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Abstract

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

26   also be applied to varying AMD matrices. The impact of AMD addition on the MWW

27   microbial community was also investigated which provided evidence of microbial

28   adaptation. This study demonstrates post-aeration co-treatment enables mitigation of mild

29   AMD without adversely affecting WWTP processes. Reported results also frame required

30   future studies to address extant questions prior to full-scale adaptation.

31

32   **Highlights**

33   • Addition of mild AMD to a secondary wastewater treatment processes examined

34   • Co-treatment removed >90% of PO_4^{3-} in wastewater via adsorption

35   • Coagulation of iron particles incomplete, dominated by sweep flocculation

36   • Secondary settling improved at highest drainage dosages

37   • Minor impact to microbial oxygen consumption rates, with adaptation noted.

38

39   **Keywords**

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

41

42   **1. Introduction**

43   Acid mine drainage (AMD) is a legacy pollution issue in many areas with a history of

44   mining activity (Johnson, 2003). AMD is generated when mining exposes pyrite rock (FeS_2)

45   to water in the presence of oxygen, thus facilitating pyrite oxidation and producing waters

46   with elevated acidity and dissolved metals (Akcil and Koldas, 2006; Evangelou and Zhang,

47   1995; Ziemkiewicz et al., 1997). Metals of concern vary geographically and often include

48   iron (Fe), aluminum (Al), manganese (Mn), copper (Cu), zinc (Zn), and lead (Pb) (Jacobs et

49 al., 2014). Climatic change, such as decreases in seasonal snow pack, can also worsen

50 mineral acidity (Todd et al., 2012). Methods for treating AMD include both passive and

51 active approaches. Passive treatment utilizes calcite rock dissolution, constructed

52 wetlands, and/or biological sulfate reduction (Hedin et al., 1994; Johnson and Hallberg,

53 2005; Watzlaf et al., 2004). Active AMD treatment utilizes addition of alkaline chemicals or

54 oxidants (Goodwill et al., 2019; Singer and Stumm, 1970) and ongoing energy inputs for

55 pumping, mixing, and/or aeration (Coulton et al., 2003; Mitsch and Wise, 1998). There are

56 several additional options for co-treating AMD with other waste streams, including the use

57 of organic solid waste substrates or flowback water produced from hydraulic fracturing

58 (Chang et al., 2000; He et al., 2016). Although these co-treatment options improve water

59 quality, disadvantages exist including the need for construction of treatment infrastructure

60 (e.g. wetlands or limestone beds) or perpetual process inputs (e.g. active treatment). These

61 requirements present difficulties for AMD treatment in economically and/or geographically

62 isolated areas.

63   A novel approach for AMD mitigation is co-treatment with municipal wastewater

64 (MWW) in existing wastewater treatment plants (WWTPs). Co-treatment is the

65 combination of AMD and MWW waste streams, turning one into a resource, best utilizing

66 extra WWTP capacity, and further leveraging existing infrastructure and energy inputs.

67 Declining industrial activity and urban population shifts has resulted in "shrinking cities"

68 for some North American municipalities with historical industrial centers (Rybczynski and

69 Linneman, 1999; Schilling and Logan, 2008). This population loss, combined with water

70 conservation efforts has decreased overall domestic sewage production and increased

71 financial stress on utilities (Faust et al., 2016). As a result, these WWTP have extra

72   treatment capacity (Dominguez and Gujer, 2006). Co-treating MWW with AMD makes use

73   of this extra capacity and may ultimately improve MWW treatment, while simultaneous

74   mitigating the ecological impact from AMD on receiving water.

75   Both AMD and MWW pose serious risks to the environment if inadequately treated.

76   Eutrophication is a problem in surface waters, globally (Dodds and Smith, 2016; Smith,

77   2003). Nitrogen and phosphorus present in MWW can cause eutrophication in downstream

78   receiving waters (Harper, 1992). Co-treatment offers WWTPs a low-cost nutrient

79   management approach utilizing another waste stream. The addition of Fe-based coagulants

80   is a relatively common approach to nutrient removal in these situations, and AMD co-

81   treatment presents a primary beneficial use of this otherwise problematic waste (de-

82   Bashan and Bashan, 2004). AMD discharges to surface waters also degrade water quality

83   by acidification and increased metal loadings which pose risks to aquatic ecosystems

84   (Azapagic, 2004; Gray, 1998). The co-treatment of AMD and MWW can remove metals from

85   low pH AMD while also decreasing effluent biochemical oxygen demand (BOD) and

86   Phosphorous (P) in higher pH MWW (Hughes and Gray, 2013a; Strosnider et al., 2013,

87   2011). AMD can also decrease fecal bacteria counts from a MWW discharge when mixed *in*

88   *situ* (i.e. within a stream) under low-flow conditions (Kruse et al., 2019).

89   The effectiveness of passive MWW and AMD co-treatment utilizing specific,

90   additional infrastructure has been quantified across several scales. Bench-scale treatment

91   wetlands with clarification, biofilm media, and limestone beds have also effectively co-

92   treated AMD and MWW by removing BOD and dissolved metals from the combined

93   wastewaters (Strosnider and Nairn, 2010; Winfrey et al., 2010). In other bench-scale

94   studies, sludge from an active AMD treatment plant was mixed with synthetic and raw

95   MWW effluent at several ratios to determine the potential for enhanced P removal, yielding

96   over 90% P removal and residual P levels below 0.5 mg/L (Ruihua et al., 2011; Wei et al.,

97   2008). Field-scale research has included the addition of AMD to an evaporation pond for

98   MWW, which increased solution pH and removed metal and sulfate concentrations from

99   the wastewaters during 18 months of monitoring (McCullough et al., 2008). A large pilot-

100 scale aerobic wetland, one of the first attempts to treat an AMD discharge with poorly

101 treated secondary MWW, removed Fe (> 60%) and BOD (> 30%) well beyond system

102 design expectations (Johnson and Younger, 2006). The first full-scale co-treatment wetland

103 provided evidence that water quality improved with co-treatment increasing BOD, NH_3-N,

104 Fe, and total P removal during a four-year monitoring period (Younger and Henderson,

105 2014). Although successful, these examples of co-treatment still require establishment of

106 new treatment infrastructure and do not adequately inform the feasibility of direct co-

107 treatment within an existing WWTP.

