

Removal of Metals and Acidity from Acid Mine Drainage Using Municipal Wastewater and Activated Sludge

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Abstract Co-treatment of acid mine drainage (AMD) and municipal wastewater (MWW) using the activated sludge process is an innovative approach to AMD remediation that utilizes the alkalinity of MWW and the adsorptive properties of the wastewater particulates and activated sludge biomass to buffer acidity and remove metals. The capacity of these materials to treat AMD was investigated in batch mode metal removal tests using high-strength synthetic AMD (pH 2.8, Al 120–200 mg/L, Cu 18–30 mg/L, Fe 324–540 mg/L, Mn 18–30 mg/L, and Zn 36–60 mg/L). Using material from a range of MWW treatment plants, the performance of screened and settled MWW, activated sludges with mixed liquor suspended solids (MLSS) concentrations of 2.0 and 4.0 g/L, and return activated sludges with 6.0 and 7.4 g/L MLSS were compared. Similar trends were observed for the MWW and activated sludges, with removal efficiency generally decreasing in the order Al = Cu > Mn > Zn > Fe. Trends in Fe removal using settled MWW and activated sludges were highly variable, with removal <30 %. Using activated sludges, average removal efficiencies for Al, Cu, Mn, and Zn were 10–65 %, 20–60 %, 10–25 %, and 0–20 %, respectively. Sludge solids concentration was an important controlling factor in metal removal, with removal of Al, Cu, Mn, and Zn increasing significantly with solids concentration. Municipal wastewaters had greater neutralization capacities than activated sludges at high AMD loading ratios. Mixing AMD with screened MWW gave the highest removal efficiency for all metals, achieving average removal of 90–100 % for Al, Cu, and Fe, 65–100 % for Zn, and

60–75 % for Mn. These empirical findings are useful for developing process design parameters in co-treatment systems. Utilizing MWW and activated sludge to remediate AMD can potentially reduce materials and energy requirements and associated costs.

Keywords Adsorption · Co-treatment · Neutralization · Treatment · Wastewater treatment plant

Introduction

Acid mine drainage (AMD) generated during the oxidation of mineral surfaces exposed during mineral extraction leads to the release of dissolved metals, sulfate, and hydrogen ions (Stumm and Morgan 1981) into overlying or infiltrating waters and can severely degrade water quality in surface waters and underlying aquifers in the vicinity of the mine (Mlayah et al. 2009; Wolkersdorfer and Bowell 2004). The key treatment processes required to remediate AMD are metal removal and acid neutralization, both of which are complex processes that depend on many factors, including concentration and solubility of metal ions, and pH (Evangelou 1998). Removal of acidity, metals, and sulfate in active and passive AMD treatment is accomplished by dosing with alkaline substances (e.g. CaO) or generating alkalinity either abiotically via passive dissolution of limestone or biotically via bacterial sulfate reduction (Hedin et al. 1994; Skousen et al. 1998; Watzlaf et al. 2004). These processes increase pH and aid in the removal of dissolved metals by precipitation and/or adsorption. The pH has a major influence on precipitation and metal adsorption; competition occurs between H⁺ and metal ions for binding sites, and metal removal by adsorption is often reported to increase with pH

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(Hawari and Mulligan 2006; Motsi et al. 2009; Rozada et al. 2008; Zhang 2011).

Municipal wastewater (MWW) is generally net-alkaline and contains low densities of fine particulate suspended solids, and so is potentially useful for AMD treatment. The pH of MWW typically ranges from 7.0 to 8.0, with alkalinity typically ranging from 200 to 250 mg/L as CaCO₃ (Henze and Comeau 2008), although higher alkalinities are observed in hardwater catchments (McKinney 2004). The neutralization capacity of MWW depends on its pH as well as its alkalinity; at a given pH, higher alkalinity results in a higher neutralization capacity (Lew et al. 2009). Mixing net-alkaline MWW (with a circumneutral pH) with AMD neutralizes acidity by buffering reactions as well as by dilution of AMD H⁺ concentrations (Strosnider et al. 2011a). As the pH of AMD is increased, the pH-dependent solubilities of many metals are decreased, lowering dissolved metal concentrations (Jiménez-Rodríguez et al. 2009; Lee et al. 2002; Strosnider and Nairn 2010).

Metal removal by adsorption onto MWW suspended solids and subsequent removal in primary sludge is also an important removal mechanism for metals in wastewater (Wang et al. 2006). Metal concentrations in MWW vary over time, but are generally low, with individual metal concentrations <500 µg/L (Chipasa 2003; Karvelas et al. 2003; Santos and Judd 2010); therefore, adsorption sites on wastewater particulates are likely to remain available for metal uptake.

As a preliminary step in biological wastewater treatment, influent raw wastewater is screened to remove large solids and grit. The predominantly settleable organic and inorganic solids (>500 µm) in screened wastewater are then removed as primary sludge by sedimentation. Settled wastewater, containing colloidal and small particles (<500 µm), then enters the secondary treatment tank, i.e. the biological reactor, where it is mixed in suspension under aerobic conditions with activated sludge, a low-density (typically 1.5–3.5 g solids/L) sludge that is comprised of a diverse population of flocculant bacteria, fungi, protozoa, rotifers, and nematodes (Gray 2004). After secondary treatment, a fraction of the activated sludge is displaced from the aeration tank into a settlement tank, where the sludge solids settle and the clarified effluent may then receive tertiary treatment or be discharged. A fraction of the settled sludge (returned activated sludge, or RAS), is returned to the aeration basin, where it serves as a microbial inoculum, and the remaining excess sludge is disposed of, and receives further treatment (e.g. dewatering and stabilization by digestion) if required. Activated sludge and the concentrated RAS are typically net-alkaline materials containing organic and inorganic particulates in aqueous suspension, and are potentially useful materials for AMD treatment. When metal-containing influent is added to the activated sludge mixed liquor (the

combined wastewater and activated sludge) during the secondary treatment stage, several metal removal processes occur simultaneously, and in practice it is difficult to identify the most significant uptake mechanisms. In general, dissolved metals and metals associated with fine particulate matter are taken up by adsorption or entrapment in the matrix of activated sludge and removed (along with any residual insoluble metals) by settling in the secondary clarifiers (Oliver and Cosgrove 1974). Brown and Lester (1979) described four possible mechanisms of metal removal in the activated sludge process, namely: (1) physical trapping of precipitated metals in the sludge floc matrix, (2) binding of soluble metal to EPS, (3) accumulation of soluble metal by cells, and (4) volatilization of metal to the atmosphere. Accumulation and transport of metals in biological wastewater treatment plants (WWTPs) is controlled largely by these mechanisms (Chipasa 2003), with biological uptake believed to play a minor role (Neufeld and Hermann 1975). Stephenson and Lester (1987a) and Santos et al. (2010) emphasized that the first mechanism, i.e. entrapment and settlement of particulate non-settleable metal-containing solids, is the most important for metal removal during the activated sludge process. In other words, it is through interaction with activated sludge solids that metals are removed. Metal precipitation must also be considered in any discussion of metal removal; otherwise, adsorption effects could be significantly overestimated (Chang et al. 2006, 2007; Cheng et al. 1975). Particularly at high influent metal concentrations in alkaline conditions, it would be expected that significant fractions of metals would be removed from solution by precipitation, in addition to removal via adsorption.

Co-treatment using the activated sludge process involves three key considerations: (1) the treatability of AMD by activated sludge, (2) the metal removal and neutralization capacities of MWW and sludges, and (3) the impacts of AMD loading on wastewater treatment performance. In AMD treatability studies, Hughes and Gray (2012) concluded that activated sludge from municipal WWTPs could withstand significant shock loadings of high-strength AMD without significant inhibition of microbial activity, and that adaptation of the microbial community occurred after an extended period of continuous AMD loading. In the present study, the results of batch mode metal removal tests mixing high-strength AMD with activated sludge, the concentrated RAS, and screened and settled MWW were compared. The capacity of each material to neutralize AMD was also considered. Compared with research into metal removal by activated sludge, there has been relatively little investigation into metal removal by wastewaters. Results from this study will be useful in the development of process design parameters for systems to co-treat AMD and MWW.

