

Coagulant recovery and reuse for drinking water treatment

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ABSTRACT

Coagulant recovery and reuse from waterworks sludge has the potential to significantly reduce waste disposal and chemicals usage for water treatment. Drinking water regulations demand purification of recovered coagulant before they can be safely reused, due to the risk of disinfection by-product precursors being recovered from waterworks sludge alongside coagulant metals. While several full-scale separation technologies have proven effective for coagulant purification, none have matched virgin coagulant treatment performance.

This study examines the individual and successive separation performance of several novel and existing ferric coagulant recovery purification technologies to attain virgin coagulant purity levels. The new suggested approach of alkali extraction of dissolved organic compounds (DOC) from waterworks sludge prior to acidic solubilisation of ferric coagulants provided the same 14:1 selectivity ratio (874 mg/L Fe vs. 61 mg/L DOC) to the more established size separation using ultrafiltration (1285 mg/L Fe vs. 91 mg/L DOC). Cation exchange Donnan membranes were also examined: while highly selective (2555 mg/L Fe vs. 29 mg/L DOC, 88:1 selectivity), the low pH of the recovered ferric solution impaired subsequent treatment performance. The application of powdered activated carbon (PAC) to

ultrafiltration or alkali pre-treated sludge, dosed at 80 mg/mg DOC, reduced recovered ferric DOC contamination to <1 mg/L but in practice, this option would incur significant costs.

The treatment performance of the purified recovered coagulants was compared to that of virgin reagent with reference to key water quality parameters. Several PAC-polished recovered coagulants provided the same or improved DOC and turbidity removal as virgin coagulant, as well as demonstrating the potential to reduce disinfection byproducts and regulated metals to levels comparable to that attained from virgin material.

Keywords Coagulant recovery and reuse; dissolution; ferric; membrane separation; DOC

1 INTRODUCTION

Coagulation-flocculation is a key process in potable water treatment. While effective, its application accounts for ~5% of operational expenditure (OPEX) at water treatment works (Niquette et al., 2004). This is attributable to the combined costs of coagulant and pH adjustment chemicals, as well as that of disposal of the resulting sludge or “water treatment residuals” (WTR). Within the UK water industry, annual coagulant consumption exceeds 0.33m tonnes (Henderson et al., 2009) and WTR production exceeds 0.18 million (m) tonnes (Pan et al., 2004), costing around £40m and £8m respectively at 2015 prices. The issue is reflected globally: annual waterworks sludge production from alum dosing alone exceeds 730m tonnes in the US (Prakash and Sengupta, 2003) and in Japan, drinking water treatment produces 0.3m tonnes of dry solids (Fujiwara, 2011).

Coagulant recovery can potentially reduce these costs by regenerating and reusing the coagulant metals in the WTRs. This is usually achieved through acidification, commonly to pH 2 (King et al., 1975; Parsons and Daniels, 1999; Keeley et al., 2014b). However, organic compounds within the sludge have similar pH solubility behaviour (Prakash and Sengupta, 2003), contaminating the acidified recovered coagulant with suspended and dissolved organic carbon (DOC). An early full-scale study of non-selective ferric recovery reported no significant impact on treated water quality but the recovered ferric coagulant free acidity increased lime demand and shortened filter run times (Saunders and Roeder, 1991).

When dosed into the potable treatment stream, elevated levels of residual DOC resulted at the final chlorination stage yielding a commensurate increase in halogenated disinfection byproducts (DBPs) in the final treated water (World Health Organization, 2000). Public health protection and abundance with water quality regulations (USEPA, 2009; DWI, 2010) demand the recovered coagulant (RC) to be appropriately purified to remove DOC and trace metal contaminants.

Conventional, pressure-filtration membranes (Keeley et al., 2014a,b), adsorbents (Lindsey and Tongkasame, 1975), chemical precipitation (Ulmert and Sarner, 2005), and ion exchange (Prakash and Sengupta, 2003) have been tested for RC purification, but have failed to combine adequate removal of organic contaminants with competitive process economics. Reuse of impure RCs for phosphorus removal in wastewater treatment is a promising circumvention to this problem (Babatunde and Zhao, 2007; Xu et al., 2009) but is less

ambitious than reuse in potable treatment which approaches the target of net chemical-free treatment stipulated by some water-related research organisations ([UKWIR, 2007](#)).

Published research into coagulant reuse for potable water applications appears to have been limited for the last decade. This study aims to provide a benchmark for the purity and treatment performance of recovered ferric coagulant and to establish which RC characteristics most affect treatment efficacy. The effect of augmenting existing RC purification technologies (ultrafiltration, UF, and Donnan dialysis, DD) with pre- and post-treatment stages was also studied by way of improving RC quality, particularly in terms of minimising DOC contamination for which a lower level of 3.5 mg/L has been identified from previous CR studies ([Prakash and Sengupta, 2003](#)). Of more practical importance is the impact of this organic contamination on DBP formation, which pertains to the residual organic compound levels from both the raw water and dosed RC and their reactivity with chlorine.

2 METHODOLOGY

2.1 Coagulant recovery and purification

Dewatered WTR cake, measured as 14% dry solids (DS) containing ~25% Fe, was collected from a 150,000 m³/d capacity water treatment works treating upland water with ferric sulfate coagulant (13% as Fe) at a coagulation pH range of 4.7-5.1 (Derbyshire, UK). The raw water had a pH of 6.26 with a zeta potential of -13.9mV. The character of the NOM within this raw water has been determined to be predominantly hydrophobic (Keeley et al., 2014b). Slurries containing 1 kg of sludge cake in 10L of deionised (DI) water were mixed for 24 h {1}

before subsequent coagulant recovery extraction using acid {3} or alkali {4} (Fig. 1; numbers in parenthesis refer to sampling points shown in the figure).

