1 # Coagulant recovery and reuse for drinking water treatment

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9 ## ABSTRACT

10 Coagulant recovery and reuse from waterworks sludge has the potential to significantly

11 reduce waste disposal and chemicals usage for water treatment. Drinking water regulations

12 demand purification of recovered coagulant before they can be safely reused, due to the risk

13 of disinfection by-product precursors being recovered from waterworks sludge alongside

14 coagulant metals. While several full-scale separation technologies have proven effective for

15 coagulant purification, none have matched virgin coagulant treatment performance.

16

17 This study examines the individual and successive separation performance of several novel

18 and existing ferric coagulant recovery purification technologies to attain virgin coagulant

19 purity levels. The new suggested approach of alkali extraction of dissolved organic

20 compounds (DOC) from waterworks sludge prior to acidic solubilisation of ferric coagulants

21 provided the same 14:1 selectivity ratio (874 mg/L Fe vs. 61 mg/L DOC) to the more

22 established size separation using ultrafiltration (1285 mg/L Fe vs. 91 mg/L DOC). Cation

23 exchange Donnan membranes were also examined: while highly selective (2555 mg/L Fe vs.

24 29 mg/L DOC, 88:1 selectivity), the low pH of the recovered ferric solution impaired

25 subsequent treatment performance. The application of powdered activated carbon (PAC) to

26 ultrafiltration or alkali pre-treated sludge, dosed at 80 mg/mg DOC, reduced recovered ferric

27 DOC contamination to <1 mg/L but in practice, this option would incur significant costs.

28

29 The treatment performance of the purified recovered coagulants was compared to that of

30 virgin reagent with reference to key water quality parameters. Several PAC-polished

31 recovered coagulants provided the same or improved DOC and turbidity removal as virgin

32 coagulant, as well as demonstrating the potential to reduce disinfection byproducts and

33 regulated metals to levels comparable to that attained from virgin material.

34

35 *Keywords   Coagulant recovery and reuse; dissolution; ferric; membrane separation;*

36 *DOC*

37

1   INTRODUCTION

39 Coagulation-flocculation is a key process in potable water treatment. While effective, its

40 application accounts for ~5% of operational expenditure (OPEX) at water treatment works

41 (Niquette et al., 2004). This is attributable to the combined costs of coagulant and pH

42 adjustment chemicals, as well as that of disposal of the resulting sludge or "water treatment

43 residuals" (WTR). Within the UK water industry, annual coagulant consumption exceeds

44 0.33m tonnes (Henderson et al., 2009) and WTR production exceeds 0.18 million (m) tonnes

45 (Pan et al., 2004), costing around £40m and £8m respectively at 2015 prices. The issue is

46 reflected globally: annual waterworks sludge production from alum dosing alone exceeds

47 730m tonnes in the US (Prakash and Sengupta, 2003) and in Japan, drinking water treatment

48 produces 0.3m tonnes of dry solids (Fujiwara, 2011).

49

50   Coagulant recovery can potentially reduce these costs by regenerating and reusing the

51   coagulant metals in the WTRs. This is usually achieved through acidification, commonly to

52   pH 2 (King et al., 1975; Parsons and Daniels, 1999; Keeley et al., 2014b). However, organic

53   compounds within the sludge have similar pH solubility behaviour (Prakash and Sengupta,

54   2003), contaminating the acidified recovered coagulant with suspended and dissolved organic

55   carbon (DOC). An early full-scale study of non-selective ferric recovery reported no

56   significant impact on treated water quality but the recovered ferric coagulant free acidity

57   increased lime demand and shortened filter run times (Saunder and Roeder, 1991).

58

59   When dosed into the potable treatment stream, elevated levels of residual DOC resulted at the

60   final chlorination stage yielding a commensurate increase in halogenated disinfection

61   byproducts (DBPs) in the final treated water (World Health Organization, 2000). Public

62   health protection and abidance with water quality regulations (USEPA, 2009; DWI, 2010)

63   demand the recovered coagulant (RC) to be appropriately purified to remove DOC and trace

64   metal contaminants.

65

66   Conventional, pressure-filtration membranes (Keeley et al., 2014a,b), adsorbents (Lindsey

67   and Tongkasame, 1975), chemical precipitation (Ulmert and Sarner, 2005), and ion exchange

68   (Prakash and Sengupta, 2003) have been tested for RC purification, but have failed to

69   combine adequate removal of organic contaminants with competitive process economics.