Materials and Methods

Municipal Wastewater and Activated Sludge Sampling

Screened and settled MWW were sampled from a range of municipal WWTPs with different process types and proportions of domestic sewage ranging from 30 to 100 % (Table 1). The selected WWTPs are of a typical European design and size for treating domestic waste streams. Screened MWW samples were collected after grit screening, and settled MWW samples were collected from the primary sedimentation tanks. Samples were cooled during transport to the laboratory, stored in airtight HDPE containers with no headspace at 4 °C, and used within 24 h.

Activated sludge and RAS were sampled from two different municipal WWTPs with different process types (Table 1). Activated sludge samples were taken from the aeration tanks, and RAS was collected from the return flow of the settling tanks. Samples were cooled during transport to the laboratory, where they were aerated with porous ceramic air diffusers at 20 ± 2 °C and used within 24 h. Mixed liquor suspended solids (MLSS) concentrations of the activated sludge and RAS were measured gravimetrically, according to Standard Methods (APHA et al. 2005). The MLSS concentrations of the activated sludge and RAS (as sampled) were approximately 2.5–4.0 and 6.0–7.5 g/L, respectively.

Batch Mode Metal Removal Studies

The removal of dissolved Al, Cu, Fe, Mn, and Zn by screened and settled MWW, activated sludge, and RAS was studied in batch mode experiments carried out at room temperature (20 ± 2 °C). High-strength synthetic AMD (pH 2.8) containing Al, Cu, Fe, Mn, and Zn was prepared fresh daily at a range of metal concentrations (Table 2) from stock metal solutions of 1,000 mg/L made using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, and distilled, deionized

water (Gray and O'Neill 1995). The metal concentrations and pH of the strongest formulation (AMD III) were selected as values representing severe AMD, after multivariate statistical analysis of a dataset of 188 real AMD cases compiled from the literature (analytical method presented in Hughes (2011)). The other formulations, i.e. AMD I and AMD II, contained the same metals in the same proportions as in AMD III, but at 60 and 80 % concentrations, respectively. This design was chosen in order to test a range of AMD 'strengths' while keeping the relative concentrations of metals the same in each. The pH was adjusted as required with sulfuric acid (H_2SO_4 , 3.6 M).

Aliquots (250 mL) of MWW, activated sludge, or RAS were placed in glass beakers and spiked with 250 mL of AMD I, AMD II, or AMD III. Prior to use, the MLSS of activated sludges was adjusted either to 2.0 g/L by dilution with distilled, deionized water or to 4.0 g/L by settling and decanting supernatant. The MLSS of RAS samples was not adjusted. The mixture was thoroughly mixed and aerated, simulating WWTP operating conditions, with the use of porous ceramic air diffusers situated at the bottom of the beakers. Removal studies were conducted at free pH, and the pH was not monitored or controlled after mixing. Removal at four time intervals (i.e. 5, 30, 60, and 120 min) was examined. These time intervals were selected so that the kinetics of metal removal, which is often reported to be a rapid process (e.g. Yuncu et al. 2006), could be observed over a relatively short time period. After each time interval, the contents of each beaker were stirred thoroughly for 2 min to homogenize the contents, and a 50 mL aliquot of the mixture was then sub-sampled from each beaker. After sub-sampling in this manner, the total volume in each beaker was decreased, but the proportion of AMD to MWW or sludge did not change. After mixing for the appropriate time interval, samples were immediately filtered through a 0.45 μm cellulose nitrate filter, using a syringe. Prior to filtering, samples containing sludge were

Table 1 Location, population equivalent, and process type of the municipal wastewater treatment plants (WWTPs), where screened and settled municipal wastewaters (MWW), activated sludge, and return activated sludge (RAS) were sampled for metal removal and neutralization

WWTP location	Population equivalent	Process type	Sample	Domestic sewage (%)	Metal removal	AMD neutralization
Greystones	30,000	Plug flow	MWW	90	+	+
Leixlip (domestic)	45,000	Completely mixed	MWW	80	+	+
Leixlip (industrial)	35,000	Plug flow	MWW	30	–	+
Swords	60,000	Extended aeration	MWW	95	+	+
			Activated sludge and RAS	–	+	+
Kildangan	500	Fine bubble diffused aeration	MWW	100	–	+
Osberstown	80,000	SBR	MWW	57	–	+
Navan	40,000	Completely mixed	Activated sludge and RAS	–	+	+

“+” indicates that the material was used for the study

Table 2 Physicochemical characteristics of high-strength synthetic AMD used in metal removal studies

Parameter (units)	AMD I	AMD II	AMD III
pH (s.u.)	2.8	2.8	2.8
Al (mg/L)	120	160	200
Cu (mg/L)	18	24	30
Fe (mg/L)	324	432	540
Mn (mg/L)	18	24	30
Zn (mg/L)	36	48	60

The characteristics of AMD III were identified using multivariate statistical analysis of real AMD cases ($n = 188$) as being representative of severe AMD. AMD I and AMD II are 60 and 80 % dilutions of AMD III

centrifuged (Mistral 2000) for 4 min at 2,000 rpm. The filtrate was acidified with 2–3 drops of 1 N nitric acid (reagent grade, Sigma-Aldrich) and stored in acid-washed polyethylene bottles at 4 °C prior to metal analysis. The filtrate and remaining solids were discarded. Background metal concentrations of MWW and supernatants of activated sludge and RAS were determined by performing the above procedure using distilled, deionized water in place of synthetic AMD, and removal calculations were corrected for background values. All samples were microwave digested in nitric acid (Ethos EZ, Milestone) prior to metal analysis using a Sequential Liberty AX inductively coupled plasma atomic emission spectrophotometry (ICP-AES), according to APHA et al. (2005). All tests were performed in triplicate. Duplicates and method blanks were analyzed for quality control, and a mixed metal solution (CertiPUR[®], Merck) was tested for quality control immediately following calibration, after every ten samples, and at the end of each sample run. Possible interference by dissolved organic compounds was checked for each material by analyzing the metal concentrations of a blank (without AMD) sample of MWW/sludge supernatant after adding a spiked addition of a certified standard solution (CertiPUR[®], Merck) to check for 100 % recovery. Control AMD solutions were also analyzed for quality control purposes. Metal removal is reported in terms of the decrease in metal concentration on mixing with MWW or sludge at a 50 % (vol AMD/total vol) loading ratio, after accounting for dilution and background metal concentrations.

Table 3 Background metal concentrations (mg/L) in the screened and settled municipal wastewaters used in metal removal studies

Wastewater type	Wastewater source	Al	Cu	Fe	Mn	Zn
Screened	Leixlip	0.30 (0.14)	0.06 (0.04)	2.45 (3.44)	0.46 (0.54)	0.66 (0.85)
Settled	Swords	1.46 (0.95)	0.27 (0.16)	4.19 (3.14)	0.23 (0.14)	0.56 (0.28)
	Greystones	1.33 (1.37)	0.20 (0.20)	3.52 (3.99)	0.19 (0.20)	0.44 (0.42)

All values are reported as the mean (standard deviation) of $n = 3$ observations

Neutralization Studies

The neutralization capacities of screened MWW from Leixlip (domestic) WWTP and settled MWW from Leixlip (domestic and industrial), Greystones, Kildangan, and Osberstown WWTPs were tested by adding AMD III (pH 2.8) at a range of loadings (vol AMD/total vol) and continuously mixing until equilibrium was reached.

To investigate the effect of adding acidity without metals, the process was repeated using settled MWW from the Swords WWTP mixed with sulfuric acid (0.0015 M) (pH 2.8) instead of AMD III. The neutralization capacities of activated sludges was tested by the same method, adding AMD III to sludge from the Swords and Navan WWTPs, and adding sulfuric acid to sludge from the Swords WWTP. Materials from the Swords WWTP were selected for the sulfuric acid experiments because it contained the highest proportion of domestic sewage (95 %) and was therefore believed to be the most representative of other WWTPs. Three replicates of each assay were performed.

