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Acidified and ultrafiltered recovered coagulants from water treatment works sludge for removal of phosphorus from wastewater

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ABSTRACT

This study used a range of treated water treatment works sludge options for the removal of phosphorus (P) from primary wastewater. These options included the application of ultrafiltration for recovery of the coagulant from the sludge. The treatment performance and whole life cost (WLC) of the various recovered coagulant (RC) configurations have been considered in relation to fresh ferric sulphate (FFS). Pre-treatment of the sludge with acid followed by removal of organic and particulate contaminants using a 2kD ultrafiltration membrane resulted in a reusable coagulant that closely matched the performance FFS. Unacidified RC showed 53% of the phosphorus removal efficiency of FFS, at a dose of 20 mg/L as Fe and a contact time of 90 min. A longer contact time of 8 h improved performance to 85% of FFS. P removal at the shorter contact time improved to 88% relative to FFS by pre-acidifying the sludge to pH 2, using an acid molar ratio of 5.2:1 mol H^+:Fe. Analysis of the removal of P showed that rapid phosphate precipitation accounted for >65% of removal with FFS. However, for the acidified RC a slower adsorption mechanism dominated; this was accelerated at a lower pH. A cost-benefit analysis showed that relative to dosing FFS and disposing waterworks sludge to land, the 20 year WLC was halved by transporting acidified or unacidified sludge up to 80 km for reuse in wastewater treatment. A maximum inter-site distance was determined to be 240 km above the current disposal route at current prices. Further savings could be made if longer contact times were available to allow greater P removal with unacidified RC.

1. Introduction

Coagulation and flocculation is a key process at potable water treatment works (WTW). Whilst still considered a low-cost treatment method (accounting for ~5% of the total cost of water production and distribution, Niquette et al., 2004), it nonetheless consumes >325,000 tonnes of coagulant annually in the UK alone (Henderson et al., 2009). This generates >182,000 tonnes of waste sludge in the form of water treatment residuals (WTRs) (Pan et al., 2004), demanding significant costs for its disposal (UKWIR, 1999).

Wastewater treatment works (WWTW) also require coagulant to remove phosphorus. In China, industrial effluents are required to meet 0.5 mg/L P (Pan et al., 2009) and for protected waters in Europe and North America consents could become 50 µg/L and 10 µg/L (Remy et al., 2014; Sengupta and Pandit, 2011). Coagulants offer a simpler means of removing P compared to biological nutrient removal (Blackall et al., 2002) but require 2–3-fold higher doses when P consents move from 2 mg/L to <1 mg/L (Ofwat, 2005) as they become less efficient at higher removals. Reuse of alternative chemical P removal agents could offer a more sustainable and cost effective treatment option for water and wastewater utility companies (Babatunde and Zhao, 2007). P removal from wastewater using WTRs is already widespread, as disposal of WTRs to sewer is convenient and frugal as it avoids sludge dewatering, haulage and disposal fees (Walsh, 2009). However, this approach is limited because fewer than 30% of the WTWs in the UK have a sewer connection. Furthermore, when WTRs are disposed to the sewer, it is usually carried out on an *ad hoc* basis with limited control on the process (UKWIR, 1999; Walsh, 2009).

Reuse of acid-recovered coagulants from WTRs has already been considered in potable treatment (Okuda et al., 2014). Recycling coagulant reduces coagulant demand and waste production. However, the acidification process required is non-selective and the carryover of organic compounds with the coagulant elevates formation of disinfection by-products if used in potable treatment (Keeley et al., 2014a). Numerous purification methods have been

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documented but at present none adequately combine selectivity with feasible implementation (Keeley et al., 2014b).

Reusing recovered coagulants (RCs) in wastewater treatment can provide similar advantages as reuse in potable treatment but is less sensitive to the presence of impurities. WTRs have proven to be effective and economically viable in a number of wastewater treatment configurations (King et al., 1975; Masides et al., 1988; Parsons and Daniels, 1999; Jiménez et al., 2007; Yang et al., 2014). However, the underlying removal mechanisms remain poorly understood (Thistleton et al., 2002; Szabo et al., 2008). This study aims to compare the removal mechanisms and the whole life cost (WLC) of several WTR reuse approaches with conventional chemical P removal using fresh coagulants.

Ferric coagulants typically remove 95–96% of P after 90 min and M^{3+}:P molar ratios of 2–4:1 (Parsons and Daniels, 1999; Szabo et al., 2008) using two main mechanisms: precipitation and adsorption (Hsu, 1976). Firstly, metal sulphate or chloride salts rapidly hydrolyse, forming metal hydroxides and, when phosphorus is present, metal phosphates. Optimal mixing (average G values > 100 s^{-1}; Szabo et al., 2008) and a pH < 9 (Galarneau and Gehr, 1997) can minimise wasted chemical and surplus sludge production (Thistleton et al., 2002) and allow rapid removal of up to 100 times more phosphate per mol of Fe than adsorption (Smith et al., 2008). Phosphate precipitation can be enhanced further by removing competing hydroxide species at pHs of 4.5–5.0 (Thistleton et al., 2002). As coprecipitation hydrolysis occurs, the precipitate particles grow in size (Takacs et al., 2006), before aggregating and settling (Jarvis et al., 2006).

Secondly, adsorption occurs through contact of phosphates with iron hydroxides (Yang et al., 2010). These have a high phosphate removal capacity (~340 mg P/g Fe after 36 h) but at a much slower rate (~0.5 mg P/g Fe/minute; Parsons and Daniels, 1999) than for precipitation (~150 mg P/g Fe/minute, initially; Szabo et al., 2008). Phosphate adsorption onto the metal hydroxide surface is fast but limited by slow phosphate migration within the metal hydroxide micropores which has been estimated to be as slow as $<4 \times 10^{-15}$ cm^2 s^{-1} (Makris et al., 2004; Wang et al., 2011).

