Potential for Co-treatment of Mine Water and Waste Water in Waste Water Treatment Works

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Abstract

Tests on a range of mine and waste waters were conducted to investigate co-treatment of phosphate and iron. Using a molar dosing ratio of 6:1 Fe:P, the best performing mine water (53 mg/L of iron) removed 73% orthophosphate (excluding dilution) from waste water with 9 mg/l of orthophosphate. Treatability tests confirmed these results and showed iron levels in the final effluent were below 1 mg/L. Effluent sulphate and some metal levels were higher than is typical for waste water treatment. The results suggest primary co-treatment may be effective for higher iron mine waters and waste water, where these issues can be managed.

Keywords: Co-treatment, phosphate reduction, efficiencies, waste water, neutral mine water

Introduction

The Coal Authority is a UK non-departmental public body responsible for managing the effects of past coal mining including the treatment of coal mine water. The Authority operates over 70 coal mine water treatment schemes that treat nearly 100,000 megalitres of mine water from emerging discharges and protect important natural resources such as drinking aquifers from contamination by mine waters. Coal mine waters contain appreciable levels of iron that need to be removed prior to discharge into the receiving water course under permit. This is predominantly achieved by passive or semi-passive (pumped) treatment using aeration, settlement and reed-beds.

The waste water industry in the UK is currently faced with the addition of an annual average total phosphorus limit to be included in the discharge consents enforced by environmental regulators. To remove phosphorus from waste water during the treatment process the water utilities most commonly use chemicals such as ferric sulphate or ferric chloride. The iron in these chemicals reacts with the orthophosphate in the waste water to form a particulate compound which is settled out in either primary or secondary treatment.

Ochre is known in the literature for its potential to bind phosphate in water (e.g. Dobbie *et al.* 2009) however there are challenges related to the formulation of the ochre to enable effective treatment that required further work to overcome (e.g. Littler *et al.* 2013). Where mine water and waste water streams are co-located, direct co-treatment could offer an alternative to combine phosphate and iron removal that avoids some of these issues.

There are a number of areas where mine water and waste water treatment operations are located close to each other and may even discharge into the same receiving water course. Passive tertiary co-treatment has been demonstrated at Lamesley, Tyne and Wear, UK (Younger *et al.* 2014, Chamberlain *et al.* 2016) and indicates that the iron in mine water can reduce phosphate levels in the co-treated scheme, beyond simple dilution. There is potential that co-treatment at waste water treatment works may be more effective at phosphate removal, reducing the requirement for ferric chemical addition.

Methods

Samples of raw mine water were taken from four treatment schemes in the Yorkshire region of the UK. The samples were fully analysed for a range of metals (total and soluble), phosphate (total and orthophosphate), and a

***Table 1** Key analyses of coal mine waters and ochre chosen for the study*

Site	Total Iron	Soluble Iron	Total Phosphorus	Ortho-Phosphate	TSS	COD	Sulphate
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Site 1	5.5	0.01	0.13	0.12	23.5	16	690
Site 2	52.7	56.8	0.46	0.14	4	19	370
Site 3	7.26	1.068	0.11	0.03	11.5	2	530
Site 4	28.3	26.76	0.23	0.09	16.5	4	720
Site 4 Ochre	59840	N/A	155	N/A	16% (Dry Solids)	N/A	200

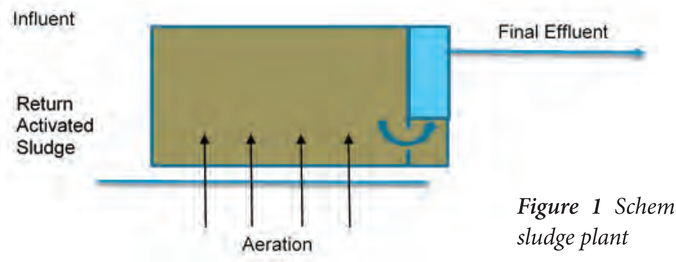

***Figure 1** Schematic of the bench-scale activated sludge plant*

range of physical parameters (including pH, electrical conductivity and dissolved oxygen (DO)). In addition, a sample of ochre from one site was also included as a comparison. The sites were selected to have a range of iron concentrations typical in UK coal mine waters. A summary of these analyses is presented in Table 1.

Raw waste water from two municipal treatment works in the Yorkshire region were sampled for use in the study. A summary of these analyses are shown in Table 2. The sites were chosen as examples of low and high phosphate waste water, however when the samples were analysed both appeared to have similar phosphate contents. This was not deemed critical for the study as both are considered typical of medium strength waste waters (Metcalfe & Eddy 2004).