Data Analysis

Summary statistics were calculated for the replicate samples. ANOVA was performed ($\alpha = 0.05$) to compare removal at different contact times, different sludge solids concentrations, and different initial metal concentrations, as well as to compare removal by MWW and sludges from different WWTPs. All statistical tests were performed using Minitab 15 (Minitab 2007).

Results

Synthetic AMD

No significant variations from the nominal metal concentrations were detected in quality control analyses of synthetic AMD; therefore, nominal concentrations were used to calculate removal.

Background Metal Concentrations

The background metal concentrations of screened and settled MWW samples (Table 3) were typically negligible

Table 4 Background metal concentrations (mg/L) in the supernatants of activated sludge (AS) and RAS used in metal removal and neutralization studies; all values are reported as the mean (standard deviation) of $n = 3$ observations

Source WWTP	Sludge type	MLSS (g/L)	Al	Cu	Fe	Mn	Zn
Swords	AS	2.0	1.01 (0.13)	0.05 (0.01)	0.06 (0.05)	0.04 (0.004)	0.06 (0.01)
		4.0	1.24 (0.22)	0.06 (0.02)	0.18 (0.42)	0.06 (0.02)	0.08 (0.05)
	RAS	6.0	0.55 (0.13)	0.04 (0.01)	0.06 (0.04)	0.03 (0.01)	0.06 (0.03)
Navan	AS	2.0	0.72 (0.26)	0.05 (0.01)	0.51 (0.14)	0.02 (0.002)	0.09 (0.02)
		4.0	0.44 (0.11)	0.05 (0.02)	0.64 (0.21)	0.01 (0.004)	0.08 (0.02)
	RAS	7.4	0.32 (0.05)	0.03 (0.004)	0.45 (0.25)	0.02 (0.01)	0.05 (0.01)

compared to the AMD concentrations, with values generally equal to 1–2 % of the AMD I concentrations. Screened MWW from Leixlip WWTP contained the lowest Al, Cu, and Fe concentrations and the highest Mn and Zn concentrations. Concentrations of all metals were similar for the settled MWW from the Swords and Greystones WWTPs.

The background metal concentrations of the activated sludge and RAS supernatants (Table 4) were also negligible compared to the AMD concentrations, with values typically <1 % of the AMD I concentrations. Metal concentrations were broadly similar in samples from different WWTPs. Differences were observed among samples from the same WWTPs having different solids concentrations, with the samples containing the highest solids concentrations often having the lowest concentrations of dissolved metals in the supernatants.

Batch Mode Metal Removal Studies

Dissolved concentrations of Al, Cu, Fe, Mn, and Zn, as measured after mixing MWW and sludges with AMD I, AMD II, and AMD III, are shown in Figs. 1, 2 and 3, respectively. Average Al, Cu, Fe, Mn, and Zn removal efficiencies (%) are shown in Figs. 4, 5, 6, 7 and 8, respectively.

Municipal Wastewaters

Effect of Mixing Time on Removal Efficiency (%) There were no statistically significant differences ($\alpha = 0.05$) among removals (%) at $t = 5, 30, 60,$ and 120 min for Al or Mn in tests with AMD I, II, and III using screened MWW from Leixlip WWTP. For Cu, Fe, and Zn, removal at 5 min was, in most cases, statistically significantly less than removal at later times for AMD I, II, and III, but after 30 min, variations in removal were insignificant. Therefore, to calculate average dissolved metal concentrations and removals (%) in tests with screened MWW, the three replicate samples for $t = 30, 60,$ and 120 min were used together as one dataset with $n = 9$ ‘replicates’.

There were no statistically significant differences ($\alpha = 0.05$) among removals (%) at $t = 5, 30, 60,$ and

120 min for any metals in tests with AMD I, II, and III when using settled MWW from Swords or Greystones WWTPs. Removal was observed to be complete within 5 min, and metals were not observed to go back into solution during the 120 min contact period. Therefore, to calculate average dissolved metal concentrations and removals (%) in tests with settled MWW, the three replicate samples for $t = 5, 30, 60,$ and 120 min were used together as one dataset with $n = 12$ ‘replicates’.

Comparison of Metal Removal Efficiency (%) by Different Materials Metal removal (%) for Al, Cu, Fe, Mn, and Zn by screened (Leixlip WWTP) and settled (Swords and Greystones WWTPs) MWW was compared. Because removal after 30 min did not vary significantly in time for any of the MWW, removal data from $t = 30, 60,$ and 120 min was used in ANOVA tests comparing removals by the different MWW. For AMD I, II, and III, the same results were obtained: metal removal was statistically significantly different ($p < 0.05$) for all MWW, with removal increasing in the order Greystones < Swords < Leixlip. This indicates that: (1) removal of Al, Cu, Fe, Mn, and Zn by screened MWW from Leixlip WWTP was statistically significantly higher than removal by settled MWW from both Swords and Greystones WWTPs, and (2) removal of all metals by settled MWW from the Swords WWTP was statistically significantly higher than removal by settled MWW from the Greystones WWTP.

For AMD I, II, and III, in terms of percentage removal, Al and Cu generally had the highest relative removals (20–100 %) by screened and settled MWW. Removals of Mn and Zn were comparatively low (<65 % in most cases). Removal of Fe by settled MWW was generally low (0–40 %), in contrast to high Fe removal (65–100 %) by screened MWW. For screened MWW from Leixlip WWTP, the general order of removals (in terms of % removal) was $Al = Cu = Fe \gg Zn > Mn$. The general order of removals (in terms of % removal) was very similar for both settled MWW, being $Al > Cu = Mn > Zn = Fe$ for MWW from the Swords WWTP and $Al = Cu = Mn > Zn > Fe$ for MWW from the Greystones WWTP.