Using a lower pH to neutralize hydroxides released by phosphate adsorption can increase adsorption efficacy by 2–3 fold (Razali et al., 2007; Babatunde et al., 2009). Unacidified WTRs and chemically similar ferric hydroxide media can match the performance of FFS (fresh ferric sulphate) in various configurations (Babatunde et al., 2009; Bai et al., 2014). However, the reliance of adsorption for P removal requires ten times higher molar doses of 50:1, M^{3+}:P (Genz et al., 2004) than coagulants with the additional capability to remove P using the precipitation pathway. Solubilisation of WTRs by acidification to pH 2 can increase the chemical efficiency of P removal by facilitating precipitation pathways (Parsons and Daniels, 1999; Jiménez et al., 2007) and by favouring phosphate uptake by adsorption. The cost of acidification may be offset by the value of greater P removal efficiency than if WTRs were dosed at ambient pH. The contribution each mechanism makes is dependent on many factors but some suggest that adsorption dominates, accounting for 65% of total P removal (Yang et al., 2010). Other studies report that when sufficiently mixed to maximize precipitation, adsorption accounts for only 25% of total removal (Smith et al., 2008).

Understanding how the P removal mechanisms operate when using recovered RCs that have undergone varying degrees of purification is a very under explored area of research but is an essential consideration for the appropriate addition of WTRs into wastewater for P removal. These varying contributions are important considerations in the use of WTR-based P removal and were examined alongside other chemical and physical factors, in terms of their effect on performance and process economics, relative to FFS.

2. Methodology

2.1. Assessing RC treatment performance

Jar tests were used to replicate chemical treatment of primary wastewater and to examine the removal performance and treated effluent quality. Various forms of ferric based RCs were compared against the performance of commercial grade FFS (measured as 20% Fe). Screened municipal wastewater was collected daily from a 2000 population equivalent WWTW (Cranfield, UK). This wastewater was used for all jar test experiments (see Supporting Information (SI) A for details on the wastewater composition).

Dewatered sludge cake (14% dry solids; DS) was taken from a 120–180 MLD WTW treating upland water (Derbyshire, UK) that used ferric sulphate coagulant. Sludge cake (1 g, wet) was dissolved in 1 L of 0.1 M analytical grade nitric acid, before analysis for dissolved organic carbon (DOC) using a Shimadzu TOC-V analyser, and Fe using a PerkinElmer atomic absorption spectrometer (AAS). Acid demand and Fe solubilisation were measured with dilute sludge (1 g/L) titrated against dilute sulphuric acid.

A range of RC options were prepared from the sludge cake. These were: i) raw dewatered sludge RC; ii) unacidified RC (dewatered sludge diluted to 2.8% DS in deionised water); iii) Acidified RC (as previous but acidified using concentrated sulphuric acid, until the required pH was held); iv) Acidified and ultrafiltered RC (as previous followed by filtration through a 2 kD molecular weight cut off (MWCO) polyethersulfone membrane (Sterlitech Corporation, Kent, WA, USA), using apparatus previously described (Keeley et al., 2014b). See SI A for details on the RC chemical composition.

Jar tests were conducted at Fe doses of 0–50 mg/L for all RCs, using a Phipps & Bird PB-700 jar tester. The jar tester mixed cylindrical beakers containing 1 L of wastewater for 1 min at 200 rpm (G = 128 s^{-1}), followed by 30 rpm (G = 7.4 s^{-1}) for 15 min, and a 30 min unmixed settlement stage. Average velocity gradient conversions (G values) were taken from a previous study, using the same apparatus (Sharp et al., 2006). Samples were taken from the supernatant and immediately analysed for total P, total N and chemical oxygen demand (COD) using Hach cell test kits. Removal of contaminants was assessed by comparing its initial concentration with the concentration in the treated water. Residual Fe was analysed using atomic absorption spectroscopy (AAS). The sample pH and turbidity was also measured.

2.1.1. Examination of P removal mechanisms

Using an adaptation of a previous method (Szabo et al., 2008), jar tests were run using the different coagulants and were mixed with wastewater using a 90 s mix (200 rpm) and a 60 min mix (30 rpm). Samples were taken 2 min and 1 h after dosing with 20 mg/L Fe to determine P removal. These samples were immediately filtered (0.45 μm, nylon) and analysed for soluble P. This process was repeated with pre-hydrolysed and precipitated coagulants. To achieve pre-hydrolysis, the coagulants were adjusted to pH 7 prior to dosing. Acidified and unacidified RCs (2.8% DS) were fractionated using successive filtration through 840, 500, 210,105, 60 and 10 μm polypropylene meshes (Spectrum Laboratories, Netherlands). Each fraction was analysed for Fe using AAS before being dosed into jar tests at normalised doses of 20 mg/L Fe.

2.1.2. Flocculation time and prolonged mixing

The optimum Fe dose was determined and repeated for all the coagulant types, with different flocculation durations of 5, 10, 30 and 120 min. Prolonged mixing for 2, 4, 8 and 24 h at 100 rpm (G = 43 s^{-1}) was studied to simulate the effect of longer contact times that occur in settlement tanks or if Fe is dosed to the sewer, upstream of the WWTW (~1 h/km; Gutierrez et al., 2010). To simulate ideal and non-ideal mixing conditions as may be experienced in full scale WTWW systems, a set of tests were carried out where the stirrer speed during the rapid mix phase of the jar test was varied from 20, 60, 140 and 300 rpm (5, 21, 72 and 250 s^{-1}, respectively), followed by 30 min flocculation at 30 rpm. Selected treated waters were analysed further for alkalinity consumption, measured by titration to pH 4.5 against 0.02 M HCl, using a pH meter. Floc size was measured using a Malvern Mastersizer.