Alkali pre-treatment {2} comprised adjustment of the WTR slurry to pH 12 with reagent-grade NaOH pellets, and mixing for 24 h, with periodic addition of NaOH to maintain the pH at 12, prior to settlement. The solids fraction was retained on a 1.2µm pore size glass fibre filter and washed with 1 L of DI water prior to digestion in 1 L of 5M H₂SO₄ for a further 24 h and dilution to 10 L with DI water. Direct solubilisation with acid was achieved by adjusting the WTR slurry to pH 2 with 18M H₂SO₄ before mixing for 24 h {4}.

Both the alkali pre-treated and direct acid extractions were purified by pressure filtration {6; 10} or cation exchange extraction {8; 12}. Pressure filtration through a 2 kDa-rated polyethersulfone membrane (Sterlitech Corporation, Kent, WA, USA) was conducted using a flat-sheet crossflow cell of 0.007 m² membrane area (Keeley et al., 2014b). The membrane cell was also adapted for use with a Nafion 115 cation exchange membrane, for which the feed-side recirculated 2 L of acidified sludge and the strip-side 1 L of 1 M H₂SO₄. Membrane specific surface area, time, feed:strip volumes and acid strength were selected according to a previous study using similar materials (Prakash and Sengupta, 2003).

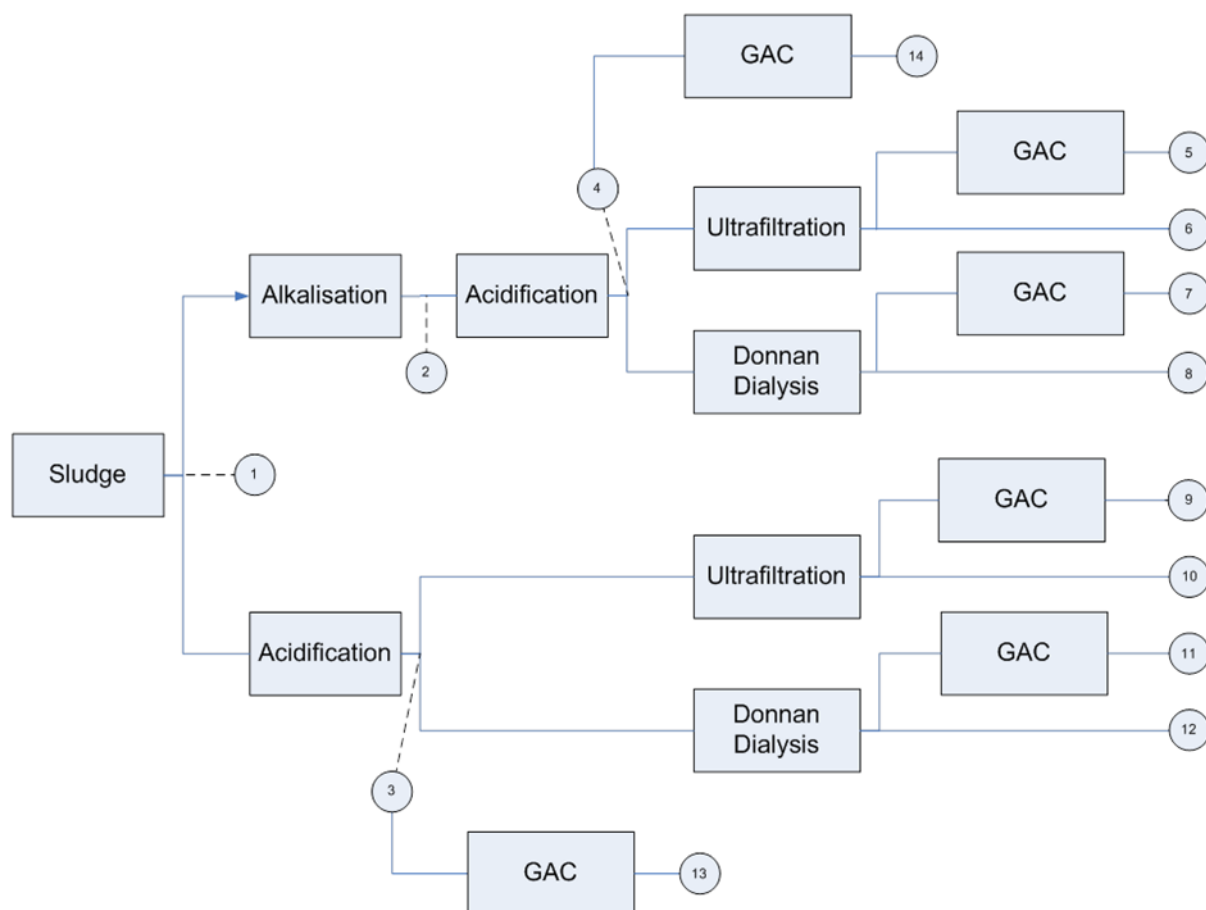


Figure 1. Recovered coagulant experimental processing scheme and sampling points:

- | | |
|--|----------------------------------|
| 1 Ferric sludge in water | 8 Alkali-purged, acidified, DD |
| 2 Ferric sludge in caustic | 9 Acidified, UF, PAC |
| 3 Acidified ferric sludge | 10 Acidified, UF |
| 4 Acidified, alkali purged | 11 Acidified, DD, PAC |
| 5 Alkali, acidified, UF (ultrafiltration), PAC (powdered activated carbon) | 12 Acidified, DD |
| 6 Alkali-purged, acidified, UF | 13 Acidified, PAC |
| 7 Alkali, acidified, DD (Donnan dialysis), PAC | 14 Alkali-purged, acidified, PAC |

Reference to these sampling points is made throughout the article, in parenthesis: {}.

