

CRANFIELD UNIVERSITY

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Coagulant Recovery from Waterworks Sludge

STREAM Industrial Doctorate Centre
School of Energy, Environment and Agrifood

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Supervisors: Dr. Peter Jarvis and Prof. Simon Judd

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ABSTRACT

Coagulation is a ubiquitous process in the treatment of raw surface water for eventual potable use. Despite its capabilities, the sheer scale of its use is manifested in the volumes of chemicals it demands and waste sludge it produces. Recovering and reusing the chemical activity of the coagulant sludge in water treatment is a logical solution but this practice has been restricted by the presence of contaminants within the sludge. This thesis has investigated methods that can separate the coagulant metals from these primarily natural organic contaminants, with an aim of producing a sufficiently pure coagulant for effective treatment performance when reused.

A process of ultrafiltration of the impure regenerated coagulant followed by a powdered activated carbon polishing stage compared favourably to a number of other separation processes and was found to remove the most dissolved organic compounds. When the purified coagulant was used to treat raw water, it provided better turbidity removal than commercial coagulant and matched its removal of trihalomethane precursors, making the process suitable for consideration at full-scale. Analysis of the whole life cost suggested that such performance could be reproduced at full-scale within a 25 year payback period.

The reuse of even purified recovered coagulants in drinking water treatment still carries risks which may deter its implementation. Therefore the efficacy of recovered coagulants in the role of phosphorus removal from wastewater was also investigated. This showed that both acidified and unacidified waterworks sludges, with sufficient contact time, could remove similar levels of phosphorus as fresh coagulants, at approximately half the whole life cost.

Keywords:

Water treatment residuals, ultrafiltration, Donnan dialysis, organo-metallic separation, phosphorus removal.

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ABBREVIATIONS AND NOTATIONS

AAS	Atomic adsorption spectroscopy
AD	Anaerobic digestion
APHA	American Public Health Association
BOD ₅	Biological oxygen demand (5 day)
BV	Bed volume
CAPEX	Capital expenditure
COD	Chemical oxygen demand
CR	Coagulant recovery
DBP	Disinfection by-product
DD	Donnan dialysis
DOC	Dissolved organic compounds
DS	Dissolved solids
DWI	Drinking Water Inspectorate
ED	Electrodialysis
EU	European Union
FFS	Fresh ferric sulfate
GAC	Granular activated carbon
GBP	Great British pounds
HPI	Hydrophilic organic fraction
HPO	Hydrophobic organic fraction
ICP	Inductively coupled plasma (mass spectroscopy)
IERAL	Ion exchange recovery of aluminium
LIE	Liquid ion exchange
M	Generic metal
MBR	Membrane bio-reactor
MLD	Mega litres per day
MW	Molecular weight
MWCO	Molecular weight cut-off

NF	Nanofiltration
NOM	Natural organic matter
NSF	National Sanitation Foundation
OPEX	Operating expenditure
PAC	Powdered activated carbon
PACl	Polyaluminium chloride
PG	Powdered graphite
PRB	Permeable reactive barrier
P _{sol}	Soluble phosphorus
PTFE	Polytetrafluoroethylene
RC	Recovered coagulant
RPM	Revolutions per minute
SD	Standard deviation
SS	Suspended solids
THM	Trihalomethane
THM-FP	Trihalomethane formation potential
TMP	Transmembrane pressure
TOC	Total organic carbon
TP	Total phosphorus
TPI	Transphilic organic fraction
TS	Total solids
UF	Ultrafiltration
UK	United Kingdom
UKWIR	United Kingdom Water Industry Research
US	United States
USD	United States dollars
USEPA	United States Environmental Protection Agency
VS	Volatile solids
WHO	World Health Organization

WLC	Whole life cost
WTR	Water treatment residuals
WTW	Water treatment works
WW	Wastewater
WWTW	Wastewater treatment works

CHAPTER 1

INTRODUCTION

1 INTRODUCTION

1.1 PROJECT BACKGROUND

Coagulation is a fundamental process for the treatment of surface water in drinking water production. The addition of ferric or aluminium salts neutralises the surface charge of raw water contaminants. These destabilised particles aggregate to form larger floc particles which can then settle more rapidly and be more effectively removed by downstream processes such as gravity filtration.

While coagulation remains a low-cost method for removing the bulk of raw water contaminants, its scale of operation accounts for proportionally large volumes of coagulant demand and waste sludge production which represent ~5% of water production and distribution operational costs (Niquette et al., 2004). Each year, the UK alone consumes > 325,000 tonnes of coagulants (Henderson et al., 2009) and produces >182,000 tonnes of sludge as dry solids (Pan et al., 2004). The annual costs of these volumes exceed £41m and £8.1m, respectively (UKWIR, 1999; adjusted for 2014 prices) and are dependent on external market forces and government policy (Henderson et al., 2009).

Tightening of consented limits on total phosphorus from 2 mg/L to <1 mg/L (Ofwat, 2005) is projected to increase demand for coagulants as they offer a simple alternative to biological P removal (Blackall et al., 2002). This is compounded by the requirement of 2-3 times higher coagulant doses to remove P to these emerging lower consented concentrations (Ofwat, 2005).

Coagulant recovery (CR) represents an opportunity to alleviate these problems by closing the loop between coagulant demand and the resulting waste sludge production. This fits into a more general goal of achieving (net) chemical-free water treatment (UKWIR, 1999), by applying the concepts of green chemistry (Anastas and Warner, 1998), to improve the sustainability of current best practices used in the industry.

The concept itself is far from novel (Jewell, 1903), with all recorded variants of the process incorporating solubilisation and regeneration of the depleted coagulant metal hydroxides, commonly using sulfuric acid. The raw recovered

coagulant (RC) product has demonstrated treatment potential when dosed in potable and wastewater (WW). However, its performance has usually been shown to be inferior to fresh coagulants, due to the presence of sludge contaminants that were solubilised alongside the RC (Petruzzelli et al., 2000). Early incarnations merely removed gross solids from the acidified sludge using depth filtration (Fulton, 1973) but at its peak CR was adopted at 15 plants in Japan (White, 1984), as well as six pilot and full-scale trials at sites in the US and the UK (Webster, 1966; Saunders and Roeder, 1991). However, the 1970s and 1980s saw the emergence of disinfection byproducts (DBPs) which alongside inorganic contaminant accumulation (White, 1984) saw the withdrawal of full-scale CR.

A particular concern and focus of this thesis is the impact of dissolved organic compounds (DOC) within the RCs and their potential to elevate the formation of DBPs upon treatment with chlorine or chloramine (Prakash and Sengupta 2003). The resulting halogenated organic compounds include but are not limited to: trihalomethane, haloacetic acids and nitrosamines (Richardson et al., 2007). These are known to be harmful to humans but due to the greater pathogenic risk if chlorination is reduced (WHO, 2007), minimisation of organic precursor compounds has been the primary method of controlling DBP formation: an approach that the recycling of impure RCs does not align with. The capability to remove organic, as well as inorganic, contaminants from RCs to match or better commercial coagulants' DOC removal performance is the key challenge for CR. For full-scale implementation to be viable, this must be achieved at a cost that can compete with commercial coagulant prices, which have rarely exceeded £100/tonne.

Various separation technologies have been studied previously, in an attempt to produce as pure an RC as possible and to treat drinking water to the same standard as fresh coagulants (Bishop et al., 1987; Prakash and Sengupta, 2003; Ulmert and Sarner, 2005). However, none of these technologies have been able to fulfil this aim on an economically competitive basis and have left

CR at the conceptual stage in the context of modern drinking water quality regulations.

1.2 RESEARCH AIM AND OBJECTIVES

The work presented in this thesis had the specific aim of developing the understanding of CR and purification, to provide an economically and technically viable method of recycling coagulants and minimising unsustainable chemical usage in water treatment.

The project was funded by the Engineering and Physical Sciences Research Council (EPSRC), Severn Trent Water, Anglian Water, Scottish Water and Northumbrian Water. The original concept of the work considered the implementation of ion exchange membrane processes: Donnan Dialysis and electrodialysis, for the purification of RC, subject to validation of preceding technical and economic investigations. These technologies were selected because ion-exchange processes had been reported to be highly selective for trivalent coagulant metals, Al and Fe, whilst rejecting the vast majority of DOC (Petruzzelli et al., 2000; Prakash and Sengupta, 2003). Their reliance on a diffusive transport mechanism also minimized the potential for membrane fouling.

As subsequent chapters will detail, the economics of implementing these technologies compared unfavourably to fresh coagulant dosing. Therefore, the project focussed on examining purification performance using the lower cost process of ultrafiltration (UF). A contingency strategy for the reuse of RCs in WW treatment was also investigated, as immediate regulatory approval of a potable CR system was deemed unlikely. As such, the overarching project objectives were to:

1. Compare the economic cost benefit and published performance data of CR processes to fresh coagulants and identify suitable processes for further investigation

2. Investigate the impact of RCs of varying purity on drinking water quality and compare their treatment performance to fresh coagulants
3. Identify the optimum mechanism to separate organic compound contaminants from trivalent coagulant metals
4. Compare and contrast the mechanistic pathways recovered and fresh coagulants use to remove contaminants from raw water
5. Determine the parameters that most affect RC performance
6. Develop and design a method to reduce coagulant demand and waste sludge volumes under favourable economic conditions, within the constraints of water quality regulations
7. Identify future risks and opportunities in coagulant usage and sludge disposal strategies.

1.3 REQUIREMENTS OF AN ENGINEERING DOCTORATE

An EngD project bears many similarities to a PhD project but has an additional taught element and a focus on delivering industrially relevant research outcomes, alongside advances in scientific novelty and understanding. This project has been conducted in close collaboration with the sponsoring water companies, with access to their internal resources ensuring that the technical and economic findings in this thesis can be replicated at full-scale and can be beneficial to their business models. These practical considerations are embedded throughout this thesis but are discussed explicitly in Chapter 7. The contribution to scientific understanding has been enhanced through dissemination and discussion of the project's key findings in various academic fora: through oral (at the American Water Works Association's Water Quality and Technology Conferences in 2011, 2012 and 2014; the 4th Developments in Water Treatment and Supply Conference in 2012; the Resource Recovery in the Water Industry Conference in 2014) and poster (at the Institute of Water's 2013 annual conference, and at the International Water Association's World Water Congress and Exhibition in 2014) presentations at international conferences; and publication in peer-reviewed journals (listed below).

1.4 THESIS STRUCTURE

This thesis is presented as a series of chapters, formatted in the style of journal papers. All Chapters were written by the first author, James Keeley and edited by Dr Peter Jarvis, Professor Simon J. Judd and Andrea D. Smith, where indicated. All laboratory work was conducted by James Keeley, with the exception of acrylamide analyses (Chapter 4) which were conducted by Severn Trent Water's Quality Assurance laboratories and inductively coupled plasma mass spectrometry analyses (Chapters 4 and 6), for which pre-prepared samples were run by Richard Andrews at Cranfield University.

The narrative between the thesis chapters is a linear investigation of coagulant recovery in potable treatment, with a single digression to examine the potential use of RCs in WW treatment (Figure 1).

The thesis commences with a critical review of existing CR technologies and management strategies for waterworks sludge (Chapter 2, published in *Critical Reviews in Environmental Science and Technology* (2014) 44, 2675-2719: *Keeley, J., Jarvis, P., Judd, S.J., Coagulant recovery from water treatment residuals: a review of applicable technologies*).

This review identified a selection of appropriate technologies for purifying RCs for reuse in drinking water treatment and contrasted them with other potential sludge reuse strategies. Before the performance of these technologies was investigated experimentally, a comparison of their operating costs was made (Chapter 3, published in *Desalination* (2012) 287, 132-137: *Keeley, J., Jarvis, P., Judd, S.J., An economic assessment of coagulant recovery from water treatment residuals*).

Analysis of process economics indicated that UF was the only CR technology that had operating costs that were competitive with commercial coagulants. Therefore, the first stage of experimental work investigated the optimum UF pore size and sludge concentration for metal recovery and organic compound rejection, and the impact RCs had on water treatment quality (Chapter 4, published in *Separation and Purification Technology* (2014) 131, 69-78: *Keeley,*

J., Smith, A.D., Jarvis, P., Judd, S.J., Reuse of recovered coagulants in water treatment: an investigation on the effect coagulant purity has on treatment performance).

While UF was partially successful in its designated role, further development or alternative reuse strategies were required to deliver the benefits of CR without risking failure of potable water quality. Reuse of waterworks sludge and its RC derivatives was suggested by the literature review to be an area of relatively unrealised potential. An analysis of the P removal performance and economic cost benefit of dosing waterworks sludge to primary WW supported this suggestion (Chapter 5, submitted for publication in Water Research, *Keeley, J., Smith, A.D., Jarvis, P., Judd, S.J., Performance and economic potential of the reuse of waterworks ferric sludge for phosphorus removal from wastewater).*

Further work was undertaken to maximise the purity of RCs by augmenting UF separation and to identify the characteristics that define an effective RC (Chapter 6, in preparation for submission to The Journal of Hazardous Materials, *Keeley, J., Smith, A.D., Jarvis, P., Judd, S.J., An examination of recovered coagulant purification techniques and their impact on drinking water treatment performance).*

Chapter 7 assimilates the scientific and economic findings of the preceding chapters, outlines implementation designs for coagulant reuse in potable and WW treatment, and assesses the risks and benefits of each. Chapter 8 provides a summary of the key conclusions of the thesis and suggested areas for future investigation.