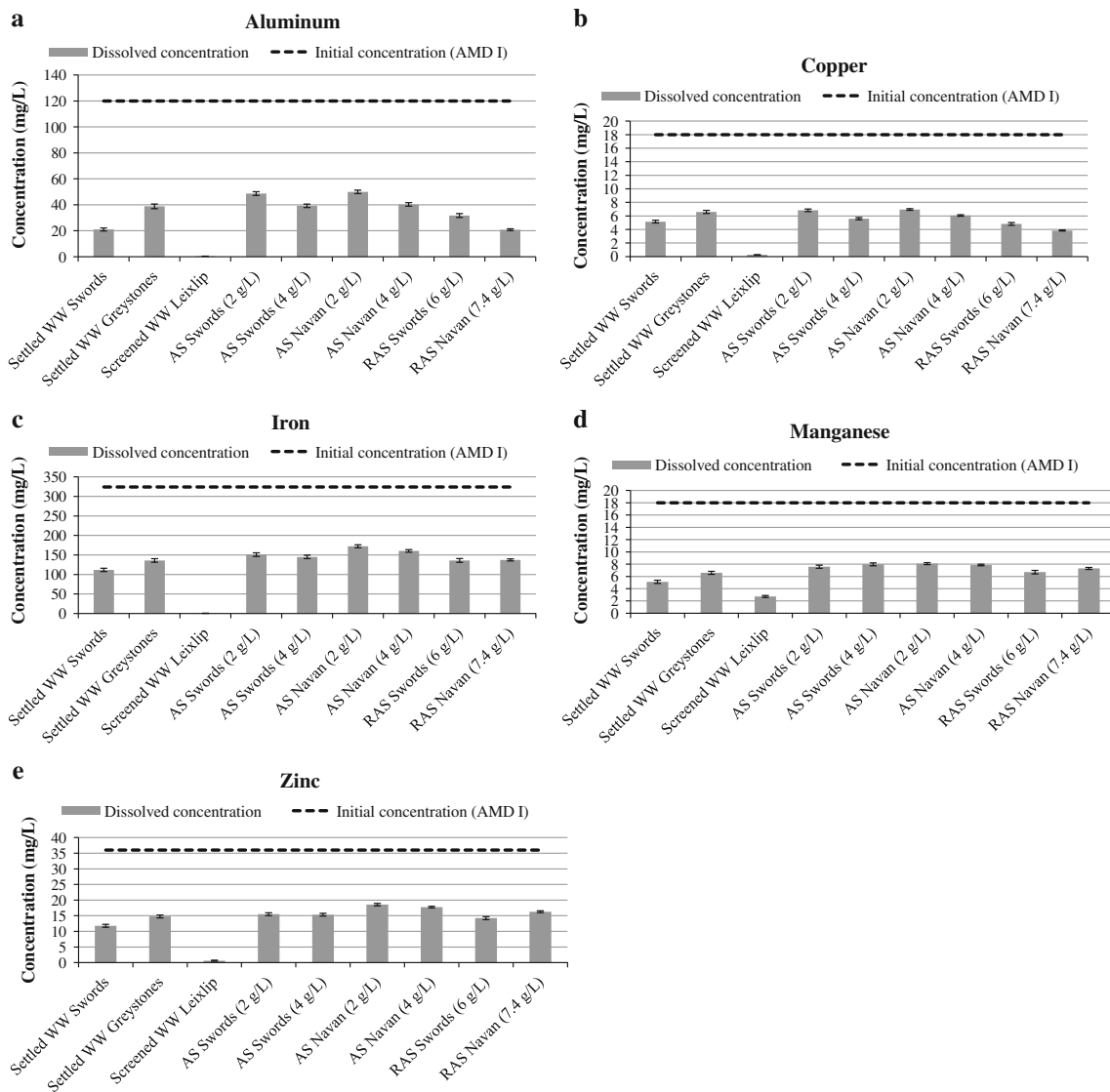


Fig. 1 Dissolved concentrations of **a** Al, **b** Cu, **c** Fe, **d** Mn, and **e** Zn after mixing AMD I with wastewater (WW), activated sludge (AS) and RAS from a range of municipal WWTPs. Results are presented as average concentrations with *standard error bars*

Effect of Initial Metal Concentration on Metal Removal Efficiency (%) Dissolved metal concentrations increased with initial metal concentrations (Figs. 1, 2, 3). Removal efficiency (%) was highest for all metals and all MWW in tests with AMD I. Removal (%) from AMD III was statistically significantly lower ($p < 0.05$) than removal (%) from AMD I in almost every case, with the exception of Al removal by screened MWW (Leixlip WWTP).

Activated Sludge and RAS

Effect of Mixing Time on Metal Removal There were no statistically significant differences ($\alpha = 0.05$) among removals (mg/L) of all metals at $t = 5, 30, 60,$ and 120 min from AMD I, II, or III, using activated sludge or RAS. Removal was complete within 5 min, and metals did

not go back into solution during the 120 min contact period. Therefore, to calculate average dissolved metal concentrations and percentage removals by sludges, the three replicate samples for $t = 5, 30, 60,$ and 120 min were used together as one dataset with $n = 12$ ‘replicates’.

Comparison of Metal Removal Efficiency (%) by Different Materials Metal removal (%) by Swords activated sludge was often significantly greater ($p < 0.05$) than removal by Navan activated sludge at the same MLSS concentration, particularly at MLSS concentrations of 2 g/L using AMD II and AMD III (Figs. 4, 5, 6, 7, 8). For AMD I, II, and III, in terms of percentage removal, Al and Cu had the highest relative removals after mixing with activated sludge and RAS from both WWTPs, with average removal efficiencies of 7–66 % and 20–57 %, respectively. In contrast, Fe, Mn,

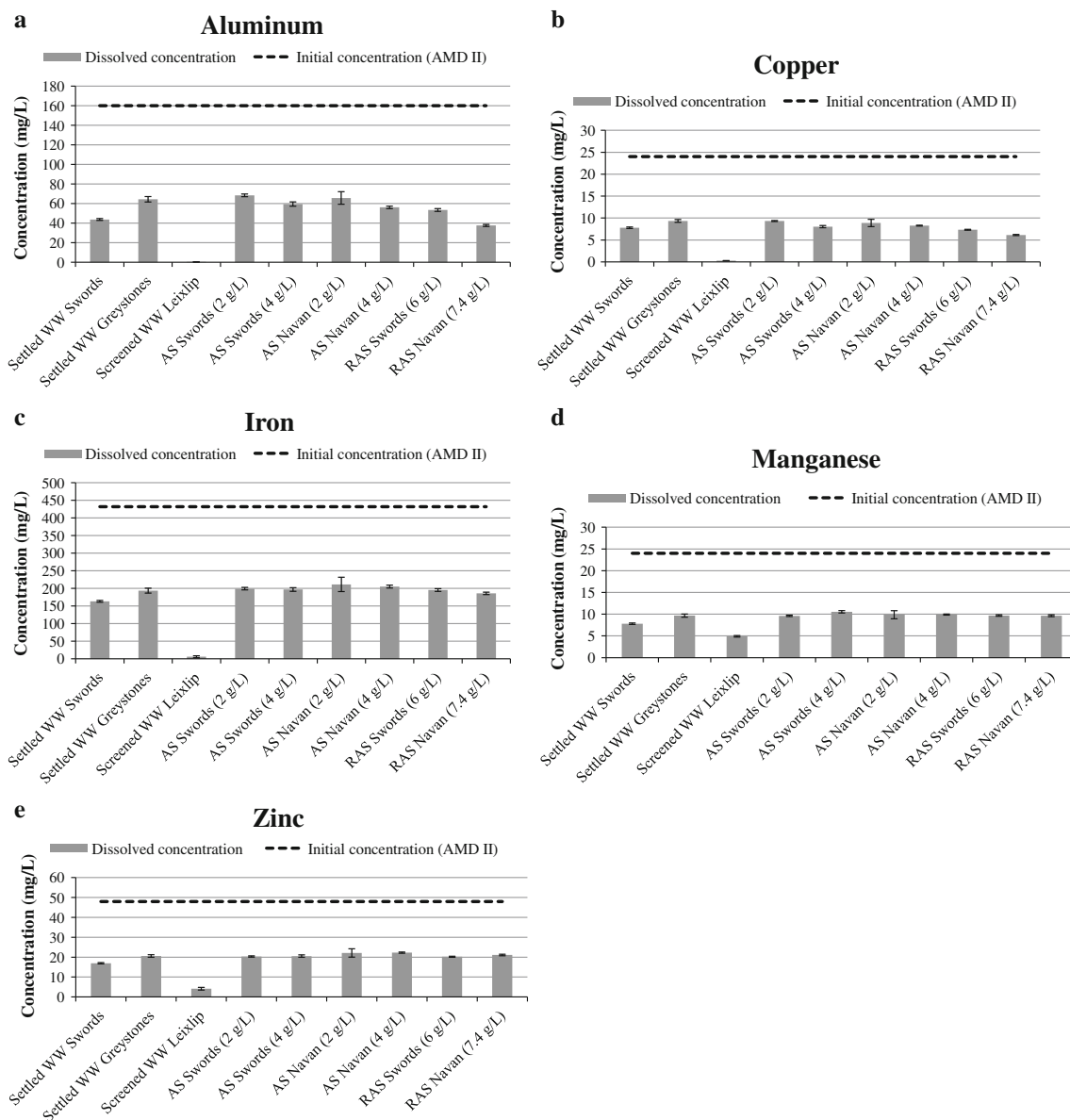


Fig. 2 Dissolved concentrations of **a** Al, **b** Cu, **c** Fe, **d** Mn, and **e** Zn after mixing AMD II with wastewater (WW), activated sludge (AS) and RAS from a range of municipal WWTPs. Results are presented as average concentrations with *standard error bars*

and Zn removals were relatively low, averaging 0–16 %, 7–26 %, and 0–21 %, respectively.

Effect of Solids Concentration on Metal Removal Efficiency (%) Solids concentration had a significant effect on metal removal (%) by activated sludge and RAS. Removal of Al, Cu, and Mn from AMD I, II, and III increased significantly ($p < 0.05$) with solids concentration for both Swords and Navan activated sludge and RAS (Figs. 4, 5, 7). Zinc and Fe removal were also strongly linked to solids concentration using Navan activated sludge and RAS; although removal of these metals was relatively low (<20 %) in all tests, removal did increase significantly ($p < 0.005$) with solids concentrations (Figs. 6, 8).