108   The addition of AMD to any portion of a conventional activated sludge treatment

109 system poses risks to the biological treatment phase, however, data quantifying these

110 potential impacts is limited. An influx of AMD constituents (e.g. metals, trace organics)

111 could impact microbial community survival, taxonomy, and/or oxygen utilization rates

112 (Ong et al., 2010; Ren and Frymier, 2005; Yuan et al., 2015). Although Fe is a crucial

113 element for growth in nearly all biological organisms, large fluxes of Fe can be detrimental

114 to microorganisms (De Freitas and Meneghini, 2001). The use of Fe-based coagulants in

115 activated sludge systems can impact microbial metabolism, decrease nitrification, and

116 degrade floc formation due to elevated Fe(III) content (Clark et al., 2000). This decreased

117 suspended solids removal is a function of excessive filamentous bacteria growth, a problem

118   that frequently plagues conventional MWW treatment facilities (Sezgin et al., 1978).

119   Similarly, Fe(III) concentrations of ~100 mg Fe/L in activated sludge can inhibit overall

120   microbial activity and nitrification (Philips et al., 2003) However, at lower Fe additions (25

121   mg Fe/L), microbial activity and nitrification were not inhibited but less stable flocs were

122   observed (Oikonomidis et al., 2010). In a simultaneous nitrification, denitrification, and P

123   removal process, high Fe(III) concentrations can decrease N removal, but this inhibition

124   can be adapted to and recovered after four, 270-minute cycles (Jia et al., 2016).

125   Furthermore, Deng and Lin (2013) demonstrated co-treating prior to an anaerobic

126   biological treatment step can maintain system performance, completely remove PO_4^{3-}

127   under certain conditions, increase alkalinity, and consistently decreasing COD by >60%.

128   Only one study has focused on AMD and MWW co-treatment in a conventional

129   activated sludge system (Hughes and Gray, 2013b). Hughes and Gray (2013) examined

130   several different options for co-treatment including (1) the addition of untreated AMD to

131   aeration tanks, (2) the pretreatment of AMD by mixing with digested sewage sludge

132   followed by sedimentation and then mixing in the aeration tank, and (3) the pre-treatment

133   of AMD by mixing with screened MWW prior to treatment in the aeration tank. In all of

134   these experiments, a synthetic AMD was made to simulate the chemistry from copper

135   mines in Ireland (pH 3.6, Fe = 130 mg/L, Al=150 mg/L, and SO_4^{2-} = 1670 mg/L). Systems

136   co-treating with MWW remained effective at removing metals and COD by precipitation

137   and adsorption mechanisms in the activated sludge reactors. In the co-treatment

138   experiments, the synthetic AMD was mixed with synthetic MWW at a 1:2 AMD:MWW

139   volumetric ratio. Metal removal by adsorption was relatively high in all experimental

140   configurations, averaging 52-84% for Al and 74-86% for Fe. Final effluent COD

141   concentrations were generally less than 50 mg/L for all treatment configurations but

142   increased on the last sampling event in experiments where AMD was pretreated before

143   addition to aeration reactors. This project concluded that co-treatment did not cause a

144   significant decrease in, nor improve, system performance for the removal of COD, total

145   organic carbon (TOC), or BOD compared to controls, but did improve P and metals removal.

146   Additional work by Hughes and Gray (2012) used Activated Sludge Respiration Inhibition

147   Tests (Organization for Economic Cooperation and Development Method 209) to show that

148   activated sludge systems could adapt to and function with AMD additions as high as 50%

149   by volume.

150   The strength of the AMD utilized in co-treatment systems may have major process

151   implications. Many of the aforementioned studies examined co-treatment utilizing a

152   narrow range of strong AMD (pH range 2-4.5), neglecting potential impacts when utilizing

153   milder (pH >4.5) Class I AMD (as defined by Watzlaf et al., 2004). Class I AMD may make

154   up >50% of discharges in the eastern United States (Herlihy et al., 1990), with the vast

155   majority in Northern Appalachia (Watzlaf et al., 2004). Mild or circumneutral discharges

156   are not a localized phenomenon and may also be found in the mid-western United States

157   (Labrenz and Banfield, 2004), Southern Africa (Madzivire et al., 2011), the United Kingdom

158   (Warrender et al., 2011), and certain regions of China (Feng et al., 2014). These mild AMD

159   discharges may be more conducive for co-treatment having bulk water qualities (e.g., pH,

160   alkalinity, etc.) more similar to MWW.

161   The small quantity of data on co-treatment with mild AMD in WWTPs leaves many

162   unanswered questions regarding the physicochemical and biological processes within an

163   existing WWTP. Also, the variability of AMD water quality leaves the opportunity for novel

164   co-treatment developments utilizing AMD of various water chemistry. The overarching

165   objectives of this study were to quantify the water quality impacts of co-treating

166   circumneutral AMD with secondary MWW MLSS and elucidate the underlying mechanisms.

167   There are many locations within a WWTP where AMD could be added, however the

168   presented study addresses mixing AMD post aeration basin and prior to secondary settling

169   (Figure S1). Laboratory work included bench-scale experimentation with robust water

170   quality analysis, in conjunction with water quality modeling. In order to fill known research

171   gaps, specific project aims included: (1) assessing changes in overall water quality, (2)

172   evaluating coagulation potential from AMD-sourced Fe, (3) demonstrating enhanced PO_4^{3-}

173   removal, and (4) characterizing the impact on MWW microbial metabolism. Results of this

174   study advance co-treatment towards potential full-scale adaptation within existing

175   WWTPs.

176

177   **2. Materials & methods**

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

179

180   2.1. Water quality and sampling

181   AMD was collected from an abandoned mining site near the core of a city with

182   declining population and industrial activity (Johnstown, PA; see Figure S3). Historic water

183   quality for the mild AMD includes a slightly acidic pH (average pH=6.1) and averages 85

184   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

185   mg/L of total Mn. The mild AMD has relatively low acidity, which is typical of AMD found in

186   coal mining regions in eastern North America (Hedin et al., 1994). AMD samples were

187 collected immediately downstream from the AMD discharge pipe. This low-pH, high-Fe

188 AMD source was selected due to its proximity to a situationally-relevant (i.e. shrinking

189 cities) WWTP. MWW were collected from a conventional WWTP (average flow = 10 MGD)

190 at the same time of AMD collection. Mixed liquor suspended solids (MLSS) was collected

191 from the WWTP aeration tank effluent, prior to the secondary clarifiers and used to

192 represent "MWW" samples. The MLSS samples were mixed to prevent the sludge from

193 becoming anoxic. Raw AMD and MLSS (MWW) samples were collected headspace free in

194 collapsible five-gallon polyethylene containers. Methods for examining the impacts on a

195 microbial community are presented in Section 2.4.