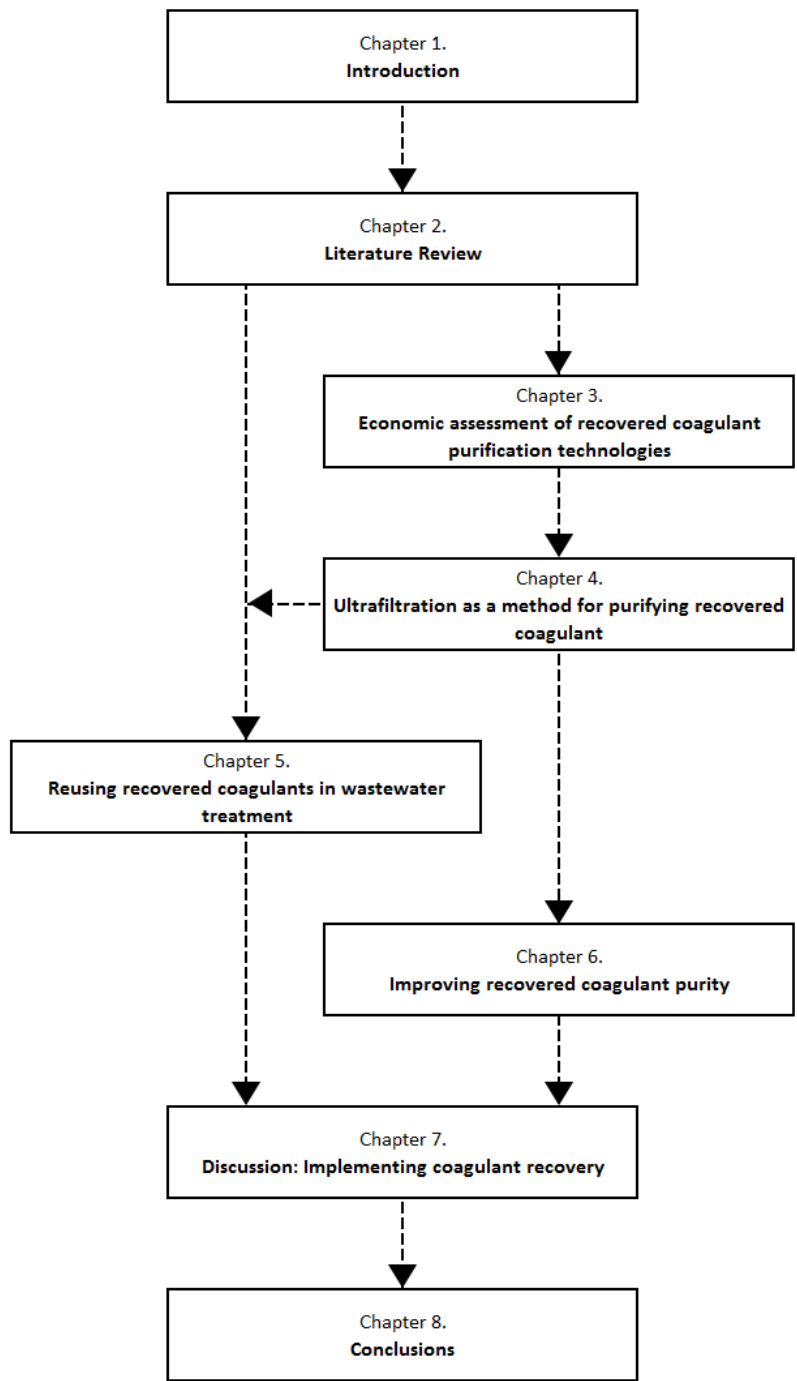


Figure 1: A diagram summarising the thesis structure

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CHAPTER 2

COAGULANT RECOVERY FROM WATER TREATMENT RESIDUALS: A REVIEW OF APPLICABLE TECHNOLOGIES

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2 COAGULANT RECOVERY FROM WATER TREATMENT RESIDUALS: A REVIEW OF APPLICABLE TECHNOLOGIES

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ABSTRACT

Conventional water treatment consumes large quantities of coagulant and produces even greater volumes of sludge. Coagulant recovery presents an opportunity to reduce both the sludge quantities and the costs they incur, by regenerating and purifying coagulant before reuse. Recovery and purification must satisfy stringent potable regulations for harmful contaminants, while remaining competitive with commercial coagulants. These challenges have restricted uptake and lead research towards lower-gain, lower-risk alternatives.

This review documents the context in which coagulant recovery must be considered, before comparing the relative efficacies and bottlenecks of potential technologies, expediting identification of the major knowledge gaps and future research requirements.

2.1 INTRODUCTION

Chemical-based treatment processes such as coagulant dosing have become well-established because they are effective, easily controlled and well understood. Historically, these practical benefits have had few drawbacks because: (1) Commercial ferric, ferrous and aluminium based coagulants have remained relatively inexpensive, with the unit cost of coagulant dosing in the order of 0.005 £/m³ of treated water (Keeley et al., 2012), two orders of magnitude less than desalination (Zhou and Tol, 2005). (2) Prior to modern environmental regulations, the vast quantities of water treatment residuals (WTRs) produced by coagulation could be returned to the point of raw water abstraction, avoiding disposal costs (Walsh, 2009). (3) If disposal is needed, WTRs are considered inert and their disposal has only incurred moderate costs.

Whilst conventional coagulant treatment is likely to remain a low-cost and popular option for contaminant removal for the foreseeable future, the process has become exposed to increased transport costs and global commodity prices as well as stricter environmental regulations and water quality standards. These challenges are common to many traditional chemical processes and typify the drivers for more sustainable, *green chemistry* (Anastas and Warner, 1998). The green chemistry concept aims to reinvent existing chemical processes with the minimum environmental impact and is defined by the 12 principles of green chemistry (Table 1). Many of these principles are applicable to chemical processes used in water treatment. Previous advances in sustainability in the water industry have focussed on minimising energy usage and reuse of wastewater (WW) sludge (Water UK, 2008). The principles of green chemistry may introduce water utilities to a more structured approach to make similar progress in the chemical processes used in potable treatment, moving towards the ideal of chemical-free treatment (UKWIR, 1999).

Table 1: A qualitative assessment of coagulant recovery against the principles of green chemistry

Principles of green chemistry (Anastas and Warner, 1998)	Comment on the potential impact of implementing in coagulant recovery
1. Prevent waste	Significant reductions in the volume and metal content of sludge requiring treatment and disposal
2. Atom economy (maximising the amount of dosed chemicals that are incorporated into the end product. Achieving this reduces waste volume and chemical demand)	This may allow more effective but expensive coagulants to be dosed, if they can be recycled more efficiently
3. Less hazardous chemical synthesis	Quantities of metals leached into the environment (from landfill) will be reduced but recovery is reliant on the use of the strong mineral acids for resolubilisation.
4. Designing safer chemicals	
5. Safer solvents and auxiliaries	
6. Design for energy efficiency	Recovered coagulant will require separation from contaminants, using energy but this may be offset by the energy required to manufacture and transport virgin coagulant
7. Use of renewable feed-stocks	The main principle of recovery is to renew coagulant supply internally
8. Reduce derivatives	-
9. Catalysis	Recycling coagulants moves their role from being a stoichiometric reagent to a retainable catalyst
10. Design for degradation	Aluminium toxicity remains debatable but reducing quantities released into the environment reduces any potential risks and the need for monitoring
11. Real-time analysis for pollution prevention	
12. Inherently safer chemistry for accident prevention	The unavoidable use of acid in coagulant recovery does carry notable risks that will require management

Conventional coagulant treatment has considerable scope for improved sustainability through coagulant recovery (CR) which enables the same atoms of coagulant metals to be repeatedly recycled and reused. To do this, acid is used to re-dissolve spent coagulant metals in waterworks sludge. Separation processes are then used to remove undesirable contaminants from the metal solution, before reuse. CR has the potential to reduce the environmental impacts of water treatment and satisfy many of the principles of green chemistry (Table 1).

When CR is viewed in the context of these principles, it becomes apparent that although it has potential to improve sustainability, it also has its own flaws. Acid-driven regeneration and purification stages must be considered holistically to ensure the benefits of CR are not offset by the chemical and energy demands of the recovery process.

This review seeks to assess the strengths and weaknesses of the available CR technologies, in relation to each other and in the wider context of WTR reuse strategies and sustainability agendas. This assessment will focus on the economic and environmental effects of CR as well as their impact on water treatment quality.

2.1.1 COAGULATION

Before CR technologies can be assessed, it is important to outline the purpose of conventional coagulant treatment and the problems that it faces. This will highlight the value of CR but also the criteria it must satisfy. The objective of coagulant enhanced flocculation and settlement is to remove the majority of suspended and colloidal particles from surface-abstracted raw water. Its effectiveness is reflected by its wide-scale application, with over 70% of water WTW dosing coagulants as part of their treatment process (Betancourt and Rose, 2004). Advancements in water treatment have ensured that increasingly stringent consents on pesticides, micro-pollutants and disinfection by-products

are met. The success of such treatments remains reliant on coagulation first removing turbidity and natural organic matter (NOM).

While coagulation-flocculation plays a key role in water treatment in removing the bulk of impurities from raw water, the process requires a large quantity of chemical and produces an even greater volume of sludge. For example, the UK uses more than 325,000 tonnes of coagulant each year. Aluminium and ferric based salts make up the majority of this total, with 107,000 and 165,000 tonnes, respectively (Henderson et al., 2009). At current prices, this equates to an annual cost of more than £28m. The handling, transport and eventual disposal of the resultant sludge pose further logistical and financial challenges.

Improved understanding of the scientific principles behind coagulation and process control has allowed dosages to be optimised. By ensuring only enough coagulant is dosed to achieve charge neutralisation, rather than less efficient sweep flocculation, coagulant usage is minimised. On-line monitoring and feedback control of coagulant dosing, using streaming current (Adgar et al., 2005) and ultraviolet absorbance at 254 nm (Wang and Hsieh, 2001) have allowed improved theoretical understanding to be put into practice. With the combination of other developments such as increased use of polymer as flocc aids and pH optimisation, coagulant dosing efficiency has been significantly improved. Changes in dosing practice can be illustrated by doses as high as 50 mg/L as Al in the 1970s (Westerhoff and Cornwell, 1978) compared to doses often below 10 mg/L as Al in current times (Jarvis et al., 2005). Dose optimisation is only a partial solution to reducing coagulant demand, and is often compromised by demand for higher doses to ensure treatment robustness during periods of water quality deterioration (Hurst et al., 2004). Hence, once such optimisation options have been fully exploited, recourse has to be made to CR as providing the only remaining option available for net coagulant demand minimisation.

2.1.2 SLUDGE DISPOSAL

The treatment and disposal of sludge is an equally important problem as coagulant usage in determining costs. In contrast to WW sludges, WTRs hold little nutritional or calorific value, making biological digestion or incineration impractical (Ulmert and Sarner, 2005). High concentrations of metals in the sludge limit the suitability for its disposal to land and the large quantities of bound water make dewatering and transport difficult and expensive (Babatunde and Zhao, 2007).

Prior to the introduction of prohibitive environmental regulations in Europe in 1946 (Babatunde and Zhao, 2007), it was common practice to return WTR to the same river that the raw water was abstracted (Elliott et al., 1990). In Europe, sludge is now mainly disposed to sewerage and landfill (Figure 2). Similarly in Japan, disposal of residuals to source was banned in 1971 by the Water Pollution Control Law (Miyanooshita et al., 2009). Japan appears to have utilized sludge reuse strategies more effectively than both the US and UK (Figure 2), driven by an extreme scarcity of landfill capacity (Miyanooshita et al., 2009). From a survey of 46 North American utilities, it seems US regulations are not at the same stage, with 46% of WTRs disposed to source (Walsh, 2009). Changes in these regulations by the US Environment Protection Agency are expected but when and to what extent remains unknown (Cornwell, 2006).

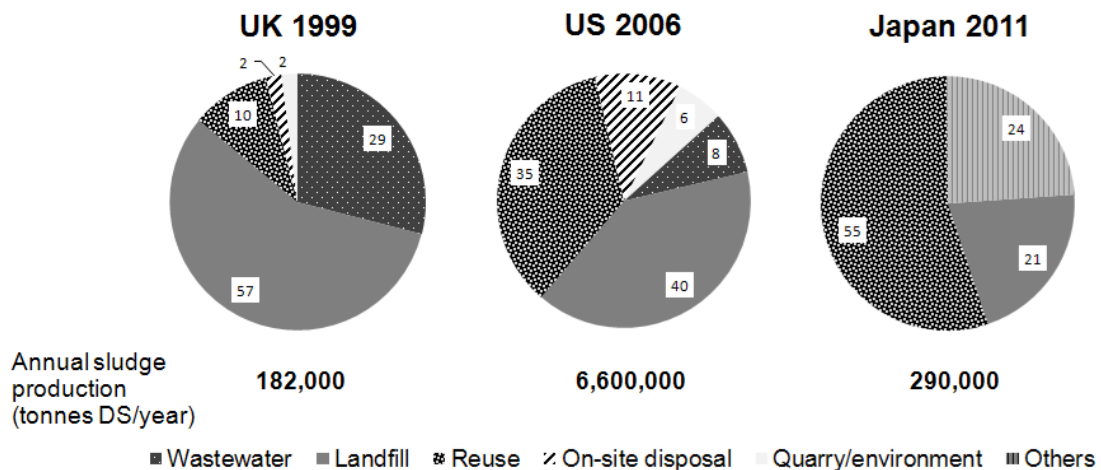


Figure 2: A comparison of final sludge disposal locations in the UK, US and Japan as percentages of total sludge in surveys of water utilities

Adapted from: Walsh, 2009; UKWIR, 1999; Fujiwara, 2011

In 2000, more than 182,000 tonnes of sludge as dry solids were generated in the UK (Pan et al., 2004) with a disposal cost exceeding £5.5m (UKWIR, 1999). The equivalent figure for the US exceeds 6.6m tonnes per annum (Prakash and Sengupta, 2003). Sludge production is increasing, with some projecting it to have doubled between 2000 and 2010 (Albertin et al., 1990). This is due to population growth, regulatory changes and increasingly variable raw water quality associated with climatic changes (Arnell, 1998; Hurst et al., 2004; Delpla et al., 2009). These increased sludge volumes, combined with rising transport costs and taxes designed to deter landfill expansion, place increasing pressure on water companies to minimise their waste production. A ten-fold increase in UK inert landfill waste fees from £8 to £80 per tonne between 1996 and 2020 has been pledged by the UK government (Her Majesty’s Treasury, 2010; Parsons and Daniels, 1999). This will force water utilities to adopt alternative disposal strategies or face the economic consequences.