A post-treatment adsorption stage was applied to all RCs to further reduce DOC concentrations {5; 7; 9; 11; 13; 14}. In addition to powdered activated carbon (PAC, Norit SA Super 94002-8), powdered graphite (PG, Fisher, UK) was also examined: previous studies had suggested PG to have a high organic acid adsorption capacity at pH values below 3 (Xiao and Pignatello, 2014). Adsorption isotherms were produced using a batch method whereby 0-200 g/L of adsorbent (pre-wetted for 24 hours in 15 mL 0.005 M H₂SO₄) were

mixed for 48 hours with 25 mL of RC at pH 2 (UF permeate for the acidified RC sample {10}). The aqueous phase was filtered through 0.45µm nylon filters (Fisher, UK) before DOC analysis using a Shimadzu TOC-V analyser and soluble Fe determination using a Perkin Elmer atomic absorption spectrometer (AAS). Other metals were extracted in nitric acid and analysed using inductively coupled plasma mass spectroscopy. The resulting isotherms were used to select the optimum adsorbent and dose (relative to RC DOC content) which were then applied to RC from all preceding stages of purification {5; 7; 9; 11; 13; 14}. RCs were then characterised in terms of pH, Fe and DOC content.

2.2 Recovered coagulant treatment performance

Jar tests were used to compare performance of RCs and virgin coagulant in terms of water treatment. Raw water and virgin ferric sulfate coagulant (VFS; measured as 20% Fe) were sampled from the same site as the WTRs. Jar tests (using a Phipps & Bird PB-700 jar tester) were conducted at room temperature, based on an existing method (Sharp et al., 2006) with a 1.5min rapid mix at 200 rpm, a 15min flocculation mix at 50 rpm and a 20min settlement stage. Treated water was analysed for DOC and turbidity, as well as zeta potential using a Malvern Zetasizer Nano ZS.

A series of jar tests with VFS were used to determine the optimum coagulant Fe dose (between 4 and 48 mg/L as Fe) and pH (between 3.5 and 5.5; corrected using dilute HCl and NaOH) for DOC and turbidity removal. This dose and pH were then used for further jar tests with RCs. Analyses comprised DOC, UV absorption at 254 nm (used to calculate specific UV adsorption; SUVA), turbidity, and zeta potential. Residual metals (Cu, Pb, Ni, Cd, Cr

and Mn) were determined using inductively-coupled plasma spectroscopy, and trihalomethane formation potential (THM-FP) measured using a protocol (Parsons et al., 2004) adapted from standard methods (APHA, 1992). Size exclusion liquid chromatography with 254 nm UV absorption detection was conducted using a Shimadzu VP series chromatogram.

3 RESULTS AND DISCUSSION

3.1 Recovered coagulant purity

Three coagulant purification unit processes were studied: 1) alkali extraction of DOC prior to acidification and solubilisation {4} of the retained solids; 2) membrane separation using UF {6; 10} or DD {8; 12}; and 3) DOC adsorption with powdered carbon {5; 7; 9; 11; 13; 14} (Fig. 1).

Alkali pre-treatment. A pH 12 NaOH solution was used to extract the bulk of the organic compounds, as DOC, from WTRs {2} leaving the less soluble iron for subsequent dissolution in H₂SO₄ {4}. The use of alkali to resolubilise and recover aluminium sludge has previously been examined (Masschelein et al., 1985) but not for iron-DOC discrimination. This combined alkali/acid process was effective in separating Fe from DOC by virtue of their differing solubilities in alkali : an equal mass of WTR produced the same volume of acidified sludge extract with 57% less DOC than extraction by acidification alone {3} (61 mg/L ± 1.4% DOC cf. 143 mg/L ± 2.8; Table 1). However, the corresponding Fe extracted was 47% lower, such that the overall Fe:DOC ratio was only slightly higher at 14.3 cf. 12.9 for single-step acidification. While solubility profiles suggest that only negligible amounts of Fe remain

in solution at pH 12 (King et al., 1976), loss of colloidal iron hydroxide and Fe-DOC through the retaining glass-fibre filter may take place.

Ultrafiltration (UF). {6; 10} Size exclusion based purification of RCs has been thoroughly investigated in previous studies (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005; Keeley et al., 2014a,b). These studies showed that within a range of <1-20 kDa MWCO UF membranes, a 2 kDa MWCO gave the optimum balance of DOC rejection and trivalent metal recovery. However, this MWCO nonetheless allowed significant DOC carryover, at 91 mg/L DOC with 1285 mg/L Fe {10}, from a feed containing 143 and 1287 mg/L DOC and Fe respectively {3} (Table 1). A similar Fe:DOC selectivity ratio before (12.9) {3} and after UF (14.1) {10} would suggest a similarly low level of selectivity by size exclusion as with alkali treatment {4}. Previous studies have highlighted the strength of Fe-DOC interactions as a contributing factor for poor selectivity for Fe by UF purification, relative to the more weakly interacting Al (Keeley et al., 2014a,b).

Donnan dialysis (DD). {8; 12} This method uses a cation exchange membrane to extract coagulant metal ions from the acidified sludge, rather than filtering through a conventional membrane. Since DD is a diffusive process and does not employ a transmembrane pressure, it avoids the membrane fouling and energy usage of pressure-filtration and their associated costs (Prakash and Sengupta, 2003). DD has additionally been reported to be the most selective method for separating trivalent coagulant metals and DOC (Schneider, 2013) with consistent Fe or Al recovery concentrations >5000 mg/L at yields of 70-75% with <5 mg/L DOC contamination (Prakash and Sengupta, 2003). Similar performance was attained in this study, with extraction from an acidified sludge feed yielding 82% Fe recovery at a

concentration of 2555 mg/L, with 29 mg/L DOC {12} (Table 1). The comparatively high yield and more dilute recovery solution are due to a lower volume ratio of feed sludge to recovery acid (2:1) than the 4:1 ratio used by Prakash and Sengupta (2003); the relative volumes affect the distribution of ions across the membrane at the point of Donnan equilibrium.