70   Reuse of impure RCs for phosphorus removal in wastewater treatment is a promising

71   circumvention to this problem (Babatunde and Zhao, 2007; Xu et al., 2009) but is less

72 ambitious than reuse in potable treatment which approaches the target of net chemical-free

73 treatment stipulated by some water-related research organisations (UKWIR, 2007).

74

75 Published research into coagulant reuse for potable water applications appears to have been

76 limited for the last decade. This study aims to provide a benchmark for the purity and

77 treatment performance of recovered ferric coagulant and to establish which RC

78 characteristics most affect treatment efficacy. The effect of augmenting existing RC

79 purification technologies (ultrafiltration, UF, and Donnan dialysis, DD) with pre- and post-

80 treatment stages was also studied by way of improving RC quality, particularly in terms of

81 minimising DOC contamination for which a lower level of 3.5 mg/L has been identified from

82 previous CR studies (Prakash and Sengupta, 2003). Of more practical importance is the

83 impact of this organic contamination on DBP formation, which pertains to the residual

84 organic compound levels from both the raw water and dosed RC and their reactivity with

85 chlorine.

86

87 2   METHODOLOGY

88 2.1   Coagulant recovery and purification

89 Dewatered WTR cake, measured as 14% dry solids (DS) containing ~25% Fe, was collected

90 from a 150,000 m^3/d capacity water treatment works treating upland water with ferric sulfate

91 coagulant (13% as Fe) at a coagulation pH range of 4.7-5.1 (Derbyshire, UK). The raw water

92 had a pH of 6.26 with a zeta potential of -13.9mV. The character of the NOM within this raw

93 water has been determined to be predominantly hydrophobic (Keeley et al., 2014b). Slurries

94 containing 1 kg of sludge cake in 10L of deionised (DI) water were mixed for 24 h {1}

95   before subsequent coagulant recovery extraction using acid {3} or alkali {4} (Fig. 1; numbers

96   in parenthesis refer to sampling points shown in the figure).

97

98   Alkali pre-treatment {2} comprised adjustment of the WTR slurry to pH 12 with reagent-

99   grade NaOH pellets, and mixing for 24 h, with periodic addition of NaOH to maintain the pH

100   at 12, prior to settlement. The solids fraction was retained on a 1.2μm pore size glass fibre

101   filter and washed with 1 L of DI water prior to digestion in 1 L of 5M H_2SO_4 for a further 24

102   h and dilution to 10 L with DI water. Direct solubilisation with acid was achieved by

103   adjusting the WTR slurry to pH 2 with 18M H_2SO_4 before mixing for 24 h {4}.

104

105   Both the alkali pre-treated and direct acid extractions were purified by pressure filtration {6;

106   10} or cation exchange extraction {8; 12}. Pressure filtration through a 2 kDa-rated

107   polyethersulfone membrane (Sterlitech Corporation, Kent, WA, USA) was conducted using a

108   flat-sheet crossflow cell of 0.007 m^2 membrane area (Keeley et al., 2014b). The membrane

109   cell was also adapted for use with a Nafion 115 cation exchange membrane, for which the

110   feed-side recirculated 2 L of acidified sludge and the strip-side 1 L of 1 M H_2SO_4. Membrane

111   specific surface area, time, feed:strip volumes and acid strength were selected according to a