2.2. Implementation modelling

A case study was used to investigate the WLC of different RC strategies for P removal. The results were validated with a water company's asset-planning business tool. This method allowed a direct comparison of options with differing operational and capital economic biases. This considered the same WTW from where the sludge samples were taken and a theoretical WWTW, 80 km away by road, that had a coagulant demand in excess of that provided by the WTW's sludge. This distance was nominally selected to allow analysis but was realistic for the European treatment context. Technical details of these sites are outlined below:

- A real WTW treating 150 MLD and generating 33,000 wet tonnes of dewatered ferric sludge per annum (14% DS, of which 25% is Fe), which is currently spread to land, 32 km away.
- A WWTW requiring $\leq$9000 t/y of 13% Fe commercial ferric sulphate, based on a molar Fe:P dose of 1.5:1 (equal to the Fe content of the WTW's sludge).

Logistical and operational parameters were analysed to indicate potential sensitivities to changes in market prices, process efficiency and inter-site distance. Bench-scale empirical data were used as design parameters for capital and operating cost models for sludge reception, acidification and purification (McGivney and Kawamura, 2008; SI D). These were used with chemical costs from water companies, and cost engineering data to calculate WLC over a typical payback period of 20 years (Gaterell et al., 2000).

Ultrafiltration performance data was taken from previous bench-scale studies, using a flux of 15 L/m^2/h and a permeate Fe concentration of 2 g/L (Keeley et al., 2014b). Sensitivity analysis was used to identify potential effects of improved efficiency and external price changes. This involved measuring the percentage difference from a baseline 20 year WLC, following a 50% increase in component cost (Verrecht et al., 2008).

Total project capital costs were based on the sum of component capital costs (SI D), plus an additional 10% for piping; 5% for groundworks; 20% for electrical and controls; and 35% for engineering, legal and administration costs (McGivney and Kawamura, 2008).

Chemical demand OPEX was scaled on the basis of specific Fe:P removal performance and acid demand, which were both experimentally determined. The cost of transport was modelled using commercial data tables (Road Haulage Association, 2013) and was validated using quotes from commercial hauliers (SI D).

3. Results and discussion

3.1. Chemical factors

For acidified RC and FFS, increasing Fe dose up to 20 mg/L significantly improved P removal (up to 2.1:1 M ratio of Fe:P, Fig. 1) and was used as the optimum dose for subsequent experiments. At 20 mg/L Fe, P removal varied between the coagulant types: FFS removed 84%; ultrafiltered RCs 84%; acidified RCs, 64%; and just 16% with raw cake. These results were consistent with removals at a similar molar dose of 3:1 Fe:P observed in previous studies (Parsons and Daniels, 1999). At 50 mg/L Fe (5:1 M Fe:P) P removals increased to 97%, 93%, 84% and 22%, respectively. Prior dilution of the sludge cake did not improve P removal but was used in subsequent experiments to ensure consistent dispersion of the coagulant. The results here therefore show that purifying acidified WTW sludge through a UF system can result in a coagulant that can perform nearly as effectively as a pure coagulant chemical at like for like doses.

The differing physico-chemical properties of the RCs can explain the different removal performances observed. The high P removal at lower Fe:P ratios of 2.1:1 observed with ultrafiltered and acidified RC was due to the iron being available entirely in soluble form, thus giving a similar removal mechanism to FFS (Thistleton et al., 2002). Lower removal with unfiltered, acidified RC compared with the ultrafiltered RC was due to the presence of more organic-Fe complexes in the unfiltered RC as well as much higher proportions of insoluble Fe (55% compared with <1% in the ultrafiltered RC). The bound and solid Fe compounds were then not available for P removal by direct precipitative mechanisms which has been observed elsewhere (Wang et al., 2012). This also accounts for the poorer performance of unacidified RC, where the insoluble Fe increased to >99%.

This was further supported from size fractionation analysis of the respective RCs. It was clear that the form of available iron was very different in acidified and unacidified RCs (Fig. 2). Over 60% of the available iron was in size fractions that were smaller than 10 μm when sludge was acidified whilst this was <10% for the unacidified form (this equates to 2.6 g/L and 0.1 g/ L Fe in this size range for acidified and unacidified RCs respectively). This indicates that for an equivalent iron dose, both more soluble iron will be available for direct reaction with P and smaller particulates will be present for surface adsorption for acidified WTRs.

COD and turbidity removal followed similar trends with increasing ferric dose (Fig. 1). At 20 mg/L Fe, FFS removed 51% of the COD and 80% of the turbidity; for ultrafiltered acidified RC removal was 32% and 68%, respectively; and for acidified RC, 43% and 68%, respectively. The organic content of wastewater treated by the raw sludge cake slightly increased COD levels by 6% and left turbidity unchanged.

Whilst ferric coagulants are effective at P removal, they can consume wastewater alkalinity and elevate residual Fe concentrations. At Fe doses of $\leq$20 mg/L, residual Fe was maintained <3 mg/L for all of the tested coagulant sludges, with FFS yielding a residual of 1.4 mg/L. These residual levels were higher than were expected and would exceed the European *Environmental Quality Standard* final effluent discharge limit of 1 mg/L as total Fe, (Environment Agency, 2007) but further physical separation by downstream settlement (Parsons and Daniels, 1999) and filtration would mitigate this. The higher values observed here were therefore likely to be due to the short reaction and settling times of 30 min used in these jar tests in comparison to a typical >2 h residence time in full-scale clarification systems (Tchobanoglous et al., 2003). For ultrafiltered and unfiltered acidified RC, Fe doses of 20–50 mg/L led to a rapid rise in residual Fe in treated wastewater, increasing by a rate of 0.05 mg/L residual Fe per additional mg/L Fe dosed, up to a maximum of 5 mg/L (Fig. 1). Here, soluble Fe-DOC complexes remained in the treated wastewater. Conversely, for FFS, higher doses led to a slight decrease in residual Fe as direct precipitation of iron hydroxide was promoted.