Table 1: Fe and DOC levels, and Fe/DOC ratios in recovered coagulant sludge product (sample numbers relate to Fig. 1).

Sam- ple	Recovered Coagulant	Fe (mg/L)		DOC (mg/L)		Fe/DOC	DOC added* (mg/L)
		Mean	S.D.	Mean	S.D.		
1	Ferric sludge in water	144	27	270	22	0.5	45
2	Ferric sludge in caustic	1094	448	1686	290	0.6	37
3	Acidified ferric sludge	1847	191	143	0.5	2.8	1.9
4	Acidified, alkali purged	874	17	61	0.1	14	1.7
5	Alkali, acidified, UF, PAC	823	26	2	0.2	341	0.06
6	Alkali-purged, acidified, UF	855	16	42	0.2	20	1.2
7	Alkali, acidified, DD, PAC	1072	19	2	0.1	597	0.04
8	Alkali-purged, acidified, DD	1056	28	4	0.3	261	0.09
9	Acidified, UF, PAC	1267	0	3	0.2	455	0.06
10	Acidified, UF	1285	34	91	0.2	14	1.7
11	Acidified, DD, PAC	2536	42	13	0.2	191	0.12
12	Acidified, DD	2555	75	29	0.2	88	0.27
13	Acidified, PAC	676	24	6	0.2	115	0.21
14	Alkali-purged, acidified, PAC	898	33	1	0.1	868	0.03

*refers to 24 mg/L Fe dosed in raw water

DD of the alkali pre-treated sludge {8} was less effective, with the same volume of sludge yielding 73% Fe at 1072 mg/L but with reduced DOC carryover of 4 mg/L (Table 1). The lower yield and concentration was due to a feed Fe concentration {4} less than half that of the single-step acidified feed {3}, due to the permeation of colloidal and solubilised Fe through the glass-fibre filter in the alkali pre-treatment process. Further reductions in process efficiency may have also been caused by the elevated levels of sodium in the RC, following

the preceding alkaline organics extraction step. These sodium ions are also extracted through the cation membrane via the same ion exchange mechanism, competing with Fe and establishing Donnan equilibrium at a lower net transfer of Fe ions (Pyrzynska, 2006).

Adsorption. Preliminary tests compared the adsorption of DOC by PG and PAC from an RC sample containing 125 mg/L DOC and 1933 mg/L Fe. Adsorption isotherms at pH 2 showed DOC removals of 90 and 86% by PAC and PG respectively at the highest adsorbent dose of 200 g/L. At lower doses PAC attained DOC removals 1.5-10 times more than those of PG (Fig. 2). This corroborates previous results of applying granular activated carbon for DOC removal from recovered alum sludge (Cornwell et al., 1981). The relative gradients of the isotherm plot (Fig. 2) indicate PAC to have a greater DOC adsorption capacity than PG.

A PAC dose of 10 g/L was selected. Higher doses yielded marginal removal improvements: a 100 g/L dose reduced the DOC residual by only 2 mg/L less than the 10 g/L PAC dose (yielding a residual DOC of 10.3 mg/L rather than 12.4 mg/L; both from a feed level of 125 mg/L). However, the 100 g/L PAC reduced the Fe yield by 330 mg/L compared with the 10 g/L PAC dose. At the dose of 10 g/L PAC removed 6 times more DOC than PG. Accordingly, PG was excluded from further testing. Both adsorbents favoured DOC adsorption over Fe adsorption, with only 9% and 15% reductions from the initial soluble Fe concentration with 10 g/L of PAC and PG respectively. Evidence suggested that the small improvement (10-15%) in Fe concentration at very high adsorbent doses (200 g/L) was primarily by water uptake by the PAC, rather than organic carbon removal. Further details are shown in Table S1 in Supporting Information.