All mine waters and ochre were individually combined with each waste water in a range of 1 litre jar tests using a series of Fe:P molar ratios of 2, 3, 4, 5 & 6. In addition a control of waste water alone was also run alongside. Each jar test was subject to the following regime considered representative of primary waste water treatment; a flash mix for 2 minutes with 100 rpm stirring; a flocculation step for 30 minutes with 30 rpm stirring and quiescent settlement for 30 minutes with no stirring. After this time a sample of the supernatant from each test was taken and analysed for pH, TSS, total phosphate, orthophosphate, total iron and soluble iron. In addition, control samples, the ochre and one of the mine waters that showed the best removal for each site were subject to detailed analysis of the supernatant and settled solids following repeat jar testing.

Treatability tests were undertaken on the best performing combination from the jar tests to simulate the downstream treatment process. Two bench-scale activated sludge reactors were set up and run for 7 days con-

***Table 2** Key analyses of waste waters chosen for the study*

Site	Total Iron	Soluble Iron	Total Phosphorus	Ortho-Phosphate	TSS	COD	BOD	Ammonia
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/l
Site A	1.62	0.671	6.95	3.7	190	530	279.4	20.6
Site B	1.04	0.316	7.3	4.5	233	626	109.0	32.1

Table 3 Activated Sludge rig operating parameters

	Target BOD: MLSS ratio	Dissolved Oxygen (DO)	Feed Volume	Return Activated Sludge Volume	Hydraulic Residence Time
	Food:Mass	mg/l	l/d	l/d	hrs
Rig 1	0.08	2-3	20	13	8
Rig 2	0.1	2-3	8	5	19

tinuously. Each reactor had a capacity of 10 litres and diffused aerators to mimic fine bubble diffused aeration typically seen in an activated sludge plant (see Figure 1). The reactors were filled with mixed liquor (a combination of waste water/mine water and sludge) at a suspended solids concentration of 2000-3000 mg/L with DO maintained between 2-3 mg/L. The food to mass ratio (biological oxygen demand (BOD) vs mixed liquor suspended solids (MLSS)) and the hydraulic retention time (HRT) were used to determine the feed rates. For waste water alone a HRT of 19 hours was used as typical of a treatment plant of this type. A shorter HRT (8 hours) was required for the mine water blend due to the dilution effects of the mine water meaning more throughput was required to maintain a minimum organic loading of 0.08 kgBOD/kgMLSS. Test parameters are listed in Table 3. During the tests the final effluent and mixed liquor were sampled regularly and at the end of the trial detailed analysis was performed on the final effluent and mixed liquor suspended solids.

Results & Discussion

Jar testing results for all mine waters with Site A waste water are shown in Figure 2. Percentage orthophosphate removal is calculated exclusive of dilution effects by calculating the removal rate from the combined waste and mine water rather than waste water alone. This ensures that genuine removal is not masked by dilution effects. Mine water from Site 2 (52.7 mg/L total Fe) showed the best performance with increasing removal rates observed as the Fe:P molar ratio is increased to a maximum of 69% at a molar ratio of 6. This performance is higher than the comparator ochre sample for all molar ratios. Site 4 (28.3 mg/L total Fe) shows some positive removal at higher molar ratios, but this is relatively marginal. Both low iron sites (1 & 3) show negative removals in all cases. The negative removal rates observed are likely due to margins of error in analysis as orthophosphate levels for these tests are typically below 1 mg/L (due to the high mine water to waste water ratio for these sites). It is considered that negative removal rates are equivalent to

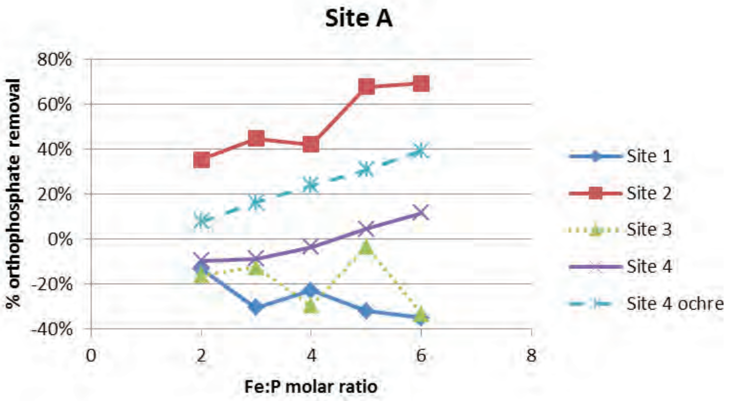

Figure 2 Jar testing results for Site A with a range of mine waters and ochre.

