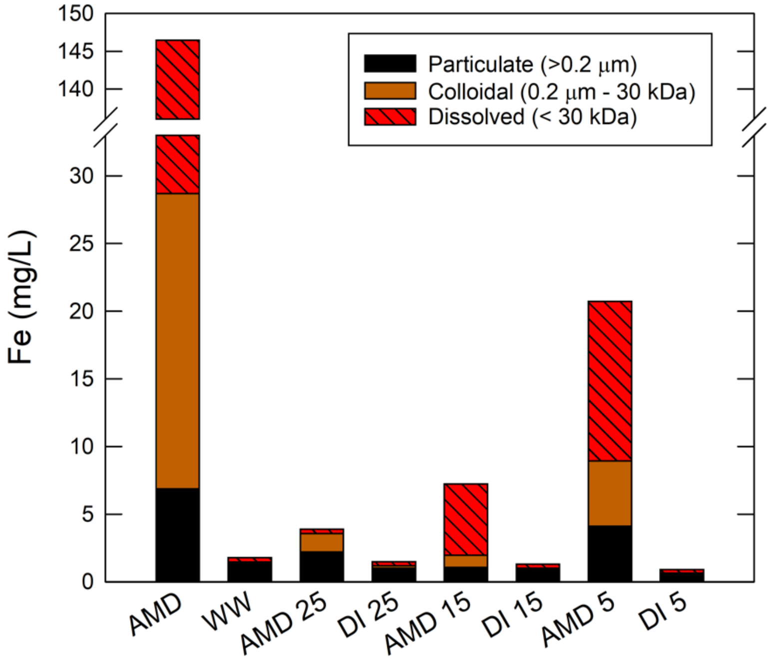

Figure 1.5: Fractionated iron content showing operationally defined particulate, colloidal and dissolved Fe. Bars represent the mean value for each of the three fractions

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 S5). 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 ($k = 1.5\text{-}3.0 \times 10^{13}\ M^{-2}\ atm^{-1}\ min^{-1}$) (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 µm) particles are no faster than 0.6 cm/day (assuming $T = 15\ °C$, $\rho_{particle} = 4250\ kg/m^3$) 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 1.6). 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. The addition of AMD diluted reactor biomass concentration by <7% compared to control, and this difference was assumed to be negligible. 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.

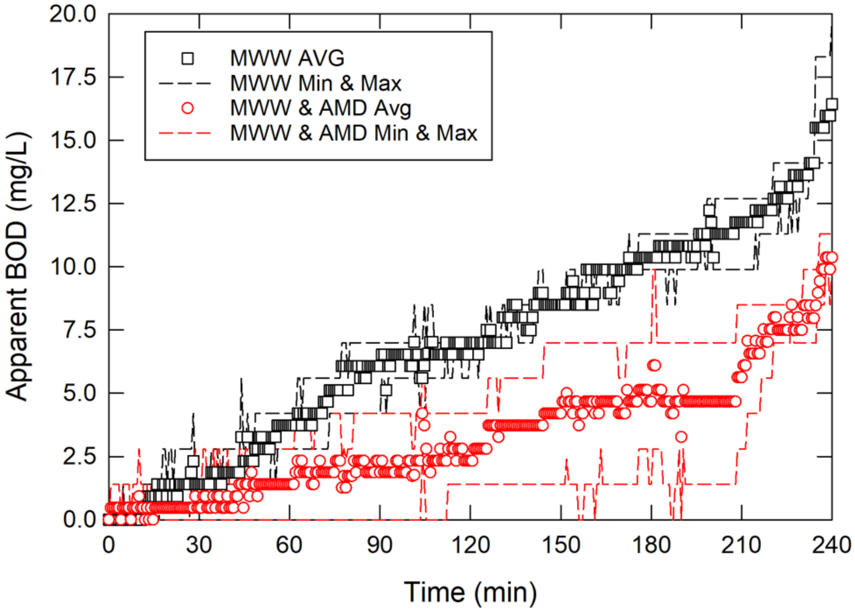

Figure 1.6: Respirometric BOD results, markers represent the mean value for each sample type, and dashed line represent the corresponding highest and lowest measured value at each point

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 1.6 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.

CHAPTER 2

“Implications of Mine Drainage Metals Addition on Waste Activated Sludge Processing & Disposal: A Brief Review”

by

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Introduction

Historic global industrialization has engendered a plethora of legacy pollution issues, including acid mine drainage (AMD). AMD formation occurs when sulfide-containing minerals, such as pyrite (FeS_2), in or around an ore deposit are exposed to oxygen and water via mining disturbance (Younger et al., 2002). The oxidation reaction can be catalyzed by a variety of environmental factors, including the presence of *Acidithiobacillus* bacteria (Younger et al., 2002). The resulting discharges can be characterized by high acidity due to release of hydronium ions during oxidation, and contains sulfate along in addition to a variety of dissolved metals including iron (Fe), aluminum (Al), manganese (Mn), copper (Cu), zinc (Zn), and lead (Pb) (Evangelou and Zhang, 1995; Jacobs et al., 2014; Younger et al., 2002). Drainage pollutants are not limited to common metals, but may also contain a variety of trace elements such as arsenic (As), silver, barium, selenium, tin, and vanadium (Strosnider et al., 2014; W. H.J. Strosnider et al., 2011).

AMD abatement can be obtained by both passive (e.g. limestone dissolution, engineered wetlands) and active (e.g., chemical addition) treatment approaches (Hedin et al., 1994; Johnson and Hallberg, 2005; Watzlaf et al., 2004). A recent novel approach has been to combine the AMD with other waste streams such as organic solid waste substrates, agricultural slurry, or fracking flowback water (Chang et al., 2000; He et al., 2016; Hughes et al., 2013). However, perhaps the most intriguing and well-documented combined treatment approach is co-treatment with municipal wastewater (MWW). AMD co-treatment enables the unique potential to enhance MWW treatment processes, including improved colloid destabilization (i.e coagulation) during metal hydrolysis (Metcalf & Eddy et al., 2013) precipitative removal of biochemical oxygen demand (i.e. "enhanced coagulation", Edzwald and Tobiason, 1999), increased nutrient removal by phosphate adsorption onto metal hydroxides (Ruihua et al., 2011), and enhanced inactivation of fecal coliforms (Winfrey et al., 2010). Although successful co-treatment has been noted in primarily passive systems (e.g. Johnson and Younger, 2006; McCullough et al., 2008; Strosnider and Nairn, 2010) effective co-treatment has also been demonstrated in more conventional MWW treatment scenarios (Deng and Lin, 2013; Ruihua et al., 2011; Wei et al., 2008). In a comprehensive bench scale examination of co-treatment, Hughes and Gray (2013b, 2013a, 2012) demonstrated improved phosphate adsorption, AMD metals (Fe & Al) removal, decreased effluent COD concentrations, and concluded co-treatment should not degrade activated sludge system performance.

Even though some success has been documented, the limited quantity of data on co-treatment leaves many research gaps regarding feasibility in existing wastewater treatment plants (WWTP). This uncertainty prohibits the potential for full scale adaptation. A noticeable literature gap exists concerning the impact AMD co-treatment could have on MWW facilities solids handling processes and subsequent solids disposal. The solids handling processes in a WWTP are equally important for protection of environmental and public health as the liquid-phase treatment steps. Although prohibitive factors are possible, the opportunity for AMD addition to support solids handling processes and improve disposal quality also exists. The objective of this mini-review is to project the potential impacts of Al and Fe from

AMD on MWW co-treatment solids handling and disposal processes by assessing existing information from previous peer-reviewed works.

Review Methodology

No known prior work has assessed the impact of AMD addition to MWW solids handling systems, but a variety of literature exists that discusses the role of AMD-related metals, primarily Fe and Al, in waste activated sludge. To identify relevant past research that examined metals within MWW solids, this literature review covered peer-reviewed sources. Sources deemed valuable were located through Google Scholar searches or extracted from bibliography sections in relevant textbooks. Keywords used (alone and in various combinations) in searches to locate literature included, but were not limited to, “activated sludge”, “trace metals”, “acid mine drainage”, “iron”, “aluminum”, “metal hydroxides”, and “sludge handling”. There was no bias towards certain publications and all works were reviewed equally. It is noted that, due to limited prior studies, the majority of the works cited were published prior to 2010, with very few sources published within the last five years. However, all cited studies were screened via the Scopus database to ensure the cited information was the most recent and relevant. Textbooks were also referenced for general information on the wastewater treatment process.

Review Results

It is not uncommon for metals, especially Fe, to appear in MWW solids in substantial amounts. Typical concentrations of Fe in biosolids have been reported to range from 1 to 300 g per dry kilogram of solids, with little information on Al and Mn

(Environmental Protection Agency, 2009). These metals are generally of little concern for WWTPs as they are relatively unregulated in sludge end products. Neither Fe nor Al content in processed sludge is currently regulated as a pollutant for land application or landfilling (U.S. Code of Federal Regulations Title 40, Part 503). These regulations contain no explicit mention of either Fe or Al (as of Jan. 17, 2020). Fe and Al are also not regulated for sludge land application in the European Union (European Union Directive 86/278/EEC). Generally, increasing the metals concentrations in a facilities secondary processes may have overall benefits for the WWTP. Elevated Fe and Al concentrations in sludge have been correlated with lower COD concentrations in plant final effluents (Park et al., 2006). Improved effluent water quality is a primary aim for a WWTP, but Al and Fe addition by co-treatment will likely benefit other MWW treatment processes, such as solids handling.

Co-treatment for Conditioning & Improved Dewatering

Introduction of increased Fe and Al concentrations from AMD could improve dewatering during co-treatment, in the same manner Al and Fe salts that undergo hydrolysis are used for sludge conditioning and coagulation of suspended particles (Davis and Edwards, 2014; Novak, 2006). The metals can improve dewatering by increasing coagulation of sludge particles (Novak, 2006). This in turn decreases raw sludges specific resistance to filtration (SRF) and lowering the amount of "bound water" within the sludge, thus reducing the amount of time needed for dewatering (Katsiris and Kouzeli-Katsiri, 1987). For example, increasing the presence of Fe(III) decreases the percent of water bound within sludge. Yu et al (2016) demonstrated a strong negative curvilinear correlation between Fe(III) and sludge water (Figure 2.1).