196

197   2.2. Experimental design

198   All experiments were performed in mixed, square 2-L batch reactors (Phipps &

199 Bird). Eight different sample matrices were tested. MWW MLSS was mixed with either AMD

200 or deionized water (DI) at ratios of 1:25, 1:15, and 1:5 (AMD:MWW; DI:MWW) in addition

201 to 100% AMD-only and 100% MWW-only as controls. Ratios were chosen based on

202 practical estimates of extra treatment capacity. All experiments were performed in

203 triplicate. Quality control experiments utilized DI water in place of AMD to address

204 potential dilutive effects from AMD. Samples were mixed for five minutes at $G \sim 120$ sec^{-1}

205 to simulate the two waste streams rapidly mixing in a pipe. They were subsequently

206 allowed to settle for 30 min, representing final clarification (Standard Method 2710D,

207 APHA, 2012). After settling, the top ~ 1 L of supernatant, representing a secondary settling

208 effluent, was decanted into a borosilicate glass beaker. The supernatant beakers were

209 placed on stir plates and mixed while sub-samples for further analysis were collected.

210

211   2.3. Supernatant analysis

212   The settled sludge blanket height was recorded prior to the supernatant being

213   decanted. Supernatant pH values were determined immediately (Mettler-Toledo LE438

214   ATC probe/FiveEasy Plus FP20 meter). Sample turbidity was determined using a portable

215   turbidimeter (Hach, 2100Q) following EPA method 180.1 (via Hach method 8195).

216   Streaming current (a method for quantifying suspended particle surface charge *in situ*;

217   (Dentel et al., 1989)) was determined using a laboratory charge analyzer (Chemtrac LCA-

218   01).

219   COD was determined for each sample by the reactor digestion method using Hach

220   low range COD vials according to Hach Method 8000. Vials were digested in a digital

221   reactor block (Hach, DRB200) and analyzed using a UV-Vis spectrophotometer (Hach,

222   DR6000). BOD was determined by the 5-day BOD test performed at 20 °C (Standard

223   Methods 5210B). Three BOD bottles were collected per beaker at varying dilutions.

224   Dissolved oxygen concentrations were collected using an optical BOD probe (YSI Pro

225   Series) with a multiparameter meter (YSI Pro Plus).

226   Anion samples for NO_3^-, SO_4^{2-} and PO_4^{3-} were collected in amber glass vials, filtered

227   through 0.45-μm nylon filters, and analyzed within 24 hours on an ion chromatograph

228   (Dionex ICS-1100) with an AS18 column following EPA method 300.

229   Samples for solids content were collected in 1000 mL HDPE bottles and stored at ~

230   4 °C for later analysis. Total solids (TS) were determined by evaporating 100 mL overnight

231   for 10-12 hours in pre-dried and pre-weighed 150 mL Erlenmeyer culture media flasks at

232   103 °C (Standard Methods 2540). Total dissolved solids (TDS) were determined in a similar

233   manner with the exception that a 50 mL sample volume was filtered through 0.45-μm

234   nylon filters (Fisher).

235   Samples for Fe, Al and Mn were collected in metals-free Nalgene LPDE bottles and

236   preserved to 2% with trace metal grade HNO_3. Fe, Al, and Mn were selected due to their

237   relative geographic abundance in AMD discharges. For each beaker, metals concentrations

238   were fractionated with various filter pore sizes to quantify the relative size distribution of

239   resulting particles under each condition (Carlson et al., 1997; Goodwill et al., 2015).

240   Fractionated particles were operationally defined as total, colloidal or dissolved. The total

241   particulate metals were unfiltered and colloidal metals were filtered 0.20-μm nylon filters,

242   and each sample was collected in triplicate. Two samples per experimental water matrices

243   (i.e. two for each tested ratio & control) were also filtered through 30 kDa ultrafiltration

244   (UF) membranes inside a 200 mL nitrogen pressurized stirred UF cell (Amicon). Total

245   metal samples were digested in a digestion/extraction microwave system (CEM, Mars 6)

246   according to EPA method 3015A. Metals concentrations were then quantified using an

247   inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific X-Series 2)

248   measuring isotopes Fe-57, Al-27 and Mn-55. While Fe speciation was not quantified,

249   thermodynamics at equilibrium under test conditions suggest the primary species to be

250   Fe(III).

251

252   2.4. Cellular respiration

253   Cellular respirometric oxygen demand (i.e. respirometry) was used to assess the

254   impact of AMD on the microbial community within an activated sludge system (Scaglione et

255   al., 2008). Respirometer experiments compared the microbial oxygen uptake between a

256   control aeration mixed liquor sample to a co-treated sample containing synthetic AMD at a

257   ratio of 1:15. Aeration tank mixed liquor samples (MLSS = 4,670 mg/L, data obtained from

258   WWTP operations report at time of collection) were collected at the Mattabassett District

259   Water Pollution Control Facility (Cromwell, CT), a conventional aeration MWW treatment

260   facility. Synthetic AMD was generated in the lab to replicate the batch study AMD using

261   ultrapure deionized water and dosed to an Fe content of 200 mg/L using a 1000 mg/L Fe

262   standard solution (in 3% HCl) and initial pH adjusted to ~6 with NaOH and H_2SO_4

263   (Karapanagioti and Atalay, 1996).