Effect of Initial Metal Concentration on Metal Removal Efficiency (%) Metal removal (%) decreased significantly ($p < 0.05$) with increasing initial metal concentration for Al and Cu in tests using activated sludge at 4.0 g/L and RAS from both WWTPs. For Fe, Mn, and Zn, removal efficiency did not vary significantly as initial metal concentration increased.

Neutralization Studies

Municipal Wastewaters

In general, the initial pH of the settled MWW ranged from pH 6.8–7.5 (Fig. 9). Adding AMD III to the

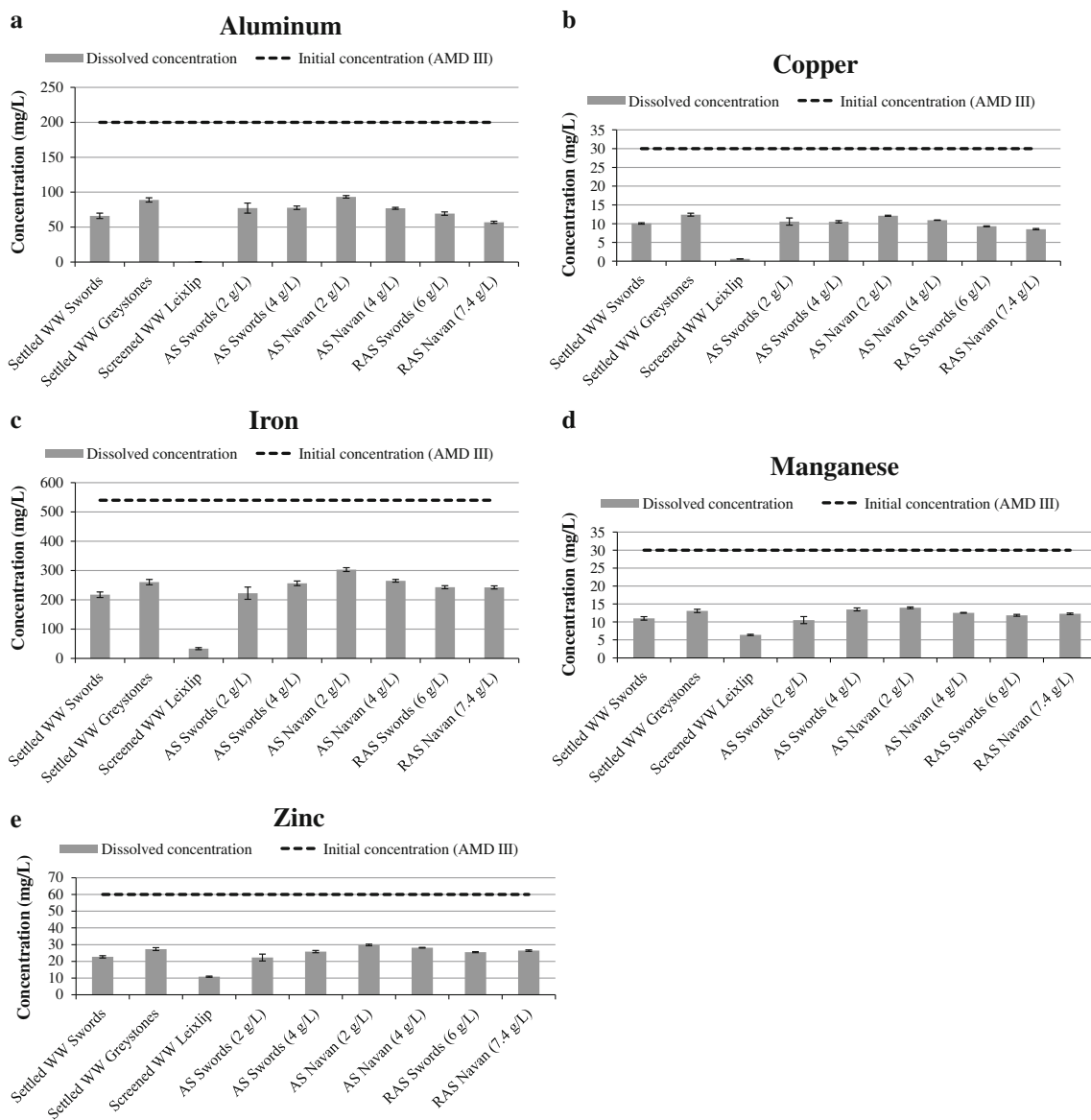


Fig. 3 Dissolved concentrations of **a** Al, **b** Cu, **c** Fe, **d** Mn, and **e** Zn after mixing AMD III with wastewater (WW), activated sludge (AS) and RAS from a range of municipal WWTPs. Results are presented as average concentrations with *standard error bars*

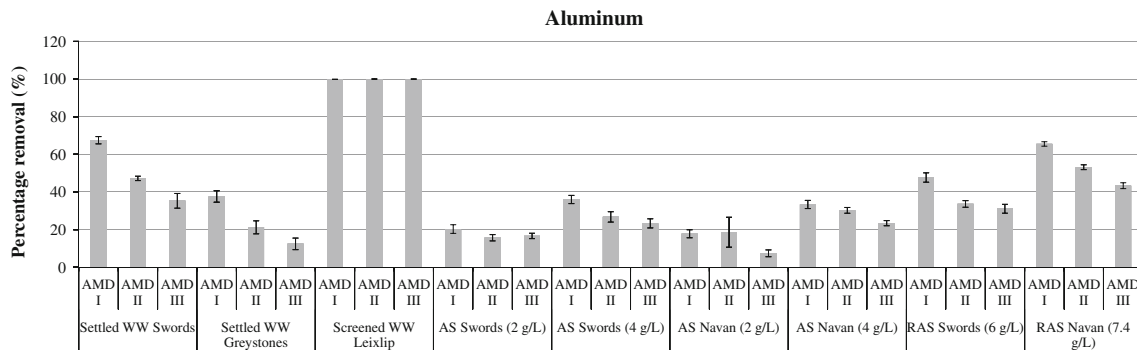


Fig. 4 Percentage Al removal (%) from AMD at a range of strengths. Removal was determined during batch tests using wastewater (WW), activated sludge (AS) and RAS from different municipal WWTPs. Results are presented as average removal with *standard error bars*

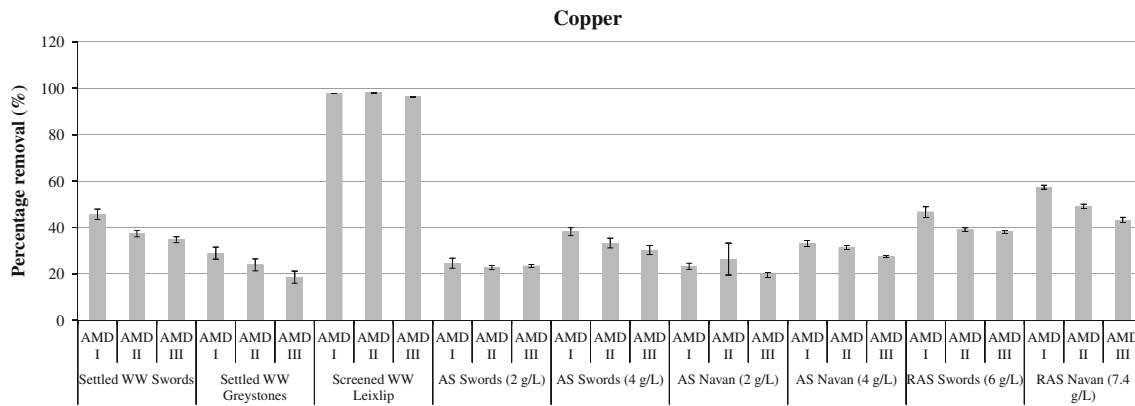


Fig. 5 Percentage Cu removal (%) from AMD at a range of strengths. Removal was determined during batch tests using wastewater (WW), activated sludge (AS) and RAS from different municipal WWTPs. Results are presented as average removal with *standard error bars*