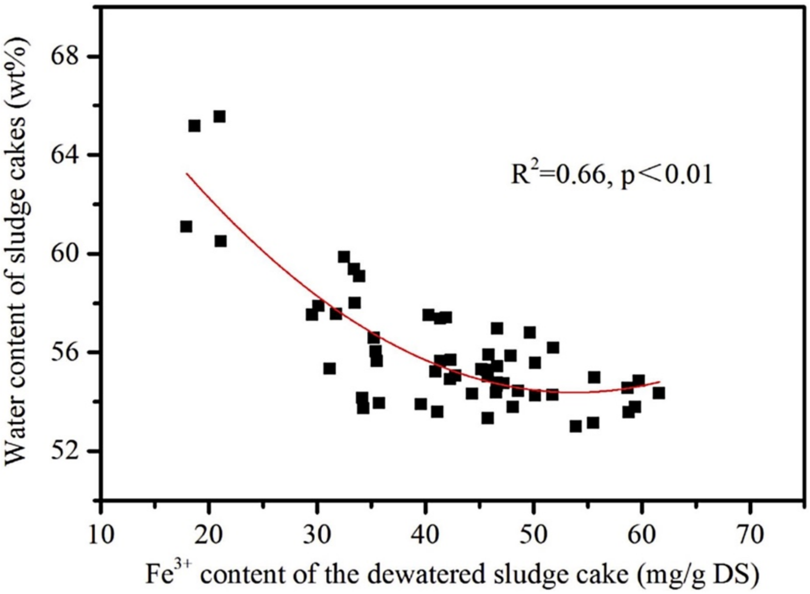

Figure 2.1: Weight % of sludge relationship with Fe(III) content (Yu et al., 2016).

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In comparison between Fe and Al coagulants, ferric Fe (Fe(III)) based coagulants remove approximately two times more bound water than those treated with Al [82% vs only 48% removal of original bound water] (Katsiris and Kouzeli-Katsiri, 1987). The decrease in bound water leads to more efficient and cost-effective sludge dewatering. Therefore, increasing Fe concentrations by co-treating may improve sludge settling and dewatering. It is not uncommon for drinking water utilities that use metal coagulants to send their Fe/Al-rich sludge to a WWTP for disposal as an alternative to landfilling, as many drinking water facilities do not operate an on-site sludge handling system. A full-scale WWTP experienced no negative impacts on treatment processes nor product quality after accepting Fe-rich drinking water sludge (Marguti et al., 2018). Al-rich sludge addition directly to MWW treatment processes at both pilot and full scale facilities did not impair system performance and increased total solids entering the sludge handling steps (Asada et al., 2010).

The presence of Al in secondary MWW waste sludge has similar benefits to Fe. Al improves sludge dewaterability, where $Al(OH)_3$ concentration was shown to have a negative linear relationship with SRF, specifically (Hsu and Pipes, 1973). Furthermore, digesting the sludge first before dewatering showed addition of increased Al concentrations improved dewaterability by nearly two orders of magnitude. When present in sludge, the Al particles act as "skeleton builders" which makes the bulk structure significantly stronger and allows water to more easily move through and out of the sludge (Lai and Liu, 2004). This enhanced structure allows the sludge to be dewatered under varying pressures and still maintain high dewaterability. It is important to note some variability in performance is possible, arising from Al speciation. Certain polymerized speciation of hydrolyzed Al perform noticeably better, having higher resistance to compression allowing for higher dewaterability (Cao et al., 2016). This, however, is not likely something that could be controlled operationally in a co-treatment scenario.

Sludge conditioning can often be improved by implementation of an advanced oxidation process (AOP) (Neyens and Baeyens, 2003), a technique that generates numerous radicals for enhanced MWW treatment through oxidation (Glaze et al., 1987). AMD co-treatment may serve as a low-cost alternative to implementation of an AOP. For example, ferrous Fe (Fe(II)) mixed with hydrogen peroxide facilitates the Fenton reaction to generate hydroxyl radicals and Fe(III), and has been utilized for sludge conditioning. Co-treatment with Fe-rich AMD could replace a Fenton AOP and retain comparable dewatering efficiency. Yu et al. (2016) directly compared sludge dewatering characteristics of Fe(III) and Fe(II) addition with several variations of the Fenton AOP process by mixing sludge and reagents (always 48 mg Fe/g sludge) in a conditioning tank, pumped the mixture to a pressure-controlled feed tank, and then dewatered via a laboratory diaphragm filter press. (Figure 2.2).

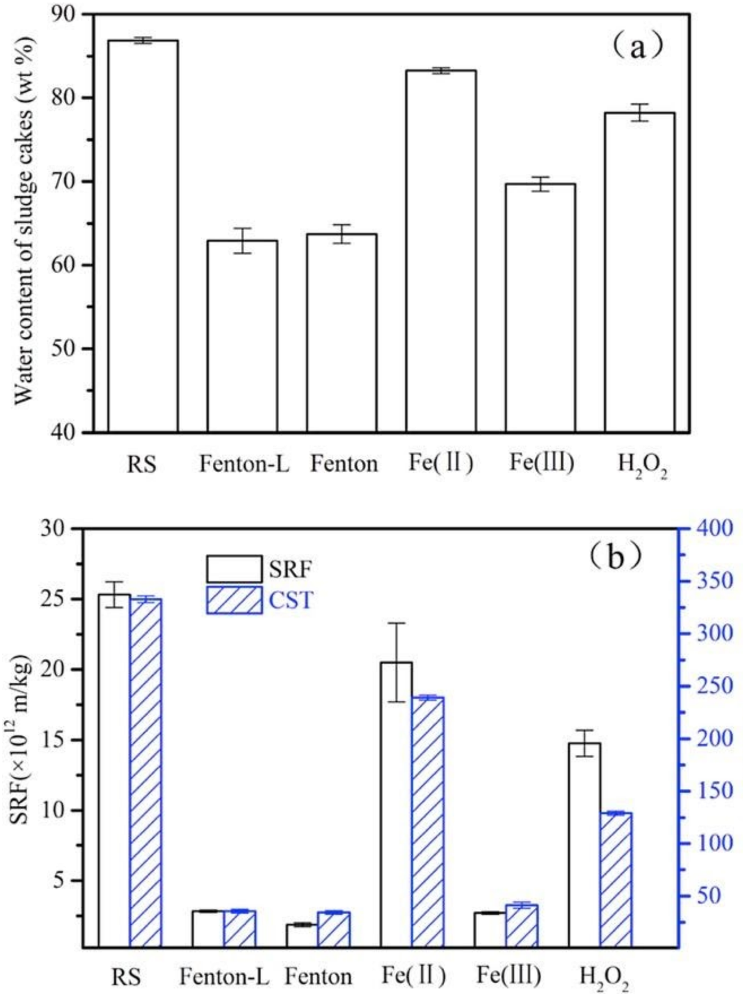

Figure 2.2: Fenton process ability to reduce sludge water content (a); and its specific resistance to filtration (SRF) & capillary suction time (CST) comparing Fenton (Fe^{2+} + H_2O_2), Fenton with lime ($Fe^{2+} + H_2O_2 + CaCO_3$), ferrous, and ferric, and peroxide (Yu et al., 2016). Included with permission under Elsevier license 4750321410053.

Although Yu et al. noted that Fenton reactions achieved the best performance, Fe(III)-alone achieved comparable performance and demonstrated significant improvement over raw sludge (RS). Increased Fe(III) content decreases the sludge cake water content by up to 15%, suggesting adding AMD through co-treatment could improve sludge processing. Conversely, Fe(II) yielded little to no improvement over the RS. An AMD discharge with an increased Fe(II) fraction would require significant oxidation for enhanced sludge processing to be seen. Although the Fe(II) results are noteworthy, it is of minimal concern for AMD co-treatment adaptability as Fe will have sufficient contact time with oxygen to oxidize to Fe(III) during co-treatment, either rapidly in an aeration basin or slowly in a settling tank, before ending up in waste activated sludge. However, this could be of concern for co-treating WWTPs that store sludge in an anaerobic system with long detention times where Fe reduction would likely occur (Rasmussen et al., 1994). As previously discussed, it would be more advantageous for facilities with anaerobic systems to prefer Al-rich AMD for co-treatment if possible, due to the relatively high stability of Al in the +3 oxidation state during anaerobic storage and processing (Park et al., 2006).

Odor Control & Anaerobic Processes

Odor control issues have always plagued WWTPs and frequently become a nuisance cost burden for many facilities (Dague, 1972). Fe from co-treatment may help mitigate these unavoidable odor-related issues arising from MWW sludge handling. Odor reduction not only removes a potential inhalation health hazard for WWTP operators, but can present positive economic benefits for the immediate community by increasing surrounding property values by up to 15% (Lebrero et al., 2011). Divalent metal species in AMD, including Fe(II), can scavenge and react with the primary odor-causing compound H_2S to form insoluble metal sulfide complexes which are non-odorous (Johnson and Hallberg, 2005). This suggests that addition of AMD Fe(II) would assist in decreasing odor causing compounds during solids processing. Similarly, the addition of zero-valent Fe (Fe0) nanoparticles at various doses to MWW sludge demonstrated improved oxidation of H_2S to form Fe sulfides and increased the final biosolids nutrient bioaccessibility (Li et al., 2007). The resultant Fe-sulfides further reacted with H_2S to form Fe polysulfides without the need for additional Fe input. Although the aforementioned study utilized Fe0, only the core of the nanoparticles contained Fe0 while the shell was oxidized and consisted of hydroxides/oxyhydroxides, similar to those that would form after oxidation of AMD Fe.

Al addition also improves the overall anaerobic sludge digestion processes. Dosing Al removes high percentages of dangerous volatile sulfur compounds from process biogas, which cause odors and corrosion issues, while maintaining system stability (Akgul et al., 2017). Furthermore, the same study showed a noticeable decrease in digestor coliform counts as well as improved dewaterability after digestion. Additionally, the total volume of biogas generated would be expected to decrease (Hsu and Pipes, 1973). All of the aforementioned improvements could equate to significant cost savings for a WWTP, in addition to benefits from reduced odors. These results suggest that Al-rich AMD co-treatment would be most advantageous at a WWTP operating an anaerobic digestion system.