Despite the cost, a significant proportion of waterworks sludge is still sent to landfill for disposal, with 57% in the UK and 40% in the US (UKWIR, 1999; Walsh, 2009). Under the current European Union Council Directive 99/31/EC,

WTRs are considered an inert waste and are charged lower rate landfill gate fees accordingly. Some have suggested that the presence of regulated heavy metals may warrant reclassification and higher gate fees for WTRs (Elliott et al., 1990). However, landfill regulations are based on the metal content in leachate (EN 12457/1-4, 2002). Because the highly complexed WTR metals are not readily leached at moderate pH values, they are unlikely to present a problem in this respect (Elliott et al., 1990). However, metal toxicity is a contentious issue for reuse options that bring WTRs in contact with humans or their food chain (Babatunde and Zhao, 2007). While this has held back WTR application to land, the concentrations of many metals (Cd, Cu, Cr, Pb, Zn, Ni) in WTRs are actually 10-35% lower than WW sludge (Elliott et al., 1990). Large amounts of WTRs are disposed to WW treatment works (WWTW) and blended with WW sludge. Ultimately these WTRs are applied to land without exceeding metal leachability regulations (Figure 2), discounting concerns over WTR metal content.

As landfill and transport fees are generally charged on a mass basis, WTRs transported off-site for disposal are often thickened and dewatered to the minimal volume that is economical. Thickening achieves dry solids concentrations of 1-6% by adding polymer and using settlement. Further dewatering is made difficult and costly by chemically bound hydrated flocs (Babatunde and Zhao, 2007). Centrifuges, filter and belt presses are used for this purpose (and at considerable expense) but dry solids above 20% are seldom reached. Less energy intensive dewatering techniques such as lagoons, drying beds and freeze-thaw have been considered (Walsh, 2009) but require large amounts of land (Fulton, 1973). Accordingly, on-site disposal is more common in the US than UK, due to differing availability of land (Figure 2).

To avoid transport costs, gate fees and on-site treatment, unthickened WTRs are disposed to sewers whenever possible, with 25% of UK and 9% of US WTRs disposed this way. The US figure is lower, presumably because disposal to source is still permitted (UKWIR, 1999; Walsh, 2009). As utilities are often combined services, the treatment cost is not charged to the WTW but instead is imparted on the WW works. The true economic cost of this has been estimated

using the Mogden formula to be ca. £35m per annum in the UK, almost ten times more than the current amount actually spent on sludge disposal, according to available historical data (UKWIR, 1999). This true cost is partially offset by the benefits of incidental WW chemical treatment (see Section 5). A recent cost analysis determined that WTR disposal to the sewer was the most economical option, even when costs are charged to the potable works (Miyano-shita et al., 2009). However, the aims of improving sustainability go beyond simply finding the disposal route with the lowest economic cost. This is the sole appeal of disposal to sewer but other reuse options can offer further benefits to overall sustainability.

Because of the concerns raised by increasing coagulant cost, supply failure and the cost of sludge disposal, many reuse options have been considered. Success has been realised in the simple strategy of using WTRs as bulking agents in aggregates and soils (Babatunde and Zhao, 2007). Over a third of sludge in the US is disposed in these ways (Figure 2). However, the actual benefit to the sludge recipient is often marginal. The true driver for reuse is the reduction in disposal costs for the potable works. Attempts have also been made to reuse the remaining or regenerated chemical activity of the sludge, as an adsorbent or coagulant. Such roles offer greater rewards but require greater development and scientific precision to ensure public health is not compromised by contaminant carryover or accumulation as the coagulant is repeatedly recycled. Ambition of this kind is essential for the progression of sustainability within the water industry and will help resist increased treatment costs, carbon emissions and waste production. Key to this is improving the scientific understanding of sludge and its constituents, allowing more efficient reuse of their unique characteristics without detriment from the associated impurities.

2.1.3 SLUDGE CHARACTERISTICS AND CONTENT

Before the challenges and solutions of WTR reuse can be properly explained, an explanation of WTR characteristics is required. The nature of sludge is dependent on the source water quality and the chemicals dosed and account for a high level of WTR variability (Table 2). Mean and standard deviations for the main chemical components of sludge have been compiled from existing literature to give an indication of typical WTR properties and to their tendency to vary (Table 2)

Geotechnical analysis of thickened sludge from an upland source water dosed with alum highlighted the challenges of bulk reuse of untreated WTRs. The analysis described sludge as having high plasticity, high compressibility and very low permeability (O'Kelly, 2008). These properties were attributed to the abundant coagulant-bound water, the high affinity of coagulant metal for water, the high organic content and the charge destabilisation within the flocs (O'Kelly, 2008). These characteristics make pure or untreated WTRs unsuitable for use as aggregates in engineering roles and help explain the difficulty in handling and transporting them. By treating WTRs or incorporating them with other materials, the impact of these characteristics can be reduced. Several trials have shown this approach to be successful and are discussed in more detail below.

Sludge bulk reuse options have recently been reviewed and are only included here to provide context for CR options (Babatunde and Zhao, 2007; USEPA, 2011). Increasingly, the feasibility comparison is not between CR and landfill disposal but to other potential reuse options such as application to land, in aggregates and for WW treatment. As these options become more established, the marginal benefit of recycling coagulants is diminished, potentially making the return on the initial capital investment for CR harder to achieve during its operational lifetime.

Table 2: Compiled sludge loadings and variability

Component	Alum			Ferric			Wastewater, dewatered and digested sludge ^a
	Number of sludge samples	Units	Mean (standard deviation)	Number of sludge samples	Units	Mean (standard deviation)	
Total solids	20 ^{b,c,d,g,h,i,k,l,n,o,p,r,s}	% w/w	5(6)	7 ^{a,h,m,p}	% w/w	4(6)	17-35
Volatile solids	13 ^{c,d,h,i,k,p}	% of TS	29(18)	5 ^{a,m,p}	% of TS	18(9)	-
Suspended solids	5 ^{h,k,p}	% of TS	84(22)	4 ^{m,p}	% of TS	97(4)	-
Al	29 ^{c,d,f,g,h,i,k,l,n,o,p,r,s,t}	% of TS	10(9)	7 ^{h,p,q}	% of TS	11(4)	0.9-1.4
Fe	21 ^{d,f,g,h,i,n,o,p,s,t}	% of TS	5(10)	10 ^{a,h,m,p,q}	% of TS	22(16)	0.6-1.7
Mn	9 ^{d,h,l,o,p,s}	% of TS	0.71(1.54)	7 ^{h,p,q}	% of TS	0.72(0.79)	0.02-0.04
Pb	9 ^{e,l,p,t}	% of TS	0.038(0.069)	6 ^{e,h,p,q}	% of TS	0.007(0.009)	0.018-0.022
Ni	5 ^{e,p,s}	% of TS	0.005(0.002)	8 ^{e,h,p,q}	% of TS	0.006(0.005)	0.002-0.003
Cr	9 ^{e,p,s,t}	% of TS	0.003(0.003)	8 ^{e,h,p,q}	% of TS	0.008(0.008)	0.005-0.044
Cd	10 ^{e,h,p,s,t}	% of TS	0.006(0.016)	5 ^{e,h,p}	% of TS	0.0002(0.0003)	0.0002-0.0009
Total Kjeldahl N	4 ^{h,s}	mg/L (N)	302(599)	2 ^h	mg/L (N)	793(858)	1.1-2.9 (% of DS)
Phosphate	8 ^{f,h,p,s}	mg/L (P)	54(104)	4 ^{h,p}	mg/L (P)	23(24)	0.06-0.09 (% of DS)
BOD₅	4 ^{g,h}	mg/L	2595(2492)	2 ^h	mg/L	211(168)	-
pH	19 ^{b,c,f,h,i,k,l,n,o,p,s}	-	6.5(1.4)	8 ^{a,m,p,q}	-	8.1(1.3)	5.9-6.7

Adapted from: a) Alonso-Alvarez et al., 2002; b) Bishop et al., 1987; c) Chen et al., 1976; d) Dymaczewski et al., 1997; e) Elliott et al., 1990; f) Gallimore et al., 1999; g) Georgantas and Grigoropoulou, 2005; h) Godbold et al., 2003; i) Jimenez et al., 2007; j) King et al., 1975; k) Lindsey and Tongkasame, 1975; l) Petruzzelli et al., 2000; m) Pigeon et al., 1978; n) Prakash and Sengupta, 2004; o) Sengupta, 1994; p) Sotero-Santos et al., 2005; q) Titshall and Hughes, 2005; r) Ulmert and Sarner, 2005; s) Wang et al., 1998; t) Xu et al., 2009a

2.2 BULK REUSE of WTRs

Bulk reuse of WTRs has seen them employed in two contrasting roles: as inert bulking material and as active substrates. The adsorbent properties and low cost of dewatered WTRs have prompted studies into their efficacy for contaminant removal from waste and ground waters. A long-term trial has shown the use of WTR sludge cake as a reed bed substrate to be effective at removing organic compounds and phosphorus (Zhao et al., 2009). Removals of 73% for chemical oxygen demand (COD), 83% for biological oxygen demand (BOD₅), 86% for reactive P, 89% for soluble reactive P and 78% for suspended solids (SS) were found. 42% of overall P removal was determined to be due to adsorption with the remainder by simple filtration. These results were considered promising but full-scale viability depends on a better understanding of bed clogging rates and lifetimes (Zhao et al., 2009). These issues should be kept in proportion however, as WTRs are in plentiful supply at only the cost of their transport and installation, making regular replacement a feasible option.

A related role is the use of WTRs permeable reactive barriers (PRBs) and the remediation of contaminated ground waters, at a lower cost than conventional zero-valent iron substrates. Using WTRs as a sorption substrate, Uranium, caesium, chlorinated phenols and nitro-benzenes have been successfully removed from contaminated ground waters at bench-scale (Hart et al., 2011).

WTRs have been applied to soil and have been shown to improve soil structure by flocculating silica particles (Elliott and Dempsey, 1991). The low dewaterability of WTRs actually benefits this application, increasing soil moisture retention (Babatunde and Zhao, 2007). Concerns regarding the presence, availability and toxicity of heavy metals from WTRs seem unfounded at this stage; while heavy metals are present in WTRs, research suggests that under neutral and alkali conditions, they are not readily bioavailable (Elliott et al., 1990). Examples of WTRs being used as inert bulking agents have been in bricks (Godbold et al., 2003) and cementous aggregates (Pan et al., 2004). When used to substitute 10% of conventional clay in bricks, no loss in structural integrity was observed (Godbold et al., 2003).

Bulk reuse strategies are limited by their failure to fully utilize the unique properties and constituents of WTRs. This makes them more a generic waste than a commodity and forces them to compete with numerous other waste producers seeking to obviate landfill disposal. There is a risk that the cost of additional transport and labour demanded by sludge reuse actually exceeds the economic benefit (Miyanoshta et al., 2009) but these costs are unlikely to be significantly more than conventional disposal to landfill. Legislation and perceived risk are also barriers to WTR bulk reuse (Babatunde and Zhao, 2007) but in comparison to the scrutiny that water treatment chemicals are subject to, these barriers can and have been negotiated (Figure 2).

2.3 CHEMICAL REUSE

Bulk reuse allows a step towards improved WTW sustainability, by reducing the amount of WTRs disposed, but it is incapable of reducing coagulant usage. In comparison, total reuse of the chemical value of WTRs could provide reductions in coagulant and disposal costs, and significant improvements to WTW sustainability. For these reasons, research into coagulant recycling technologies has a long history. The first patent in the area was granted in 1903, for the acidification of filter backwash water to resolubilise the precipitated hydroxides of metal coagulants (Jewell, 1903). Aluminium and iron both have a linear solubility with acid dose: more coagulant is regenerated and returned to the aqueous phase as the pH is lowered. However, other sludge components such as NOM are also solubilised in acid, both increasing the acid requirement and contaminating the recovered coagulant (RC). Contaminant co-solubilisation is key to the economics and quality of recovering coagulant for reuse in modern water treatment (USEPA, 2011) and remains the most critical barrier to CR for potable reuse.

2.3.1 RECOVERED COAGULANT QUALITY

In the 1970s and 1980s, when water quality regulations were less focussed on disinfection by-products and metals, non-selective CR was capable of providing acceptable levels of coagulant quality (King et al., 1975; Bishop et al., 1987). At its peak, the practice was adopted at 15 plants in Japan (White, 1984), as well as six pilot and full-scale trials at sites in the US and UK (Webster, 1966; Saunders and Roeder, 1991). Improved sludge dewaterability was the primary aim of sludge acidification in Japan but the reuse of solubilised coagulant also bore a significant economic benefit (Tomono, 1977). Despite this success and progress, CR adoption and operation has been abandoned due to: (1) the failure of process control to manage the variability of WTRs (Chen et al., 1976), and (2) the accumulation of acid-soluble impurities, particularly manganese (Tomono, 1977; White, 1984). Acidification remains a possible dewatering aid (Fujiwara, 2011) but the solubilised liquor is unusable unless subsequently purified. This makes the practice economically viable in only when disposal routes are extremely limited.

In recent years, the control of disinfection by-products (DBPs) in drinking water (particularly trihalomethanes; THMs) has become a focal point of modern potable quality. DBPs are formed from oxidation of organic material by chlorine and other oxidising disinfectants. The resulting halo-organic compounds are suspected carcinogens and research has shown that at sufficiently high exposure, these compounds can heighten the risk of several cancers, particularly of the bladder (World Health Organization, 2000). DBP formation can be minimized by limiting the availability of their reactants; the chlorine dose and the DBP organic precursors. While chlorine doses are already trimmed to prevent taste and odour complaints, the need for effective disinfection far outweighs any other treatment goals. The WHO has stated that the risk from pathogens, due to ineffective disinfection, is far greater than the risks caused by carcinogenic activity of DBPs, at the levels typically seen in treated water (World Health Organization, 2000).

Therefore, the emphasis for DBP management is on organic precursor removal, prior to disinfection. This is particularly important for the most reactive hydrophobic fractions with the highest THM formation potential (THM-FP). The risk of innovative treatment processes, such as CR, is the unknown impact they will have on DOC levels in treated water. CR, as any recycling process would, poses a particular risk of recycling DOC alongside RC. This could lead to accumulation of DOC and elevation of the DBP formation potential of the treated water.

With the continued discovery and toxicological understanding of emerging DBPs, regulations are likely to become more comprehensive and stringent in the coming decades, putting further pressures on CR selectivity. With this regulatory background and future, utilities cannot afford to use unproven processes that pose any risk to treatment quality. Even in simple economic terms, any efficiency gains could quickly be outweighed by fines for breaching DBP regulations.