264   Trials were performed in specialized, air tight 250mL sample bottles (Xylem WTW,

265   MF45). Each bottle was equipped with a CO_2 absorbent quiver, filled with NaOH pellets

266   (98%, Fisher Chemical) to absorb CO_2 gas during experimentation, and sealed with a

267   calibrated WTW OxiTop-C measuring head. Each sample was run in triplicate. The samples

268   were continuously mixed for 4 hours to simulate the hydraulic retention time of typical

269   aeration tanks (Ten State Standards, 2014). Results were gathered using the OxiTop OC100

270   controller and data was reported in mg/L of BOD (Spanjers and Vanrolleghem, 1995).

271

272   2.5. Statistical presentation of data

273   All reported values represent the mean of triplicate experimental replicates. All error

274   bars represent the 95% confidence interval (2 standard deviations (σ)), unless otherwise

275   noted. Within each triplicate, any individual value that was more than 3 σ, or outside the

276   99.7% confidence interval (Pukelsheim, 1994) from the mean was considered an outlier.

277

278   2.6. Water quality modeling

279   Iron speciation, pH, PO_4^{3-} were modeled to further understand the impacts of co-

280   treatment, and elucidate mechanisms underlying laboratory measurements. The influence

281   of varying AMD acidity on pH was examined by calculating the alkalinity and total H^+ that

282   would result from mixing AMD of several pH's with pH 6.7 MWW, under open-system

283   carbonate buffering conditions (Stumm and Morgan, 1996), using Equation S5. Changes in

284   PO_4^{3-} concentration were used to create an adsorption isotherm, in a manner similar to

285   Yang et al. (2006). Experimental data was fitted to the Langmuir isotherm (see SI S5,

286   Equation S7) where a high (>0.95) linear coefficient of determination would indicate

287   adsorption as the primary mechanism. The resulting regression also allowed for the

288   determination of the maximum adsorption capacity under tested conditions. It was

289   assumed experimental mixing and settling was sufficient for the adsorption reaction to

290   reach equilibrium. Fe speciation resulting from co-treatment was determined by combining

291   applicable pK_s values (Stumm and Morgan, 1996) with empirical models for Fe stability

292   and coagulation (Johnson and Amirtharajah, 1983). This allowed further assessment of

293   dominate coagulation mechanisms.

294

295 **3. Results & Discussions**

296   3.1. Supernatant water quality

297   Figure 1 reports impacts of AMD's on general supernatant water quality

298   characteristics. Co-treating had little influence on pH (Figure S4). All pH values were above

299   6.0, a typical Environmental Protection Agency (EPA) National Pollutant Discharge

300   Elimination System (NPDES) permit limit for MWW facilities (Environmental Protection

301   Agency, 2019; EPA Region 3, 2016). The negligible pH change in this study is attributed to

302 relatively low acidity and high pH of the AMD. Measured results closely follow the modeled

303 pH (Figure S4).
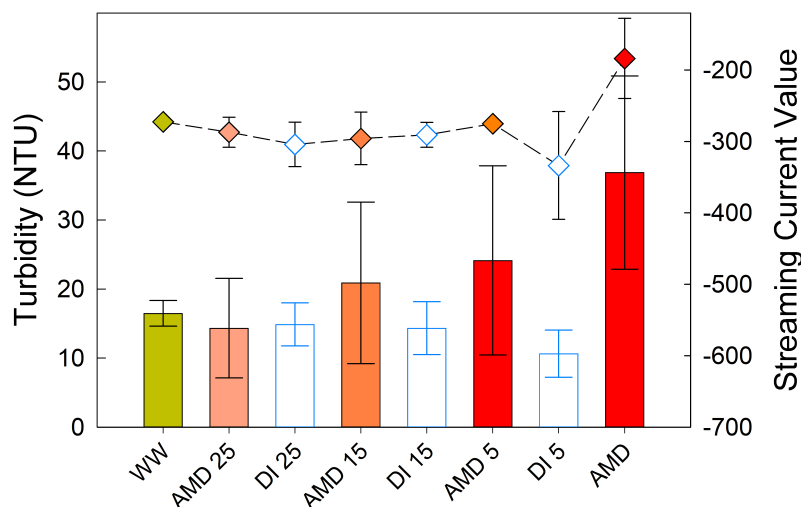
304

305 Figure 1: Sample turbidity (bars) and streaming current surface charge (points). Dashed

306 line represents trend between experimental data points.

307   Higher strength AMD than the matrix used in this work could still be feasible in co-

308 treatment. Alkalinity and pH modeling results show that co-treating at 1:25 with AMD of a

309 pH as low as 2.7 would still leave MWW (with a similar pH and alkalinity to experimental

310 MWW) effluent above discharge minimums of pH 6.0 (Figure S4). Mild AMD with a pH

311 similar to that of AMD used in this study could theoretically be used up to AMD:MWW

312 ratios beyond 1:1 whereas co-treatment with stronger AMD of pH 3.0 could likely not

313 exceed 1:25. Moderate strength AMD at a pH of 4.0 could still be feasible for co-treatment

314 at ratios up to 1:3 where the mixed pH would remain above the target minimum, pH 6.0.

315 These modeled results are in agreement with co-treatment performed with lower pH AMD

316 (Deng and Lin, 2013).

317   No significant difference in AMD nor DI supernatant turbidity relative to the MWW-

318   only (MLSS) control was noted (Figure 1). Although all co-treated turbidity values were

319   statistically similar to each other (within 2 σ, see section 2.5), the averages appear to trend

320   upwards with higher values of AMD resulting from the relatively high turbidity of the AMD-

321   only control. The turbidity trends of the co-treated trials agree with predictions from a

322   simple mass balance on TSS (turbidity of AMD added with turbidity of MWW at each ratio,

323   Equation S7). The similarity of settled turbidity values across all experiments indicates a

324   stable colloidal suspension.

325   The addition of positively charged hydrolyzed Fe (and Al) species from AMD could

326   serve as a coagulant and destabilize particles in the co-treated mixture via charge

327   neutralization and or "sweep-flocculation" mechanisms (Davis and Edwards, 2014).