Biosolids and Application

Typical processed MWW sludge (biosolids) may contain anywhere from 1 to 300 g of Fe per dry kilogram of solids (Environmental Protection Agency, 2009), but very few studies have actually examined how high Fe (and Al content) will influence biosolids. Potential pH changes to biosolids resulting from AMD co-treatment would likely have been neutralized by lime addition during stabilization. As previously discussed, there is minimal regulatory concern for common AMD metals in biosolids. Yet it is possible on a case-by-case basis that a facility may have Fe or Al limits in their biosolids disposal permit.

Trace metals and metalloids (e.g. Pb, Hg and As) in biosolids can have environmental and human health implications if they bioaccumulate or leach after land application (Arulrajah et al., 2011). Both As and Hg have frequently been investigated for their role in biosolids toxicity in land use scenarios. AMD from the eastern part of the United States rarely has notable As and Hg concentrations, often below drinking water standards (Herlihy et al., 1990), but elevated concentrations can be found in other situations (Cheng et al., 2009; Rytuba, 2000). The ability to reduce the bioavailability of trace metals and metalloids in soil is a key consideration in land application of any compost. Increasing Biosolids Fe content impacted bioavailability of both Pb and As. Figure 2.3 demonstrates The difference in bioavailability of Pb during a field study when increased loads of Fe (109 g/kg) were added to biosolids compost (Brown et al., 2012). This study applied biosolids compost at several amounts (50 and 100 g compost per kg soil) to the top layer of soil. Experimental analysis showed 75% of the Fe in the high-Fe biosolids was Fe(III), similar to what might be expected of co-treatment biosolids.

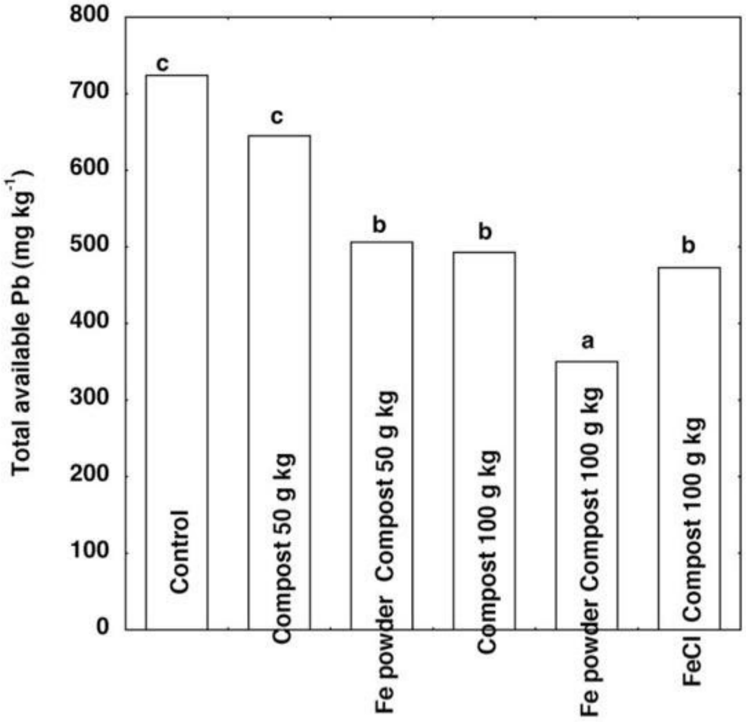

Figure 2.3: Fe's improvement of soil metal bioavailability. Bars with the same letter are not statistically different. Increased Fe content in compost significantly reduced availability of Pb in soil (Brown et al., 2012). Included with permission under John Wiley and Sons license 4750330261796.

Brown et al concluded there was little difference in the bioavailability of As, but significant decreases in total available Pb. The increased soil retention of toxic compounds after application of biosolids with elevated Fe concentrations makes them marketable not just as compost but also as remediation substrate for sequestering metals (e.g. Pb) in soils (Farfel et al., 2005). It is important to note that the substantial concentration of Fe added (>80 g/kg) in the successful Brown et al. experiment would only be expected under high-volume, Fe-rich AMD co-treatment scenarios. However, the Fe concentration is likely orders of magnitude higher than what a typical AMD discharge (221 mg/L Fe in AMD, per Watzlaf et al., 2004) might contribute in a co-treatment system. In these situations, solids trace metal bioavailability would likely not be improved as demonstrated in the Brown et al. low Fe (5 g Fe/kg) experiments. These results imply that decreased toxic compound concentrations could only be expected during co-treatment on a case by case basis as a function of AMD and MWW influent Fe concentrations and system Fe removal capabilities.

Both Fe and Al may benefit agricultural land application of biosolids. AMD metals have demonstrated potential related to improving soil P availability. Adler and Sibrell (2003) showed addition of neutralized AMD "flocs" to high-P soil (20 g floc / kg soil) could sequester roughly 70% of water-extractable P. A similar result was noted in a larger scale study, where application of manure mixed with AMD treatment residuals to a large parcel of farmland decreased the water-soluble P content (Sibrell et al., 2015). Similarly, a study that mixed MWW biosolids with water treatment alum sludge, the addition of Al to the biosolids improved crop yields in agricultural soils by retaining higher concentrations of P in both laboratory (60 days) and greenhouse (105 days) scale studies (Farfel et al., 2005). Furthermore, the Al-hydroxides, which were applied at a low ratio (1 to 4% by weight), assisted in reducing the total nutrient runoff. Fe and Al can decrease the soluble P concentration in land applied biosolids by formation and precipitation of Al/Fe-P complexes or P adsorption unto hydroxides (Huang et al., 2007). However, it is important to note that results can vary depending on soil pH, and the final Fe-P ratio. Biosolids enriched with Fe(III), which exists as several commercially available products, demonstrated some influence on certain fruits that suffer from Fe deficiencies. The growth size of oranges were positively impacted by Fe(III), meanwhile there was no impact on pears (Pérez-Sanz et al., 2002). However, most biosolids results showed non-negative but neutral impacts on fruit growth and the total Fe uptake was less effective compared to manufactured Fe-enriched fertilizers. There is a strong potential for AMD co-treatment biosolids to support localized agriculture. Co-treatment could reduce demands for artificial fertilizers and potentially decrease nutrient loading on waterways without negatively impacting agriculture processes.

Incineration Considerations

Co-treatment has the potential to impact sludge incineration operations. As previously discussed, the addition of metals decreases the amount of sludge bound water which thus increasing the percent solids. Increased solids makeup improves dewatering and the quality of dry sludge produces, thus reducing stress on incinerator processes. Furthermore, after incineration the amount of extractable P from ash is increased when sludges contain elevated levels of Fe and Al (Farfel et al., 2005). Co-treatment incineration ash could improve nutrient recovery and be viewed as a beneficial reuse product. Due to increasing global stress on P demand, WWTP processes have long been a point of focus as a source of potential P recovery and recycling (Farfel et al., 2005). Ash product produced from a co-treating incineration facility with a high percent of extractable P could alleviate this demand by increasing localized P availability. Incinerated sludge ash can contain up to 10% P by mass

(Donatello and Cheeseman, 2013) and the amount of P that is recoverable is directly proportional to ash value. Sludge ash can successfully be applied to land as a fertilizer (Bierman and Rosen, 1994). Therefore, this beneficial use ash also carries economic incentives, as it is now a product to boost revenue rather than a waste. Furthermore, the extractable P-rich ash is significantly less dense than a dried & stabilized sludge making it more economically viable to transport.

However, there are disadvantages to be considered for incineration facilities. Depending on the water chemistry of the AMD, the ash could contain higher weight-percentages of toxic trace metals (e.g. As & Pb). This results in disposal considerations that were not present before. Ash containing > 100 mg/kg of Pb would be considered a hazardous waste and could not be disposed of in a traditional municipal landfill. Landfill Pb can be indirectly associated with a variety of health issues for neighboring communities (Kim and Williams, 2017), and remains a liability for the generator. is a primary contaminant in landfill leachates (Pinel-Raffaitin et al., 2006), and a landfill would likely not willing accept wastes due to the associated costs required for As treatment after leaching.

Conclusions

Fe and Al are already abundant constituents within WWTP from both influential waste sources and in-situ treatment from chemical treatment processes. Addition of AMD to the waste stream may not increase waste sludge metal concentrations above what is typically seen in most treatment facilities, depending on the AMD water chemistry and loading. Furthermore, the addition of these metals may enhance a facility’s solids handling processes and impact the end products use.

Additional metals present in processed waste sludge could increase toxicity of soils after application. However, the opportunity to improve sludge dewatering, remove odor-causing compounds, and reduce COD exists. Furthermore, elevated Fe in biosolids can be economically valuable as a soil remediation tool by immobilizing trace metals in contaminated soils. Sludge incineration facilities that add AMD (with low levels of Pb, As and other trace metals) can generate economically valuable ash, which would otherwise be landfilled. However, there remains a gap in the research on co-treatment metals and biosolids. Future research should include laboratory experiments to investigate the true impact of AMD on waste activated sludge.