From an initial pH value of 7.8 and at 20 mg/L Fe, all coagulants maintained an end pH within the starting value by < 0.6 units. Alkalinity titrations with treated wastewater against dilute HCl gave final alkalinity of 416, 428, 340 and 456 mg/L as $CaCO_3$, for FFS, acidified, ultrafiltered and raw sludge cake RCs, respectively,

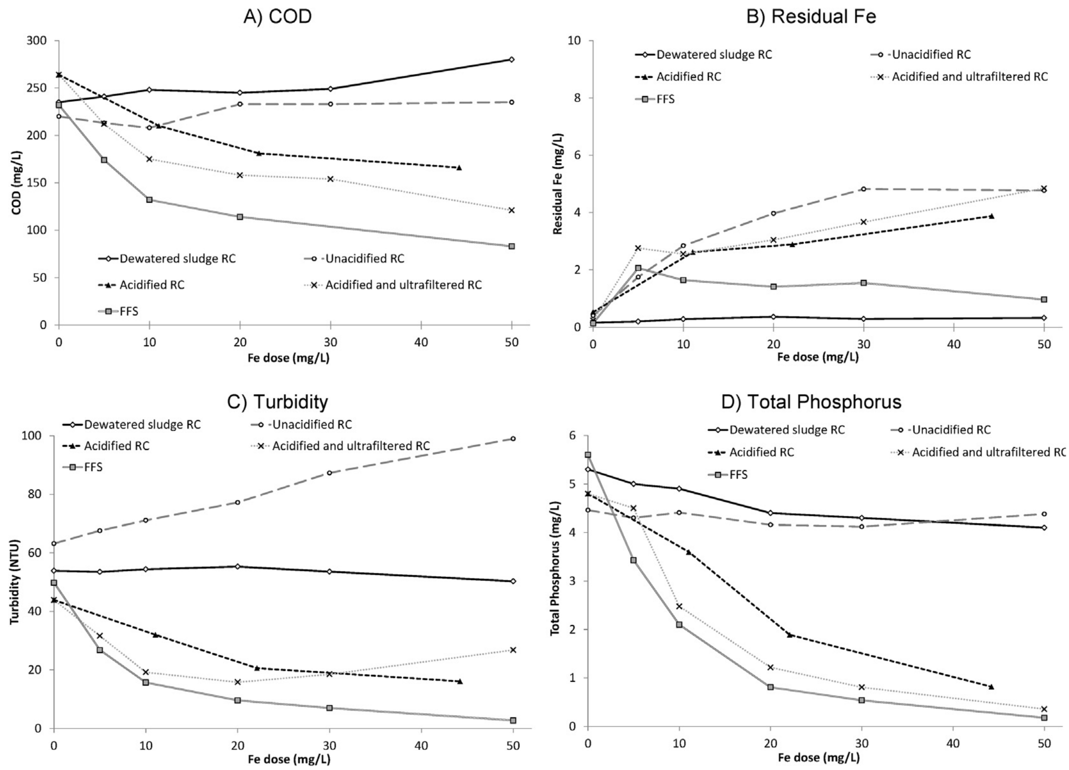

Fig. 1. Removal of COD, turbidity and total phosphorus with increasing doses of recovered and fresh coagulants following jar test mixing. Residual iron concentration after coagulation and settlement is also shown.

compared to an undosed blank value of 524 mg/L. These all left sufficient alkalinity for subsequent nitrification, given that the measured total nitrogen was 48 ± 4 mg/L and a requirement for 7 mg $CaCO_3$ per g of NH_4^+-N (Liu and Wang, 2012).

To discriminate between the P removal mechanisms seen when using various RCs, P removal after 2 min was compared to that after 1 h. Removal was stopped at the time of sampling by filtration, so only soluble P (P_{sol}) removal can be discussed, however this was >70% of TP for the wastewater. FFS achieved 90% overall P_{sol} removal within 2 min of dosing (Fig. 3). Formation of ferric-phosphate precipitates was the main removal route, due to the high stoichiometric efficiency (~225 mg P/g Fe in 2 min) which was achieved much faster than for adsorption, which is typically <30 mg P/g Fe per hour (Parsons and Daniels, 1999; Smith et al., 2008). This was confirmed when FFS was pre-hydrolysed before dosing, such that P removal via precipitation could not occur. While some P removal still occurred, through adsorption onto the pre-formed ferric hydroxide, it accounted for 20% of the removal achieved using FFS. In addition, there was only marginal subsequent removal (0.6 mg/L P_{sol}) after 1 h with FFS. This confirmed the predominance of the precipitation mechanism for FFS giving >65% of overall P_{sol} removal.