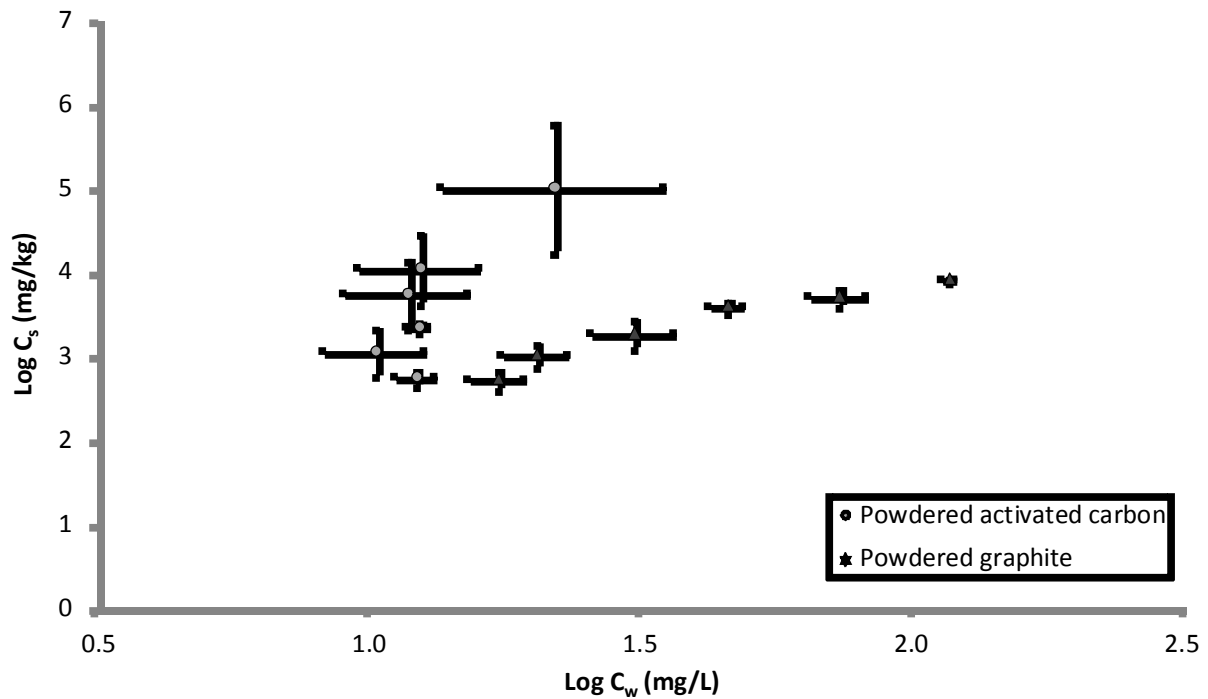


Figure 2. Adsorption of DOC by PAC and powdered graphite at pH 2

The isotherms showed that a PAC dose of 80 mg/mg DOC was most effective at DOC removal from RCs, without significant uptake and loss of Fe. At this dose, removals of 94-98% were achieved from acidified {13}, alkali pre-treated {14}, and ultrafiltered RCs {5; 9} (Table 1). DD RCs were less effectively purified by PAC {7; 11}, with DOC removals of 54-56%, due to the low DOC concentrations of 4 and 29 mg/L, prior to PAC treatment {8; 12}. Low pH values make DOC and PAC more electropositive, increasing electrostatic repulsion to a point that adsorption is inhibited (Xiao and Pignatello, 2014). Additionally, the DD-treated RCs had significantly lower initial pH of ~0.5, compared to 1.5-2.8 for other PAC-treated RCs. The hydrophilic, low molecular weight/electronegativity nature of the residual DOC in DD-treated RCs may also negatively affect its ability to be adsorbed, although of all the purification methods evaluated in this study, DD RC {12} had the lowest DOC residual and may not require additional purification

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249 The residual DOC concentrations for PAC-treated RCs {5; 7; 9; 11; 13; 14} were in the range
250 of 1-13 mg/L, comparable to the lowest reported DOC values in RCs of 3.5 mg/L (Prakash
251 and Sengupta, 2003) and 17 mg/L (Prakash et al., 2004). The lowest DOC concentrations for
252 PAC-treated RCs were from alkaline pre-treatment {5; 7; 14}, both with and without UF or
253 DD treatment. Alkaline pre-treatment thus removes DOC of different character to PAC, or
254 else chemically alters the residual DOC through hydrolysis and saponification (Randtke and
255 Jepsen, 1981; Schafer, 2001), such that enhanced overall DOC removal is attained from their
256 combination.

257

258 **Relative separation performance of individual processes.** All of the individual processes
259 were capable of recovering >70% of the feed Fe, other than alkali pre-treatment {4} and
260 direct PAC treatment of acidified sludge {13} which respectively recovered only 57% and
261 35% of the Fe. These yields do not take into account the yield from acidifying the base
262 sludge, which never exceeded 53% in this experiment. More importantly, in terms of their
263 impact on treated water quality, there was significant DOC rejection from each stage. UF {6;
264 10} gave the least effective DOC exclusion of 31-36% due to the comparable molecular
265 weight distributions of DOC compounds and Fe colloids. PAC treatment of DD-treated RCs
266 {8; 12} gave almost as poor DOC removals of 50-55%, due to low initial DOC levels (<29
267 mg/L) and the extensive electropositive repulsion between the DOC and PAC adsorption
268 sites at the low pH of the recovered DD solutions (Xiao and Pignatello, 2014). Alkali pre-
269 treatment gave similarly low levels of rejection, with incomplete alkali solubilisation of
270 organic compounds in the sludge {3} leading to carry-over into the recovered solid phase and
271 subsequent organic compound solubilisation upon acidification {4}. Far better DOC rejection

was provided by DD (80-93% {8; 12}) and PAC treatment at pH values of 2 and higher initial DOC loadings (90-98% {5; 9; 13; 14}). These data indicate that charge or adsorptive DOC removal is important in minimising DOC levels in the RC final product.

While individual CR process selectivity is an important consideration, the selectivity of multiple processes in series has also been examined. A multistage RC purification train would be a likely requirement to ensure reliable delivery of RCs with sufficient quality for potable treatment by diversifying the modes and extent of DOC removal (Ulmert and Sarner, 2005; Cornwell et al., 1981). With the obvious practical constraints of a multistage recovery process, more pragmatic water quality regulations may be prerequisite for full-scale potable coagulant recycling.

3.2 Coagulant recovery option assessment

The combined performance of a number of CR treatment trains was evaluated in terms of RC Fe concentration, DOC carryover and pH, as previously proposed by Cornwell et al (1981), as well as Fe/DOC ratio (Table 1). These measures were then compared to coagulant treatment performance and benchmarked against virgin ferric coagulant.

Fe concentration. For fully acidified and solubilised ferric RCs, soluble Fe concentration could be indicative of RC ability to destabilise impurities, via surface charge neutralisation, when dosed into raw water. By this measure, DD was the most effective treatment option: DD without alkali pre-treatment {12} and DD followed by PAC polishing {11} gave the highest Fe concentrations of 2555 and 2536 mg/L, respectively, although the incremental

reduction in DOC concentration was minor. The next highest was the unpurified sludge acid extract with 1847 mg/L {3}. These results highlight the inevitable losses of Fe for alkaline pre-treatment {4} or, to a lesser extent, UF {10}. The concentrations of Fe recovered using UF {10} and DD {12} are comparable with previous studies using similar approaches reporting RCs of 3500 mg/L Al with UF (Ulmert and Sarner, 2005) and 5400 mg/L Fe with DD (Prakash and Sengupta, 2003), with feed concentration, pH and volume being key determinants of RC concentration (King et al., 1975). More concentrated RCs (up to 30,000 mg/L Al) have been achieved through RC extraction from an ion exchange resin (Petruzzelli, 2000) or nanofiltration dewatering and precipitation of the RC salts (Ulmert and Sarner, 2005). These were not attempted in this study since the cost-benefit of producing RCs at these high concentrations, whilst reducing transport volumes and allowing centralised processing, is questionable.