APPENDICES

Appendix A: Chapter 1 Supporting Information

S1. Options for co-treatment

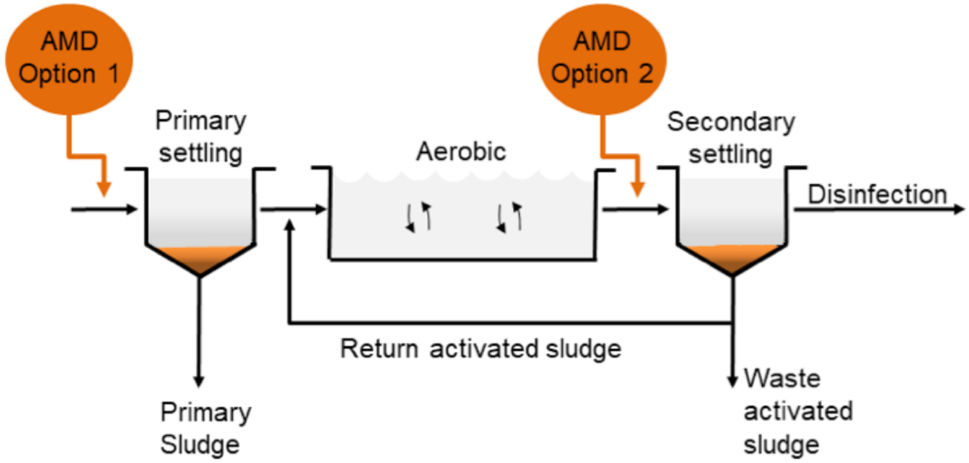

Figure S1: Options for co-treatment in a conventional MWW treatment plant. This study examined “AMD Option 2”.

S2. Experimental setup

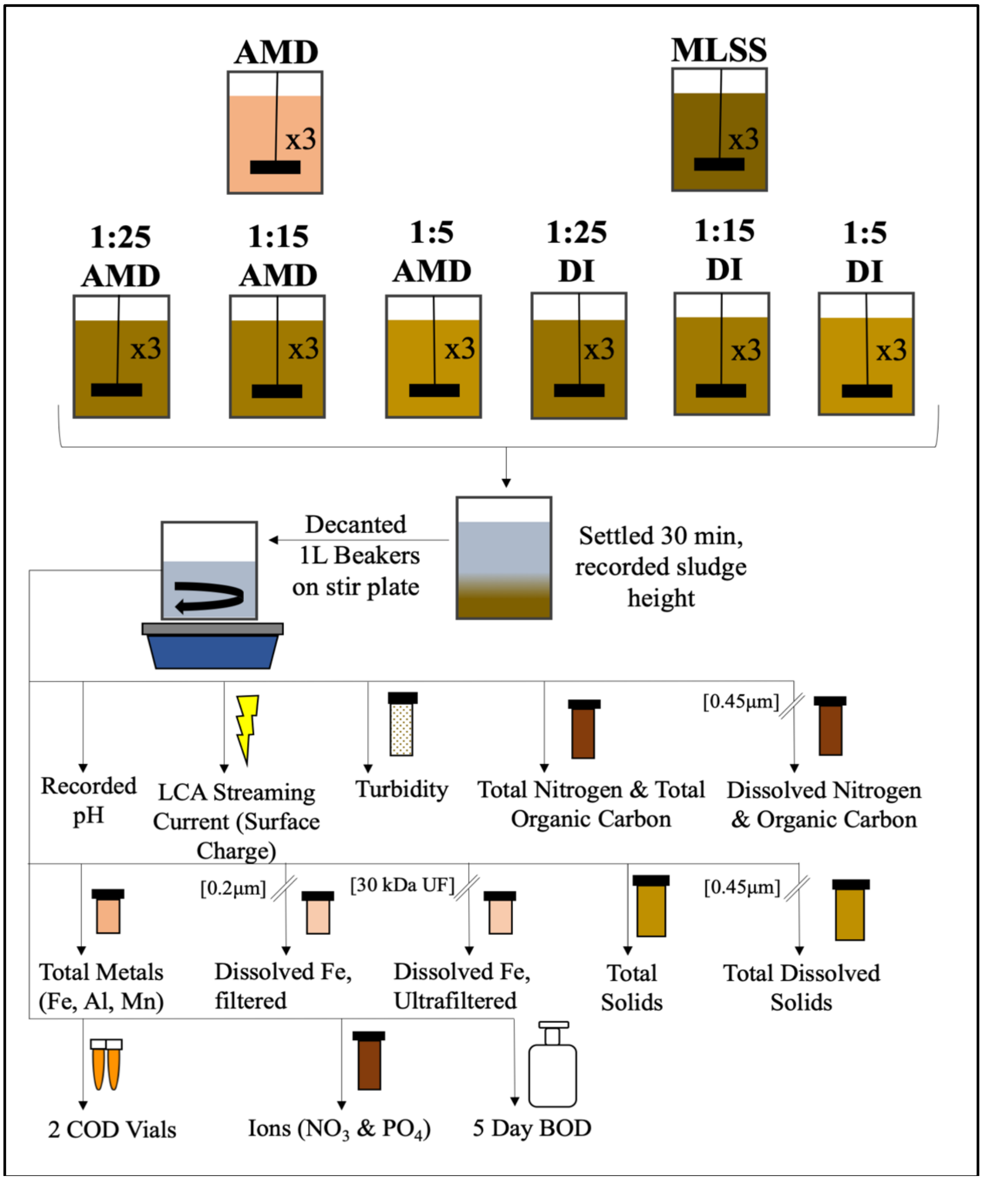

Figure S2: Flow diagram of experimental setup of acid mine drainage (AMD) and wastewater (MWW) controls and all three tested ratios (each tested in triplicate). Samples were settled, the supernatant decanted, and analyzed for pH, streaming current, turbidity, metals, solids, ions, and oxygen demand.

S3. Research site

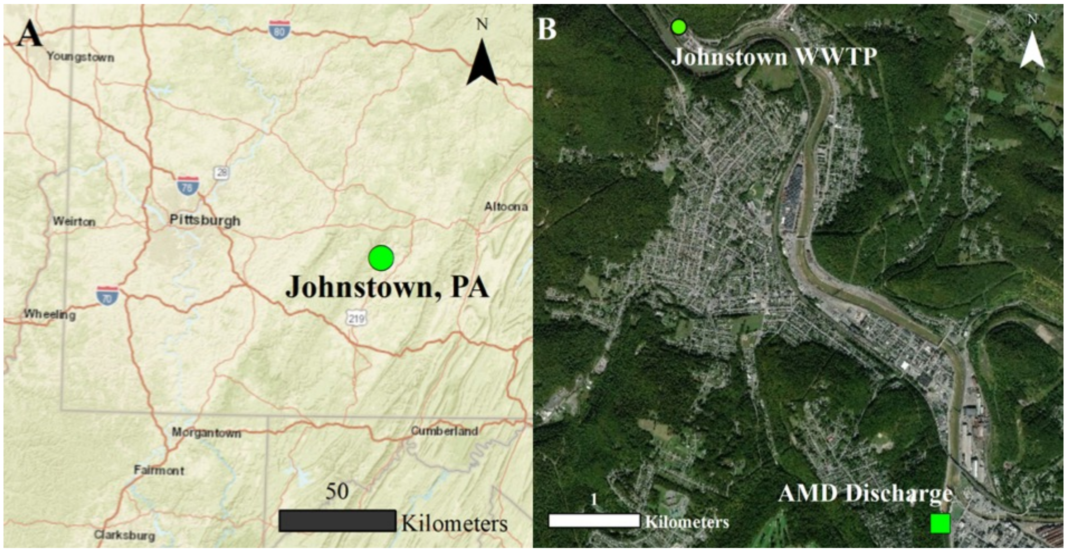

Figure S3: (A) Location of Johnstown, PA in the Appalachian Region, USA; (B) Proximity of the Johnstown Wastewater Treatment Plant ((near 40° 21' 52"N 78° 57' 9"W) and the Inclined Plane AMD discharge (near 40° 19' 41"N, 78° 55' 34"W) along the Conemaugh River

S4. pH modeling

As discussed in section 3.1, pH was not below a typical discharge limit in all experimental trials. In order to determine the amount of AMD that could be added until the mixed solution would exceed discharge minimums minimum pH, predictions were made based on the concentrations of H^+ resulting from mixing the MWW and AMD alkalinity's under open-system, aqueous carbonate buffering conditions. Alkalinity of the AMD and MWW alone were determined from starting pH using equation S1-S4, assuming a system open to the atmosphere with MWW pH = 6.7 and $pCO2 = 10^{-3.8}$

$$\boxed{\text{Alkalinity} = (\alpha_1 + 2 * \alpha_2) * C_T + \frac{K_W}{[\mathrm{H^+}]} - [\mathrm{H^+}]} \tag{S1}$$

$$\boxed{\alpha_1 = \left(\frac{[\mathrm{H^+}]}{K_1} + 1 + \frac{K_2}{[\mathrm{H^+}]}\right)^{-1}} \tag{S2}$$

$$\boxed{C_T = \frac{K_H * p_{CO_2}}{\alpha_0}} \tag{S3}$$

$$\boxed{\alpha_0 = \left(1 + \frac{K_1}{[\mathrm{H^+}]} + \frac{K_1 * K_2}{[\mathrm{H^+}]^2}\right)^{-1}} \tag{S4}$$

α_2 was assumed to be zero as within the pH range (4.5-7), the influence of CO_3^{2-} was determined to be negligible based on aqueous carbonate equilibrium diagrams. After determining the mixed solution alkalinity, the mixed solution pH was calculated by substituting equations S2-S4 into equation S1 and then rearranged to equation S5.

$$\boxed{[\mathrm{H}^+] = \frac{1}{2}\left(\sqrt{4 * K_1 * K_H * p_{CO_2} + 4 * K_W + (\mathrm{Alk}_{AMD+MWW})^2} - \mathrm{Alk}_{AMD+MWW}\right)} \quad \text{(S5)}$$