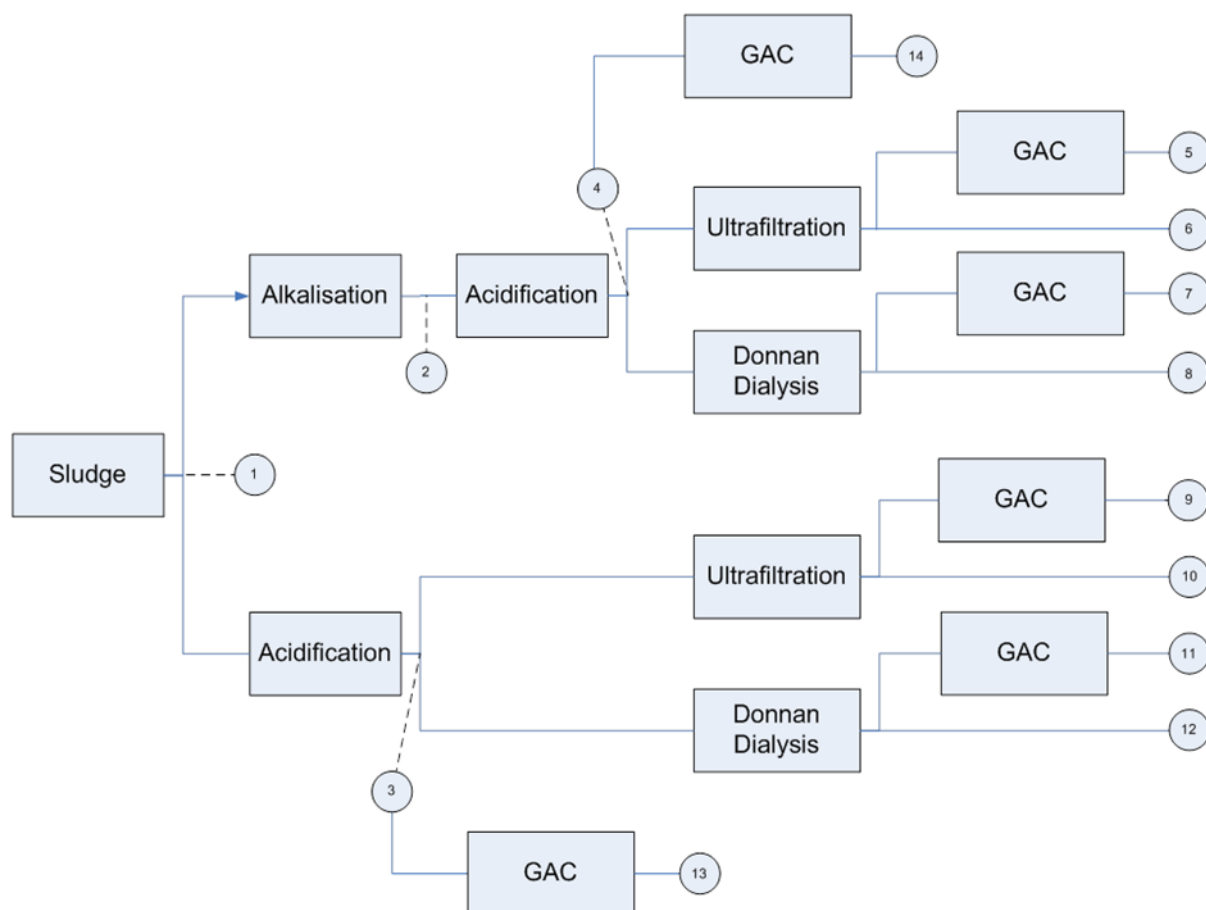112   previous study using similar materials (Prakash and Sengupta, 2003).

113

114
115 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

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

117

118 A post-treatment adsorption stage was applied to all RCs to further reduce DOC

119 concentrations {5; 7; 9; 11; 13; 14}. In addition to powdered activated carbon (PAC, Norit

120 SA Super 94002-8), powdered graphite (PG, Fisher, UK) was also examined: previous

121 studies had suggested PG to have a high organic acid adsorption capacity at pH values below

122 3 (Xiao and Pignatello, 2014). Adsorption isotherms were produced using a batch method

123 whereby 0-200 g/L of adsorbent (pre-wetted for 24 hours in 15 mL 0.005 M H_2SO_4) were

124 mixed for 48 hours with 25 mL of RC at pH 2 (UF permeate for the acidified RC sample

125 {10}). The aqueous phase was filtered through 0.45μm nylon filters (Fisher, UK) before

126 DOC analysis using a Shimadzu TOC-V analyser and soluble Fe determination using a

127 Perkin Elmer atomic absorption spectrometer (AAS). Other metals were extracted in nitric

128 acid and analysed using inductively coupled plasma mass spectroscopy. The resulting

129 isotherms were used to select the optimum adsorbent and dose (relative to RC DOC content)

130 which were then applied to RC from all preceding stages of purification {5; 7; 9; 11; 13; 14}.

131 RCs were then characterised in terms of pH, Fe and DOC content.

132

2.2   *Recovered coagulant treatment performance*

134 Jar tests were used to compare performance of RCs and virgin coagulant in terms of water

135 treatment. Raw water and virgin ferric sulfate coagulant (VFS; measured as 20% Fe) were

136 sampled from the same site as the WTRs. Jar tests (using a Phipps & Bird PB-700 jar tester)

137 were conducted at room temperature, based on an existing method (Sharp et al., 2006) with a

138 1.5min rapid mix at 200 rpm, a 15min flocculation mix at 50 rpm and a 20min settlement

139 stage. Treated water was analysed for DOC and turbidity, as well as zeta potential using a

140 Malvern Zetasizer Nano ZS.

141

142 A series of jar tests with VFS were used to determine the optimum coagulant Fe dose

143 (between 4 and 48 mg/L as Fe) and pH (between 3.5 and 5.5; corrected using dilute HCl and

144 NaOH) for DOC and turbidity removal. This dose and pH were then used for further jar tests

145 with RCs. Analyses comprised DOC, UV absorption at 254 nm (used to calculate specific

146 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 H_2SO_4 {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

170   in solution at pH 12 (King et al., 1976), loss of colloidal iron hydroxide and Fe-DOC through

171   the retaining glass-fibre filter may take place.