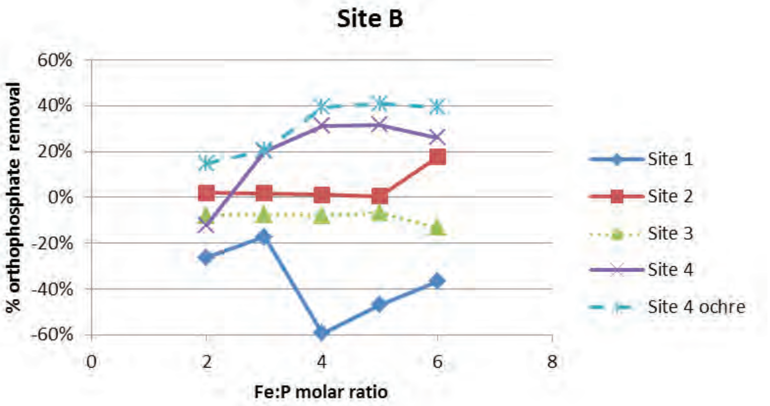

***Figure 3** Jar testing results for Site B with a range of mine waters and ochre.*

zero removal for the purposes of discussion.

Figure 3 shows the equivalent jar test results for Site B. The performance of the low iron site mine waters (sites 1 & 3) was similar to the results from Site A, with negative removal rates observed. The medium iron site (site 4) and the site 4 ochre also showed similar performance as for Site A but with a different trends in relation to molar ratio. The high iron site (site 2) showed a markedly different behaviour compared to Site A. This behaviour may be due to the interference of the increased BOD in the Site B waste water. This increased BOD could be indicative of increased levels of organic material with chelating properties that could reduce the availability of the iron to bind phosphate. If correct, it is plausible that this would affect the site 2 tests more than others due to the reduced dilution by mine water required to achieve the molar ratios. Alternatively, the Site B waste water had higher alkalinity, which could have impacted binding. This effect requires further investigation, which was not possible in this study due to time constraints.

Table 4 shows the relative volumes on mine and waste water used in all the jar tests performed with an Fe:P molar ratio of 6, where the most effective phosphate removal was observed. It can be seen that the relative volumes are strongly dependent on the iron concentration of the mine water and that higher iron concentrations are required to achieve a ratio of less than 1. The relatively high volumes of mine water required pose issues for co-treatment in existing WWTP where there is likely to be limited additional hydraulic capacity. This suggests that purpose built co-treatment facilities may be required; however these could still offer cost savings compared to separate treatment plants.

Repeat Jar testing with detailed analysis was performed on the best performing combinations and a control with waste water alone. This required further samples of waste water to be collected with Site A and Site B

***Table 4** Volumes and ratios of mine water and waste water added to achieve Fe:P of 6 for all sites*

	Site A			Site B		
	Waste water (ml)	Mine water (ml)	Mine water: waste water ratio	Waste water (ml)	Mine water (ml)	Mine water: waste water ratio
Site 1	109	791	7.26	91	809	8.89
Site 2	512	388	0.76	468	432	0.92
Site 3	138	762	5.52	117	783	6.69
Site 4	373	527	1.41	331	569	1.72

Table 5 Analytical results from jar retests of optimum phosphate removal combinations

		Site A Control	Site A + Site 2 Fe:P=6	Site A + Site 4 ochre Fe:P=6	Site B Control	Site B + Site 4 Fe:P=6	Site B + Site 4 ochre Fe:P=6
Ortho-phosphate, as P	mg/l	8	1.6	1.9	5.7	1.7	2.7
% ortho phosphate removal (exc. dilution)		11%	73%	79%	12%	25%	70%
Phosphorus, Total as P	mg/l	9.79	2.34	2.99	7.67	2.39	3.77
Iron , Total as Fe	mg/l	0.6	5.95	4.41	0.28	19.7	2.06
Iron, Filtered as Fe	mg/l	<0.23	0.85	1.11	<0.23	15	0.26
Arsenic, Total as As	mg/l	0.0012	0.0013	0.0015	<0.0010	0.0019	0.0012
Barium, Total as Ba	mg/l	0.026	0.011	0.019	0.062	0.023	0.041
Boron, Total as B	mg/l	<0.23	<0.23	<0.23	<0.23	<0.23	<0.23
Cadmium , Total as Cd	mg/l	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006	<0.0006
Copper, Total as Cu	mg/l	0.013	<0.009	0.013	0.025	<0.009	0.01
Lead , Total as Pb	mg/l	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Mercury, Total as Hg	mg/l	<0.00010	<0.00010	<0.00010	<0.00010	<0.00010	<0.00010
Nickel, Total as Ni	mg/l	0.01	0.026	0.011	0.008	0.051	0.006
Sulphate as SO4	mg/l	34.8	313	83.4	155	446	158
Zinc, Total as Zn	mg/l	0.07	0.03	0.05	0.07	0.04	0.02

samples having orthophosphate concentrations of 9 mg/L and 6.5 mg/L respectively. Repeat testing was undertaken on combinations of Site A with Site 2 mine water and Site 4 ochre and of Site B with Site 4 mine water and ochre, all at a Fe:P of 6.