328   However, co-treatment had no influence on particulate surface charge (Figure 1) which

329   indicates that charge neutralization was not significant. No change of particulate surface

330   charges can be explained by several factors. The experimental water chemistry (pH and Fe

331   concentration) was not favorable for adsorption-destabilization (charge neutralization)

332   mechanisms, as shown in Figure S5 (Johnson and Amirtharajah, 1983). Rather,

333   experimental conditions were more likely to have encouraged sweep flocculation, where

334   the kinetic energy of larger falling particles is adequate to overcome electrostatic surface

335   repulsive forces of suspended particles (Gregory and O'Melia, 1989). Additionally, NOM in

336   MWW exhibits coagulant demand, which likely dominates surface charge neutralization,

337   making destabilization even less favorable (Stumm and O'Melia, 1968). These elevated

338   concentrations of organic matter require increased coagulant doses compared with what

339   would typically be required to achieve destabilization (Fettig and Ratnaweera, 1993).

340   Furthermore, the presence of PO_4^{3-} likely impacted charge neutralization potential. Fe(III),

341   and other metals, have a strong affinity for available PO_4^{3-} , and the majority of PO_4^{3-} would

342   need to be adsorbed and precipitated before Fe(III) would begin to destabilize suspended

343   MWW colloids (Tenney and Stumm, 1965). Higher AMD:MWW ratios would theoretically

344   provide increased particle destabilization, however these ratios were not studied

345   experimentally due to the perceived practical limits on WWTP capacity. pH modeling

346   demonstrates the addition of higher strength AMD will further suppress pH (SI S4), shifting

347   water chemistry into regions favorable for charge neutralization (Figure S5).

348

349   3.2. Supernatant solids characterization

350   Sludge settling was not significantly impacted by AMD co-treatment, with the

351   exception of the highest AMD addition ratio (Figure 2A). The highest AMD dose improved

352   settling by 20% over MWW-only, while other co-treatment conditions showed negligible

353   improvement. No settling is reported for the AMD as the discharge contained only small

354   and dissolved solids. The significant settling improvement noted at the highest AMD ratio

355   was not seen with the same significance in DI water at that same ratio, suggesting

356   improvement was not a function of dilution. Improved settling with increasing AMD ratio,

357   despite little change in surface charge, demonstrates sweep flocculation as the controlling

358   particle destabilization mechanism, in agreement with coagulation modeling (Figure S5).
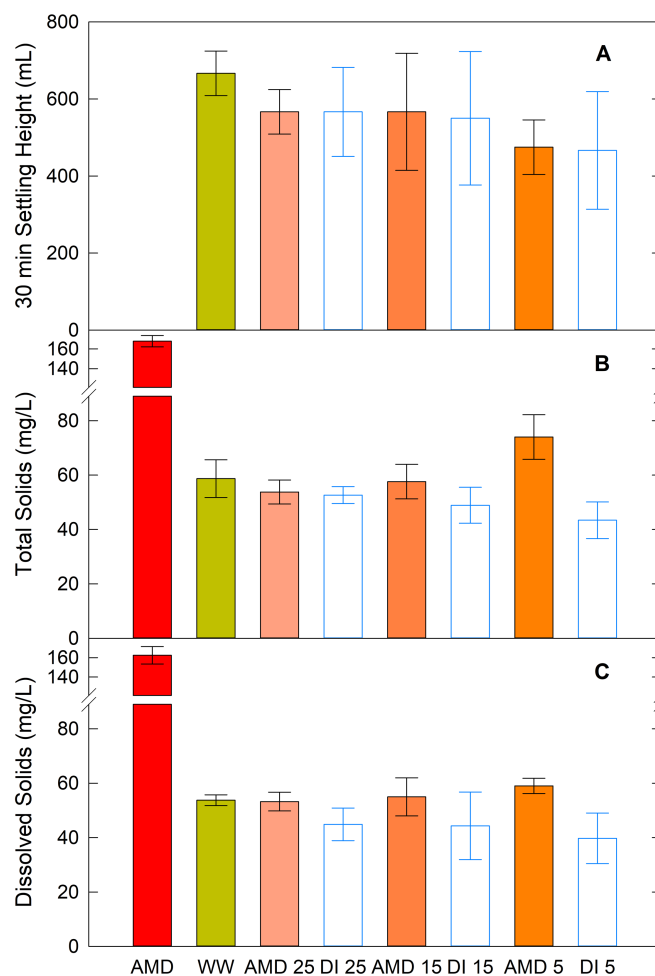
Figure 2: (A) Recorded sludge height in mL after 30 min of settling; (B) Experimentally determined total solids remaining in supernatant; (C) Experimentally determined dissolved solids remaining in supernatant

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

369   quality consideration. A relatively constant TDS concentration suggests AMD addition does

370   not significantly increase the effluent ionic strength, which is proportional to TDS (Kemp,

371   1971; Langelier, 1936). If the TDS and subsequent ionic strength were to have increased,

372   this could have decreased adsorption of PO_4^{3-} onto Fe(III) and promote destabilization

373   (break up) of aggregates (Zhang et al., 2010; Zita and Hermansson, 1994). MWW can be co-

374   treated with high volumes of AMD without TDS being of concern.

375   Although some changes in solids concentration were experienced, both the TS and

376   TDS concentrations in all co-treatment trials were lower than what was predicted by mass

377   balance (Tables S1 & S2). AMD 1:25 and 1:15 trials had 15% fewer TS while the AMD 1:5

378   had just ~10% less. A decrease in supernatant solids was likely a function of improved

379   coagulation by sweep flocculation, as discussed in section 3.1. An increased concentration

380   of settling solids would result in increased resultant sludge, in agreement with the minimal

381   changes seen in sludge blanket height (Figure 2A). TDS were proportional to the amount of

382   AMD added. As the AMD ratio increased, the amount of post-settling TDS was 9% to 24%

383   less than predicted by mass balance calculations (e.g. 10-15 mg/L TDS). The majority of

384   this apparent loss in TDS corresponds to the mass of PO_4^{3-} removed via adsorption onto Fe

385   particles (see Section 3.4).