172

173   **Ultrafiltration (UF).** {6; 10} Size exclusion based purification of RCs has been thoroughly

174   investigated in previous studies (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005;

175   Keeley et al., 2014a,b). These studies showed that within a range of <1-20 kDa MWCO UF

176   membranes, a 2 kDa MWCO gave the optimum balance of DOC rejection and trivalent metal

177   recovery. However, this MWCO nonetheless allowed significant DOC carryover, at 91 mg/L

178   DOC with 1285 mg/L Fe {10}, from a feed containing 143 and 1287 mg/L DOC and Fe

179   respectively {3} (Table 1). A similar Fe:DOC selectivity ratio before (12.9) {3} and after UF

180   (14.1) {10} would suggest a similarly low level of selectivity by size exclusion as with alkali

181   treatment {4}. Previous studies have highlighted the strength of Fe-DOC interactions as a

182   contributing factor for poor selectivity for Fe by UF purification, relative to the more weakly

183   interacting Al (Keeley et al., 2014a,b).

184

185   **Donnan dialysis (DD).** {8; 12} This method uses a cation exchange membrane to extract

186   coagulant metal ions from the acidified sludge, rather than filtering through a conventional

187   membrane. Since DD is a diffusive process and does not employ a transmembrane pressure, it

188   avoids the membrane fouling and energy usage of pressure-filtration and their associated

189   costs (Prakash and Sengupta, 2003). DD has additionally been reported to be the most

190   selective method for separating trivalent coagulant metals and DOC (Schneider, 2013) with

191   consistent Fe or Al recovery concentrations >5000 mg/L at yields of 70-75% with <5 mg/L

192   DOC contamination (Prakash and Sengupta, 2003). Similar performance was attained in this

193   study, with extraction from an acidified sludge feed yielding 82% Fe recovery at a

194 concentration of 2555 mg/L, with 29 mg/L DOC {12} (Table 1). The comparatively high

195 yield and more dilute recovery solution are due to a lower volume ratio of feed sludge to

196 recovery acid (2:1) than the 4:1 ratio used by Prakash and Sengupta (2003); the relative

197 volumes affect the distribution of ions across the membrane at the point of Donnan

198 equilibrium.

199

200 **Table 1: Fe and DOC levels, and Fe/DOC ratios in recovered coagulant sludge product (sample**

201 **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

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

203

204 DD of the alkali pre-treated sludge {8} was less effective, with the same volume of sludge

205 yielding 73% Fe at 1072 mg/L but with reduced DOC carryover of 4 mg/L (Table 1). The

206 lower yield and concentration was due to a feed Fe concentration {4} less than half that of the

207 single-step acidified feed {3}, due to the permeation of colloidal and solubilised Fe through

208 the glass-fibre filter in the alkali pre-treatment process. Further reductions in process

209 efficiency may have also been caused by the elevated levels of sodium in the RC, following

210 the preceding alkaline organics extraction step. These sodium ions are also extracted through

211 the cation membrane via the same ion exchange mechanism, competing with Fe and

212 establishing Donnan equilibrium at a lower net transfer of Fe ions (Pyrzynska, 2006).

213

214 **Adsorption.** Preliminary tests compared the adsorption of DOC by PG and PAC from an RC

215 sample containing 125 mg/L DOC and 1933 mg/L Fe. Adsorption isotherms at pH 2 showed

216 DOC removals of 90 and 86% by PAC and PG respectively at the highest adsorbent dose of

217 200 g/L. At lower doses PAC attained DOC removals 1.5-10 times more than those of PG

218 (Fig. 2). This corroborates previous results of applying granular activated carbon for DOC

219 removal from recovered alum sludge (Cornwell et al., 1981). The relative gradients of the

220 isotherm plot (Fig. 2) indicate PAC to have a greater DOC adsorption capacity than PG.

221

222 A PAC dose of 10 g/L was selected. Higher doses yielded marginal removal improvements: a

223 100 g/L dose reduced the DOC residual by only 2 mg/L less than the 10 g/L PAC dose

224 (yielding a residual DOC of 10.3 mg/L rather than 12.4 mg/L; both from a feed level of 125

225 mg/L). However, the 100 g/L PAC reduced the Fe yield by 330 mg/L compared with the 10

226 g/L PAC dose. At the dose of 10 g/L PAC removed 6 times more DOC than PG.