Public health is protected by regulation of these harmful compounds. National regulatory bodies have put limits on total THM levels at 100 µg/L in the UK (Drinking Water Inspectorate, 2010) and 80 µg/L in the US (United States Environmental Protection Agency, 2011). US regulations also place a limit of 60 µg/L on the total concentration of five haloacetic acids, another group of DBPs. It is likely that as more emerging DBPs are characterized and their toxicity is better understood, there will be more prescriptive regulatory guidelines.

CR causes varying amounts of organic compounds to be carried over with the coagulant dosed into the treatment stream, depending on recovery process performance (Table 3). Since only organic compounds that can be removed by coagulation will be present in WTRs and be present in the recycled coagulant, it could be surmised that the impact on treated water may be minimal since organic contaminants would be removed by the coagulant (Lindsey and Tongkasame, 1975). However, no research has been carried out on the effect that pH and interactions have on the transformation of NOM character during recovery. Contaminant loadings would have to be compensated by higher

overall coagulant doses. Despite this, the reduced cost of RC can allow higher doses, while still reducing chemical costs, in comparison to solely dosing fresh coagulant (Table 4).

Table 3: Recovered coagulant quality at typical coagulant doses vs. current water quality standards for the US and UK

Contaminant	Units	US Maximum Contaminant Level (brackets denote guideline) (USEPA, 2009)	UK Standard (DWI, 2010)	Commercial alum worst-case potential conc. in treated water when dosed at 3.9 mg/L Al (Eyring et al., 2002)	Unselectively recovered alum worst-case potential conc. in treated water when dosed at 26 mg/L Al (Bishop et al., 1987)	Selectively recovered alum diluted when dosed at 3.9 mg/L recovered Al (Prakash and Sengupta, 2004)
Aluminium	µg/L	(50-200)	200	3900*	26000*	3900*
Iron	µg/L	(300)	200	7	3800	80
Colour	Colour units	(15)	20	-		-
Turbidity	NTU	0.3-1-5	1†	-		-
THM	µg/L	80	100	- ‡	214 (as THM-FP)	14 (as DOC) §
Manganese	µg/L	(50)	50	0.2	3300	-
Nickel	µg/L	-	20	0.7	0.8	-
Mercury	µg/L	2	1	-	0	-
Copper	µg/L	1300 (1000)	2000	1.0	7.8	0.9
Chromium	µg/L	100	50	0.2	7.8	-
Lead	µg/L	15	10	0.2	0.5	-
Cadmium	µg/L	5	5	0.04	0	-

*Will largely be removed by precipitating as an insoluble hydroxide, meeting consented levels. Other components will also, to varying extents. † Upon entering the distribution network. ‡ Required by NSF Standard 60 to contribute less than 10% of final treated levels; here <8 µg/L. § Used as a proxy in the absence of THM data.

Table 4: Dosing mass balance with and without coagulant recovery

Alum dosed (mg/L)	Coagulant Dosing and Recovery Approach (DOC contaminant load mg/L in parenthesis)		
	Conventional	Recovered	Recovered with 20% extra dose of fresh alum*
Recovered (81% of total)	0	3.2 (11.5)	3.2 (11.5)
Fresh	3.9	0.7	1.5
Total	3.9	3.9 (11.5)	4.7 (11.5)

*A hypothetical extra dose of coagulant to compensate for removal of organic contaminants carried over in RC. Doses and recovery yield adapted from: Eyring et al., 2002; Prakash and Sengupta, 2004.

Despite this, some studies have suggested that recycled coagulant does have a detrimental impact on treated water quality with respect to colour (Lindsey and Tongkasame, 1975), although reported increases in THM-FP have been small (Bishop et al., 1987). It is possible that current consents, of 80 and 100 µg/L total THMs (in the US and UK, respectively), would be breached failed if the organic matter retained in the RC is not removed prior to chlorination. Indeed, the increasingly stringent water quality regulations have put pressure on commercial coagulant producers to reduce metal and organic contaminant levels in their products, which may be contributing to the increases in prices.

The quality standards that CR must adhere to, for potable use, go beyond THMs. For a recycled coagulant to be considered for dosing, it must meet the same quality assurance regulations as for virgin coagulants, as set out by Article 10 of the Council of the European Union Drinking Water Directive (1998). This implies that acid extraction alone is insufficient, as it could result in elevated DBP levels and impact public health. In the UK, coagulant quality regulation is implemented by British Standards for each coagulant type and the Drinking Water Inspectorate's (DWI) Regulation 31(4). In contrast, the US uses a more general National Sanitation Foundation and American National Standards Institute, *Standard 60*, which considers coagulant purity in terms of their percentage contribution to treated water quality contaminant loadings (Table 3). Such standards are specifically aimed at commercial coagulants and

make no mention of RCs and the issues surrounding their use, such as DOC concentrations. However, the recurrent message of water treatment chemical and treated water regulations is clear: treated water quality is of paramount importance and should be protected as much as is reasonably practicable. If they are to be implemented, CR technologies must satisfy this requirement and at least match conventional coagulant performance.

2.3.2 SOLUBILISATION

The process of metal solubilisation is an unavoidable stage of CR but is unselective, with other contaminants solubilised as well. Recent CR research has focussed on developing efficient methods of metal-contaminant separation to prevent contamination of treated water by dosing RC.

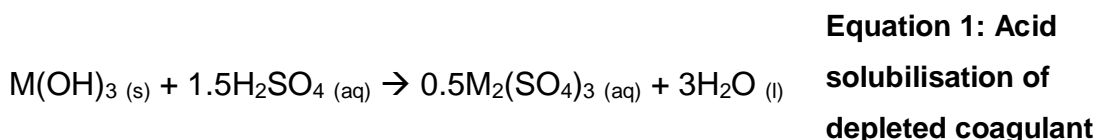
The end-products of coagulant reactions with raw water are flocs of precipitated metal hydroxides, entrapped organic and inorganic contaminants, as well as insoluble metal-DOC (dissolved organic carbon) complexes. All CR technologies require the coagulant metals to be firstly returned to the aqueous phase. This stage accounts for at least 25% of the total operating costs for selective CR (Keeley et al., 2012). The most common method has been acidification using sulfuric acid, due to it being the cheapest acid available (Parsons and Daniels, 1999). Acidification is also responsible for reducing sludge volumes, as large amounts of suspended solids are dissolved (Saunders and Roeder, 1991).

For aluminium hydroxide, which is amphoteric, solubilisation can also be achieved by raising the pH to form soluble aluminate salts $[\text{Al}(\text{OH})_4]^-$. At pH values above 11.4, Al recoveries of 80% have been achieved (Masschelein et al., 1985), at concentrations of 950 mg/L Al (Saunders and Roeder, 1991). However, the cost of sodium hydroxide is almost double that of sulfuric acid, per mol of acid or hydroxide (Alibaba, 2012; Keeley et al., 2012), making the process uncompetitive. Calcium hydroxide is a lower-cost alternative (Keeley et al., 2012) but offers only 50% Al recovery at pH values of 11.4 (Masschelein et

al., 1985) and recovered concentrations of no more than 30 mg/L Al (Wang and Yang, 1975) due to the lower solubility of calcium over sodium aluminates. It has been reported that alkaline solubilisation reduces the carryover of heavy metals, which are acid soluble (Masschelein et al., 1985), but coagulant quality is nonetheless impaired by increased solubilisation of organic compounds (Isaac and Vahidi, 1961).

While acidification with sulfuric acid is the universal means of coagulant re-solubilisation, there is a lack of consensus on the optimum operational pH. More metal coagulant can be solubilised at lower pH values but this effect has been reported to diminish below pH values of 1, at concentrations of approximately 2,500 mg/L Al (Saunders and Roeder, 1991). Lower pH values require exponentially greater volumes of acid and drive up the process cost, as well as increasing organic solubilisation. Optimum values between pH 2 and 4 have been reported to offer a compromise between metal and contaminant solubilisation (Westerhoff and Cornwell, 1978; Bishop et al., 1987; Saunders and Roeder, 1991; Sengupta and Sengupta, 1993; Vaezi and Batebi, 2001). This is contrary to the theoretical pH-solubility curves for aluminium that suggest a linear increase in solubilisation to a maximum at pH 2.75. This has been attributed to mass transfer limitations, such that once aluminium hydroxide salts are solubilised only the less reactive oxide forms remain (Saunders and Roeder, 1991).

Acid solubilisation has also been considered in terms of the stoichiometric ratio between the trivalent coagulant metal hydroxides and the added sulfuric acid. Stoichiometry would suggest 1.5 mols of acid are required to solubilise 1 mol of trivalent metal (M) (Equation 1).



Experimental data has shown higher molar ratios are usually required, with the actual molar ratio being closer to 2:1 (Bishop et al., 1987): additional acid is required to overcome the buffering capacity of the sludge, reflecting the original

raw water characteristics. However, other studies have found the 1.5:1 stoichiometric amount to be sufficient for 100% coagulant solubilisation (Ulmert and Sarner, 2005). Since the specific acid requirement for metal solubilisation is a major cost factor, attempts have been made to actively reduce the dose required. Sodium sulfide has been used to reduce the oxidation state of ferric salts to ferrous, reducing the acid:metal molar ratio to 1:1. The settled volume of the remaining insoluble fraction was reduced to 20% of the original (Pigeon et al., 1978). However, removal of residual sulfide was required before the RC could be reused, to prevent iron sulfide formation (Pigeon et al., 1978). The demand for costly sodium sulfide by this process also significantly compromises the cost benefit.

The extent of solubilisation is not the only consideration for pH adjustment. If acid insoluble recovery residuals are disposed to landfill as inert waste, a minimum pH limit may be imposed to prevent metal leaching (Bishop et al., 1987). It may be more economical not to acidify the sludge below this limit to avoid neutralisation later. Sludge settleability is also dependant on pH and, while acid extraction reduces the mass of suspended solids in the sludge, residual solids require removal and disposal. Studies have shown that optimum settling rates of the acid insoluble WTR fraction occurred at pH values of 2-3, providing another incentive for restraint in acidification (Sengupta and Sengupta, 1993).

Another way of improving the process economics is to consider re-using the acid used to recover coagulant. Suitable selective acid recovery technologies are discussed alongside CR below.

2.4 COAGULANT RECOVERY SEPARATION TECHNOLOGIES

The success of recovering coagulant to a standard satisfying modern potable regulations depends on efficient metal-contaminant separation within the acidified sludge solution. Achieving this requirement allows the full benefits of CR to be realised and the satisfaction of many of the principles of green

chemistry (Table 1). The earliest, simpler coagulant recycling technologies used solid-liquid filtration or settlement to remove only gross solids from the RC (Jewell, 1903; Fulton, 1973). This is still practiced but modern systems also use molecular charge and size to discriminate metal coagulants from contaminants. These principles have been applied using membranes and adsorbents.

The heterogeneous nature of potential contaminants in RC poses a significant challenge. Natural organic compounds vary widely in molecular weight, functionality and depend heavily on environmental conditions, while heavy metals share similar cationic and molecular weight characteristics with coagulants. These characteristics make total exclusion from the recovery of trivalent metal coagulants difficult. Despite this, several separation processes have reported recovery of high purity coagulant, with minimal heavy metal and organic compound contaminants (Prakash and Sengupta, 2003; Ulmert et al., 2005). These can be categorised as either pressure-driven membranes or charge-based methods.

2.4.1 PRESSURE-DRIVEN MEMBRANE SEPARATION

Pressure-driven membranes are widely-used separation technologies in water treatment. The combined benefit of a near absolute barrier and simple and well-understood operation seemingly make them candidates for CR. However, issues such as fouling, energy demand and limited selectivity have been cited as reasons to disregard conventional membrane treatment for CR (Prakash and Sengupta, 2003).

There have been a number of studies of the performance of ultrafiltration (UF) for CR at bench and pilot scale (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005). In these studies the rationale was to select UF pore sizes allowing trivalent metal permeation whilst retaining NOM. A range of membranes with differing molecular weight cut-offs (MWCO) between 10-50 kDa have been investigated to determine the greatest margin of metal-contaminant separation achievable. Membranes with MWCO of 10 kDa allowed

aluminium permeation exceeding 90% and TOC rejections of 50-66% (Lindsey and Tongkasame, 1975).

Jar tests were used to compare the efficacy of recovered and fresh coagulant at various doses. At doses that gave the best level of treatment, the presence of organic contaminants in the RC had no detrimental effect on treated water quality. At doses below the optimum, there was an increase in treated water residual colour, which worsened with repeated recycles (Lindsey and Tongkasame, 1975). Subsequent runs showed sharp declines in fluxes, due to the concentrated feed solution forming a gel layer on the membrane surface. This was shown to be managed effectively with water washes every 12 hours and weekly washes with 0.01M sodium hydroxide (Lindsey and Tongkasame, 1975). It should be noted that this study was carried out before DBPs were a water quality issue. Therefore the research did not focus on the impact the recovered alum had on DOC levels in the treated water.

Economic management of the inevitable fouling of pressure-filtration membranes is key to successful treatment of a concentrated, acidified sludge feed. Contradictory arguments have been made regarding the positive (Lindsey and Tongkasame, 1975) and negative (Ulmert, 2005) cost benefit of pressure-filtration for CR. This debate is likely to continue, but even based on pessimistic performance estimates, membrane filtration appears to offer the lowest cost of all options (Keeley et al., 2012).

A study of an aluminium recovery process (known as the *ReAl* process), used UF followed by diafiltration, nanofiltration (NF) and precipitation to purify and concentrate alum to a crystalline form (Ulmert and Sarner, 2005). Again, a range of UF membrane MWCOs between 2-100 kDa were considered. The membranes with a cut-off less than 5 kDa allowed only 55-65% Al recovery and COD rejections of 80%. Since even the most hydrated form of aluminium sulfate (heptadecahydrate) has a molecular weight well below 1 kDa (Smith, 1942), the retention of aluminium at larger MWCOs strongly suggests that aluminium is complexed with larger organic molecules. Further Al recovery may be achieved

by degrading these organo-metallic complexes but also risks reducing DOC molecular weights and increasing DOC permeation.