DOC concentration. Since the principal concern of using RC in potable water treatment is elevated DBP (disinfection by-product) formation from DOC, residual DOC provides a useful indication of CR efficacy. Processes using PAC and alkali pre-treatment gave the lowest DOC concentrations, viz: alkali pre-treatment coupled with PAC post-treatment (1 mg/L {14}); alkali pre-treatment with UF or DD and PAC post-treatment (2 mg/L {5; 7}); and non-pre-treated UF with PAC post-treatment (3 mg/L {3}). This suggests that PAC treatment is integral to reaching the highest purity of RC and corroborates previous assertions that an activated carbon polishing stage is required, although in these earlier studies the stage was used to remove a synthetic organic extractant which has different characteristics to NOM (Cornwell et al., 1981). While PAC provides effective polishing, it nonetheless demands reasonable DOC removal from preceding treatment processes, whether that is alkali pre-

treatment, membrane separation or a combination of both. Without such pre-treatment the high DOC load in the RC and thus higher PAC dose relative to Fe, produces significantly greater Fe adsorption and less complete DOC removal. Since UF and PAC utilize different mechanisms of DOC removal (size and adsorption, respectively) they remove DOC different fractions from RC and so maximize overall removal. Removal of the high molecular weight DOC by UF reduces the load onto the PAC and ameliorates pore clogging, analogous to coagulation and filtration prior to GAC in potable water treatment (Newcombe and Drikas, 1997).

Fe/DOC ratios. The efficacy of the RC increases with increasing Fe/DOC ratio due to the associated reduced RC demand and DOC carryover. Because DOC concentrations are more variable than Fe levels between the CR processes (between 1 and 143 mg/L in acidified RCs, cf. 676-2555 mg/L for Fe) Fe/DOC ratios correlate more closely with DOC concentrations than Fe (Table 1). Accordingly, the highest Fe/DOC ratios pertain to alkali-PAC {14} and DD treatment {7} (868 and 597 respectively), both achieved primarily through extensive DOC rejection. UF-PAC treatment {9} achieved a lower ratio of 455 due to the higher DOC carryover (3 mg/L), albeit offset by a higher Fe concentration yield than the alkali pre-treated RCs.

3.3 Recovered coagulant treatment performance

RC coagulant performance was benchmarked against virgin material (VFS). A VFS coagulant dose of 24 mg/L as Fe and pH of 4.5 were selected from within the optimum operating region with reference to zeta potential and DOC and turbidity removals (Fig. 3).

The relatively high dose was employed to ensure that coagulant performance was affected only by coagulant quality, rather than external factors such as minor variations in raw water character. This dose and pH combination was used for all subsequent jar tests using RCs.

RC treatment performance with PAC post-treatment, in terms of DOC and THM-FP removal and treated water turbidity and Fe residual, revealed no significant trend with either RC Fe dose, DOC concentration or Fe/DOC ratio. For alkali-pretreated coagulants % DOC removal from the raw water was in the region of 66-77% {5; 6; 7; 8; 14} at Fe doses of 800-2600 mg/L with associated DOC concentrations of up to 91 mg/L and Fe/DOC ratios between 14 and 870 (Table 2). This compares with a value of 76% recorded for VFS dosed at a concentration of 24 mg/L as Fe. The %THM-FP removal was within 18% of that determined for VFS for all RCs, whilst residual turbidity was comparable (Table 2). In some cases {5; 9; 14} the %THM-FP removal with RCs was equal to the removal achieved with VFS. Residual Fe concentrations were more variable, with generally higher concentrations than with VFS but in some cases, including for the best DOC-removing RCs, residual Fe was comparable to those for VFS.