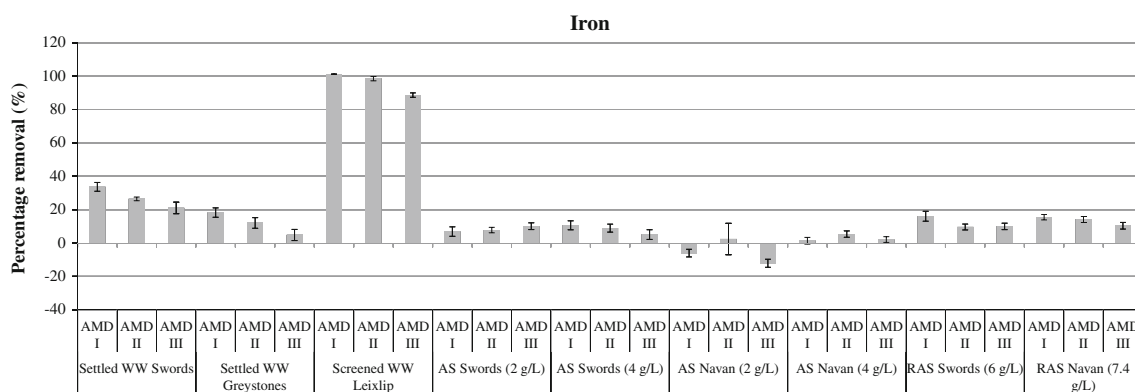


Fig. 6 Percentage Fe removal (%) from AMD at a range of strengths. Removal was determined during batch tests using wastewater (WW), activated sludge (AS) and RAS from different municipal WWTPs. Results are presented as average removal with *standard error bars*

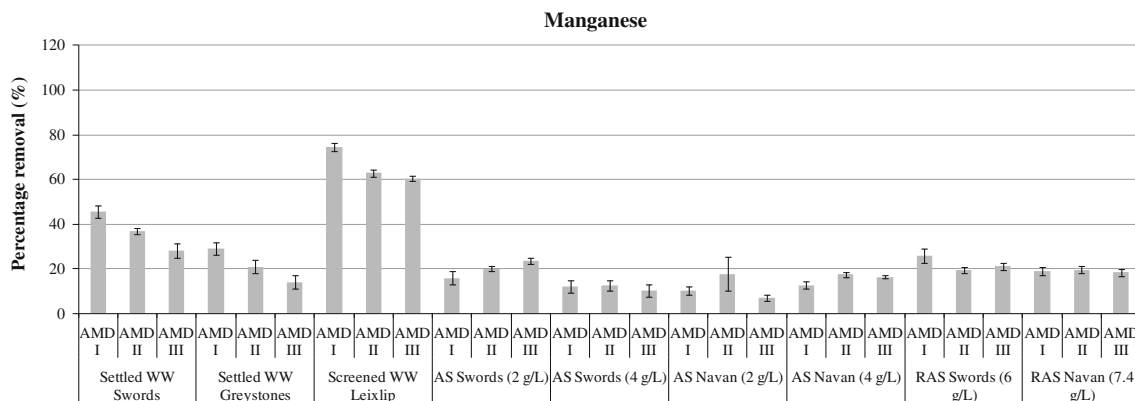


Fig. 7 Percentage Mn removal (%) from AMD at a range of strengths. Removal was determined during batch tests using wastewater (WW), activated sludge (AS) and RAS from different municipal WWTPs. Results are presented as average removal with *standard error bars*

MWW caused a decrease in pH, with higher AMD loads resulting in pH <6 at 30 % (vol AMD/total vol) for all settled MWW. Slight variations were observed between samples, with Kildangan MWW having the highest equilibrium pH. The screened MWW had the highest initial pH value, and also had a higher pH

than all settled MWW after being mixed with AMD III.

Adding sulfuric acid (H_2SO_4) (0.0015 M) to settled MWW from the Swords WWTP (initial pH 7.2) did not cause a significant drop in pH (Fig. 10). In contrast, adding AMD III to the settled MWW from both the

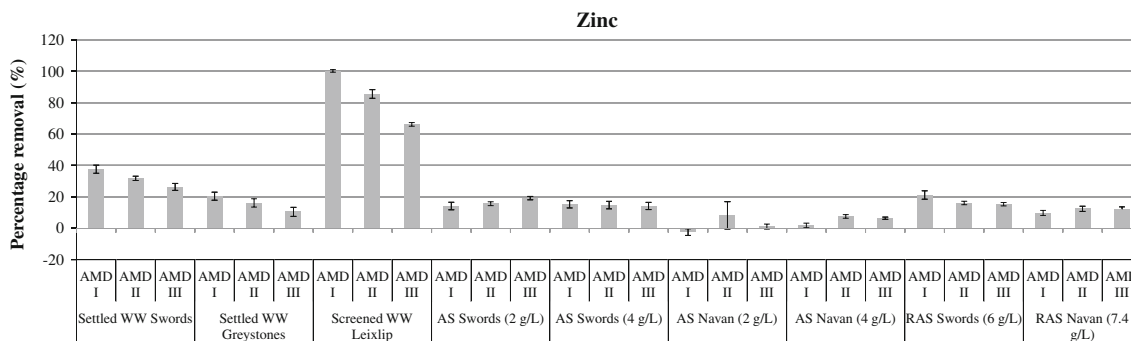


Fig. 8 Percentage Zn removal (%) from AMD at a range of strengths. Removal was determined during batch tests using wastewater (WW), activated sludge (AS) and RAS from different municipal WWTPs. Results are presented as average removal with *standard error bars*

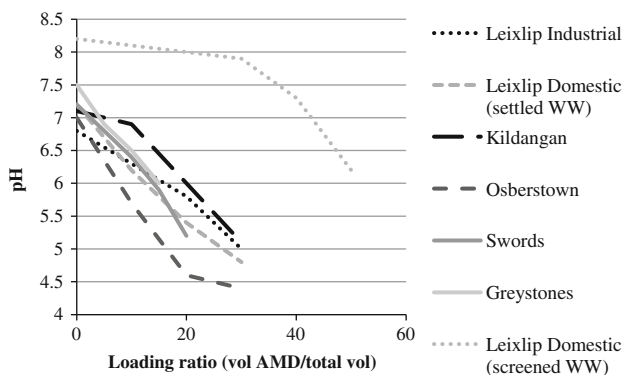


Fig. 9 Equilibrium pH at a range of loading ratios (vol AMD/total vol) adding AMD III to settled and screened wastewater (WW) from six different municipal WWTPs

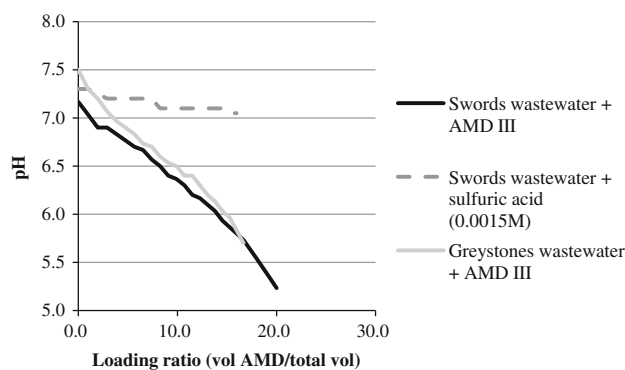


Fig. 10 Equilibrium pH at a range of loading ratios (vol AMD/total vol) adding AMD III and sulfuric acid to settled MWW from the Swords and Greystones WWTPs

Swords WWTP and Greystones WWTP (initial pH 7.5) caused a significant drop in pH, which decreased to pH \approx 6.0 in both samples at 15 % (vol AMD/total vol).