For the *ReAl* process, optimum separation was achieved using a membrane with a MWCO range of 15-30 kDa, giving Al recovery of 94% and COD rejection of 78%. Without further purification, this was deemed to be of insufficient quality for potable treatment but was suitable for dosing into WW for P removal. For further purification, the *ReAl* process concentrates the RC using NF (by permeation of water), cooling the retentate to 0°C and adding potassium sulfate to induce alum precipitation. The crystals were then filtered and washed with cold water to remove aqueous organic contaminants. Ultimately a sufficiently high level of purity was reached, with a heavy metal content was below European regulations for coagulants and TOC content was in the order of 100 mg/kg of Al (Ulmert and Sanders, 2005). Approximately 10% of Al permeated through the NF membrane but it was proposed that some use could still be made of it in WW treatment. The economics of such a thorough purification process were not described in the paper, though process costs would be expected to be high.

2.4.2 CHARGE BASED SEPARATION

While conventional membranes can be used for coagulant-contaminant separation, such processes face the challenge of overcoming fouling and quality issues. Due to the overlap in molecular weights of coagulants and organic contaminants, some of the most successful coagulant separation technologies have used molecular charge as the principal means of discriminating between cationic coagulant metals and anionic or neutral contaminants. These have been in the form of ion-exchange media - as liquids, resins and dialysis membranes.

2.4.2.1 LIQUID ION EXCHANGE

The first charged-based separation technology used to remove organic contaminants from acidified sludge was liquid ion exchange (LIE; Cornwell, 1979). Firstly, the impure acidified coagulant is mixed with an organically-soluble extractant liquid, into which the coagulant metals are adsorbed, forming organic-metal complexes. When saturated with metal, the extractant is dissolved in an organic hydrophobic solvent (such as kerosene) and removed from the acidified sludge. The organic solution is then mixed with an acid stripping solution that recovers the coagulant and regenerates the extractant. The purified recovered alum is then ready for reuse or further purification, if required and the stripped extractant can be recycled back to the first step. Because the extractant is specific for Al, the organic matter rejection, heavy metal rejection and coagulant quality are high. Alum recoveries of >90% were achieved, at concentrations and quality equal to, or better than, commercial-grade equivalents of the time (Westerhoff and Cornwell, 1978). This favourable comparison may not be valid against modern commercial coagulants which have to treat water to satisfy DBP consents.

More detailed research for full-scale LIE plants support the positive outcomes of bench-scale studies, with alum recoveries still in excess of 90% (Cornwell et al., 1981). Coagulant performance, in terms of THM precursor concentrations, colour and turbidity removals, was comparable to commercial coagulants at the same dose. The conclusions of an economic assessment in the same report suggested that LIE recovery of alum would offer operating cost reductions over conventional coagulant use, provided Al concentration in WTRs exceeded 1,200 mg/L and the WTR flow was at least 37 litres per minute. Increasing these two parameters was shown to increase operating cost savings (Cornwell et al., 1981). Criticism aimed at the inability of LIE to concentrate recovered aluminium seems unfounded (Sengupta and Prakash, 2002). No concentration takes place during the extraction phase but four-fold concentration increases have been reported in the stripping phase, producing recovered alum concentrations above 30,000 mg/L as Al (Cornwell et al., 1981).

Concern has been expressed over the nature of the chemicals used in the LIE process (Sengupta and Sengupta, 1993). There is potential for entrainment of organic solvent in the coagulant during the stripping stage and contamination of the treated water (Prakash and Sengupta, 2003), although an activated carbon polishing stage was originally suggested to prevent this (Cornwell et al., 1981). Similar techniques are used in extractive hydrometallurgy, where these limitations are less important. In hydrometallurgy, end-products do not have to be fit for human consumption and process complexity is justified by the recovery of higher value metals (Tasker et al., 2007).

Although capable of impressive recovery rates and yields, LIE is vulnerable to entrainment of liquid organic extractants and solvents, elevating the risk of taste and odour complaints and DBP formation. Polishing stages can be used to help mitigate this risk but would worsen the already marginal cost benefit of recovering low-value coagulants. Accordingly, research has focussed on more robust solid-phase ion-exchange systems.

2.4.2.2 ION EXCHANGE RESINS

Attached and suspended ion-exchange media were a logical progression from LIE. Because the extractants (resins beads) are less toxic and more readily retained, the danger of treatment stream contamination is minimised, allowing a more simple and safe recovery process.

Adsorbent resins have been used in a number of ways to purify RC. This includes selective adsorption of cationic coagulant metals from an acidified solution, leaving anionic contaminants in solution (Sengupta, 1994; Petruzzelli et al., 2000) or selective adsorption of anionic contaminants, leaving cationic coagulant metals in solution (Anderson and Kolarik, 1994). Once saturated, the resins can then be stripped and regenerated on-site. The relative concentration of metal coagulant to anionic contaminants governs which process is most suitable, making adsorption of anionic contaminants a possible polishing stage that could be used after other separation techniques.

Column-based weak carboxylate Purolite C106 and strong sulfonic Purolite C100X10 cation-exchange resins have both demonstrated >90% recovery of Al from acidified alum sludge, but the sulfonic resin required more sodium hydroxide for regeneration (Petruzzelli et al., 2000). Aluminium concentrations of 5,000 mg/L as Al were recovered in hydroxide form, but would require acidification and further chemical treatment to generate an acidic sulfate or chloride coagulant salt. A 50 L/d pilot-scale *ion exchange recovery of aluminium process (IERAL)* employing Purolite C106 resins reportedly achieved Al recovery yields of 95%. Using hydroxide precipitation and acid resolubilisation, aluminium sulfate concentrations of 99% were achieved, equalling commercial coagulant purity (Petruzzelli et al., 2000). When operated as an exchange column at a flow of 5 bed volumes (BV) per hour, breakthrough started at 80 BV and total Al breakthrough occurred at 150 BV, yielding a very low capacity and treatment rate. This protracted period of breakthrough is indicative of the declining rates of adsorption as the ion-exchange resins approach Al saturation and equilibrium - a limitation common to all ion exchange processes (Prakash and Sengupta, 2003). Resin regeneration and metal stripping is carried out with sodium hydroxide, forming metal hydroxide precipitates that can be filtered before acid solubilisation. While this extra stage allows higher coagulant concentrations than other processes, it requires an additional adjustment of pH, additional chemicals and increased costs.

An alternative to column processes are conveyor belts with attached resins. These allow simultaneous loading and stripping of the resins, as they cycle between tanks of acidified sludge feed (with 90% of the Al in the original sludge extracted) and stripping acid (Sengupta and Sengupta, 1993). A bench-scale simulation of this process, using weak acid resin beads (iminodiacetyl) attached to a porous PTFE (polytetrafluoroethylene) membrane, recovered 68% of Al with 12% DOC and almost total exclusion of heavy metals, independent of their feed concentrations. Although selective, this process provided low concentrations of recovered Al, at only 400 mg/l after 30 cumulative cycles. Further cycles increased the Al concentration but at the expense of decreased NOM exclusion (Sengupta and Sengupta, 1993). However, this system does

have the advantage of using an acidic stripping agent, reducing the need for further pH manipulation, in contrast to the Purolite resins used in columns.

Although there are no examples of using ion exchange resins for ferric CR, there are numerous examples of ferric extraction from similar acidified waste streams, e.g. electroplating (Saji et al., 1998; Agrawal and Sahu, 2009; Navarro et al., 2009). The principles of these processes are transferrable to ferric CR but with certain constraints: co-extraction of other metal species and the use of toxic or easily entrained extractant or stripping agents are unacceptable. These constraints, combined with the requirement for acidification prior to separation (whereas electro-plating streams are already acidified), greatly impair the economics of technology transfer.

Anion exchange resins show potential at selectively adsorbing organic contaminants from otherwise pure acidified coagulant. Because selective recovery processes are still prone to some organic carryover, anion exchange resins may prove valuable in ensuring the absence of THM precursors in recycled coagulant. Following previous purification by polyelectrolyte and pH induced contaminant precipitation, TOC levels in RC were reduced from 120 mg/L to 40 mg/L by passing through a column of Amberlite *IRA 910* resin in the hydroxyl form (Anderson and Kolarik, 1994). In conjunction with more effective pre-treatment, anionic resins could help reduce the RC organic content to beneath regulated levels. However, the heterogeneity of NOM character should be remembered. The DOC fractions that have not been removed by other technologies are likely to be low-molecular weight hydrophilic compounds and will not be removed effectively by anionic resins either.

A more crude method demonstrated that charcoal dosed at 10,000 mg/L into a solution containing 6,000 mg/L as Al was capable of removing 34% of the colour from the coagulant in 5 minutes of mixing (Abdo et al., 1993). Although the performance is comparable to anion exchange membranes, recovery and regeneration of the charcoal would be more costly. In this example, further purification was achieved by evaporation and crystallisation.

Ion exchange resins and adsorbents allow improved retention over LIE and are capable of recovering relatively pure coagulant without undue process complexity. Like most ion exchange processes, practical applicability is limited by slow diffusion kinetics for extraction and stripping. The cost of using a stoichiometric excess of sodium hydroxide to strip bound coagulant metals and to regenerate the resin largely offsets the value of the RC (Petruzzelli et al., 2000). At current alum and sodium hydroxide prices, the cost of using of 6 mols of hydroxide to recover 1 mol of aluminium approaches parity with commercial coagulant, limiting its appeal (Petruzzelli et al., 2000; Alibaba, 2012; Keeley et al., 2012). Such inefficient use of chemicals would also undermine any potential benefits brought about by CR, in terms of striving for a green chemical process. Until more efficient media and regeneration techniques are developed, ion exchange does not appear to be viable for CR.

2.4.2.3 DONNAN MEMBRANE PROCESSES

Resin-based recovery processes are simpler processes when compared to LIE but are still based on a two-step, extract/strip operation. Donnan dialysis (DD) membranes allow these two steps to occur simultaneously through an ionic membrane that separates the feed and stripping solutions. This configuration makes plug-flow operation easier to implement, ameliorating the kinetic limitations of resin-based batch processes.

Donnan membranes are ion-selective (for cations in the case of CR) and ion flux is driven by electrochemical gradients, as opposed to pressure differentials of conventional membrane processes. The lack of transmembrane pressure helps minimise fouling; the flux is determined only by the electrochemical gradient and the membrane characteristics (Prakash and Sengupta, 2003).

Metal recovery is driven by the Donnan co-ion exclusion principle (Donnan, 1925). The recovery solution, containing a more concentrated acid solution than the feed, creates an H^+ concentration gradient across the membrane. The cation-selective membrane allows H^+ ions to diffuse across it, to achieve

thermodynamic equilibrium. The sulfate co-ions are rejected by the cation-selective membrane, creating an electrochemical gradient across the membrane (Figure 3). Another application of this principle, hydrogen fuel cells, employs this electrochemical gradient to produce electrical work. For CR it is used to drive coagulant metal ions from the feed to the recovery solutions (Prakash et al., 2004).

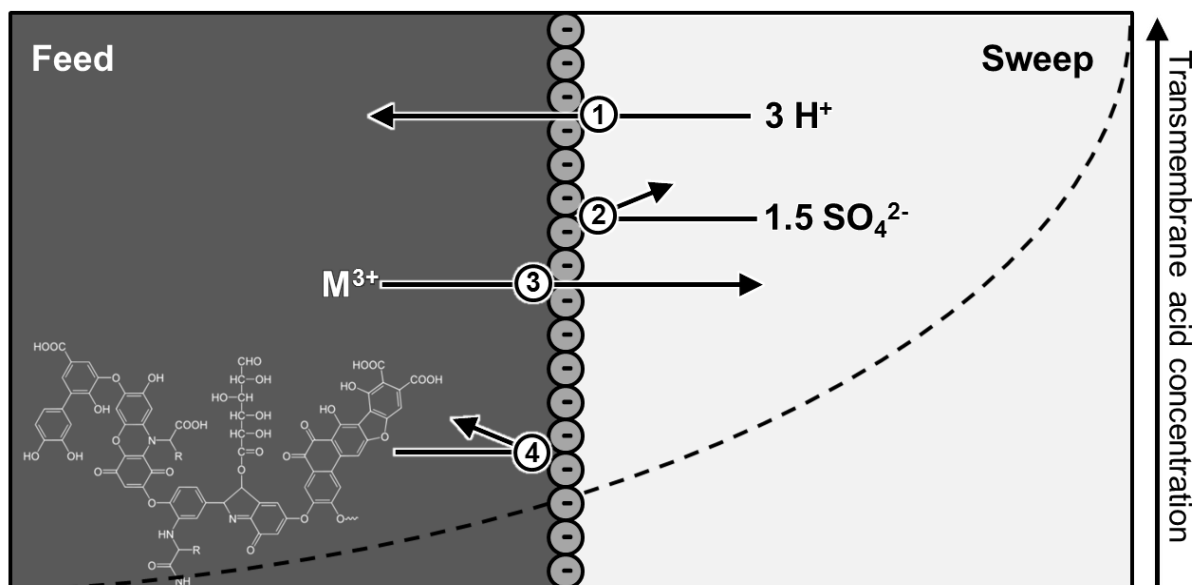


Figure 3: Donnan equilibria-driven trivalent metal recovery across a cation-selective membrane

1. Sweep-side acid protons move down their concentration gradient across the cation-selective membrane, creating a charge imbalance across the membrane
2. Acid counter-ions are rejected by the membrane, preventing them moving to correct the charge imbalance
3. Trivalent metals move in the opposite direction to acid, neutralizing the trans-membrane charge
4. Organic material in the feed is rejected by the membrane due to its bulk and negative/neutral charge

Because metal ion movement across the membrane is driven by electrochemical potential, metals can be transported against their concentration gradient, allowing concentrated solutions to be recovered. Organic contaminants are largely rejected by the cation-selective membranes along with di- and mono-valent heavy metals (Prakash and Sengupta, 2003), which remain

in stable organic complexes (Elliott et al., 1990). Bench-scale performance studies have shown recovered concentrations of 5,650 mg/L Al (72% recovery) with only 3.5 mg/L DOC, from a feed solution with initial concentrations of 2,500 mg/L Al and 190 mg/L DOC, with no noticeable membrane fouling. Incidental recovery of ferric ions was also reported, to a concentration of 97 mg/L, but this was deemed to benefit coagulant performance rather than impair it.