386   The TSS values were not directly measured in this study, but approximated by

387   calculating the difference between the TDS and TS values. The WWTP influent TSS,

388   obtained from the facilities DEP/EPA reports, generally contains 166 mg/L. All calculated

389   experimental TSS concentrations were below 15 mg/L, within a typical NPDES permit

390   weekly TSS discharge limits of 40-50 mg/L (Environmental Protection Agency, 2019; EPA

391   Region 3, 2016). These results demonstrate co-treatment positively impacted MWW

392 effluent solids and retained TSS removals (compared to influent) of over 90%. It is

393 important to note TSS removal may have been influenced by experimental mixing

394 conditions. The velocity gradients generated during rapid mixing (G > 100 sec^{-1}) could have

395 caused orthokinetic flocculation (i.e. fluid shear), an increase in collision frequency

396 between suspended particles, resulting in larger flocs (Han and Lawler, 1992; Teh et al.,

397 2016). The noted improvement in TSS removal was likely a function of both orthokinetic

398 flocculation and differential sedimentation (i.e., sweep flocculation).

399

400   3.3. Co-treatment impacts on oxygen demand

401   Co-treatment had minimal impact on both BOD and COD of the MWW (Figure 3).

402 The COD remained relatively constant under all conditions. However, the average COD in

403 all AMD experiments was lower than theoretically determined values (Table S3, Equation

404 S3) by ~10%. The slight loss of COD suggests that there was some removal during the co-

405 treatment process. COD removal is likely a mechanism of either microbial-mediated

406 aggregation of organics resulting in bioflocculation, or through adsorption of biomaterial

407 onto Fe (Choo and Kang, 2003; Jimenez et al., 2007). BOD results were similar (Figure 3).

408 The BOD between all samples was similar relative to the MWW-only control, meaning co-

409 treatment did not further increase oxygen demand. This is an important operational

410 consideration as BOD is one of the most critical effluent water-quality parameters.
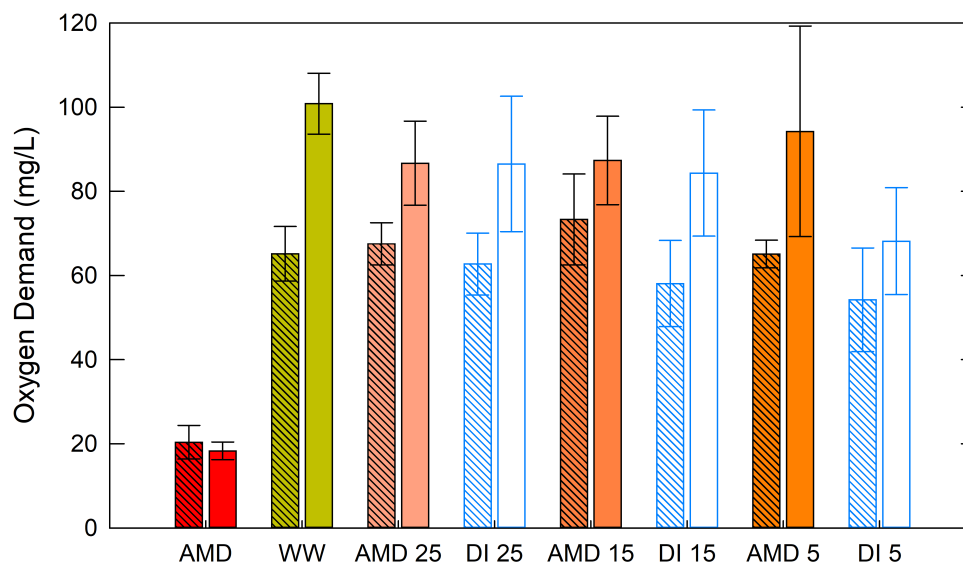
Figure 3: Oxygen demand remaining for each sample after treatment

3.4. Influence on ion concentrations

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

426   environments are conducive for sulfate reduction (Schramm et al., 1999). One potential

427   issue that could arise from increased SO_4^{2-} reduction is the resultant sulfide (S)

428   concentrations that can disrupt floc formations and Fe-based coagulation processes by the

429   formation of FeS (Nielsen and Keiding, 1998).

430   Results from PO_4^{3-} analysis demonstrate the potential of co-treatment to

431   significantly decrease PO_4^{3-} (and total P) concentrations in MWW (Figure 4A). Although

432   PO_4^{3-} exists as inorganic and organic forms in MWW, the non-speciated total PO_4^{3-} was

433   deemed sufficient for this study as typical MWW effluent discharge limits are set in terms

434   of total P. All three AMD ratios exhibited PO_4^{3-} removal, with the 1:15 condition averaging

435   ~84% decrease and the 1:5 trials averaging >97% decrease, significantly improved over

436   the MWW control. DI trials showed no improvement over dilution alone. These results

437   support the use of AMD co-treatment as a lower cost alternative for tertiary treatment

438   focused on P-removal, especially in shrinking cities or other economically and

439   geographically disadvantaged areas. Decreasing P discharges into water where it is a

440   limiting nutrient is of increasing concern, globally, as a strategy to control harmful algal

441   blooms and eutrophication (Alexander et al., 2008; Anderson et al., 2008).
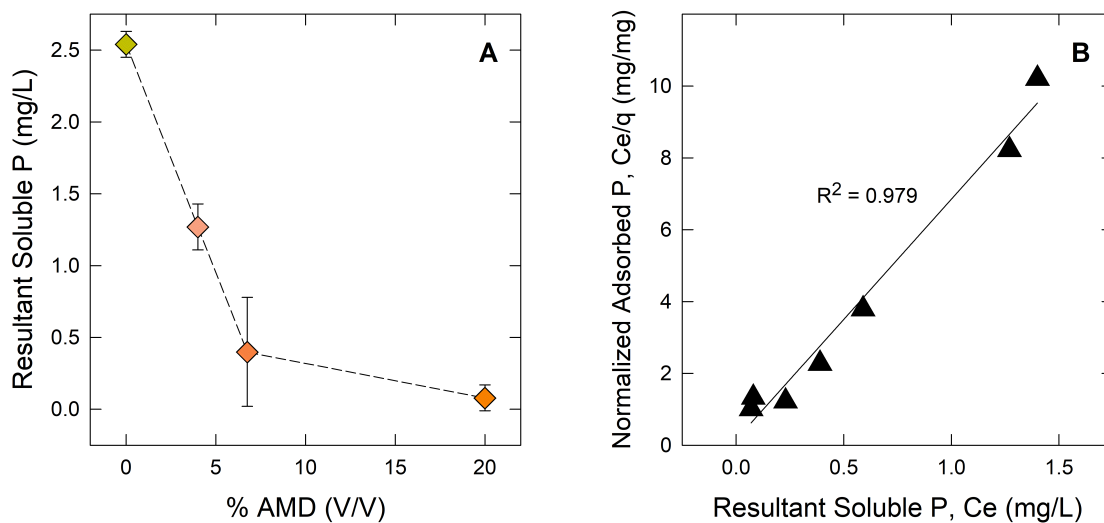
442