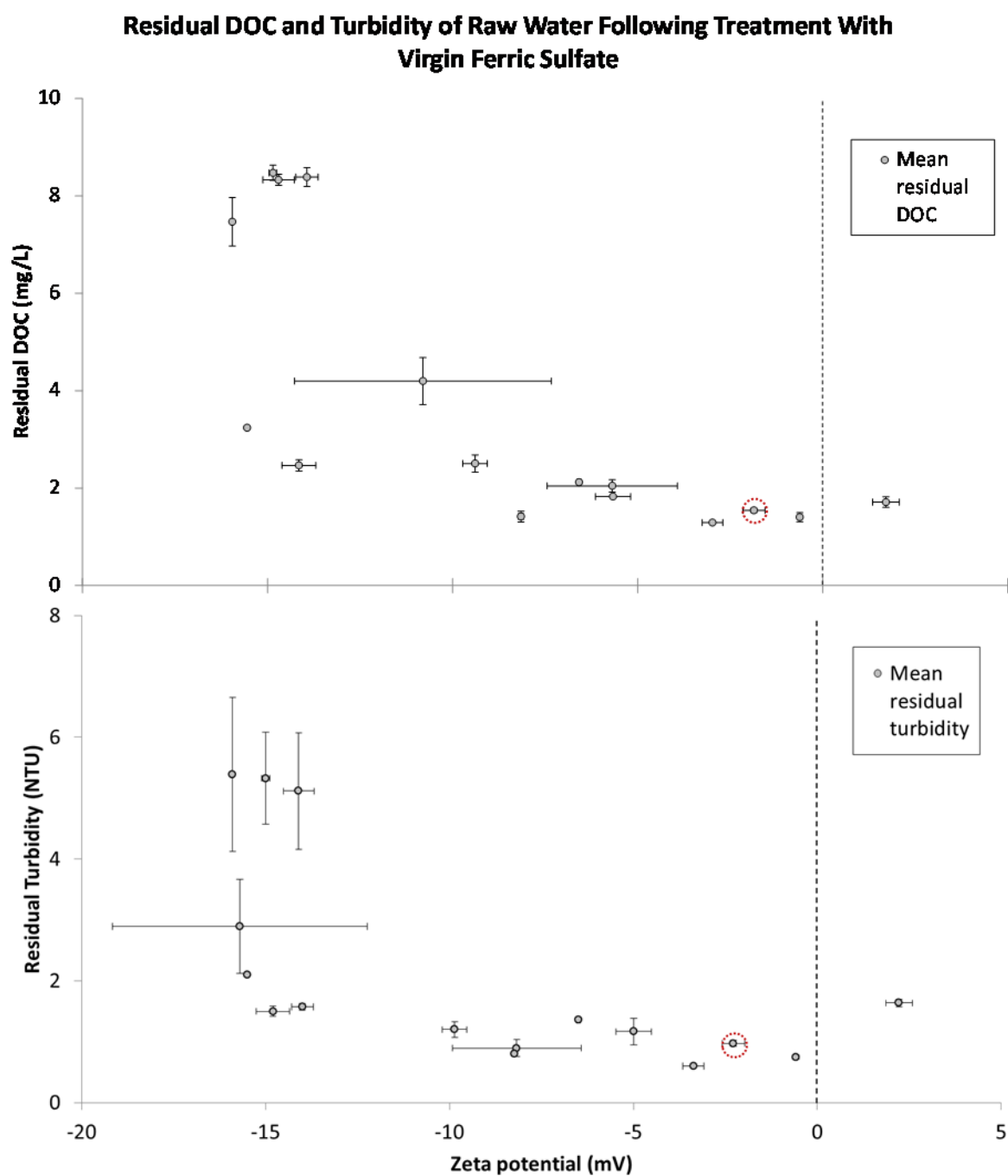


Figure 3. Coagulation optimisation for DOC and turbidity removal using virgin ferric sulphate (VFS); circled data point indicates dose selected for subsequent tests (24 mg/L Fe).

363 **Table 2 Mean percentage removals and residual treated water quality for recovered coagulants and virgin ferric sulfate.**

Sample	Recovered Coagulant	DOC removal	THM-FP removal	DOC (mg/L)	Specific DOC-THM-FP reactivity $\mu\text{g}/\text{mg}$	Turbidity (NTU)	Residual Fe (mg/L)
	Raw water	-	-	8.1	6.7	0.76	0.46
	Virgin ferric sulfate	76%	77%	2.0	6.5	0.6	0.2
3	Acidified ferric sludge	29%	<1%	5.8	9.4	9.2	12.0
4	Acidified, alkali purged	69%	64%	2.5	7.9	0.4	1.6
5	Alkali, acidified, UF, PAC	75%	73%	2.1	7.1	0.3	0.8
6	Alkali-purged, acidified, UF	72%	64%	2.2	8.8	0.3	0.3
7	Alkali, acidified, DD, PAC	66%	67%	2.7	6.7	0.6	0.4
8	Alkali-purged, acidified, DD	67%	64%	2.7	7.4	0.6	0.7
9	Acidified, UF, PAC	77%	74%	1.9	7.6	0.3	3.7
10	Acidified, UF	67%	58%	2.7	8.4	0.6	6.7
11	Acidified, DD, PAC	71%	65%	2.3	8.2	0.5	1.1
12	Acidified, DD	69%	67%	2.5	7.2	0.5	1.7
13	Acidified, PAC	74%	69%	2.1	7.9	0.4	0.2
14	Alkali-purged, acidified, PAC	77%	76%	1.9	6.9	0.4	0.2

Table 2 indicates that the best treatment performance is attained from PAC polishing downstream of alkali pre-treatment. The related RCs {5; 14} provided 74-77% DOC removal, comparable to VFS. For the DD RCs the amount of NaOH to maintain a coagulation pH of 4.5 was 150 times (mol:mol) the Fe concentration for a dose of 24 mg/L Fe. Aside from the additional cost this would incur at full-scale, the resulting concentration of Na in the treated water (>1.4 g/L) would contravene most drinking water regulated limits (DWI, 2010), though the use of lime would circumvent this issue. Acid recovery, already proposed to improve the chemical efficiency of the feed side of the DD CR process (Schneider, 2013), may reduce the acidity of the DD RC product and thus the requirement for NaOH to achieve the pH window for coagulation. A further option is to use sodium ions on the acidic strip side of the DD process to help drive the recovery of trivalent ferric ions without imparting additional excess acidity to the end RC solution (Tor et al., 2004).

Reductions in THM-FP followed a similar pattern to DOC (Table 2), suggesting that the RCs removed DOC of a similar reactivity. Based on previously determined DOC reactivity (Keeley et al., 2014b) and DOC residuals, coagulants reducing THM-FP by ~75% would be expected satisfy the THM limits of 80 and 100 µg/L for final treated water in the US and UK, with THM-FPs of 65-70 µg/L (USEPA, 2009; DWI, 2010, respectively). These coagulants comprised VFS (THM-FP reduction: 77%), alkali pre-treated with PAC polishing (76% {14}), UF with PAC polishing (75% {9}), and alkali pre-treated with UF and PAC (72% {5}).

The purest RCs appear able to match the THM precursor removal performance of commercial VFS and may allow their use at full-scale to be reconsidered. Furthermore,

because THM-FP is a measure of the maximum possible THM levels, under more realistic conditions with intermediate treatment (such as GAC or advanced oxidation) and less complete chlorination, the absolute THM levels would be expected to be lower. Under these circumstances the necessity and additional expensive of a two-stage RC purification approach is questionable, particularly since they provide only minor improvements to THMFP ([Table 2](#)).