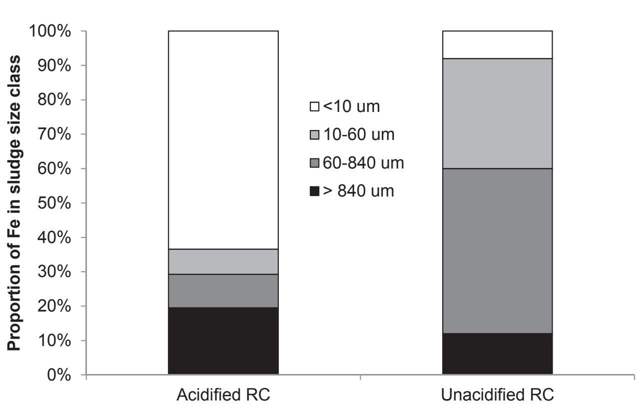

Fig. 2. The available iron concentration in acidified and unacidified RCs, size fractionated by membrane filtration (2.8% dry solids initial sludge solids content).

The RCs gave slower removal (2 mg/L/h), with a greater proportion of P_{sol} removal achieved after 1 h when they were directly dosed (between 50 and 80% of the overall removal). Similar removals to FFS were observed for the acidified RCs (filtered and unfiltered) when coagulants were pre-hydrolysed, with most removal occurring after 2 min (Fig. 3). For the unfiltered acidified pre-hydrolysed RC, there was a slight increase in the average soluble P concentration in the wastewater after 1 h of mixing. This may have been caused by some release of P into the wastewater from the sludge or within the error of measurement of the P concentration given that the increase was only 0.2 mg/L P. Very low levels of P removal were observed for the pre-hydrolysed unacidified RC. These results were expected for the unacidified RC, which was predominantly organic laden ferric hydroxide but more surprising for the soluble Fe^{3+} dominated acidified RCs. Inhibition of precipitation through complexing with organic compounds may account for this (Wang et al., 2012) but the ultrafiltered RC, with a lower organic content, did not show any greater P_{sol} removal at 2 min (Fig. 3). The additional water in the acidified RCs (>10 times more dilute than FFS) offers a further explanation. The increased water content would mediate the hydrolysis of ferric sulphate on addition to the wastewater and impede contact with P_{sol} while precipitation occurred. For the directly dosed RCs, subsequent removal after 1 h gave a greater contribution to overall P_{sol} removal (~50%). This was due to more favourable equilibrium conditions driving adsorption onto solids in the RC (metal hydroxides and

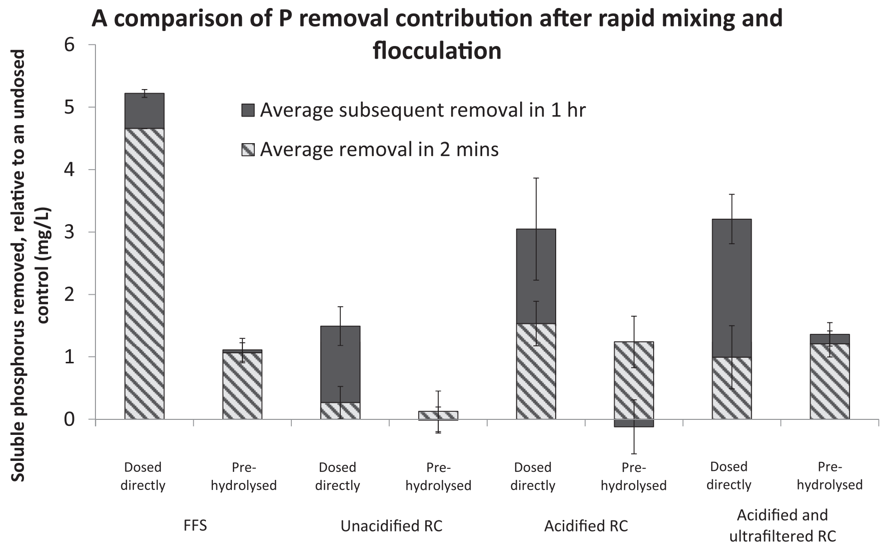

Fig. 3. Comparison of the soluble phosphorus removal contributions of fresh and recovered coagulants after 2 min and then after 1 h. In all systems, coagulants were added at 20 mg/L as Fe.

other complexes).

Previous work investigating specific removal rates of P using conventional coagulants agrees with the findings here. Specific removals of ~160 mg P/g Fe (after 1 h) for the acidified RC were intermediate between those for FFS (276 mg P/g Fe; Parsons and Daniels, 1999) and metal hydroxides (13–20 mg P/g Fe; Genz et al., 2004), suggesting a combination of mediated precipitation and adsorption as the removal mechanisms. The closest comparative specific removal in the literature was for a wastewater treated with fresh ferric chloride under poor mixing conditions (163 mg P/g Fe), where a similar combination of mechanisms was proposed to occur (Smith et al., 2008).

Precipitation and adsorption of phosphate can be increased by 2–3-fold by removing competing hydroxide species at lower pH values (Parsons and Daniels, 1999; Razali et al., 2007). Therefore, P removal was examined over a range of acidic pH (Fig. 4 and SI B). Ultrafiltered RC closely tracks the performance of FFS, removing 81% and 74% of P at a sludge pH of 2, respectively. This similarity was due to the exclusion of insoluble Fe from the sludge as well as 50% DOC removal by the ultrafiltration membrane (Keeley et al., 2014a). When dosed, normalised to total Fe, this ensured similar Fe availability and minimal interference from organic compounds (Wang et al., 2012). P removals with FFS and ultrafiltered RC remained unchanged from pH 4.5 to 3 but removed a further 1.5 mg/L P as the pH was lowered to 2. The end pH for the jar tests was similar for all coagulants tested at each pH (Fig. 4). A pH of 1 enabled even greater P removals but was associated with a significant decrease in average treated wastewater end pH to below 6.8 (Fig. 4), 0.5 units below the pH values recommended to ensure sufficient alkalinity for downstream processes. P removal with unfilterered RC increased more steadily with progressively lower pH values. This was due to an increased proportion of soluble Fe available (from 16 to 173 and 265 mg/L at pH 4.8, 3 and 2, respectively) for precipitation and reductions in the wastewater pH.