Following mixing and settling, the supernatant was sampled from each test and analysed for phosphate removal and a range of metals (Table 5). For Site A orthophosphate removal was seen to improve for both Site 2 mine water and Site 4 ochre to 73% and 79% respectively. It is likely that the increased phosphate concentration in the new waste water samples accounts for this change, although the improvement in ochre performance is large and is likely to require further investigation. For Site B, a similar behaviour is observed; again the increased phosphate levels in the new samples are likely to account for this. Total phosphorous levels are above 2 mg/L in all cases suggesting that further treatment would be required to reduce phosphate to levels acceptable in the UK (<1 mg/L).

Iron levels are increased from the controls in all cases although with the exception of Site B with Site 4 mine water (19.7 mg/L total Fe) these would be considered reasonable (typical limits enforced in the UK are between 4-6 mg/L total iron). The high Fe levels in the Site B + Site 4 supernatant may arise from the relatively low removal rates resulting in reduced precipitation of iron phosphate. Sulphate levels are substantially increased in the mine water/ waste water blends compared to the controls and above typical maximum sulphate levels in UK waste waters (50 mg/L), this could lead to operational issues related to odour under anaerobic conditions and requires further investigation.

Metals levels in the supernatant of all tests are shown to be reduced by the addition of mine water or ochre with the exception of Ni (in mine water blends) and As (in all blends) where increases are observed. The levels observed are above Environment Agency recommended surface water levels in England (20 µg/L Ni and 10 µg/L As) indicating that the supernatant may not be suitable for final effluent discharge. Further investigation over a longer sampling period is recommended to confirm these results.

A further treatability study using a bench-scale activated sludge reactor was undertaken using a blend of Site A and Site 2 waters with a control with Site A waste water alone following pre-treatment as per the jar tests. The purpose of this study was to determine the impact of blending mine water with waste water on the downstream treatment process as well as providing some indicative results on potential sludge quality. The treatment performance of both reactors was generally good with BOD and COD removal found to be over 90% and 79% respectively. Orthophosphate removal in rig 1, fed with mine water was found to be an additional 68% beyond that achieved in the jar tests, compared to the control in rig 2, which showed 0% additional removal. Total Fe and P values in the rig 1 effluent were found to be below typical discharge limit values (4-6 mg/L and 1 mg/L respectively). Nickel levels in the rig 1 effluent were found to be marginally above recommended surface water levels at 22 µg/L. Sulphate levels in the final effluent for rig 1 were found to be high compared to rig 2 (330 mg/L and 94 mg/L respectively) in line with the jar test findings and similar levels were found in the biomass for both rigs implying the potential for odour issues if anaerobic conditions are present.

Due to the low % dry solids in the biomass in both rigs it was not possible to directly measure metals in the biomass. Conservative calculations indicate that if all the metals were associated with the dry weight, key metal concentrations would be 687 mg/kg Zn, 169 mg/kg Cu and 44 mg/kg Ni. Both Zn and Cu levels exceed the maximum permissible concentrations for sludge to land in England, Wales and N. Ireland at 200 mg/kg and 80 mg/kg respectively (Defra 2017). It is recommended further investigation is done into the fate of trace metals from mine water throughout the waste water process to determine metal concentrations in the final effluent and sludge.

Conclusions & Recommendations

The above results indicate that mine water does show some potential for the removal of orthophosphate from waste water during primary treatment, particularly for higher iron mine waters. Based on this study the substantial increase in hydraulic loading required for primary co-treatment means that this is most likely to find application where new treatment facilities are to be built or there is hydraulic capacity available in existing infrastructure. The impact of BOD levels, alkalinity, effluent and sludge metals and elevated sulphate also need to be considered before this option can be applied.

In addition, this study provides further data to indicate the potential for ochre to be used to treat phosphate in waste water. Ochre dosing would not present the same hydraulic issues as mine water co-treatment and if costs associated with transport and dosing are less than the OPEX costs of dosing ferric chemicals, this could be advantageous.

It is recommended that further investigations are undertaken on the impact of waste water quality, metals and sulphate on sludge and effluent in co-treatment. Also, further studies of the impact of ochre on secondary treatment should be undertaken to determine the impact on overall treatment and effluent quality.

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