443 Figure 4: A) Total P concentrations remaining in each sample supernatants, measured

444 as mg/L PO₄ on IC. Dashed line represents trend between experimental data points B)

445 Langmuir isotherm behavior of experimental data, demonstrating adsorption

446 mechanism of P removal. Further explanation in SI S5.

447   PO_4^{3-} removal closely follows Langmuir isotherm behavior. The relative linearity (R^2 =

448 0.979) confirms that PO_4^{3-} adsorption unto *in situ* AMD-generated Fe oxides is the

449 mechanism for nutrient removal in co-treatment (de-Bashan and Bashan, 2004; Kavanaugh

450 et al., 1978). PO_4^{3-} removal via adsorption further explain the streaming current and

451 settling results discussed in section 3.1, as PO_4^{3-} adsorption unto Fe(III) drastically impedes

452 coagulation (Tenney and Stumm, 1965). Furthermore, the Langmuir relationship

453 quantified the maximum adsorption capacity of the co-treatment system as 0.15 mg P per

454 mg Fe added (0.46 mg PO_4^{3-}/mg Fe; see SI S5).

455

456   3.5. Supernatant metals concentrations

457   Total Mn and Al in both the AMD and secondary MWW were low, making AMD Fe

458   the primary constituent of concern. Total Fe in AMD was 147 mg/L while there was little Fe

459   in the raw MWW (< 2 mg/L). Settled, total Fe increased with increasing ratio to a maximum

460   of 21 mg/L (Figure 5). The majority of Fe was operationally defined as dissolved,

461   comprising 57% and 73% of the total Fe content in the AMD 1:15 and AMD 1:5,

462   respectively. This is similar to the raw AMD in which over 80% of Fe passed through the UF

463   membrane.
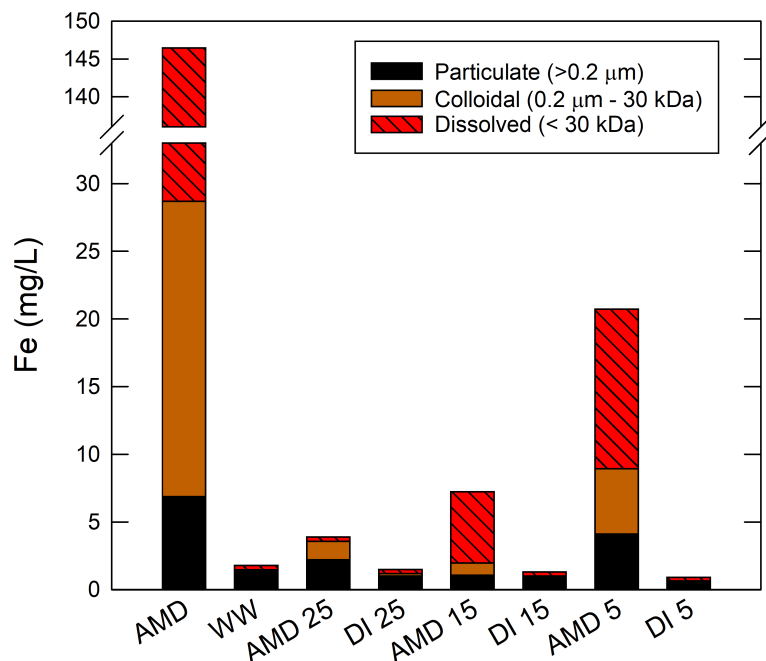
464

465   Figure 5: Fractionated iron content showing operationally defined particulate, colloidal

466   and dissolved Fe. Bars represent the mean value for each of the three fractions

467   The amount of dissolved Fe is orders of magnitude higher than what would be

468   thermodynamically expected from an Fe(III) solubility diagram at pH ~6.5 (Figure S5),

469   suggesting that operationally defined "dissolved" Fe is actually amorphous nanoscale

470 Fe(III). This is supported by the stable colloidal conditions demonstrated by the streaming

471 current results (Figure 1, surface charge), where aggregation is expected to be quite

472 limited. The presence of PO_4^{3-} during Fe precipitation can result in particles operationally

473 defined as dissolved despite thermodynamic predictions to the contrary (Jiang et al., 2015).

474   Mass balance calculations showed a significant portion of the Fe gravimetrically

475 separated with the sludge (see SI S7, Table S4). The fraction of total Fe removed from the

476 bulk solution ranged from ~50% (AMD 1:25) down to ~30% in the AMD 1:5. The AMD

477 1:15 ratio settled out approximately 38% of Fe added. Although AMD could have

478 contributed insoluble Fe(II) to the system (Watzlaf et al., 2004), this was unlikely under

479 experimental conditions. Since the solutions were open to the atmosphere, rapid mixed for

480 several minutes, and under circumneutral pH, the oxygenation of Fe(II) to Fe(III) would

481 have quickly proceeded to equilibrium (k = 1.5-3.0 x 10^{13} M^{-2} atm^{-1} min^{-1}) (Davison and

482 Seed, 1983; Moses and Herman, 1989; Stumm and Lee, 1961). Under equilibrium

483 conditions at experimental pH, both Fe(II) solubility (O'Melia, 1973) and Fe redox potential

484 (pE) indicate high percentages of Fe(II) were unlikely. This low percentage of Fe settling

485 with MWW sludge was more likely a result of suspended, nanoscale Fe particles. The

486 approximate Stoke's law terminal settling velocities of these small (< 0.2 μm) particles are

487 no faster than 0.6 cm/day (assuming T = 15 °C, $\rho_{particle}$ = 4250 kg/m^3) meaning an

488 operationally longer settling time would not significantly improve Fe concentrations in

489 effluent. Although it is uncommon for WWTPs to have Fe discharge limits, removal of Fe is

490 important to maintain high effluent quality and decrease the total Fe load on the receiving

491 water body; however, the hypothetical co-treatment effluent Fe loading from supernatant

492   produced in this study represents an order of magnitude improvement over an unabated

493   AMD discharge.

494

495   3.6. Co-treatment impact on microbial activity

496   Co-treating MWW with AMD can impact the metabolism of activated sludge

497   microbes. In respirometric experiments where AMD was mixed with MWW (MLSS), BOD

498   consumption rates were impeded compared to trials where no AMD was added (Figure 6).