Ultrafiltered RC gave consistently higher Fe in the treated wastewater by between 0.5 and 1.0 mg/L than the other coagulants between coagulant pH values of 2 and 4.5. This correlated with the higher residual Fe (Fig. 1B) and turbidity (Fig. 1C) seen at higher doses for ultrafiltered sludge. These data suggest that while the most effective RC in terms of P removal, ultrafiltered sludge produces weaker flocs that are prone to releasing colloidal metal-organic complexes at higher mixing velocities. Alternatively, some stable ferric–organic complexes may remain unreactive and soluble in the acidified RC (Keeley et al., 2014b).

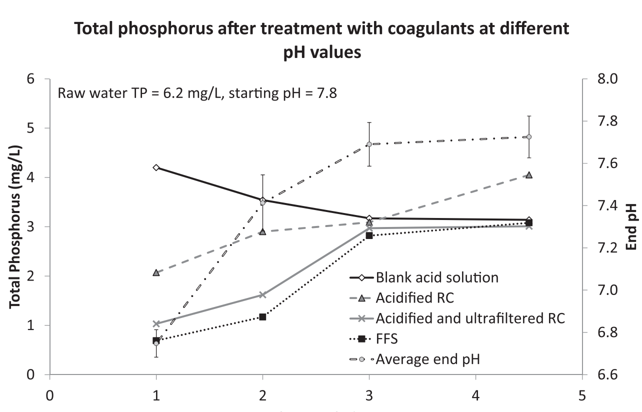

Fig. 4. Residual total phosphorus at different coagulant pH values (prior to dosing) for different recovered coagulant options. Results are compared with those for fresh ferric sulphate.

3.2. Physical factors

Non-ideal mixing conditions are a common cause of coagulant inefficiencies at treatment works (Szabo et al., 2008) and can reduce chemical removal efficiency by 5-fold (Smith et al., 2008). Using a similar method used to examine P_{sol} removal within 2 min, removals immediately after different rapid mix intensities were examined to determine the importance of effective mixing when using RCs. Both FFS and RCs had increased removals as mixing intensity increased from 5 s^{-1} to 75 s^{-1} (Fig. 5) which is comparable to the optimum requirement (100 s^{-1}; Szabo et al., 2008). For FFS, removals increased by 3.5 mg/L (3 times the 5 s^{-1} mixing condition), while the RCs increased from 0.0 to 0.5 mg/L, at 5 s^{-1} to ~1.0 mg/L at 75 s^{-1} and above. In the case of FFS, good mixing is required to promote dispersal of the coagulant for reaction with P. For RCs, where adsorption processes are more important, increased mixing improves mass transfer of P onto the surface of available adsorbent materials.

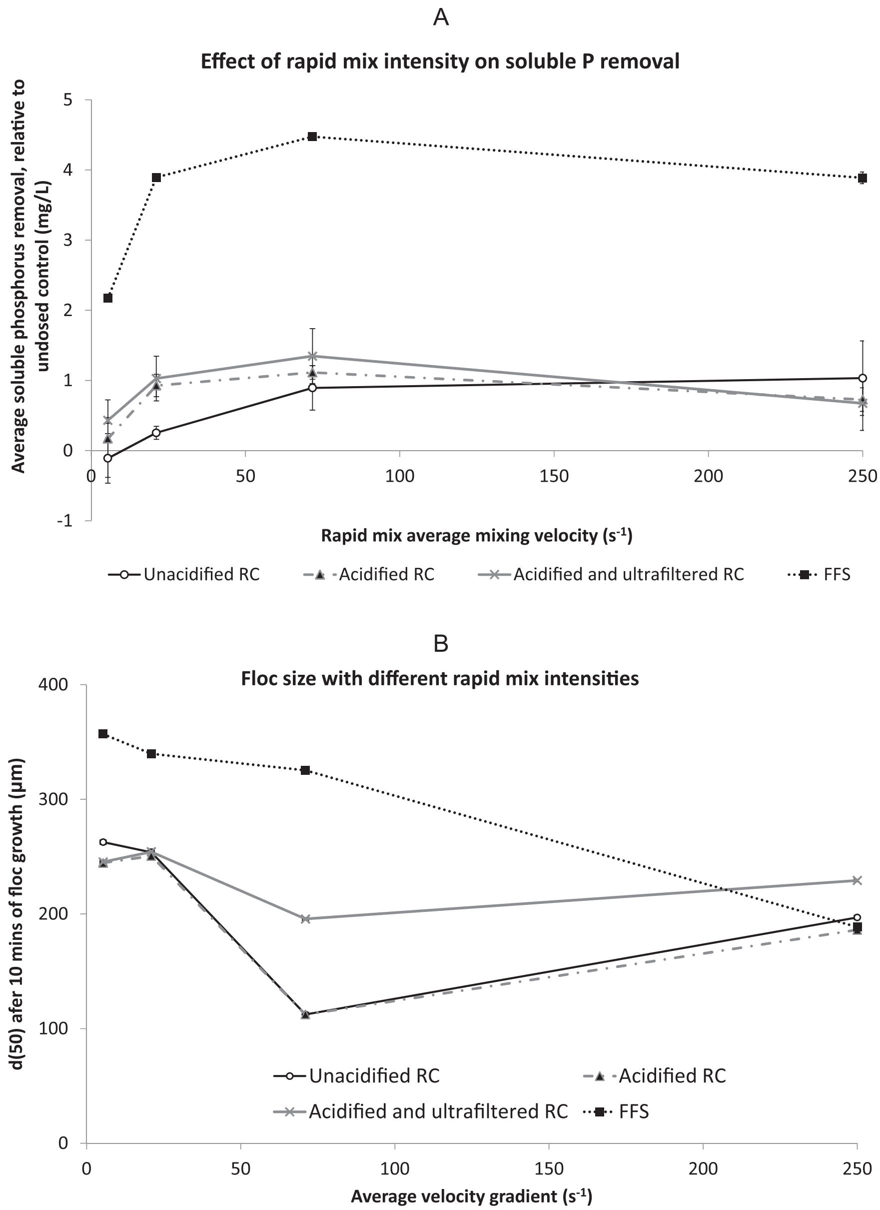

Fig. 5. The effect of rapid mix intensity on soluble phosphorus removal and the subsequent floc size when using different coagulation options following 10 min flocculation time.