Activated Sludge

The average pH of activated sludge from the Swords WWTP (MLSS 4.0 g/L) decreased from pH 6.1 to 4.8 at 8.3 % (vol AMD/total vol) (Fig. 11). When the same AMD load was added to activated sludge from the Navan WWTP (MLSS 4.0 g/L), the average pH of activated sludge decreased from pH 6.1 to 5.1. In contrast, when sulfuric acid (0.0015 M) (pH 2.8) was added to activated sludge from the Swords WWTP, the pH dropped only slightly, to pH 6.0 at 8.3 % (vol AMD/total vol). The initial pH and the capacities of the activated sludge from both the Swords and Navan WWTPs to neutralize AMD III were very similar.

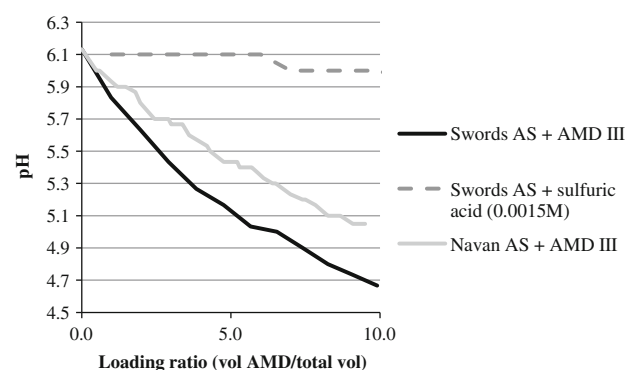


Fig. 11 Equilibrium pH at a range of loading ratios (vol AMD/total vol) adding AMD III and sulfuric acid to activated sludge (AS) from Swords and Navan WWTPs

Discussion

Neutralization during co-treatment of AMD and MWW is a critical parameter for process design, is required to protect

the biological wastewater treatment process from shocks due to low pH, and is also the key factor controlling metal removal processes during wastewater treatment. The results of neutralization and batch mode metal removal studies using MWW and sludges are discussed below. The key metal removal processes relevant during co-treatment, e.g. precipitation, co-precipitation, and adsorption, are considered.

In neutralization studies, there were no significant differences in pH among the settled MWW samples from different WWTPs, and adding AMD caused a similar drop in pH for all settled MWW samples. However, screened MWW had a higher initial pH and a higher neutralization capacity for AMD over a range of AMD loads than the settled MWW. The most likely reason for the difference in neutralization capacities between screened and settled MWW is that screened MWW contains more suspended solids, consisting of organic and inorganic matter in the form of fine particulates, which can adsorb metals and H^+ , thereby decreasing the overall acidity of the mixture. Differences in MWW neutralization capacities were reflected in metal removal efficiencies (%). Significant differences in metal removal efficiency were observed, with significantly greater removal efficiency achieved using screened MWW in every case. This suggests that significant metal removal from AMD is likely to occur during primary treatment; further investigations are recommended to investigate the impacts of AMD on the primary sedimentation process. In contrast to MWW, activated sludge had a limited neutralization capacity. While having circumneutral pH values, activated sludge samples evidently had lower alkalinities and lower associated buffering capacities. With MWW and activated sludge, the effect of hydrolyzable metals (e.g. Fe^{2+} , Fe^{3+} , Al, Cu, Mn, and Zn) on neutralization capacity was clearly evident (Hedin et al. 1994; Rose and Cravotta 1998).

Overall, Al was the most efficiently removed metal (in terms of % removal) in tests with MWW and with sludges. Removal most likely occurred via several mechanisms, i.e. precipitation with phosphates to form stable solids, complexation with particulate organic matter, and precipitation as hydrobasaluminite and/or $Al(OH)_3$ (Clark et al. 1999; Omoike and Vanloon 1999; Sánchez-España et al. 2011; Strosnider et al. 2011b; Stumm and Morgan 1981).

Copper removal by MWW and sludges was also relatively efficient. Significant removal of Cu by MWW can occur during primary treatment (Nielsen and Hrudey 1983; Oliver and Cosgrove 1974). The pH is the major controlling factor, with Cu hydrolysis, co-precipitation, and sorption with Fe/Al solids likely to occur in the typical pH range of MWW (Burgos et al. 2012; Munk et al. 2002). Solubility and speciation of Cu in WWTPs is also related to the suspended solids and dissolved organic matter (DOM) concentrations in raw sewage, with the formation of soluble Cu-DOM complexes an important process which can limit Cu removal (Kempton et al. 1983; Kunz and Jardim 2000; Sterritt and Lester 1982). When metals bind to DOM, they are not removed from MWW unless the complexes dissociate to form species with higher affinity for settleable material and/or biomass. Where Cu removal in MWW is poor, the possibility of complexation onto DOM

in MWW should be investigated as a potential cause. Copper is known to have a good affinity for EPS (Crane et al. 2010) and for activated sludge in general (Hammami et al. 2002), and is often observed to having a higher affinity for binding sites on organic materials in the presence of competing metals such as Zn, Ni, and Cd (Cheng et al. 1975; Gibert et al. 2005a; Zhang 2011). Copper can also precipitate as a hydroxide in sludge at $pH > 5.5$ (Bouزيد et al. 2008).

Efficient Fe removal (e.g. as schwertmannite, ferrihydrite, goethite, and phosphate precipitates) was expected to occur (Caravelli et al. 2010; Evangelou 1998; Sánchez España et al. 2006; Stumm and Morgan 1981; Younger et al. 2002). After mixing AMD and MWW, Strosnider et al. (2011b) concluded that Fe removal was occurring via several mechanisms, including flocculation with phosphate, iron sulfide precipitation, Fe oxyhydroxide precipitation, and sedimentation. However, in the present study, Fe removal by MWW and sludges was highly variable and overall very low. Evidently, settled MWW from Greystones WWTP has some characteristics which prevent Fe precipitation, effectively keeping Fe in solution. One possible factor limiting Fe removal could be the formation of soluble Fe-DOM complexes (Kleja et al. 2012) or colloidal Fe complexes (small enough to pass through 0.45 μm filters) (Schemel et al. 2007). Another possible cause of poor Fe removal by MWW and sludges is interference by high concentrations of ammonia in MWW; where ammonia concentrations are high (i.e. 2 mg/L), oxidation of Fe is prevented (Johnson and Younger 2006). Removal of Fe is important in co-treatment, because the removal of trace metals in AMD is significantly enhanced by co-precipitation and sorption onto Fe precipitates (Burgos et al. 2012; Sánchez España et al. 2006). Further work is recommended to investigate ways to improve Fe removal efficiency.

Manganese is typically reported to react less than other metals with raw sewage, thus entering WWTPs primarily in a dissolved state (Oliver and Cosgrove 1974; Stephenson and Lester 1987b) and remaining in solution, making removal efficiency poor compared to other metals such as Zn, Cu, Cr, Pb, and Cd (Kempton et al. 1983; Mariner et al. 2008; Oliver and Cosgrove 1974; Stephenson and Lester 1987b; Sterritt and Lester 1982). Removal can occur by precipitation (Brown and Lester 1982a, b) or by adsorption onto biomass (Sterritt et al. 1981); however, adsorption is limited by the relatively low affinity of Mn for binding sites on EPS compared to Co, Cd, and Ni, or by binding to DOM (Sterritt and Lester 1982). Removal of Mn from AMD has also been described as problematic (Bamforth et al. 2006; Hallberg and Johnson 2005); this is partly because uncatalyzed oxidation of soluble Mn(II) to insoluble Mn(IV) does not occur readily below pH 9 (Brezonik 1994), thus giving Mn a high solubility over a wide pH range. Another problem is that high concentrations of dissolved Fe can

reduce oxidized forms of Mn (Watzlaf et al. 2004), preventing removal of Mn as hydroxide. If the Fe:Mn ratio is too high, Mn oxidation and precipitation is limited (Nairn and Hedin 1993), and in the presence of high concentrations of Fe^{2+} , Mn oxides will dissolve (Stumm and Morgan 1981). It was observed in this study that Mn removal often was the least efficient where dissolved Fe concentrations remained high (e.g. in tests using activated sludge (2 g/L) from the Navan WWTP). Although precipitation of Mn as a hydroxide does not occur in pure solution below pH 7.5, Mn can be trapped by Fe hydroxides (by co-precipitation or adsorption) at low pH (Azzam et al. 1969). Therefore, Mn removal by MWW and sludges in this study was most likely limited by the high concentrations of dissolved Fe, but if more efficient Fe oxidation and precipitation is achieved, better removal of Mn can be expected. Alternatively, removal of Mn can be enhanced by the addition of carbonate alkalinity to enhance Mn removal as MnCO_3 (Bamforth et al. 2006).