499   The respirometer reactors with no AMD added achieved a higher realized-BOD

500   consumption over the 4-hr period and consumed oxygen at a faster average rate than those

501   with AMD. There is also a much larger variance in the co-treatment reactors relative to the

502   narrow variation in the MLSS-only controls. Reactors with AMD consumed oxygen at a

503   slower rate initially, likely due to the stress induced by a perturbation in water quality.

504   Over the four hours, the MWW samples consumed oxygen (O_2) at an average rate of 3.5

505   mg/L of O_2 per hour [(O_2)/hr] while the co-treated reactors consumed at only 1.9 (O_2)/hr.

506   In the first hour, oxygen consumption was nearly three times faster in reactors with only

507   MWW (i.e., 3.7 (O_2)/hr in MWW reactors vs 1.2 (O_2)/hr in AMD:MWW reactors). However,

508   the difference between the two sample rates began to decrease over time. During the last

509   hour the co-treated samples consumed O_2 at a rate similar to the MWW samples, 5.5 vs 4.9

510   (O_2)/hr. The 5.5 (O_2)/hr is also the highest average hourly rate exhibited by any sample.

511   This suggests that the bacteria in co-treated samples had begun to acclimate. Acclimation

512   time at full-scale would be impacted by hydraulic residence time (4-8 hours), solids

513   retention time (3-15 days (Metcalf & Eddy et al., 2013)), and sludge recycle rates.

514
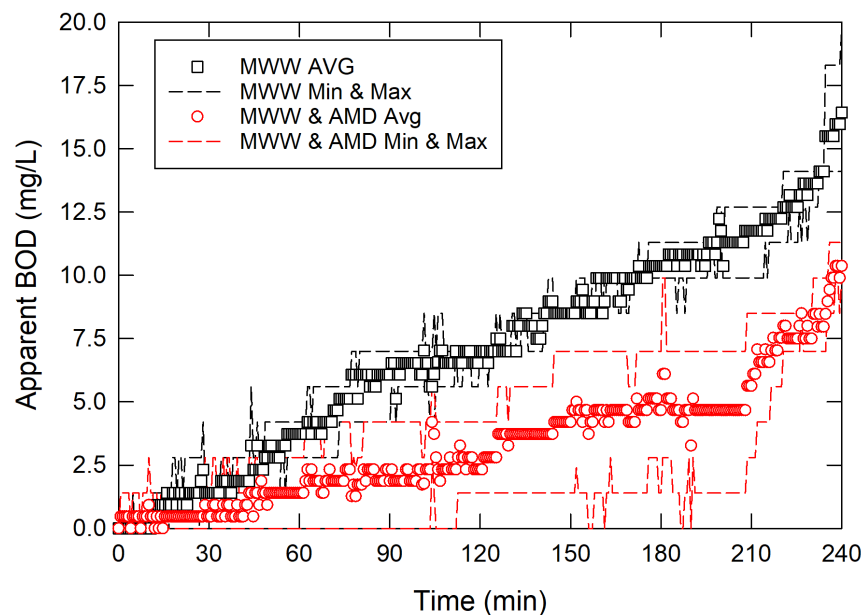
Figure 6: Respirometric BOD results, markers represent the mean value for each sample

type, and dashed line represent the corresponding highest and lowest measured value at

each point

Respirometric results also inform full-scale adaptation. Co-treating with AMD at

WWTPs with longer mean cell residence times would better accommodate cellular

acclimation upon initiation of AMD addition. The increased O_2 consumption after 200

minutes in Figure 6 suggest microbial community adaptation to the addition of AMD,

without long-term negative impacts. Gradual increases in AMD:MWW ratio may improve

microbial adaptation. Although the reaction times (days compared to hours) and AMD

differed (Fe dominant versus various metals in excess), MWW bacteria in experiments by

Hughes and Gray (2012) behaved similarly, requiring an initial acclimation period after

addition of AMD with very different quality. Further assessment of microbial community

adaptation to AMD inputs over longer time scales should be a focus of future research.

4. Conclusions

528

529

530   This work addressed primary knowledge gaps related to co-treatment of AMD in

531 existing WWTPs. Co-treatment resulted in a stable colloidal suspension, and conditions

532 where differential settling is the primary mechanism for particle aggregation. Co-treatment

533 led to improved settling when the highest ratio was evaluated, despite extant repulsive

534 surface charges. However, this condition also yielded the highest effluent Fe loading.

535 Resulting supernatant Fe was nanoscale. Over 90% removal of phosphate was

536 demonstrated, and described by Langmuir adsorption isotherm unto iron oxides. AMD co-

537 treatment represents a novel form of nutrient removal from wastewater effluents. Impact

538 on other studied wastewater quality parameters (TS, BOD, COD) broadly indicated

539 insignificant impact. In this way, co-treatment also represents a novel form of AMD

540 disposal. Introduction of AMD into activated sludge communities caused a short-term

541 decrease in oxygen consumption rate, with recovery noted after several hours, suggesting

542 adaptation. Further research on microbial community impacts is required. Ultimately, the

543 understanding of physio-chemical processes and other water quality results in this work

544 support the feasibility of full-scale co-treatment, which may be especially advantageous to

545 communities with declining MWW production.

546

547   **Declaration of Interests**

548   None.

549

550   **Acknowledgements**

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