The selectivity of this process has been shown to be variable however, with a subsequent trial recovering less aluminium (4,725 mg/L concentration and 81% yield) with more DOC carried over (17 mg/L), from a feed of 1,900 mg/L Al and 150-600 mg/L DOC, in the same period of dialysis (Prakash et al., 2004). The correlation between elevated feed DOC and increased DOC permeation would suggest feed quality has a significant impact on the quality of RC. Recovery of ferric ions, from a sludge where ferric was used as a coagulant, gave almost identical performance to that of alum sludges, with recovered concentrations of 5,500 mg/L Fe from a feed of 1,800 mg/L (76% yield) (Prakash and Sengupta, 2003).

Yield percentages and concentrations are important but process kinetics are also key to full-scale success. In the case of Donnan diffusion, rates are dependent on many factors. These include feed and recovery-side concentrations, membrane thickness and ionic capacity, and recovered metal valency. Aluminium-acid interdiffusion rates in the kinetic region of exchange (Figure 4) approached those of protons (Prakash and Sengupta, 2003). This was attributed to the high affinity of trivalent metals for the strong-acid ionic groups on the Nafion 117 ion exchange membrane, saturating all the available sites and ensuring that only the rapid interdiffusion of protons limit the reaction. However, the same data also showed that this accelerated rate is short-lived. After 6 hours and approximately 65% Al recovery (Prakash and Sengupta, 2003), the batch ion exchange system approached equilibrium, slowing interdiffusion (Figure 4). If diffusion is allowed to continue beyond this point, background osmotic leakage overcomes the diminished ionic transfer rates and dilutes the recovered solution (Figure 4).

Published Donnan performance is impressive and its resilience to fouling is an attraction in the CR role. However, when the diffusion time (24 hours) and specific membrane area (120 cm²/L of feed) are taken into consideration (Prakash and Sengupta, 2003), the cost benefit of the process is questionable (Keeley et al., 2012). Reasons such as these have limited the practical application of the Donnan process (Strathmann, 2010), particularly in the recovery of ions from concentrated wastes (Wang et al., 2010). Slow kinetics can be compensated for by using greater membrane area contact time but this requires greater quantities of expensive membranes. Diffusion rates will also decline as the process reaches equilibrium. This requires a balance to be struck between recovery yield (i.e. acid requirement) and specific membrane area requirements.

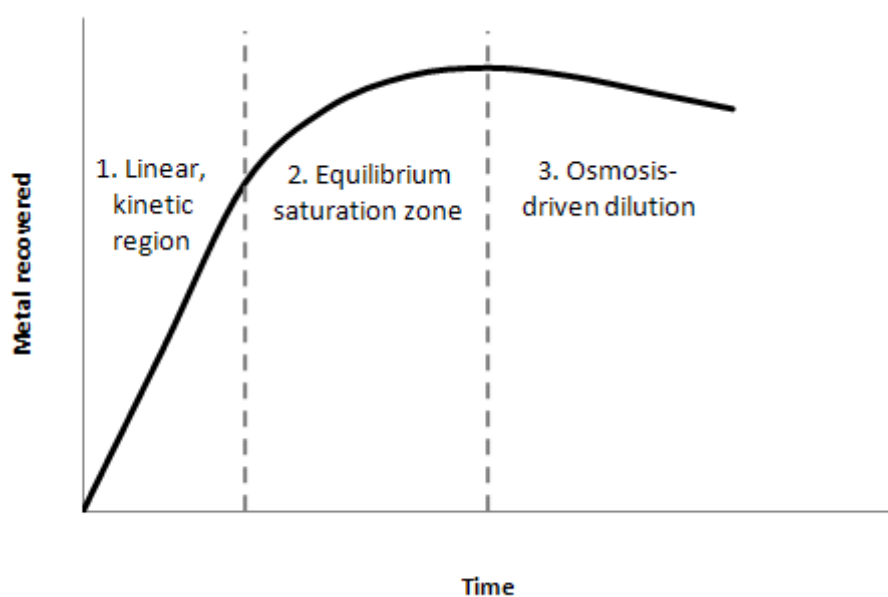


Figure 4: Kinetic regions that occur as batch Donnan dialysis progresses (adapted from Prakash and Sengupta, 2004).

Membrane functionality is important, with superior diffusion rates for aluminium recovery (Table 5) demonstrated by homogeneous sulfonated membranes. These membranes have demonstrated rates 5 to 10 times greater than heterogeneous alternatives as well as being 30 times more selective for Al (Prakash and Sengupta, 2005). This was attributed to Nafion membranes being

more hydrophilic and the even distribution of sulfonate ionogenic groups, throughout the membrane cross-section, allowing more direct diffusion paths for ions (Prakash and Sengupta, 2005). This effect was less pronounced in a similar study investigating the relative performance of heterogeneous and homogeneous membranes for the Donnan transport of Cr^{3+} ions (Table 5) due to the importance of other factors such as ion characteristics, membrane thickness and hydrophilicity. The four-fold variation of diffusion rates for aluminium and ferric ions diffusing through the same membrane (Table 5) contradicts the theory that valency is the principle rate-determining characteristic for interdiffusion rates (Prakash and Sengupta, 2003). The practical outcome of this difference is a further increased specific membrane requirement for ferric coagulant recovery over alum.

Table 5: Normalised Donnan dialysis initial flux performance comparison for trivalent metal recovery with a 1M sulfuric acid sweep solution

Membrane Type	Functionality or other variable	J_{sat} (eq/m ² /s) over initial 4hr with 1 M H ₂ SO ₄ sweep solution	Ion	Reference
DuPont Nafion 117	Homogeneous sulfonated PTFE	8.27×10^{-04}	Al ³⁺	Prakash and Sengupta, 2003
DuPont Nafion 117	Homogeneous sulfonated PTFE	2.13×10^{-04}	Fe ³⁺	
DuPont Nafion 117	Homogeneous sulfonated PTFE	8.46×10^{-04}	Al ³⁺	
Sybron Chemicals Ionac MC 3470	Heterogeneous sulfonated (reinforced) polymer	7.34×10^{-05}	Al ³⁺	Prakash et al., 2004
Gelman Sciences ICE-450 SA ₃ S	Homogeneous sulfonated polyester	2.25×10^{-05}	Cr ³⁺	Tor et al., 2004
Gelman Sciences ICE-450 SA ₃ T	Heterogeneous sulfonated polyester	2.07×10^{-05}	Cr ³⁺	

A study of divalent magnesium and calcium recovery from lime softening sludge, using Nafion 117 homogenous membrane, showed notably lower flux performance over the initial four hours, at just 2.31×10^{-5} eq/m²/s (Wang et al., 2010). This may be due to limiting mass transfer, caused by the feed solution being almost four times more dilute than other experiments using the same

membrane (normalised in terms of eq/L; Prakash and Sengupta, 2003) or the higher stability of divalent organic complexes over trivalent (Elliott et al., 1990). These effects were sufficient to offset the hypothesised higher flux of the lower valence magnesium and calcium species, in comparison to aluminium and ferric, due to the divalent species having less electrostatic attraction to the counter ions within the membrane, allowing for more labile transfer (Tor et al., 2004).

Because the direction of acid transport is in the opposite direction to recovered metal, DD will generate an acidified waste stream at the end of the recovery process. At the point that the recovery system reaches thermodynamic equilibrium the aluminium depleted feed solution is highly acidified, requiring neutralisation prior to disposal. Like all selective recovery processes, there are significant issues regarding the degree of contamination and coagulant concentration: both must be addressed for reuse. Although DOC transport is minimal with DD, even levels as low as this may be sufficient to fail coagulant quality regulations or THM consents.

Selective anion adsorbents may be a necessary augmentation to ensure that the product is acceptably pure. This would add another level of complexity to the process but, since only a small amount of NOM is required to be removed, the adsorbent would require less frequent regeneration compared to less-selective separation processes. Furthermore, while DD facilitates metal ion concentration, typically by a factor of three (Prakash and Sengupta, 2003), it still does not match the concentration of commercial coagulants of ca. 40,000 mg/l as Al for alum. This dilution may help ensure better distribution of coagulant, particularly with static mixers but would impair the ease of handling and transport and must be considered before full-scale implementation.

DD also shows potential to recover acid from the RC stream and the wasted feed stream. Using an anion-selective (but proton permeable) membrane to separate the impure acid solution from a solution of deionised water creates a sulfate concentration gradient and anion movement across the membrane. To maintain electroneutrality across the membrane, protons diffuse through the

membrane via a tunnelling mechanism. This has been used to recover sulfuric acid, at yields of 85% and concentrations of 4 mol/L as H^+ , from a feed of 4.78 mol/L H^+ (Xu et al., 2009b). In this example, leakage of the contaminant ion, (Al^{3+}) was less than 5%. If applied to acid recovery from WTRs, contaminant leakage may be significantly higher since charge rejection of anionic organics from the anion-exchange membrane would be minimal. There is also a significant issue surrounding progressive dilution of acid, due to recycle losses. However, just as in CR, this can be offset by supplementing with fresh acid.

2.4.2.4 ELECTRODIALYSIS

Thermodynamically driven ion exchange processes such as Donnan membranes, LIE and resins show potential for CR because they are charge-selective and resilient to fouling. However, the kinetics of exchange decrease as thermodynamic equilibrium is reached, making high yields and fast kinetics mutually exclusive. To compensate for this, greater media volumes or membrane areas are required to provide sufficient capacity at full-scale. Active processes such as electrodialysis (ED) may allow the same advantages of ion-selective processes but greater control over the process kinetics and process costs, by being able to control kinetics independently of yields (through the applied potential).

ED has not been tested for CR but is a well-established concept in the recovery of cations (nickel, copper, aluminium and acid) in the electroplating and anodizing industries (Lancy and Kruse, 1973; Itoi et al., 1980; Franken, 2003; Agrawal and Sahu, 2009). ED has been employed to create closed-loop electroplating processes which offer similar reductions in waste and chemical requirements to CR. To do this, electric current is applied across stacks of cells containing acidified solutions of metals, forcing the movement of cations through cation-selective membranes towards the anode and away from immobile and anionic contaminants (Figure 5).

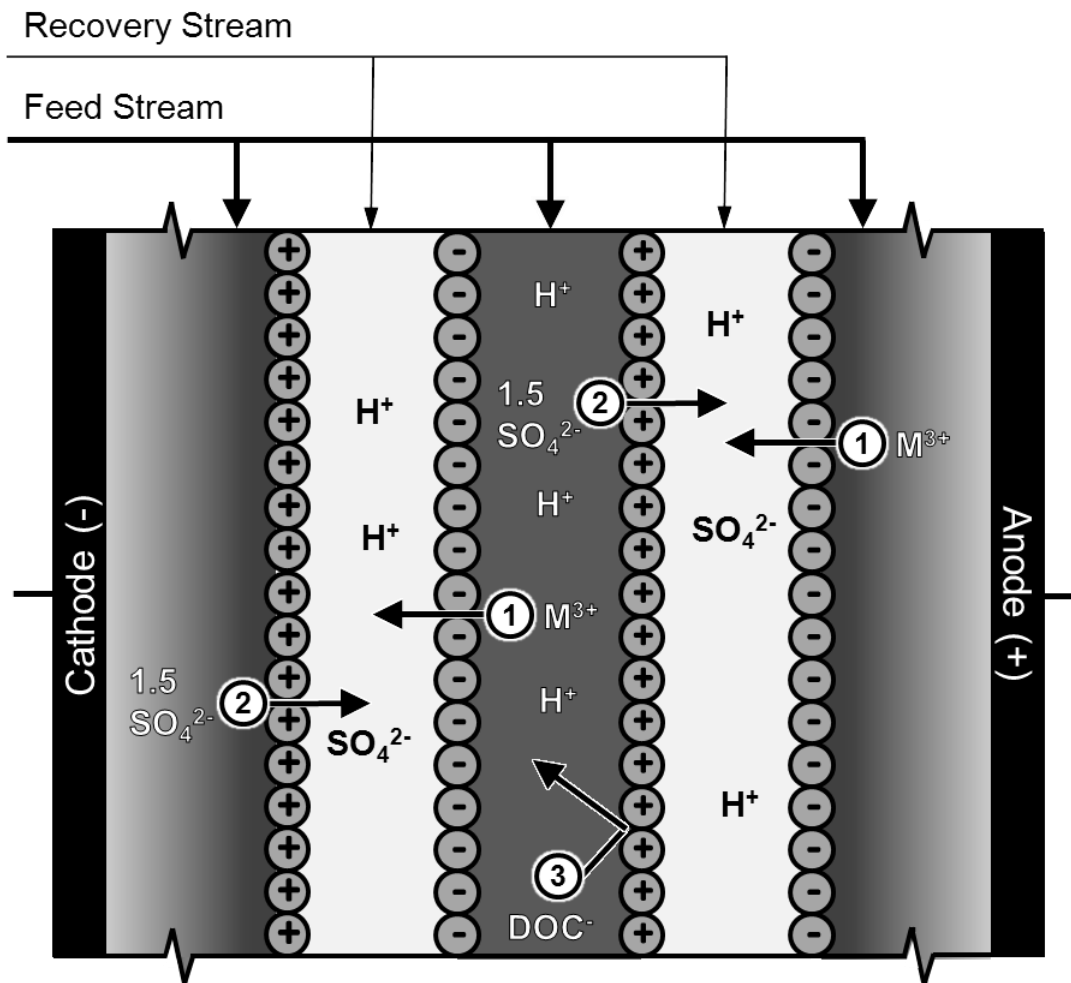


Figure 5: Theorized electrodialysis recovery of trivalent coagulant metals

1. Trivalent coagulant metals move from the acidified feed, towards the cathode, until their path is blocked by an anion selective membrane
2. Acid /coagulant counter ions move from the acidified feed, towards the anode, until their path is blocked by a cation selective membrane
3. Despite having the correct charge, organic material in the feed is rejected by the membrane due to its bulk

Metal recovery yields in excess of 90% have been reported using ED, though recoveries diminish with increasing feed concentration (Itoi et al., 1980). Concerns arise over membrane fouling due to organic compounds and anode scaling due to aluminium hydroxide. However, ED reversal, pulsing and cleaning have been implemented to control fouling when analogous streams are

treated with ED (Lee et al., 2002; Lee et al., 2003; Strathmann, 2010). Using these methods, successful ED treatment of aluminium-containing solutions has been documented, although with a focus on acid rather than metal recovery (Franken, 2003). ED-based processes have also been used to de-salt organic-rich fermentation broths, demonstrating that the problem of organic fouling can be managed (Lee et al., 2003).