Dissolved Zn removal during co-treatment is likely to occur via sorption or co-precipitation in Fe/Al solids (Carroll et al. 1998; Gibert et al. 2005a), as well as by association with sludge biomass (Katsou et al. 2011; Lei et al. 2008). In the present study, Zn removal increased with solids concentration, especially for the Navan sludges, suggesting that adsorption onto sludge biomass is an important removal mechanism. Relatively poor Zn removal by MWW and sludges was most likely inhibited by the presence of other competing ions, such as Cu (Hammami et al. 2002, 2003; Zhang 2011), as well as by binding of Zn to DOM (Antoniadis and Alloway 2002; Crane et al. 2010).

Comparison of metal removals by sludges at different solids concentrations showed that metal removal increased significantly with solids concentration for Al, Cu, Mn, and Zn for sludges from both Swords and Navan WWTPs. The link between metal removal and sludge solids concentration has been observed in other studies (Al-Qodah 2006; Katsou et al. 2011), and is to be expected where adsorption is the main removal process. Because metal removal by adsorption is controlled by the availability and affinity of binding sites, an increase in the sludge solids concentration leads to an increase in the number of available sites for ion exchange. However, increased adsorption capacity only occurs up to an optimum point; at higher concentrations, there may be a screening effect between cells, limiting the number of available binding sites and effectively decreasing adsorption capacity (Hammami et al. 2007). Optimization of sludge use will depend on the removal performance of sludge from a given WWTP.

Metal removal by MWW, activated sludge, and RAS occurred rapidly, with removal being complete within 30 min for MWW and 5 min for sludges. Rapid (3–10 min) metal uptake by activated sludge has been observed in other

studies (Chang et al. 2007; Cheng et al. 1975); Yuncu et al. (2006) reported that uptake of high concentrations of Cd, Cu, Ni and Zn was almost 85 % complete within 5 min of mixing and almost 100 % complete within 90 min (initial metal concentration 200–400 mg/L). Rapid removal processes are a major advantage during the co-treatment process, because the need for large mixing/storage tanks is eliminated.

Highly efficient metal removal and neutralization achieved by mixing AMD with MWW were strong indicators of the feasibility of co-treatment. However, it is important that alkalinity concentrations in MWW are not entirely depleted during co-treatment. An adequate concentration of alkalinity must be maintained during secondary treatment to prevent drops in pH below normal operating conditions, i.e. >pH 6.5 (Ekama and Wentzel 2008; Garcia Orozco 2008; Lew et al. 2009). The alkalinity budget of a WWTP is extremely important, and if final effluents are net-acidic or net-alkaline with low concentrations of alkalinity (i.e. <50 mg/L as CaCO_3) (Gerardi 2002), the pH stability of the WWTP will be adversely affected, especially in WWTPs that are designed for acid-forming processes such as nitrification (Ekama and Wentzel 2008; Lew et al. 2009). Significant concentrations of metals were removed on mixing AMD with sludges; however, complete removal was not achieved for any metal in the batch tests. The effect of H^+ ions competing with metal ions for binding sites evidently limits metal removal by adsorption onto sludge. Results from this study indicate a need for supplemental alkalinity during co-treatment of MWW and highly acidic AMD, or a pre-treatment stage to remove significant fractions of acidity and metals prior to AMD entering the aeration tanks. Hughes et al. (2013) performed batch tests using digested sewage sludges and cattle slurry and reported moderate neutralization capacity and significant removal of Al, Cu, and Pb, indicating the potential of these materials for AMD pre-treatment.

Metal removal is not easily predicted when treating a complex, multi-factorial pollutant such as AMD. In AMD treatment systems that incorporate an adsorbent material as well as alkali addition, there are several important metal removal mechanisms: precipitation (e.g. as (oxy)hydroxides, hydroxysulfates, or carbonates), co-precipitation or sorption of trace metals with Fe/Al solids, and adsorption (e.g. onto biomass). The situation becomes more complex as more metal species are considered, with pH and redox having major effects on the chemical and sorptive processes. The key factors that affect metal removal during secondary treatment (i.e. in activated sludge) in WWTPs are those factors that influence metal speciation, solids concentrations, settling, and solids removal, including: process parameters (i.e. sludge volume index, sludge age, suspended solids removal, dissolved oxygen concentration, hydraulic retention time and settling time) (Brown and Lester 1982b; Lawson et al. 1984; Özbelge et al. 2005; Santos et al. 2010;

Santos and Judd 2010; Sterritt et al. 1981; Stoveland and Lester 1980), physical and chemical factors (i.e. temperature; pH; metal concentration, solubility, and valency; concentration of complexing and chelating agents; and particle size) (Al-Qodah 2006; Cheng et al. 1975; Crane et al. 2010; Gibert et al. 2005b; Hammami et al. 2007; Jiménez-Rodríguez et al. 2009; Pambrun et al. 2008), and biological properties (i.e. concentration of EPS) (Brown and Lester 1982b; Chang et al. 2007; Yuncu et al. 2006). With respect to the present study, any of these factors could have influenced the metal removal capacity of the Swords and Navan WWTP sludges, particularly factors associated with the composition of the sludge and the supernatant. Significant differences in metal removal by digested sewage sludges from different municipal WWTPs was also reported in Hughes et al. (2013). The presence of soluble chelating agents in the MWW and sludge supernatants was not investigated, but is a possible factor in removal performance and merits investigation. In practice, regardless of the mechanism(s) by which influent metals are removed from the dissolved phase, removal during the activated sludge process is primarily controlled by entrapment and settlement of particulate non-settleable metal-containing solids (Brown and Lester 1979; Santos et al. 2010). Removal ultimately occurs when the metals settle out of suspension and accumulate in the primary and secondary sludges; therefore, optimization of sludge settling will enhance metal removal efficiency (Goldstone et al. 1990).

Finally, it is important to consider the effects of metal loading and an associated increase in sludge metal concentrations on the anaerobic digestion process (Chiu-Yue 1992; Hayes and Theis 1978) and on sludge disposal. Toxicity thresholds and methods of avoiding toxic effects of metals on the anaerobic digestion process require further investigation. Disposal of metal-enriched sludges is discussed in Hughes et al. (2013).

Conclusions

The main findings from this study are:

- Mixing AMD with screened and settled MWW rapidly removed Al, Cu, Fe, Mn, and Zn from high-strength synthetic AMD, with removal complete within 5 min for settled MWW and within 30 min for screened MWW.
- Metal removal efficiency by mixing with MWW varied for each metal, with removal of Al and Cu generally the most efficient and removal of Mn and Zn generally the least efficient.
- Metal removal efficiency was statistically significantly higher ($p < 0.05$) for screened MWW compared to the settled MWW.
- Mixing high-strength AMD with settled MWW caused a drop in pH to pH <6 at relatively low loading ratios of

20 % (vol AMD/total vol)), while pH remained high with screened MWW, even at the very high loading ratio of 50 % (vol AMD/total vol)).

- Metal removal by mixing with activated sludge is a rapid process, and maximum removal was achieved within 5 min of contact time. Metal removal is significantly different for sludges from different WWTPs and also varies significantly with sludge solids concentration for Al, Cu, Mn, and Zn.
- Removal efficiency by mixing with activated sludge varies, generally occurring in the order Al > Cu > Mn > Zn > Fe.
- Loading of AMD to activated sludge in aeration tanks could cause a significant decrease in sludge pH; this should be prevented and may require AMD pre-treatment (e.g. by oxidation and precipitation of Fe (oxy)hydroxides, and/or addition of alkali agents).

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