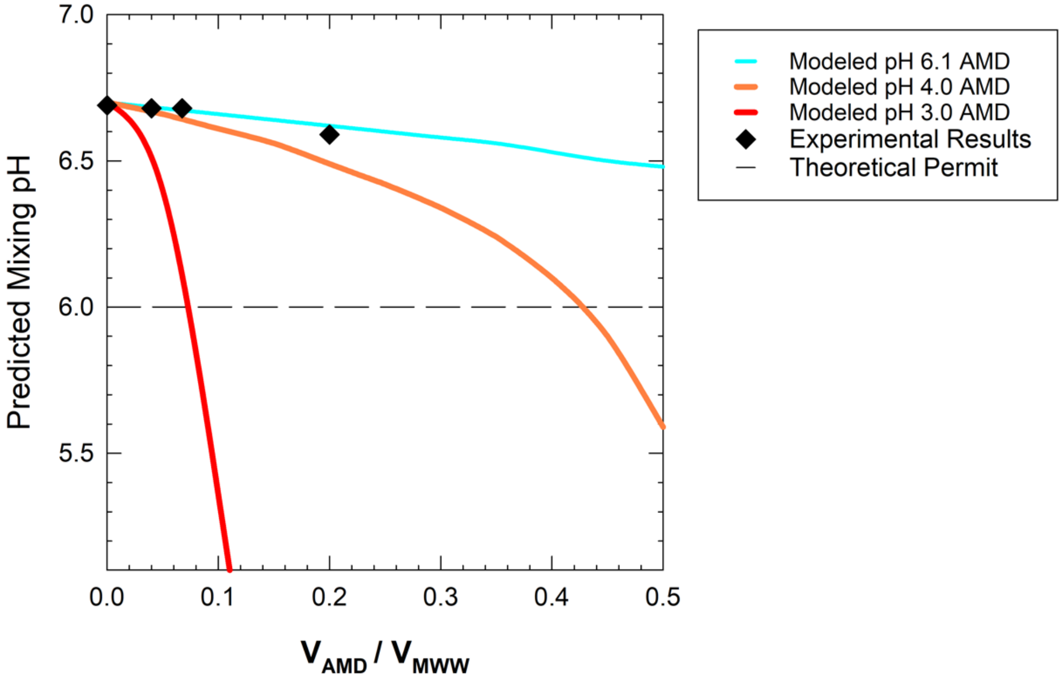

Figure S4: Modeled co-treated effluent pH at various initial AMD pH's and when a typical NPDES permit minimum of pH 6.0 is exceeded.

S5. PO_4 adsorption isotherm modeling

The Langmuir equilibrium adsorption isotherm is defined as:

$$\boxed{q_e = \frac{Q_M * b * C_e}{1 + b * C_e}} \quad \text{(S6)}$$

Where q_e represents the amount of solid-phase adsorbate (mg adsorbed per mg of absorbent), Q_M is the maximum adsorption capacity (mg/mg), b is a Langmuir adsorption constant (L/mg) and C_e is the equilibrium concentration of adsorbate.

The isotherm can be linearized to:

$$\boxed{\frac{C_e}{q_e} = \frac{1}{Q_M} * C_e + \frac{1}{Q_M * b}} \quad \text{(S7)}$$

PO_4 removal by adsorption can be confirmed if plotting experimental (C_e/q_e) vs C_e and yielding a highly-linear relationship, thus fitting the Langmuir adsorption isotherm behavior (similar methodology to Yang et al., 2006). The slope of the resulting regression line would be equal to $1/Q_M$, allowing for the determination of the maximum adsorption capacity for the experimental system.

S6. Dissolved Fe speciation modeling

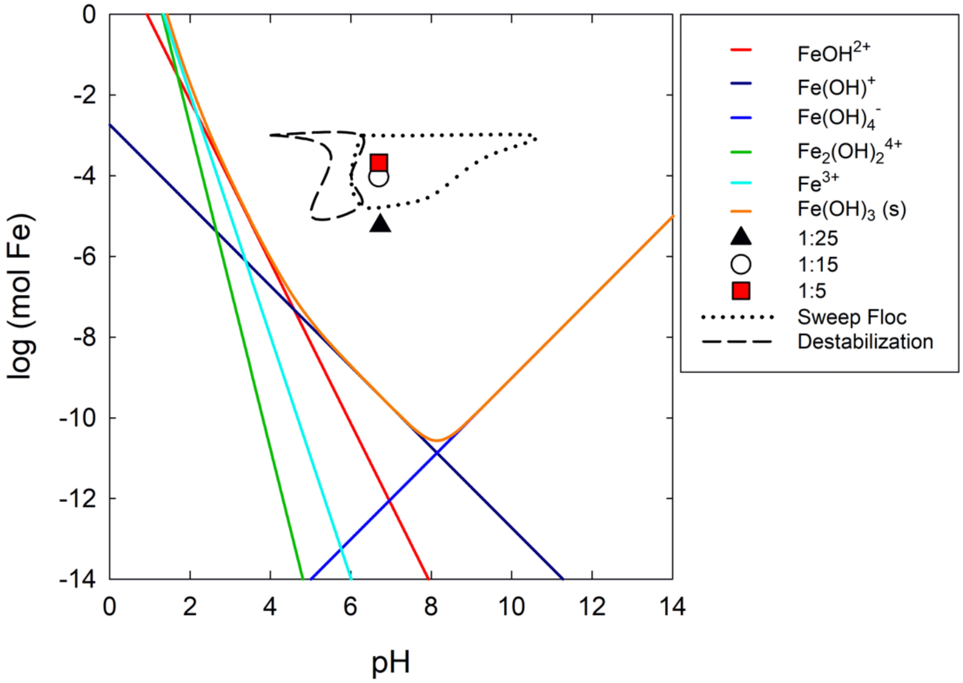

Figure S5: Various Fe hydroxide species solubility at different pH's, determined using K values from Snoeyink and Jenkins (1980). If the Fe in our experiments was oxidized to Fe(III), the concentrations of experimentally determined dissolved Fe at respective pH suggest the Fe should not be dissolved, but in solid $Fe(OH)_3$. Sweep flocculation and destabilization regions based on those of Johnson and Amirtharajah, 1983. The boundary of destabilization with respect to pH decrease is also a function of particulate surface area concentration.

S7. Mass balance calculations

$$\boxed{\text{Predicted } X_{total} = (Vol_{MWW} * \text{MWW } X_{total}) + (Vol_{AMD} * \text{AMD } X_{total})} \quad \text{(S8)}$$

Mass balance of total solids used the mean total solids concentrations from experimental trials. Each calculation used experimentally determined solids of 167.8 mg/L and 58.7 mg/L in AMD and MWW, respectively. Theoretical values were calculated using the dilution equation (Eq. S3).

Table S1: Total solids mass balance

Trial	**1:25**	**1:15**	**1:5**
Theoretical total solids (mg/L)	63.1	66.1	80.5
Experimental total solids (mg/L)	54.1	57.6	74.0
% difference	-15%	-14%	-8%

Total dissolved solids mass balance was performed in the same manner as total solids with Eq. S3, using dissolved solids of 162.4 mg/L in AMD and 53.7 mg/L in MWW.

Table S2: Total dissolved solids mass balance

Trial	**1:25**	**1:15**	**1:5**
Theoretical total solids (mg/L)	58.1	61.0	75.4
Experimental total solids (mg/L)	52.9	55.0	59.0
% difference	-9%	-11%	-24%

The mass balance of chemical oxygen demand was determined in the same manner as solids, and calculations used experimentally determined COD's of 18.3 mg/L for AMD and 100.8 mg/L for MWW, and then calculated using the dilution equation.

Table S3: COD mass balance

Trial	**1:25**	**1:15**	**1:5**
Theoretical COD (mg/L)	97.5	95.3	84.3
Experimental COD (mg/L)	86.7	87.33	94.3
% difference	-12%	-11%	-9%

Mass balance of total Fe during settling, assuming Fe not remaining in solution settled with sludge. All values use the mean total Fe concentrations from experimental trials. Each calculation used experimentally determined total Fe, 146.5 mg/L in AMD and 1.80 mg/L in MWW, and then calculated using the dilution equation (Eq. S3).

Table S4: Fe mass balance

Trial	**1:25**	**1:15**	**1:5**
Theoretical total Fe (mg/L)	7.59	11.6	30.7
Experimental Total Fe (mg/L)	3.90	7.24	20.7
Assumed settled total Fe (mg/L)	*3.69*	*4.36*	*10.0*
% settled total Fe	49%	38%	33%

S8. Sulfate data

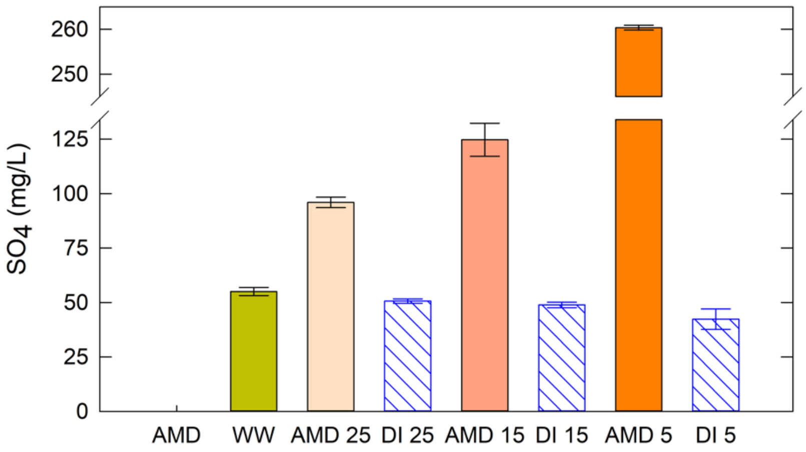

Figure S6: Total SO_4 concentrations in each sample, determined by IC. AMD concentrations were not determined due to analytical interferences caused by the extremely high dissolved Fe content

REFERENCES

Adler, P.R., Sibrell, P.L., 2003. Sequestration of Phosphorus by Acid Mine Drainage Floc. J. Environ. Qual. 32, 1122–1129. https://doi.org/10.2134/jeq2003.1122

Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. J. Clean. Prod. 14, 1139–1145. https://doi.org/10.1016/j.jclepro.2004.09.006

Akgul, D., Abbott, T., Eskicioglu, C., 2017. Assessing iron and aluminum-based coagulants for odour and pathogen reductions in sludge digesters and enhanced digestate dewaterability. Sci. Total Environ. 598, 881–888. https://doi.org/10.1016/j.scitotenv.2017.04.141

Alexander, R.B., Smith, R.A., Schwarz, G.E., Boyer, E.W., Nolan, J. V, Brakebill, J.W., 2008. Differences in Phosphorus and Nitrogen Delivery to The Gulf of Mexico from the Mississippi River Basin. Environ. Sci. Technol. 42, 822–830. https://doi.org/10.1021/es0716103