The fundamental challenge for ED recovery is energy consumption. If fouling can be controlled, the high concentrations of ions will reduce the resistance of the WTR stream compared to conventional ED feeds, such as brackish water. However, a far greater amount of ions require transportation for ED applied to WTR and, as Faradaic principles govern the process, the minimum electricity requirement and cost can be accurately predicted (Audinos, 1986). Using these principles and chemical prices, the overall cost of CR using ED can be calculated. For alum the cost of recovery equals the value of coagulant recovered and for ferric the cost exceeds the value recovered (Keeley et al., 2012). Selectivity and RC purity are likely to be comparable to those of dialysis processes that use similar ion-exchange membranes (Prakash and Sengupta, 2003). The combination of a predictable high energy demand and the unknown extent of fouling and scaling have left ED CR at the conceptual stage of development.

Acid recovery is readily achievable with ED, with the use of less porous ion-exchange membranes allowing rejection of multivalent cations but permeation of protons. When ion complexation is minimised, acid recoveries above 90% can be achieved (Pierard et al., 2002). ED acid recovery has also been achieved simultaneously with metal recovery, with acid yields of 66-72% and nickel losses of 4% (Xu and Yang, 2004). However, acid recovery from CR residuals is subject to the same potential problems as CR itself, i.e. fouling, scaling and energy demand.

2.5 COAGULANT RECYCLING IN WASTEWATER TREATMENT

As previously highlighted, coagulant reuse in potable treatment is challenged by numerous regulatory and economic issues. Although coagulant dosing in WW treatment is less prevalent than in potable water production, demand is growing in response to tighter final effluent consents and it remains a practical target for RC reuse. The absence of DBP limits and less stringent heavy metal regulations reduce the requirement for coagulant-contaminant separation, commensurately lowering both recovery costs and the risk of failing quality regulations.

Coagulant can be recovered for reuse from both WW and potable sludges. Alum was recovered from primary WW sludge with a yield of 70% at a pH of 2 (Jimenez et al., 2007). The RC not only performed comparably to fresh coagulant (when supplemented with 30% fresh material) but also reduced residual sludge volume and mass by 45% and 63% respectively. The study was only partly successful in its aim to inactivate helminith ova in the insoluble sludge fraction to enable the residual sludge to meet agricultural standards for application to crops for human consumption. For this, further stabilisation with lime would be required (Jimenez et al., 2007).

The acid requirement was found to correspond to the stoichiometric dose. Addition of acid beyond this solubilised no more aluminium. This is contrary to what might be expected for WW sludge which has higher alkalinity levels (Slechta and Culp, 1967) but was explained by a low WW pH of 5, indicating minimal buffering capacity (Jimenez et al., 2007). The study also found that increased solids above 5.9% in the sludge feed led to reduced recovery efficiencies at the mixing conditions and duration tested. This suggests that mass transfer becomes a key consideration when acidifying thicker sludges. This parameter will need to be balanced with the cost of transporting WTR, which would benefit from the highest possible sludge thickness to minimise volume.

Other studies have examined the effect of dosing acidified and raw WTRs to WW. Jar tests examining total orthophosphate removal from a synthetic WW

containing 10 mg/L as P required a dose of 75 mg/L Al with unacidified alum sludge and only 15 mg/L Al with fresh alum. The same dose of unacidified sludge also removed 40-60% total P and 35-40% COD from two different municipal WWs (Table 6). This performance data could be used to estimate the benefit of direct WTR disposal to sewers, which is poorly documented but practiced widely (Figure 2).

Table 6: A comparison of commercial and recovered coagulants in wastewater treatment

Sludge type and dose (mg/L as Al or Fe)	Alum			Ferric		
	Non-acidified	Commercial	Recovered	Commercial	Recovered*	
4	75	30	30	30	30	
Removals						
SS (%)		97	97	90	25 (67)	
COD (%)	53	35-40	62	62	48	55
Soluble P (%)			96	99	95	81 (66)
Total P (%)	95	40-60				
Reference	Xu et al., 2009a	Georgantas and Grigoripoulou, 2005	Parsons and Daniels, 1999		Parsons and Daniels, 1999	

* Parenthesis denote removals when neutralised

While dosing of unacidified WTRs enhances treatment, prior regeneration of the constituent coagulants with acid improves removals of solids, COD and P by a further 20-30% at much lower doses (Table 6). Under these circumstances, recovered alum matches commercial alum performance at equal doses, in terms of removal of solids, COD and P (Table 6). This performance was maintained for the coagulant recovered from the WW sludge even after four cycles (Xu et al., 2009a). The same study reported that potable sludge provided no performance advantages over that from WW, such that transporting of sludge from potable to WW sites could be unnecessary, although doing so would provide a plentiful source of RCs. Recovered, unfiltered ferric coagulants compared less favourably with commercial equivalents, particularly for solids removal. Filtering the recovered ferric coagulant improved solids and COD removal (the latter to beyond commercial coagulant levels) but to the detriment of P removal (Parsons and Daniels, 1999; Table 6).

CR in WW shows great promise by offering greater economic rewards than bulk reuse strategies, by reducing demand for fresh coagulant. Although purification stages have been shown to improve RC performance, the less strict WW quality regulations permit less expensive, unselective technologies such as simple

acidification. Further work is required to ascertain the effects of sludge acidification on anaerobic digestion, since biogas production and energy offsetting are key objectives in WW treatment and their potential impairment by CR would jeopardize its acceptance by the industry. The particular concerns are the low pH (and possible requirement of neutralisation) and the accumulation of heavy metals and aluminium, which have been shown to potentially inhibit anaerobic digestion (AD) (Chen et al., 2008). Using recovered potable coagulants in WW treatment would negate the need to acidify WW sludge and may prevent many of these potential problems for AD. However, even if CR is successful in the context of WW, it would not fully solve the problems of coagulant demand in potable treatment.

2.6 DISCUSSION

There is a wide range of technologies available that may be considered for CR, each with advantages and disadvantages, as highlighted by SWOT analysis (Table 7). Most of these are capable of consistently recovering >70% of coagulant metals and reducing sludge volumes by 60%. These levels of recovery performance would allow significant improvements to water treatment sustainability and partial fulfilment of many of the principles of green chemistry, as set out in the introduction (Anastas and Warner, 1998). CR technologies broadly fulfil these principles in terms of waste reduction, atom economy and a movement towards using coagulants as non-consumable catalysts. The key shortfalls of CR in these terms are: incomplete recovery (~30% is a loss), the use of concentrated acid, electricity usage and the risk of elevated DBPs. Reuse of WTRs in WW treatment could nullify many of these shortfalls, including use of acid but at the cost of less complete atom economy and recycling efficiency.

Table 7: A performance summary and SWOT analysis of key coagulant recovery options

Recovery approach	Typical Recovery performance			Strengths	Weaknesses	Opportunities (common to all)	Threats (common to all)	Reference
	M ³⁺ yield (%)	M ³⁺ conc. (mg/L)	DOC conc. (mg/L)					
Simple acid solubilisation	90	2500	500	Simple, low-cost, relatively well understood	Non-selective, heavy metal and organic compound contamination	Developments in other fields that can be transferred to CR. Increased commercial coagulant prices Decreased commercial coagulant quality Increased landfill costs More stringent landfill regulations	Increased acid and alkali costs relative to commercial coagulants More stringent treated water and coagulant quality regulations Competition from alternative reuse options Diminished raw water quality placing greater stress on metal-contaminant separation processes	Saunders and Roeder, 1991; King et al., 1975.
Simple alkali solubilisation	80	950	Higher than acid	Simple, rejects heavy metals	Higher cost, specific to alum, low recovery concentrations, worse DOC contamination			Masschelein et al., 1985; Isaac and Vahidi, 1961.
Ultrafiltration	80	560	75	Relatively selective, low cost and well understood technology	Considerable organic compound permeation and fouling			Lindsey and Tongkasame, 1975
ReAl process	85	12,500	<2	Capable of recovering very pure and concentrated alum	Multi-stage approach elevates costs and complexity			Ulmert and Sarner, 2005
Liquid ion exchange	90	30,000	-	Allows high concentrations to be achieved in the stripping stage, quite selective	Risk of toxic solvent carryover, and process complexity			Westerhoff and Cornwell, 1978; Cornwell, 1979
Cation exchange resins	95	5000	-	Capable of high yields and purity	Regeneration is inefficient and costly. Problems with scale-up			Petruzzelli et al., 2000

Anion exchange resins	90	-	60% removal	Potential to reduce organic contaminant levels in other processes	Inadequate performance to stand alone, adds complexity when used as a polishing stage			Anderson and Kolarik, 1994
Donnan membranes	80	4700	17	Robust performance in terms of purity and concentration	Slow kinetics require large membrane areas or contact time, harming process economics			Prakash and Sengupta, 2004
Electro-dialysis	-	-	-	May be able to accelerate the slow kinetics of other ion exchange membrane processes	Poorly understood in this role and likely to face problems with fouling, scaling and high energy demand			-
Dosing to WW	-	-	-	By-passes many of the quality issues faced in potable CR while still yielding significant treatment benefits	Fails to solve the problem of coagulant demand at potable works. RC transport between sites is dependent on proximity			Babatunde and Zhao, 2007; Parsons and Daniels, 1999

The recovery technologies investigated have reported a wide range of selectivity and process complexity. Ion-exchange has shown the highest degree of RC purification but at a cost that is currently unrealistic at full-scale (Table 8). Pressure-filtration recovery of alum shows potential to reduce operating costs when compared to conventional practice but is yet to demonstrate adequate selectivity. Even the most selective technology, the Donnan membrane process, has been shown variable purity in response to differing feed sludge DOC loadings. Reliance on a single separation stage leaves RC purity vulnerable to variability of raw water quality. This has been alleviated by multi-stage separation (such as the *ReAl* process) but to the likely detriment of process economics, which are already critical for more basic CR technologies (Table 8). Furthermore, technology transfer into CR is restricted by the low value of ferric and alum compared to the high-value metals commonly recovered in other industries using similar processes.

Although the approaches are diverse, the common challenge for potable reuse is achieving a high level of contaminant rejection without inferring excessive costs. The literature has shown (highlighted in Tables 7 and 8) that these two aims are mutually exclusive, with current prices and technology. It is only when recovery costs change, in relation to coagulant prices, that potable reuse of RC can be considered a viable option.

Table 8 A Comparison of operating costs for key coagulant reuse options against conventional coagulant dosing practice

Coagulant operating costs as £/1000 mols of M ³⁺ recovered or purchased	Pressure filtration	Donnan dialysis	Electro-dialysis	Dosing to WW	Conventional practice	
					Alum	Ferric
Solubilisation acid	20	20	36	20		
Recovery chemicals (cleaning chemicals ^a ; dialysis acid)	2	20	2			
Electricity	3		8			
Membranes^b	26	34	11			
Landfill gate fees^c	10	10	10	10	20	20
Inter-site transport^d				20		
Commercial coagulant					60	35
Total	61	84	67	50	80	55

Adapted from current prices and published performance data as listed in Keeley et al. (2012), unless stated otherwise:

- a) Estimated to be 3% of total operating costs (Verrecht et al., 2010)
- b) Considered as a consumable
- c) Including neutralisation to moderate pH, if required. Excluding transport costs.
- d) Based on transporting 20% DS WTRs to a WWTW 20 miles away, in 30 tonne loads, using fuel consumption data from Coyle (2007)

Available literature for CR has also shown a disparity between apparent promise in short-term lab-scale trials and process reliability at full-scale, with full-scale CR's initial successes being better documented than ultimate failures. The few available accounts of failed full-scale CR operation give only a qualitative indication of the circumstances that lead to process failure (for example diminished raw water quality, problematic sludge handling and marginal economic benefit). Although of some use, the lack of quantitative data highlights a knowledge gap that must be filled before any CR technology can be operated reliably and safely at full-scale. It may be that the cause of failure in RC quality is discrete, predictable and detectable. For instance, if raw water DOC or heavy metal loadings exceed a certain level, CR systems could then be paused, mitigating the risk of quality failures. This more reactive approach is likely to be more economic than investing in CR capable of meeting quality standards under all conditions.

While important, CR and engineered solutions are not the only means for improving coagulant management: supply-side forces must be understood, anticipated and mitigated. The widespread use of coagulation in water treatment has made the industry reliant on the supply of coagulants. The dynamics of coagulant supply are complex and often poorly understood by water utilities. Previous near-misses in supply integrity and price rises have not been predicted by the utilities (Henderson et al., 2009). A significant attraction of CR is its potential to reduce dependence on external market forces, though there will always be a requirement for some fresh coagulant.

Commodity chemicals such as alum and ferric are often sourced from only a few distributors, weakening the utilities' market position. On an international scale, coagulant supply and prices are affected by global economic conditions. As shown in a comprehensive study by the Water Research Foundation (Table 9), coagulant supply is dependent on the supply and prices of many other commodities (Henderson et al., 2009). The study notes that many raw chemicals involved in coagulant manufacture are demanded by competing industries which often dwarf the market share and power of the water industry

(e.g. manufacturing and construction for iron and aluminium, and the production of fertiliser uses 60% of the total of sulfuric acid produced). The impact of these dominant and competing industries on commodity markets is passed onto the market price for coagulants, causing them to inflate with global economic growth. This is particularly true for fuel prices and transport costs, which for coagulants bearing a low value to mass account for a significant contribution to the overall cost.