A further consideration is the impact mixing has on resultant floc size given that effective P removal relies on separation of the solids in (and on) which the P is present (Fig. 5). The FFS formed the largest flocs, with a median size of 330–350 μm for initial rapid mixing intensity between 5 and 75 s^{-1}. RCs generally had smaller floc sizes, with a maximum median size of 250 μm after poor mixing (<20 s^{-1}). Increased mixing to 75 s^{-1} appeared to impede floc growth, giving a smaller median size of 100 μm for acidified RCs and 200 μm for unacidifed sludge. This was a reflection of the increased proportion of insoluble fractions in the unacidified RCs. Increased mixing intensity up to 250 s^{-1} led to a decrease in the size of the FFS flocs. Similar observations have been seen before as rapid mixing intensity increases during coagulation experiments, such that at high mixing intensity, flocs form then break within the rapid mix period that are then unable to effectively regrow (Aktas et al., 2014). The same observation was seen for the RC flocs, albeit at lower mixing intensity thresholds. However, for the RCs, floc size then increased at the highest mixing intensity. This was likely to be due to the breakage of the particulates/colloidal aggregates already present in the RCs releasing more Fe surface area that was then available to aggregate particles into larger flocs. These results indicate that RCs will produce flocs that will not be as effectively removed in clarification systems than for FFS due to the smaller floc size.

The hydraulic retention time in settlement tanks at WWTWs is typically 2 h, following a flocculation time of typically >30 min, providing sufficient contact time for P adsorption (Tchobanoglous et al., 2003). Extended jar tests at a moderate mixing intensity of 43 s^{-1} gave an insight to the changing rates of P removal over several hours. All coagulants showed fastest removal rates in the first 2 h, with 3.6, 3.1, 2.5 and 1.9 mg/L/h for FFS, ultrafiltered, acidified and unacidified RCs, respectively (SI C). While FFS and ultrafiltered RCs provided no further removal, acidified and unacidified RCs continued for a further 6 h, at 0.2 and 0.4 mg/L/h, respectively. After 2 h, this equated to 82%, 71%, 56% and 52% TP removal with fresh, ultrafiltered, acidified and unacidified RCs,

Table 1
Whole life cost estimations for implementation of five different phosphorus removal strategies using fresh and recovered coagulants.

		Component cost (£)	Basis of cost	Ref.	FFS for WWTW, with WTW sludge disposed to land	Unacidified sludge RC	Acidified RC	Acidified and ultrafiltered RC	Direct connection
CAPEX[a] **(£)**	Sludge reception	80,000	Based on dewatered sludge conveyor	1	–	80,000	80,000	80,000	–
	Acidification	350,000	5 L acid/min		–	–	350,000	350,000	–
	Ultrafiltration	2,000,000	15 $L/m^2/h$, 2 g/L Fe		–	–	–	2,000,000	–
	Ferric dosing system	260,000			260,000	260,000	260,000	260,000	260,000
	Rapid mix ($G = 900$)	75,000	10x sludge volume		–	80,000	80,000	80,000	–
	Connecting buried sewer	16,100,000	£200/m	2	–	–	–	–	16,100,000
	Total				260,000	420,000	770,000	2,770,000	16,360,000
Value of TP removal (based on performance relative to fresh) - Not directly included in OPEX total -		730	£/tonne, as Fe	2	330,000	180,000	290,000	320,000	180,000
OPEX (£)	Fresh ferric required	730	£/tonne, as Fe	2	330,000	160,000	40,000	20,000	160,000
	Acid	105	£/tonne, as H_2SO_4		–	–	80,000	80,000	–
	Transport	0.13	£/tonne/km apart	3	40,000	90,000	90,000	90,000	–
	Labour		£30/man hour		10,000	10,000	10,000	10,000	10,000
	Mixing electricity		Nominal estimate		–	10,000	10,000	10,000	
	UF electricity	0.5	£/m^3 (2 g/L Fe)		–	–	–	110,000	–
	Chemical cleaning		Nominal estimate		–	–	–	10,000	–
	Disposal to land	9	£/tonne	2	120,000	–	–	–	–
	Total annual OPEX				500,000	260,000	230,000	330,000	170,000
	Total OPEX over 20 years	Adjusted for 3% annual inflation			13,390,000	7,090,000	6,170,000	8,870,000	4,460,000
Estimated whole life cost over 20 years (£)					13,650,000	7,510,000	6,930,000	11,630,000	20,820,000

1. McGivney and Kawamura, 2008.
2.Commodity prices and construction estimates provided by UK water companies.
3. Road Haulage Association, 2013.
[a] Based on published cost curves, plus an additional: 10% piping; 5% groundworks; 20% electrical and controls; 35% engineering, legal and admin.

respectively. After 8 h, all RCs except the dewatered sludge cake RC achieved P removals within 15% of FFS, showing the importance of adsorption mechanisms for the unfiltered RCs.