Anderson, D.M., Burkholder, J.M., Cochlan, W.P., Glibert, P.M., Gobler, C.J., Heil, C.A., Kudela, R.M., Parsons, M.L., Rensel, J.E.J., Townsend, D.W., Trainer, V.L., Vargo, G.A., 2008. Harmful algal blooms and eutrophication: Examining linkages from selected coastal regions of the United States. Harmful Algae 8, 39–53. https://doi.org/10.1016/j.hal.2008.08.017

APHA, 2012. Standard Methods for Examination of Water and Wastewater (Standard Methods for the Examination of Water and Wastewater). Am. Public Heal. Assoc. Washington, DC, USA. https://doi.org/ISBN 9780875532356

Arulrajah, A., Disfani, M.M., Suthagaran, V., Imteaz, M., 2011. Select chemical and engineering properties of wastewater biosolids. Waste Manag. 31, 2522–2526. https://doi.org/10.1016/j.wasman.2011.07.014

Asada, L.N., Sundefeld, G.C., Alvarez, C.R., Filho, S.S.F., Piveli, R.P., 2010. Water Treatment Plant Sludge Discharge to Wastewater Treatment Works: Effects on the Operation of Upflow Anaerobic Sludge Blanket Reactor and Activated Sludge Systems. Water Environ. Res. 82, 392–400. https://doi.org/10.2175/106143009X12487095236838

Azapagic, A., 2004. Developing a framework for sustainable development indicators for the mining and minerals industry. J. Clean. Prod. 12, 639–662. https://doi.org/10.1016/S0959-6526(03)00075-1

Bierman, P.M., Rosen, C.J., 1994. Phosphate and Trace Metal Availability from Sewage-Sludge Incinerator Ash. J. Environ. Qual. 23, 822–830. https://doi.org/10.2134/jeq1994.00472425002300040030x

Brown, S.L., Clausen, I., Chappell, M.A., Scheckel, K.G., Newville, M., Hettiarachchi, G.M., 2012. High-Iron Biosolids Compost–Induced Changes in Lead and Arsenic Speciation and Bioaccessibility in Co-contaminated Soils. J. Environ. Qual. 41, 1612. https://doi.org/10.2134/jeq2011.0297

Cao, B., Zhang, W., Wang, Q., Huang, Y., Meng, C., Wang, D., 2016. Wastewater sludge dewaterability enhancement using hydroxyl aluminum conditioning: Role of aluminum speciation. Water Res. 105, 615–624. https://doi.org/10.1016/j.watres.2016.09.016

Carlson, K.H., Knocke, W.R., Gertig, K.R., 1997. Optimizing treatment through Fe and Mn fractionation. J. Am. Water Works Assoc. 89, 162–171.

https://doi.org/10.1002/j.1551-8833.1997.tb08216.x

Chang, I.S., Shin, P.K., Kim, B.H., 2000. Biological treatment of acid mine drainage under sulphate-reducing conditions with solid waste materials as substrate. Water Res. 34, 1269–1277. https://doi.org/10.1016/S0043-1354(99)00268-7

Chapman, P.M., Bailey, H., Canaria, E., 2000. Toxicity of total dissolved solids associated with two mine effluents to chironomid larvae and early life stages of rainbow trout. Environ. Toxicol. Chem. 19, 210–214. https://doi.org/10.1002/etc.5620190125

Cheng, H., Hu, Y., Luo, J., Xu, B., Zhao, J., 2009. Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. J. Hazard. Mater. https://doi.org/10.1016/j.jhazmat.2008.10.070

Choo, K.-H., Kang, S.-K., 2003. Removal of residual organic matter from secondary effluent by iron oxides adsorption. Desalination 154, 139–146. https://doi.org/10.1016/S0011-9164(03)80014-0

Clark, T., Burgess, J.E., Stephenson, T., Arnold-Smith, A.K., 2000. The Influence of Iron-Based Co-Precipitants on Activated Sludge Biomass. Process Saf. Environ. Prot. 78, 405–410. https://doi.org/10.1205/095758200530916

Coulton, R., Bullen, C., Hallett, C., 2003. The design and optimisation of active mine water treatment plants. L. Contam. Reclam. 11, 273–279. https://doi.org/10.2462/09670513.825

Dague, R.R., 1972. Fundamentals of Odor Control. J. (Water Pollut. Control Fed. 44, 583–594.

Davis, C.C., Edwards, M.A., 2014. Coagulation with hydrolyzing metal salts:

Mechanisms and water quality impacts. Crit. Rev. Environ. Sci. Technol. 44, 303–347. https://doi.org/10.1080/10643389.2012.718947

Davison, W., Seed, G., 1983. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. Geochim. Cosmochim. Acta 47, 67–79. https://doi.org/10.1016/0016-7037(83)90091-1

de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res. 38, 4222–4246. https://doi.org/10.1016/j.watres.2004.07.014

De Freitas, J.M., Meneghini, R., 2001. Iron and its sensitive balance in the cell. Mutat. Res. Mol. Mech. Mutagen. 475, 153–159. https://doi.org/10.1016/S0027-5107(01)00066-5

Deng, D., Lin, L.-S., 2013. Two-stage combined treatment of acid mine drainage and municipal wastewater. Water Sci. Technol. 67, 1000–1007. https://doi.org/10.2166/wst.2013.653

Dentel, S.K., Thomas, A. V, Kingery, K.M., 1989. Evaluation of the streaming current detector—I. Use in jar tests. Water Res. 23, 413–421. https://doi.org/10.1016/0043-1354(89)90132-2

Dodds, W., Smith, V., 2016. Nitrogen, phosphorus, and eutrophication in streams. Inl. Waters 6, 155–164. https://doi.org/10.5268/IW-6.2.909

Dominguez, D., Gujer, W., 2006. Evolution of a wastewater treatment plant challenges traditional design concepts. Water Res. 40, 1389–1396. https://doi.org/10.1016/j.watres.2006.01.034

Donatello, S., Cheeseman, C.R., 2013. Recycling and recovery routes for incinerated sewage sludge ash (ISSA): A review. Waste Manag. 33, 2328–2340. https://doi.org/10.1016/j.wasman.2013.05.024

Edzwald, J.K., Tobiason, J.E., 1999. Enhanced coagulation: US requirements and a broader view. Water Sci. Technol. 40, 63–70. https://doi.org/10.1016/S0273-1223(99)00641-1

Environmental Protection Agency, 2019. National Pollutant Discharge Elimination System (NPDES) [WWW Document]. URL https://www.epa.gov/npdes

Environmental Protection Agency, 2009. Targeted National Sewage Sludge Survey Sampling and Analysis Technical Report, EPA-822-R-08-016. Washington, DC 20460.

EPA Region 3, 2016. Region 3 NPDES Permit Quality Review: Pennsylvania. Philadelphia, PA.

Evangelou, V.P. (Bill), Zhang, Y.L., 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. Crit. Rev. Environ. Sci. Technol. 25, 141–199. https://doi.org/10.1080/10643389509388477

Farfel, M.R., Orlova, A.O., Chaney, R.L., Lees, P.S.J., Rohde, C., Ashley, P.J., 2005. Biosolids compost amendment for reducing soil lead hazards: A pilot study of Orgro® amendment and grass seeding in urban yards. Sci. Total Environ. 340, 81–95. https://doi.org/10.1016/j.scitotenv.2004.08.018

Faust, K.M., Abraham, D.M., McElmurry, S.P., 2016. Water and Wastewater Infrastructure Management in Shrinking Cities. Public Work. Manag. Policy 21, 128–156. https://doi.org/10.1177/1087724X15606737

Feng, Q., Li, T., Qian, B., Zhou, L., Gao, B., Yuan, T., 2014. Chemical Characteristics and Utilization of Coal Mine Drainage in China. Mine Water Environ. 33, 276–286. https://doi.org/10.1007/s10230-014-0271-y

Fettig, J., Ratnaweera, H., 1993. Influence of Dissolved Organic Matter on Coagulation/Flocculation of Wastewater by Alum. Water Sci. Technol. 27, 103–112. https://doi.org/10.2166/wst.1993.0269

Glaze, W.H., Kang, J.-W.W., Chapin, D.H., 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Sci. Eng. 9, 335–352. https://doi.org/10.1080/01919518708552148

Goodwill, J.E., Jiang, Y., Reckhow, D.A., Gikonyo, J., Tobiason, J.E., 2015. Characterization of particles from ferrate preoxidation. Environ. Sci. Technol. 49, 4955–4962. https://doi.org/10.1021/acs.est.5b00225

Goodwill, J.E., Labar, J., Slovikosky, D., Strosnider, W.H.J., 2019. Preliminary Assessment of Ferrate Treatment of Metals in Acid Mine Drainage. J. Environ. Qual. 1–34. https://doi.org/10.2134/jeq2019.02.0079

Gray, N.F., 1998. Acid mine drainage composition and the implications for its impact on lotic systems. Water Res. 32, 2122–2134. https://doi.org/10.1016/S0043-1354(97)00449-1

Gregory, J., O'Melia, C.R., 1989. Fundamentals of flocculation. Crit. Rev. Environ. Control 19, 185–230. https://doi.org/10.1080/10643388909388365

Han, M., Lawler, D.F., 1992. (Relative) insignificance of G in flocculation. J. / Am. Water Work. Assoc. 84, 79–91. https://doi.org/10.1002/j.1551-8833.1992.tb05869.x

Harper, D., 1992. What is eutrophication?, in: Eutrophication of Freshwaters. Springer

Netherlands, Dordrecht, pp. 1–28. https://doi.org/10.1007/978-94-011-3082-0_1

He, C., Zhang, T., Vidic, R.D., 2016. Co-treatment of abandoned mine drainage and Marcellus Shale flowback water for use in hydraulic fracturing. Water Res. 104, 425–431. https://doi.org/10.1016/j.watres.2016.08.030

Hedin, R.S., Nairn, R.W., Kleinmann, R.L.P., 1994. Passive treatment of coal mine drainage, Infromation Circular 9389.