Trace metals determination in the treated waters revealed concentrations of Cu, Pb, Cd and Cr to be well within the statutory potable water limits for both the US and UK ([Table S2](#); Supporting Information). The slightly elevated levels for Ni recorded in some instances (up to 31 µg/L, cf. the UK regulatory limit of 20) were attributed to acid corrosion of the brass fittings used. Mn levels were elevated above that for VFS-treated water for all RCs except alkali pre-treated ones, suggesting Mn removal downstream of coagulation would be required to meet the regulatory limit of 50 µg/L. However, this treatment stage is often required for potable water treatment since commercial ferric coagulants can contain Mn concentrations of up to 2% w/v. No work was performed to determine the phase of residual Mn in the treated waters but given the low coagulation pH of the waters used in this study it is likely that pre-oxidation would be required to destabilise Mn colloids for effective removal using filtration. Similarly, the regulatory limit of 0.2 mg/L for Fe was exceeded for all coagulants – including the virgin reagent; values ranged between 0.22 for VFS to 12 mg/L for acidified sludge. However, residual iron would also be removed by the Mn removal.

4 CONCLUSIONS

The selectivity of a number of novel CR processes has been studied with respect to the Fe and DOC concentration in the RC product, and the RC performance compared to virgin reagent. PAC was found to be more effective than powdered graphite. A PAC dose of 80 mg PAC/mg DOC consistently reduced RC DOC levels to below 15 mg/L with increased removals to <6 mg/L at RC pH values above 1, with minimal loss of Fe. When used in conjunction with alkali pre-treatment or ultrafiltration, PAC-treated RCs provided DOC and turbidity removal from raw water equal to or greater than that attained by virgin coagulant. UK and US regulatory limits for residual metals levels and THMs were sufficiently satisfied by the purest of the RCs, albeit with some requirement for downstream removal of Mn and Fe. The study outcomes suggest that a relatively simple, multistage RC purification technology can be applied to recover coagulant from potable water sludge and reused for potable water treatment.

Extraction through Donnan dialysis membranes yielded the highest selectivity for Fe and rejection of DOC in a single process, corroborating previous research. However, the current study determined that the potentially high ratio of acidity to Fe in the resulting RC demanded excessive alkaline dosing to achieve the normal coagulation pH window for DOC removal, to the detriment of both the process economics. In this respect, while a certain acidity level (pH ~2) is required for Fe solubilisation, an excessive acid content is undesirable. The economic burden of high PAC doses is also likely to be punitive.

The heterogeneous nature of organic and inorganic contaminants within raw RC dictates that Fe RC of the appropriate purity is best achieved using a series of separation processes. The efficacy of alkali extraction and UF appear to be similar in terms of DOC rejection per loss of Fe, such that the inclusion of both in the same CR purification train is of marginal value. Instead, either of these treatment method could be used upstream of a PAC polishing stage, thereby reducing the DOC load on the PAC and commensurately reducing both the required PAC dose and the loss of Fe by adsorption.

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533 **SUPPORTING INFORMATION**

534 **Table S1** Sorption data used to determine the C_s and C_w values referred to in Fig. 2

	Powdered Activated Carbon		Powdered Graphite	
Adsorbent dose in recovered coagulant (g/L)	End DOC (mg/L)	DOC removal per mass of adsorbent (mg/g)	End DOC (mg/L)	DOC removal per mass of adsorbent (mg/g)
200	12.2	0.6	17.2	0.5
100	10.3	1.1	20.3	1.0
50	12.4	2.2	30.6	1.9
20	11.8	5.6	45.6	4.0
10	12.4	11.2	73.0	5.2
1	21.9	102.8	116.4	8.3
0	124.7	0	124.7	0

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537 **Table S2 Residual metal content in water treated with recovered coagulants.**

Sample		Zn		Cu		Pb		Ni		Cd		Cr		Mn		Fe	
		Value	SD	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.	Value	S.D.
	Virgin ferric sulfate	261	41	2	1	N.D.		8	3	0.0	0.01	0.9	0.5	89	3	0.22	0.0
3	Acidified ferric sludge	235	11	3	1	N.D.		6	1	0.1	0.00	0.9	0.2	188	1	12.01	1.8
4	Acidified, alkali purged	206	38	2	0	N.D.		3	1	0.1	0.00	0.5	0.1	74	3	1.57	0.6
5	Alkali, acidified, UF, PAC	1070	10	174	5	1	0.1	24	1	0.1	0.01	1.1	0.1	82	2	0.75	0.1
6	Alkali-purged, acidified, UF	961	77	136	1	1	0.0	19	0	0.0	0.00	0.9	0.2	60	1	0.26	0.1
7	Alkali, acidified, DD, PAC	191	116	6	2	1	0.1	6	0	0.1	0.00	1.2	0.1	84	2	0.39	0.0
8	Alkali-purged, acidified, DD	131	48	6	2	N.D.		6	0	0.1	0.01	1.1	0.3	87	2	0.69	0.2
9	Acidified, UF, PAC	1360	87	215	11	N.D.		31	0	0.1	0.00	1.0	0.1	150	4	3.74	0.8
10	Acidified, UF	1407	59	240	9	0	1.1	30	1	0.1	0.00	1.4	0.1	138	4	6.72	0.5
11	Acidified, DD, PAC	293	166	4	2	N.D.		5	0	0.1	0.01	1.0	0.2	148	5	1.10	0.5
12	Acidified, DD	282	119	4	1	N.D.		5	0	0.1	0.01	0.9	0.2	152	4	1.70	1.0
13	Acidified, PAC	582	116	4	0	N.D.		15	0	0.3	0.02	0.8	0.1	582	3	0.23	0.1
14	Alkali-purged, acidified, PAC	285	126	3	1	N.D.		6	0	0.1	0.01	0.7	0.1	105	5	0.23	0.1
	Raw water	282	118	1	0	N.D.		1	0	0.0	0.00	1.2	0.0	6	1	0.46	0.1
Units		µg/L														mg/L	
DWI limit				2000		10		20		5		50		50		0.20	
USEPA limit				1300 (1000)		15				5		100		50		(0.30)	

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