227 Accordingly, PG was excluded from further testing. Both adsorbents favoured DOC

228 adsorption over Fe adsorption, with only 9% and 15% reductions from the initial soluble Fe

229 concentration with 10 g/L of PAC and PG respectively. Evidence suggested that the small

230 improvement (10-15%) in Fe concentration at very high adsorbent doses (200 g/L) was

231 primarily by water uptake by the PAC, rather than organic carbon removal. Further details are

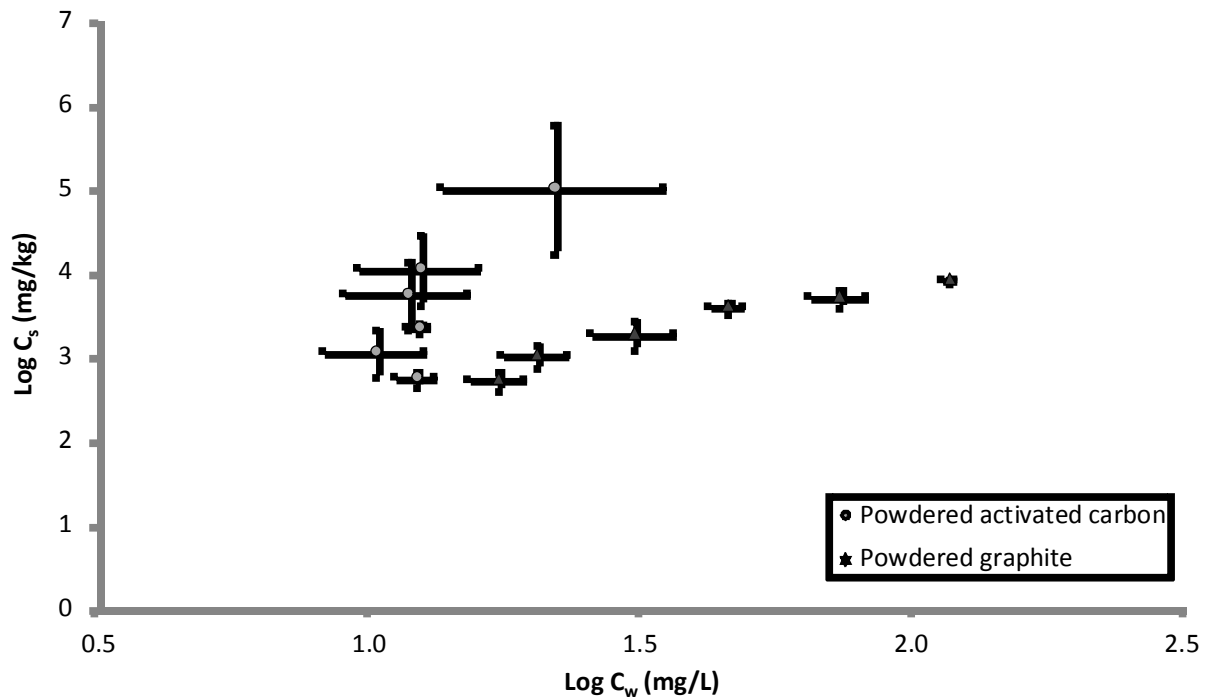232 shown in Table S1 in Supporting Information.

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

248

The residual DOC concentrations for PAC-treated RCs {5; 7; 9; 11; 13; 14} were in the range

of 1-13 mg/L, comparable to the lowest reported DOC values in RCs of 3.5 mg/L (Prakash

and Sengupta, 2003) and 17 mg/L (Prakash et al., 2004). The lowest DOC concentrations for

PAC-treated RCs were from alkaline pre-treatment {5; 7; 14}, both with and without UF or

DD treatment. Alkaline pre-treatment thus removes DOC of different character to PAC, or

else chemically alters the residual DOC through hydrolysis and saponification (Randtke and

Jepsen, 1981; Schafer, 2001), such that enhanced overall DOC removal is attained from their

combination.