Herlihy, A.T., Kaufmann, P.R., Mitch, M.E., Brown, D.D., 1990. Regional estimates of acid mine drainage impact on streams in the mid-atlantic and Southeastern United States. Water. Air. Soil Pollut. 50, 91–107. https://doi.org/10.1007/BF00284786

Hsu, D.Y., Pipes, W.O., 1973. Aluminum Hydroxide Effects on Wastewater Treatment Processes. J. Water Pollut. Control Fed. 45, 681–697.

Huang, X.L., Chen, Y., Shenker, M., 2007. Solid phosphorus phase in aluminum- and iron-treated biosolids. J. Environ. Qual. 36, 549–556. https://doi.org/10.2134/jeq2006.0155

Hughes, T.A., Gray, N.F., 2013a. Removal of Metals and Acidity from Acid Mine Drainage Using Municipal Wastewater and Activated Sludge. Mine Water Environ. 32, 170–184. https://doi.org/10.1007/s10230-013-0218-8

Hughes, T.A., Gray, N.F., 2013b. Co-treatment of acid mine drainage with municipal wastewater: Performance evaluation. Environ. Sci. Pollut. Res. 20, 7863–7877. https://doi.org/10.1007/s11356-012-1303-4

Hughes, T.A., Gray, N.F., 2012. Acute and Chronic Toxicity of Acid Mine Drainage to the Activated Sludge Process. Mine Water Environ. 31, 40–52.

https://doi.org/10.1007/s10230-011-0168-y

Hughes, T.A., Gray, N.F., Sánchez Guillamón, O., 2013. Removal of Metals and Acidity from Acid Mine Drainage Using Liquid and Dried Digested Sewage Sludge and Cattle Slurry. Mine Water Environ. 32, 108–120. https://doi.org/10.1007/s10230-013-0217-9

Jacobs, J.A., Lehr, J.H., Testa, S.M., 2014. Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation, Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation. https://doi.org/10.1002/9781118749197

Jia, W., Wang, Q., Zhang, J., Yang, W., Zhou, X., 2016. Nutrients removal and nitrous oxide emission during simultaneous nitrification, denitrification, and phosphorus removal process: effect of iron. Environ. Sci. Pollut. Res. 23, 15657–15664. https://doi.org/10.1007/s11356-016-6758-2

Jiang, Y., Goodwill, J.E., Tobiason, J.E., Reckhow, D.A., 2015. Effect of Different Solutes, Natural Organic Matter, and Particulate Fe(III) on Ferrate(VI) Decomposition in Aqueous Solutions. Environ. Sci. Technol. 49, 2841–2848. https://doi.org/10.1021/es505516w

Jimenez, J.A., La Motta, E.J., Parker, D.S., 2007. Effect of Operational Parameters on the Removal of Particulate Chemical Oxygen Demand in the Activated Sludge Process. Water Environ. Res. 79, 984–990. https://doi.org/10.2175/106143007x175717

Johnson, B.D., 2003. Chemical and Microbiological Characteristics of Mineral Spoils and Drainage Waters at Abandoned Coal and Metal Mines. Water, Air Soil Pollut. Focus 3, 47–66. https://doi.org/10.1023/A:1022107520836

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338, 3–14. https://doi.org/10.1016/j.scitotenv.2004.09.002

Johnson, K.L., Younger, P.L., 2006. The co-treatment of sewage and mine waters in aerobic wetlands. Eng. Geol. 85, 53–61. https://doi.org/10.1016/j.enggeo.2005.09.026

Johnson, P.N., Amirtharajah, A., 1983. Ferric chloride and alum as single and dual coagulants. J. Am. Water Works Assoc. 75, 232–239. https://doi.org/10.1002/j.1551-8833.1983.tb05122.x

Karapanagioti, H.K., Atalay, A., 1996. Adsorption of Acid Mine Drainage Metals on Fly Ash. J. Am. Soc. Min. Reclam. 1996, 659–670. https://doi.org/10.21000/jasmr96010659

Katsiris, N., Kouzeli-Katsiri, A., 1987. Bound water content of biological sludges in relation to filtration and dewatering. Water Res. 21, 1319–1327. https://doi.org/10.1016/0043-1354(87)90004-2

Kavanaugh, M.C., Krejci, V., Weber, T., Eugster, J., Roberts, P. V., 1978. Phosphorus Removal by Post-Precipitation with Fe(III). J. (Water Pollut. Control Fed. 50, 216–233.

Kemp, P.H., 1971. Chemistry of natural waters—I. Water Res. 5, 297–311. https://doi.org/10.1016/0043-1354(71)90175-8

Kim, M.A., Williams, K.A., 2017. Lead Levels in Landfill Areas and Childhood

Exposure: An Integrative Review. Public Health Nurs. 34, 87–97. https://doi.org/10.1111/phn.12249

Kjeldsen, K.U., Joulian, C., Ingvorsen, K., 2004. Oxygen Tolerance of Sulfate-Reducing Bacteria in Activated Sludge. Environ. Sci. Technol. 38, 2038–2043. https://doi.org/10.1021/es034777e

Kruse, N.A., Reber, R., Schlater, N., Spencer, R., Steinmaus, M., Imhoff, D., 2019. In stream dynamics of acid mine drainage and untreated sewage. Environ. Earth Sci. 78, 659. https://doi.org/10.1007/s12665-019-8680-7

Labrenz, M., Banfield, J.F., 2004. Sulfate-Reducing Bacteria-Dominated Biofilms That Precipitate ZnS in a Subsurface Circumneutral-pH Mine Drainage System. Microb. Ecol. 47, 205–217. https://doi.org/10.1007/s00248-003-1025-8

Lai, J.Y., Liu, J.C., 2004. Co-conditioning and dewatering of alum sludge and waste activated sludge. Water Sci. Technol. 50, 41–48. https://doi.org/10.2166/wst.2004.0530

Langelier, W.F., 1936. The Analytical Control of Anti-Corrosion Water Treatment. J. Am. Water Works Assoc. 28, 1500–1521. https://doi.org/10.1002/j.1551-8833.1936.tb13785.x

Lebrero, R., Bouchy, L., Stuetz, R., Muñoz, R., 2011. Odor Assessment and Management in Wastewater Treatment Plants: A Review. Crit. Rev. Environ. Sci. Technol. 41, 915–950. https://doi.org/10.1080/10643380903300000

Lens, P.N., De Poorter, M.P., Cronenberg, C.C., Verstraete, W.H., 1995. Sulfate reducing and methane producing bacteria in aerobic wastewater treatment systems. Water Res. 29, 871–880. https://doi.org/10.1016/0043-1354(94)00195-

D

Li, X.Q., Brown, D.G., Zhang, W.X., 2007. Stabilization of biosolids with nanoscale zero-valent iron (nZVI). J. Nanoparticle Res. 9, 233–243. https://doi.org/10.1007/s11051-006-9187-1

Madzivire, G., Gitari, W.M., Vadapalli, V.R.K., Ojumu, T. V., Petrik, L.F., 2011. Fate of sulphate removed during the treatment of circumneutral mine water and acid mine drainage with coal fly ash: Modelling and experimental approach. Miner. Eng. 24, 1467–1477. https://doi.org/10.1016/j.mineng.2011.07.009

Marguti, A.L., Ferreira Filho, S.S., Piveli, R.P., 2018. Full-scale effects of addition of sludge from water treatment stations into processes of sewage treatment by conventional activated sludge. J. Environ. Manage. 215, 283–293. https://doi.org/10.1016/j.jenvman.2018.03.072

McCullough, C.D., Lund, M.A., May, J.M., 2008. Field-scale demonstration of the potential for sewage to remediate acidic mine waters. Mine Water Environ. 27, 31–39. https://doi.org/10.1007/s10230-007-0028-y

Metcalf & Eddy, I., Tchobanoglous, G., Stensel, H.D., Tsuchihashi, R., Burton, F., 2013. Wastewater Engineering: Treatment and Resource Recovery, 5th ed. McGraw-Hill Education, New York, NY.

Mitsch, W.J., Wise, K.M., 1998. Water quality, fate of metals, and predictive model validation of a constructed wetland treating acid mine drainage. Water Res. 32, 1888–1900. https://doi.org/10.1016/S0043-1354(97)00401-6

Moses, C.O., Herman, J.S., 1989. Homogeneous oxidation kinetics of aqueous ferrous iron at circumneutral pH. J. Solution Chem. 18, 705–725.

https://doi.org/10.1007/BF00651804

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Hazard. Mater. 98, 33–50. https://doi.org/10.1016/S0304-3894(02)00282-0

Nielsen, P.H., Keiding, K., 1998. Disintegration of activated sludge flocs in presence of sulfide. Water Res. 32, 313–320. https://doi.org/10.1016/S0043-1354(97)00235-2

Novak, J.T., 2006. Dewatering of Sewage Sludge. Dry. Technol. 24, 1257–1262. https://doi.org/10.1080/07373930600840419

O'Melia, C.R., 1973. Coagulation and Flocculation, in: Weber Jr., W.J. (Ed.), Physicochemical Processes for Water Quality Control. John Wiley & Sons, Ltd, New York, NY, pp. 101–103.