The continued removal contribution from adsorption onto ferric precipitates in the sludge over the timescales typical of full scale WWTWs offers the potential to obviate the need for acidification of WTRs, provided the treatment stream allows sufficient contact time. A key consideration for determining the optimal ferric-based phosphorus removal approach is the available contact time within existing treatment stages: for FFS and ultrafiltered sludge this is relatively unimportant but for acidified and unacidified sludges, extended contact time will benefit removal performance.

3.3. Implementing recovered coagulant

The assessment of treatment efficacy and acid demand enables a direct comparison of the efficiency of FFS to RCs. Relative to P removal performance of FFS, at a dose of 20 mg/L and 1 h of mixing, unacidified RC was 53% as efficient; acidified RC 88%; and ultrafiltered RC 95% (Fig. 3). The molar requirement of H_2SO_4:Fe required to acidify RC to pH to 2 was 2.6:1 (SI B). This exceeds the 1.5:1 stoichiometric requirement but compares to empirical values seen previously (Parsons and Daniels, 1999).

The value of RC was considered in terms of its P removal performance when compared to FFS. For example, if 1 tonne of FFS costs £100 and can remove ‘x’ amount of P and if 1 tonne of RC can remove 0.75 of ‘x’, then it's value is £75/tonne. In other words it can offset that value of FFS. In this case, the FFS required would be £25 or 0.25 tonne; the amount required to supplement the recovered coagulant. The case study considered a WWTWs that dosed FFS for P-removal and used that as a base level cost. Each coagulant recovery scenario measured the cost benefit of offsetting some of the FFS demand with RC. In each case, some FFS is required to supplement the recovered RC and this incurs a cost, the “FFS required”.

For the hypothetical, but realistic situation considered, it was shown that the acidification step plays a critical role in the viability of using RCs (Table 1). The whole life cost (WLC) of using three coagulant recovery techniques was lower than for dosing FFS including disposal of the resultant sludge to landfill. The lowest WLC was given by dosing acidified RC, closely followed by transport and dosing of unacidified RC. Such similarity in WLC shows that the acidification cost is almost equal to the value of improved P removal performance. These reuse strategies nearly halve the 20 year WLC of the FFS option. The ultrafiltered RC also gave a lower WLC than for FFS, but was closer than for the other two RC options. The improved treatment performance of ultrafiltered sludge was counteracted by the high CAPEX and OPEX of the UF system. Although the obvious conclusion from this being that ultrafiltered RC is not as viable as unfiltered options, additional benefits from the membrane filtration not included in the analysis may still make the process worthy of consideration. This includes a more reliable and purer Fe coagulant being dosed, more reliable solid liquid separation from a more robust floc forming and improved removal of other impurities (chemical and biological) from the RC that will not be added to treated wastewater.

Direct connection of the WTW and WWTW sites with a sewer provided the lowest OPEX but this was insufficient to offset the construction CAPEX and gave rise to the highest WLC: £5.5 m above conventional treatment. However, it is noted that if sludge was sent to sewers instead of land, the significant OPEX of WTRs dewatering at the WTW would be saved (Babatunde and Zhao, 2007).

Reuse of sludge within WWTW is dependent on external market forces and operational parameters. Sensitivity analysis highlighted the variables that WLC was most vulnerable to (SI E). Acid and the inferior P removal of RCs compared to FFS were the main contributors to overall costs for reuse of acidified and raw sludge, respectively. A 50% increase in acid unit price would increase the 20 year WLC of acidified RC by 16%. A 50% increase in FFS price would increase unacidified RC WLC by 28% due to the requirement of having to top-up the dose with fresh coagulant. The other main variable is inter-site distance, which determines transport costs. A 50% increase in distance or cost would increase WLC for all sludge transport reuse strategies by 10–17%. In the case of a connecting sewer, distance is the main determinant of CAPEX, with a 50% increase in distance leading to a 39% increase in WLC. Further analysis was used to determine the maximum inter-site distance that would still allow 20 year WLC reductions over FFS. This gave the maximum distance above the existing route to disposal to be: 240 km for acidified and unacidified RCs; 50 km for acidified and ultrafiltered RC; and 16 km for a connecting sewer (SI E). Shorter distances would significantly improve the processes' WLC.

Mechanistic, empirical, and economic analyses have shown that recovered ferric coagulants and raw WTRs are effective at removing P from wastewater under economically viable conditions. Within the limitations defined by the economic analysis, this will allow utilities to develop strategies that minimize coagulant demand and disposal of WTRs, whilst better protecting the aquatic environment through more extensive nutrient removal. The impact of the formation of smaller flocs on full scale wastewater clarification and dewatering systems and high residual metals when using RCs needs further investigation. These effects may be mitigated by the addition of low doses of supplementary fresh coagulant or from longer flocculation times. These areas should be the focus of future research in coagulant recovery.

4. Conclusions

Experimental and economic analyses have highlighted a number of factors regarding the reuse of WTRs for wastewater nutrient removal.

- Acidified and ultrafiltered sludge resulted in similar P removal as for FFS when dosed under short contact periods (16 min of mixing).
- Adsorption controlled P removal for unacidified RCs (slow). Precipitative driven processes (fast) dominated for fresh coagulants. While for acidified RCs a combination of processes was evident.
- For fresh coagulants floc size was significantly larger than for the RCs, which has significant implications on the downstream settleability of flocs.
- Reuse of acidified or unacidified RCs can reduce the 20 year WLC by almost 50% in comparison to using conventional use of FFS and WTR disposal to land. Ultrafiltration increased WLC but was still significantly lower than conventional practice.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.10.039.

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