257

Relative separation performance of individual processes. All of the individual processes

were capable of recovering >70% of the feed Fe, other than alkali pre-treatment {4} and

direct PAC treatment of acidified sludge {13} which respectively recovered only 57% and

35% of the Fe. These yields do not take into account the yield from acidifying the base

sludge, which never exceeded 53% in this experiment. More importantly, in terms of their

impact on treated water quality, there was significant DOC rejection from each stage. UF {6;

10} gave the least effective DOC exclusion of 31-36% due to the comparable molecular

weight distributions of DOC compounds and Fe colloids. PAC treatment of DD-treated RCs

{8; 12} gave almost as poor DOC removals of 50-55%, due to low initial DOC levels (<29

mg/L) and the extensive electropositive repulsion between the DOC and PAC adsorption

sites at the low pH of the recovered DD solutions (Xiao and Pignatello, 2014). Alkali pre-

treatment gave similarly low levels of rejection, with incomplete alkali solubilisation of

organic compounds in the sludge {3} leading to carry-over into the recovered solid phase and

subsequent organic compound solubilisation upon acidification {4}. Far better DOC rejection

272 was provided by DD (80-93% {8; 12}) and PAC treatment at pH values of 2 and higher

273 initial DOC loadings (90-98% {5; 9; 13; 14}). These data indicate that charge or adsorptive

274 DOC removal is important in minimising DOC levels in the RC final product.

275

276 While individual CR process selectivity is an important consideration, the selectivity of

277 multiple processes in series has also been examined. A multistage RC purification train

278 would be a likely requirement to ensure reliable delivery of RCs with sufficient quality for

279 potable treatment by diversifying the modes and extent of DOC removal (Ulmert and Sarner,

280 2005; Cornwell et al., 1981). With the obvious practical constraints of a multistage recovery

281 process, more pragmatic water quality regulations may be prerequisite for full-scale potable

282 coagulant recycling.

283

3.2   Coagulant recovery option assessment

285 The combined performance of a number of CR treatment trains was evaluated in terms of RC

286 Fe concentration, DOC carryover and pH, as previously proposed by Cornwell et al (1981),

287 as well as Fe/DOC ratio (Table 1). These measures were then compared to coagulant

288 treatment performance and benchmarked against virgin ferric coagulant.

289

290 **Fe concentration.** For fully acidified and solubilised ferric RCs, soluble Fe concentration

291 could be indicative of RC ability to destabilise impurities, via surface charge neutralisation,

292 when dosed into raw water. By this measure, DD was the most effective treatment option:

293 DD without alkali pre-treatment {12} and DD followed by PAC polishing {11} gave the

294 highest Fe concentrations of 2555 and 2536 mg/L, respectively, although the incremental

14

295   reduction in DOC concentration was minor. The next highest was the unpurified sludge acid

296   extract with 1847 mg/L {3}. These results highlight the inevitable losses of Fe for alkaline

297   pre-treatment {4} or, to a lesser extent, UF {10}. The concentrations of Fe recovered using

298   UF {10} and DD {12} are comparable with previous studies using similar approaches

299   reporting RCs of 3500 mg/L Al with UF (Ulmert and Sarner, 2005) and 5400 mg/L Fe with

300   DD (Prakash and Sengupta, 2003), with feed concentration, pH and volume being key

301   determinants of RC concentration (King et al., 1975). More concentrated RCs (up to 30,000

302   mg/L Al) have been achieved through RC extraction from an ion exchange resin (Petruzzelli,

303   2000) or nanofiltration dewatering and precipitation of the RC salts (Ulmert and Sarner,

304   2005). These were not attempted in this study since the cost-benefit of producing RCs at

305   these high concentrations, whilst reducing transport volumes and allowing centralised

306   processing, is questionable.

307

308   **DOC concentration.** Since the principal concern of using RC in potable water treatment is

309   elevated DBP (disinfection by-product) formation from DOC, residual DOC provides a

310   useful indication of CR efficacy. Processes using PAC and alkali pre-treatment gave the

311   lowest DOC concentrations, viz: alkali pre-treatment coupled with PAC post-treatment (1

312   mg/L {14}); alkali pre-treatment with UF or DD and PAC post-treatment (2 mg/L {5; 7});

313   and non-pre-treated UF with PAC post-treatment (3 mg/L {3}). This suggests that PAC

314   treatment is integral to reaching the highest purity of RC and corroborates previous assertions

315   that an activated carbon polishing stage is required, although in these earlier studies the stage

316   was used to remove a synthetic organic extractant which has different characteristics to NOM

317   (Cornwell et al., 1981). While PAC provides effective polishing, it nonetheless demands

318   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).

16

342   The relatively high dose was employed to ensure that coagulant performance was affected

343   only by coagulant quality, rather than external factors such as minor variations in raw water

344   character. This dose and pH combination was used for all subsequent jar tests using RCs.