Oikonomidis, I., Burrows, L.J., Carliell-Marquet, C.M., 2010. Mode of action of ferric and ferrous iron salts in activated sludge. J. Chem. Technol. Biotechnol. 85, 1067–1076. https://doi.org/10.1002/jctb.2399

Ong, S.-A., Toorisaka, E., Hirata, M., Hano, T., 2010. Adsorption and toxicity of heavy metals on activated sludge. ScienceAsia 36, 204. https://doi.org/10.2306/scienceasia1513-1874.2010.36.204

Park, C., Muller, C.D., Abu-Orf, M.M., Novak, J.T., 2006. The Effect of Wastewater Cations on Activated Sludge Characteristics: Effects of Aluminum and Iron in Floc. Water Environ. Res. 78, 31–40. https://doi.org/10.2175/106143005X84495

Pérez-Sanz, A., Álvarez-Férnandez, A., Casero, T., Legaz, F., José Lucena, J., 2002. Fe enriched biosolids as fertilizers for orange and peach trees grown in field conditions. Plant Soil 241, 145–153. https://doi.org/10.1023/A:1016055607447

Philips, S., Rabaey, K., Verstraete, W.H., 2003. Impact of iron salts on activated sludge and interaction with nitrite or nitrate. Bioresour. Technol. 88, 229–239. https://doi.org/10.1016/S0960-8524(02)00314-0

Pinel-Raffaitin, P., Ponthieu, M., Le Hecho, I., Amouroux, D., Mazeas, L., Donard, O.F.X., Potin-Gautier, M., 2006. Evaluation of analytical strategies for the determination of metal concentrations to assess landfill leachate contamination. J. Environ. Monit. 8, 1069–1077. https://doi.org/10.1039/b606106k

Pukelsheim, F., 1994. The Three Sigma Rule. Am. Stat. 48, 88. https://doi.org/10.2307/2684253

Rasmussen, H., Bruus, J.H., Keiding, K., Nielsen, P.H., 1994. Observations on dewaterability and physical, chemical and microbiological changes in anaerobically stored activated sludge from a nutrient removal plant. Water Res. 28, 417–425. https://doi.org/10.1016/0043-1354(94)90279-8

Ren, S., Frymier, P.D., 2005. Toxicity of metals and organic chemicals evaluated with bioluminescence assays. Chemosphere 58, 543–550. https://doi.org/10.1016/j.chemosphere.2004.07.005

Ruihua, L., Lin, Z., Tao, T., Bo, L., 2011. Phosphorus removal performance of acid mine drainage from wastewater. J. Hazard. Mater. 190, 669–676. https://doi.org/10.1016/j.jhazmat.2011.03.097

Rybczynski, W., Linneman, P.D., 1999. How to save our shrinking cities. Public Interest 30–44.

Rytuba, J.J., 2000. Mercury mine drainage and processes that control its environmental impact. Sci. Total Environ. https://doi.org/10.1016/S0048-9697(00)00541-6

Scaglione, D., Caffaz, S., Ficara, E., Malpei, F., Lubello, C., 2008. A simple method to evaluate the short-term biogas yield in anaerobic codigestion of was and organic wastes. Water Sci. Technol. 58, 1615–1622. https://doi.org/10.2166/wst.2008.502

Schilling, J., Logan, J., 2008. Greening the rust belt: A green infrastructure model for right sizing America's shrinking cities. J. Am. Plan. Assoc. 74, 451–466. https://doi.org/10.1080/01944360802354956

Schramm, A., Santegoeds, C.M., Nielsen, H.K., Ploug, H., Wagner, M., Pribyl, M., Wanner, J., Amann, R., De Beer, D., 1999. On the occurrence of anoxic microniches, denitrification, and sulfate reduction in aerated activated sludge. Appl. Environ. Microbiol. 65, 4189–4196.

Sezgin, M., Jenkins, D., Parker, D.S., 1978. A unified theory of filamentous activated sludge bulking. J. Water Pollut. Control Fed. 50, 362–381.

Sibrell, P.L., Penn, C.J., Hedin, R.S., 2015. Reducing Soluble Phosphorus in Dairy Effluents through Application of Mine Drainage Residuals. Commun. Soil Sci. Plant Anal. 46, 545–563. https://doi.org/10.1080/00103624.2014.998339

Singer, P.C., Stumm, W., 1970. Acidic Mine Drainage: The Rate-Determining Step. Science (80-.). 167, 1121–1123. https://doi.org/10.1126/science.167.3921.1121

Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. Environ. Sci. Pollut. Res. 10, 126–139. https://doi.org/10.1065/espr2002.12.142

Soucek, D.J., Kennedy, A.J., 2005. Effects of hardness, chloride, and acclimation on the acute toxicity of sulfate to freshwater invertebrates. Environ. Toxicol. Chem. 24, 1204. https://doi.org/10.1897/04-142.1

Spanjers, H., Vanrolleghem, P., 1995. Respirometry as a tool for rapid characterization of wastewater and activated sludge. Water Sci. Technol. 31, 105–114. https://doi.org/10.1016/0273-1223(95)00184-O

Strosnider, W.H.J., Llanos López, F.S., LaBar, J.A., Palmer, K.J., Nairn, R.W., 2014. Unabated acid mine drainage from Cerro Rico de Potosí, Bolivia: uncommon constituents of concern impact the Rio Pilcomayo headwaters. Environ. Earth Sci. 71, 3223–3234. https://doi.org/10.1007/s12665-013-2734-z

Strosnider, W. H.J., López, F.S.L., Nairn, R.W., 2011. Acid mine drainage at Cerro Rico de Potosí I: Unabated high-strength discharges reflect a five century legacy of mining. Environ. Earth Sci. 64, 899–910. https://doi.org/10.1007/s12665-011-0996-x

Strosnider, W.H.J., Nairn, R.W., 2010. Effective passive treatment of high-strength acid mine drainage and raw municipal wastewater in Potosí, Bolivia using simple mutual incubations and limestone. J. Geochemical Explor. 105, 34–42. https://doi.org/10.1016/j.gexplo.2010.02.007

Strosnider, W.H.J., Nairn, R.W., Peer, R.A.M., Winfrey, B.K., 2013. Passive co-treatment of Zn-rich acid mine drainage and raw municipal wastewater. J. Geochemical Explor. 125, 110–116. https://doi.org/10.1016/j.gexplo.2012.11.015

Strosnider, William H. J., Winfrey, B.K., Nairn, R.W., 2011. Biochemical oxygen demand and nutrient processing in a novel multi-stage raw municipal wastewater and acid mine drainage passive co-treatment system. Water Res. 45, 1079–1086. https://doi.org/10.1016/J.WATRES.2010.10.026

Stumm, W., Lee, G.F., 1961. Oxygenation of Ferrous Iron. Ind. Eng. Chem. 53, 143–146. https://doi.org/10.1021/ie50614a030

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley.

Stumm, W., O'Melia, C.R., 1968. Stoichiometry of Coagulation. J. Am. Water Works Assoc. 60, 514–539. https://doi.org/10.1002/j.1551-8833.1968.tb03579.x

Teh, C.Y., Budiman, P.M., Shak, K.P.Y., Wu, T.Y., 2016. Recent Advancement of Coagulation–Flocculation and Its Application in Wastewater Treatment. Ind. Eng. Chem. Res. 55, 4363–4389. https://doi.org/10.1021/acs.iecr.5b04703

Ten State Standards, 2014. Recommended Standards for Wastewater Facilities. Albany, NY.

Tenney, M.W., Stumm, W., 1965. Chemical flocculation of microorganisms in biological waste treatment. J. Water Pollut. Control Fed. 37, 1370–1388.

Todd, A.S., Manning, A.H., Verplanck, P.L., Crouch, C., McKnight, D.M., Dunham, R., 2012. Climate-Change-Driven Deterioration of Water Quality in a Mineralized Watershed. Environ. Sci. Technol. 46, 9324–9332. https://doi.org/10.1021/es3020056

Warrender, R., Pearce, N.J.G., Perkins, W.T., Florence, K.M., Brown, A.R., Sapsford, D.J., Bowell, R.J., Dey, M., 2011. Field Trials of Low-cost Reactive Media for the Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK. Mine Water Environ. 30, 82–89. https://doi.org/10.1007/s10230-011-0150-8

Watzlaf, G.R.G., Schroeder, K.K.T., Kleinmann, R.L.P., Kairies, C.L., Nairn, R.W., 2004. The Passive Treatment of Coal Mine Drainage, … States Department of …. Pittsburgh, PA.

Wei, X., Viadero, R.C., Bhojappa, S., 2008. Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants. Water Res. 42, 3275–3284. https://doi.org/10.1016/j.watres.2008.04.005

Winfrey, B.K., Strosnider, W.H.J., Nairn, R.W., Strevett, K.A., 2010. Highly effective reduction of fecal indicator bacteria counts in an ecologically engineered municipal wastewater and acid mine drainage passive co-treatment system. Ecol. Eng. 36, 1620–1626. https://doi.org/10.1016/j.ecoleng.2010.06.025

Yang, Y., Zhao, Y.Q., Babatunde, A.O., Wang, L., Ren, Y.X., Han, Y., 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Sep. Purif. Technol. 51, 193–200. https://doi.org/10.1016/j.seppur.2006.01.013

Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. Mine Water, Environmental Pollution. Springer Netherlands, Dordrecht. https://doi.org/10.1007/978-94-010-0610-1

Younger, P.L., Henderson, R., 2014. Synergistic wetland treatment of sewage and mine water: Pollutant removal performance of the first full-scale system. Water Res. 55, 74–82. https://doi.org/10.1016/j.watres.2014.02.024

Yu, W., Yang, J., Shi, Yafei, Song, J., Shi, Yao, Xiao, J., Li, C., Xu, X., He, S., Liang, S., Wu, X., Hu, J., 2016. Roles of iron species and pH optimization on sewage sludge conditioning with Fenton's reagent and lime. Water Res. 95, 124–133. https://doi.org/10.1016/j.watres.2016.03.016

Yuan, L., Zhi, W., Liu, Y., Karyala, S., Vikesland, P.J., Chen, X., Zhang, H., 2015. Lead Toxicity to the Performance, Viability, And Community Composition of Activated Sludge Microorganisms. Environ. Sci. Technol. 49, 824–830. https://doi.org/10.1021/es504207c

Zhang, T., Ding, L., Ren, H., Guo, Z., Tan, J., 2010. Thermodynamic modeling of ferric phosphate precipitation for phosphorus removal and recovery from wastewater. J. Hazard. Mater. 176, 444–450. https://doi.org/10.1016/j.jhazmat.2009.11.049

Ziemkiewicz, P.F., Skousen, J.G., Brant, D.L., Sterner, P.L., Lovett, R.J., Skousen, J.G., Sterner, P.L., Lovett, R.J., 1997. Acid Mine Drainage Treatment with Armored Limestone in Open Limestone Channels. J. Environ. Qual. 26, 1017. https://doi.org/10.2134/jeq1997.00472425002600040013x

Zita, A., Hermansson, M., 1994. Effects of ionic strength on bacterial adhesion and stability of flocs in a wastewater activated sludge system. Appl. Environ. Microbiol. 60, 3041–3048.