345

346   RC treatment performance with PAC post-treatment, in terms of DOC and THM-FP removal

347   and treated water turbidity and Fe residual, revealed no significant trend with either RC Fe

348   dose, DOC concentration or Fe/DOC ratio. For alkali-pretreated coagulants % DOC removal

349   from the raw water was in the region of 66-77% {5; 6; 7; 8; 14} at Fe doses of 800-2600

350   mg/L with associated DOC concentrations of up to 91 mg/L and Fe/DOC ratios between 14

351   and 870 (Table 2). This compares with a value of 76% recorded for VFS dosed at a

352   concentration of 24 mg/L as Fe. The %THM-FP removal was within 18% of that determined

353   for VFS for all RCs, whilst residual turbidity was comparable (Table 2). In some cases {5; 9;

354   14} the %THM-FP removal with RCs was equal to the removal achieved with VFS. Residual

355   Fe concentrations were more variable, with generally higher concentrations than with VFS

356   but in some cases, including for the best DOC-removing RCs, residual Fe was comparable to

357   those for VFS.

358

Residual DOC and Turbidity of Raw Water Following Treatment With Virgin Ferric Sulfate
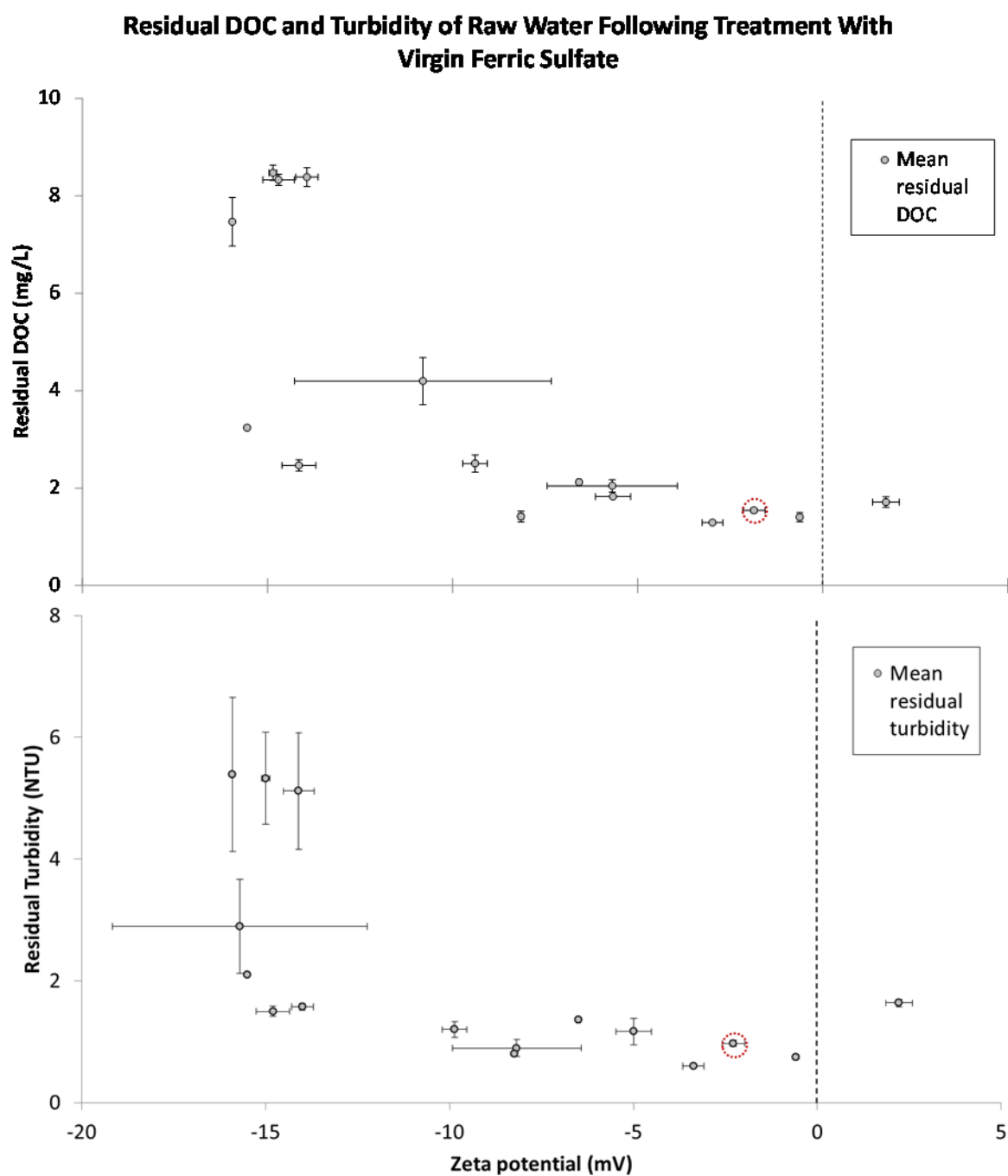
359

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

362

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 μg/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

364   Table 2 indicates that the best treatment performance is attained from PAC polishing

365   downstream of alkali pre-treatment. The related RCs {5; 14} provided 74-77% DOC

366   removal, comparable to VFS. For the DD RCs the amount of NaOH to maintain a

367   coagulation pH of 4.5 was 150 times (mol:mol) the Fe concentration for a dose of 24 mg/L

368   Fe. Aside from the additional cost this would incur at full-scale, the resulting concentration of

369   Na in the treated water (>1.4 g/L) would contravene most drinking water regulated limits

370   (DWI, 2010), though the use of lime would circumvent this issue. Acid recovery, already

371   proposed to improve the chemical efficiency of the feed side of the DD CR process

372   (Schneider, 2013), may reduce the acidity of the DD RC product and thus the requirement for

373   NaOH to achieve the pH window for coagulation. A further option is to use sodium ions on

374   the acidic strip side of the DD process to help drive the recovery of trivalent ferric ions

375   without imparting additional excess acidity to the end RC solution (Tor et al., 2004).

376

377   Reductions in THM-FP followed a similar pattern to DOC (Table 2), suggesting that the RCs

378   removed DOC of a similar reactivity. Based on previously determined DOC reactivity

379   (Keeley et al., 2014b) and DOC residuals, coagulants reducing THM-FP by ~75% would be

380   expected satisfy the THM limits of 80 and 100 µg/L for final treated water in the US and UK,

381   with THM-FPs of 65-70 µg/L (USEPA, 2009; DWI, 2010, respectively). These coagulants

382   comprised VFS (THM-FP reduction: 77%), alkali pre-treated with PAC polishing (76%

383   {14}), UF with PAC polishing (75% {9}), and alkali pre-treated with UF and PAC (72%

384   {5}).

385

386   The purest RCs appear able to match the THM precursor removal performance of

387   commercial VFS and may allow their use at full-scale to be reconsidered. Furthermore,

388   because THM-FP is a measure of the maximum possible THM levels, under more realistic

389   conditions with intermediate treatment (such as GAC or advanced oxidation) and less

390   complete chlorination, the absolute THM levels would be expected to be lower. Under these

391   circumstances the necessity and additional expensive of a two-stage RC purification approach

392   is questionable, particularly since they provide only minor improvements to THMFP (Table

393   2).

394

395   Trace metals determination in the treated waters revealed concentrations of Cu, Pb, Cd and

396   Cr to be well within the statutory potable water limits for both the US and UK (Table S2;

397   Supporting Information). The slightly elevated levels for Ni recorded in some instances (up to

398   31 µg/L, cf. the UK regulatory limit of 20) were attributed to acid corrosion of the brass

399   fittings used. Mn levels were elevated above that for VFS-treated water for all RCs except

400   alkali pre-treated ones, suggesting Mn removal downstream of coagulation would be required

401   to meet the regulatory limit of 50 µg/L. However, this treatment stage is often required for

402   potable water treatment since commercial ferric coagulants can contain Mn concentrations of

403   up to 2% w/v. No work was performed to determine the phase of residual Mn in the treated

404   waters but given the low coagulation pH of the waters used in this study it is likely that pre-

405   oxidation would be required to destabilise Mn colloids for effective removal using filtration.

406   Similarly, the regulatory limit of 0.2 mg/L for Fe was exceeded for all coagulants – including

407   the virgin reagent; values ranged between 0.22 for VFS to 12 mg/L for acidified sludge.

408   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.

431 The heterogeneous nature of organic and inorganic contaminants within raw RC dictates that

432 Fe RC of the appropriate purity is best achieved using a series of separation processes. The

433 efficacy of alkali extraction and UF appear to be similar in terms of DOC rejection per loss of

434 Fe, such that the inclusion of both in the same CR purification train is of marginal value.

435 Instead, either of these treatment method could be used upstream of a PAC polishing stage,

436 thereby reducing the DOC load on the PAC and commensurately reducing both the required

437 PAC dose and the loss of Fe by adsorption.

438

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442

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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**

Adsorbent dose in recovered coagulant (g/L)	Powdered Activated Carbon		Powdered Graphite	
	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

535

536

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

Sample		Zn Value	SD	Cu Value	S.D.	Pb Value	S.D.	Ni Value	S.D.	Cd Value	S.D.	Cr Value	S.D.	Mn Value	S.D.	Fe 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)	

538

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