Table 9: Coagulant Markets and Price Dynamics

Coagulant	North American market share (%)	Average US price increase 2008-09 (%) ¹	Average UK price increase 2008-09 (%) ²	Cost Drivers (coagulant type affected, in parenthesis)
				Fuel (universal)
Aluminium coagulants	20-25	14-51	5-18	Bauxite (alum) Sulfuric acid (alum) Aluminium trihydrate (PACl*) Aluminium metal (ACH†) Hydrochloric acid; chlorine (PACl, ACH)
Ferric Chloride	10-15	22	N/A	Scrap steel/pickle liquors Hydrochloric acid; chlorine
Ferric Sulfate	10-15	40	13	Sulfuric acid Iron ore

Adapted from: Henderson et al. (2009); ¹ Association of Metropolitan Water Agencies (AMWA) survey with 42 responses from water utilities; ² AMWA survey with 7 responses from water utilities (Walsh, 2009). *Poly aluminium chloride, †Aluminium chlorohydrate

Other coagulant raw materials are sourced as by- or co-products from other processes, further diminishing the utilities' market control. Metal chloride coagulants are particularly dependant on the availability of waste pickle liquors from metal finishing industries. Hydrochloric acid is another key commodity for coagulant production and its price is a function of chlorine. The supply of chlorine is related to the demand for its co-product sodium hydroxide in the energy-intensive chlor-alkali process (Henderson et al., 2009).

Complex and inter-linked markets are a challenge to predict accurately but the disruption caused by supply fluctuations can be alleviated by flexible usage strategy. Reliance on a single coagulant type or supplier can leave water utilities vulnerable to external market forces, with shortages posing a risk to water treatment capacity, quality and cost (Henderson et al., 2009). As the changes in commodity prices illustrate, all commodities have experienced price inflation over the last 30 years but some more than others (Table 10).

Long-term flexibility in coagulant dosing strategy has allowed water utilities to avoid the most inflation-afflicted commodities by switching coagulant types. This is demonstrated by the producer price index for water-treating compounds rising significantly less than inorganic chemical and metal price indices would suggest. CR would allow even greater flexibility and a shift of reliance from coagulants to sulfuric acid, which has historically been less prone to inflation (Table 10). Increasing demand for coagulants, in response to more widespread restrictions on final effluent consents for P, is likely to put further inflationary pressure on prices in Europe, in the coming years (European Commission, 2000). Transporting WTRs to WWTWs for P removal would offset coagulant demand, without having to negotiate the stringent DBP regulations of potable reuse. This will reduce costs (Table 8) and secure fresh coagulant supply for the role its purity is most valuable in: potable treatment.

Table 10: U.S. Producer Price Indices (PPI) for Commodities Related to Water-Treatment

Commodity	Base year (PPI=100)	PPI in January 2012
All industrial commodities	1982	201
Water-treating compounds	1985	191
Sulfuric acid	1987	165
Petroleum products, refined	1982	294
Basic inorganic chemicals	1982	339
Iron and steel	1982	257
Non-ferrous metals	1982	254

Adapted from: Bureau of Labor Statistics (2012)

When discussing price changes, it is also important to remember the relative volumes of chemicals used. For CR, the cost of sulfuric acid required to regenerate coagulant, in relation to the cost of equivalent virgin coagulant, is between 30 and 60% for alum and >60% for ferric (Keeley et al., 2012) – demonstrating the impediment to CR implementation at full-scale by the relatively low cost of coagulant (USEPA, 2011). The development of novel, high-performance zirconium-based coagulants (Jarvis et al., 2012), with increased value relative to recovery costs, may improve the economics of CR.

A holistic approach is also required when considering the CR residuals. Acid recovery and recycling would reduce waste acidity, allowing easier disposal and reduced demand for virgin acid and reducing process costs to help drive CR towards better fulfilling the principles of green chemistry. In pure economic terms, acid recovery alongside CR appears to be highly beneficial, though acid recovery is itself subject to efficiency limitations. As with CR, acid recovery operations add complexity and capital costs that will be further obstacles to CR implementation.

Potable regulations will play an important role in the success and failure of CR for reuse. British Standards have been developed with commercial coagulants in mind, leaving the targets for CR purity uncertain. The USEPA approach of allowing no more than a 10% contribution from treatment chemicals to regulated

parameters seems more pragmatic. If a low level of DOC contamination in RC proves to have no effect on treated water quality, a regulatory focus solely on final treated water quality may encourage CR. Current standards allow an insufficient margin of error for existing CR technologies, making the risks of failure outweigh the benefits in cost savings.

However, it would be naïve to assume regulations will change to facilitate the potential sustainability benefits of CR. Public health and trust are the foremost priorities of potable treatment and quality regulations are designed to enforce this philosophy. While water utilities are obliged to minimise costs and protect the environment, these cannot be at the expense of risk to public health. Only a few of the many known DBPs are currently regulated and more comprehensive regulations are expected in the future. This implies that CR processes must be developed to not only offer better value than conventional coagulation practice but also to offer consistently better treatment quality. The extent to which RC contaminant levels and treated water quality are linked must be determined. A thorough understanding of this relationship will allow the minimum recovery cost to be balanced with the requirements of modern potable treatment.

Coagulant reuse strategies besides potable treatment should also be considered. While direct recycling of coagulant from WTRs for potable treatment may be the most complete form of reuse, the economic implications of meeting regulated quality standards currently make non-potable reuse of RCs and WTRs more achievable. In this respect, dosing RC at WWTWs seems particularly promising in the short term, subject to favourable logistical conditions. Such practices would allow sustainable disposal of WTRs and reduce fresh coagulant demand for WW treatment but still fall short of reducing net-chemical demand in potable treatment itself.

2.7 CONCLUSIONS AND RESEARCH NEEDS

Currently, potable reuse of RC is not at a stage where it can be implemented at full-scale. Its ability to recover coagulant at sufficient purity and costs has been demonstrated individually with different technologies but not simultaneously. Current regulations and prices continue to make the risk of implementing CR outweigh the potential benefits; fresh coagulants remain the best-value, lowest-risk solution. If the economics and selectivity of recovery can be improved or if market forces increase the cost of coagulants, in relation to recovery costs, then it may become viable. Research is required in the following areas to better understand and mitigate the process costs and risks:

- Effective acid recovery
- Improving ion exchange performance; in terms of exchange rates and selectivity
- The potential and costs of successive polishing stages, after less selective processes such as pressure filtration

Holistic research approaches will also improve the viability of CR for potable reuse:

- Identifying the impact of site raw water characteristics on CR quality
- Negotiation with regulators with regard to RC and their requirements for coagulant purity or actual impact on treated water quality

In contrast, the application of RC in WW shows immediate promise. While it does not fully meet the ambitions of green technology and zero net chemical usage in potable treatment, it does provide a disposal route for WTRs and reduces external demand for coagulant (which will help secure coagulant supply and prices for potable treatment). The comparatively lenient requirements of WW treatment allow non-selective and frugal recovery methods, minimising regulatory and economic risks. Provided logistical conditions are favourable (which must be verified on a case-by-case basis) it is advisable that this is the focus of future research and trials. The key research needs in these terms are:

- Ascertaining the optimum logistical configuration to transport and acidify WTRs to WWTWs
- The cost benefit of acidifying WTR prior to dosing to WW
- The impact RCs have on downstream WW processes, in comparison to commercial alternatives. There are specific concerns with regard to their effect on AD biogas production, metals loadings in digestate and residual metals in final effluent

This study has systematically examined the aims and benefits of coagulant recovery, against the technological and economic environment the water industry currently faces. This has allowed the limitations of CR to be identified and thus the reuse strategy that offers the greatest benefit, in terms of green technology, economics and operational risk.

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CHAPTER 3

AN ECONOMIC ASSESSMENT OF COAGULANT RECOVERY FROM WATER TREATMENT RESIDUALS

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3 AN ECONOMIC ASSESSMENT OF COAGULANT RECOVERY FROM WATER TREATMENT RESIDUALS

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ABSTRACT

Coagulant recovery from waterworks sludge for reuse is a key option towards the reduction of chemical usage in the water industry. Whilst this concept is not novel, process economics and recovered product quality issues have limited its implementation. Whilst ion selective membranes have recently been shown to satisfactorily address the latter, economic feasibility remains a key issue which has been largely overlooked.

This study used empirical data taken from bench-scale tests of coagulant recovery using Donnan dialysis (DD) with bulk chemical prices to determine the operational expenditure (OPEX) for full-scale recovery. Calculated values were compared with existing coagulant dosing procedures, as well as potential alternative recovery technologies based on electrodialysis (ED) and ultrafiltration (UF), to determine the cost benefit.

It was determined that under current commodity and technology prices, coagulant recovery by DD offers no cost benefit in comparison to conventional practice. Process improvements, such as incorporating acid recovery, identifying alternative waste disposal routes and improving membrane performance, can significantly increase economic viability. UF was shown to provide OPEX reductions of around 40% when compared to conventional practice, and ED found to be cost neutral. None of the assessed technologies are currently able to offer cost benefit for ferric coagulant.

3.1 INTRODUCTION

Over 70% of water treatment works (WTWs) use coagulant-enhanced solid-liquid separation in their flowsheet for water purification (Cornwell and Westerhoff, 1981) and the process is likely to remain an essential water treatment process for the foreseeable future. It is therefore important that the management of chemical usage and resultant sludge production is continuously improved. Large quantities of coagulants are used in the water industry. For example, >326,000 tonnes of coagulant is used per annum across water and wastewater treatment in the UK (Henderson et al., 2009) and proportionally large quantities of sludge are produced (>182,000 tonnes as dry solids per annum from UK water treatment; Godbold et al., 2003). On a global scale approximately 10,000 tonnes of waterworks sludge are produced each day (Dharmappa et al., 1997). With increasing demand on the quantity and quality of potable water (Fabrizi et al., 2010), a deterioration in water quality coupled with rising commodity and landfill prices, water utilities are actively seeking alternative coagulant options (Jarvis et al., 2008). A 10% reduction in net coagulant usage across UK water and wastewater treatment would allow annual savings exceeding £2.5m to be made (Henderson et al., 2009), with additional benefits of improved security of supply and reduced environmental impact.

A number of sludge reduction and reuse strategies have been previously considered, offering varying degrees of success (Babatunde and Zhao, 2007). Reuse in bricks and other construction materials have shown no loss in quality but their economics are dependent on their manufacture being close to the source of sludge (Godbold et al., 2003). Reuse applications for the improvement of soil structure and immobilization excess fertilizer nutrients have also been documented (Henderson et al., 2009). Reuse of sludge in wastewater treatment for phosphorus adsorption, coagulation, sewage sludge co-conditioning and wetland media, have all been successfully trialled but progression to full-scale implementation remains limited (Henderson et al., 2009). The majority of water treatment sludge is still disposed to landfill (UKWIR, 1999) and to sewers, providing incidental benefits to downstream

wastewater treatment (Simpson et al., 2009). More formal reuse in this manner is still under development (Parsons and Daniels, 1999; Georgantas and Grigoropoulou, 2005; Babatunde et al., 2009).

Whilst sludge reuse strategies and reductions of waste to landfill are undoubtedly of benefit, the applications are often dependant on co-operation of external parties and also fail to realise the total value of the constituents within the sludge. A potentially more rewarding approach is recovery and reuse of the coagulant itself, which reduces both the volume of waste requiring disposal (Cornwell and Westerhoff, 1981) and the virgin coagulant demand by 70% (Prakash and Sengupta, 2003). For reuse in drinking water treatment, this requires adequate purification to comply with potable treatment chemical standards without incurring disproportionate costs.

Re-solubilisation of coagulant metals with acid and reuse of the supernatant saw full-scale use in the 1970's but was withdrawn due to concern surrounding its lack of specificity (Prakash and Sengupta, 2003). Whilst acid is able to solubilise the coagulant metal precipitates in the sludge, many other sludge contaminants are also dissolved at low pHs. Of particular concern is the re-solubilisation of natural organic matter (NOM), which may introduce potential disinfection by-product precursors to the water, heavy metals and non-metallic inorganic material (turbidity). This has led to the study of a number of separation technologies applied to the acid eluate in order to remove these contaminants. These processes can be broadly categorized into charge and size exclusion. Ion exchange liquids (Sthapak et al., 2008), resins (Petruzzelli et al., 2000) and membranes (Prakash and Sengupta, 2003), as well as pressure driven membranes are all theoretically applicable to this role. Of the separation technologies considered, the Donnan dialysis (DD) membrane process (Prakash and Sengupta, 2003) has shown the most potential.

Research has shown the DD to be capable of recovering a relatively pure coagulant solution (5500 mg/L aluminium and 3.5 mg/L dissolved organic carbon, DOC) from acidified waterworks sludge (2400 mg/L aluminium and 200 mg/L DOC), without membrane fouling (Parsons and Daniels, 1999). Feasibility

studies performed for non-selective acid extraction from water and wastewater sludges (King et al., 1975; Masides et al., 1988) have been positive, and suggest non-selective coagulant recovery to be economically viable for plants of >95 million litres per day (MLD) capacity (King et al., 1975), or offering payback periods of less than 2 years for a 90 MLD plant (Masides et al., 1988). However, these studies are somewhat out of date, with unrepresentative commodity/energy costs, and have ignored the requirement for recovered coagulant quality improvement.

This assessment aims to combine the costs associated with the predicted performance of three prospective coagulant recovery processes with current commodity prices alongside sludge management and disposal costs to provide a cost benefit appraisal for coagulant recovery. The three membrane-based processes considered are DD, ultrafiltration (UF) and electro dialysis (ED) processes.

ED provides an alternative means of extracting coagulant from the organic-rich acidified sludge solution. The technical capability of the technology has been demonstrated in a similar role for recovery of metals from electroplating liquors (Itoi et al., 1980; Pierard et al., 2002), and is widely used to desalt organic-rich solutions (Xu and Huang, 2008). The NOM contaminants have a lower charge to mass ratio than the metal coagulants, such that they would be expected to be retained while the trivalent metal cations would be extracted under the action of the electromotive force (Xu and Huang, 2008). NOM fouling would be expected to be minimal since, as with DD, bulk transport is ostensibly diffusive rather than convective as in a pressure-driven process. Also, the chemical requirements are lower than for DD. Against this, metal hydroxide scaling near the cathode demands control and, most significantly, the process OPEX is constrained by Faradaic principles: the electrical power requirement is proportional to the amount and valency of ions transported.

UF operates by exclusion of the larger NOM contaminant particles whilst selectively permeating the smaller coagulant metal and acid ions. However, lower molecular weight NOM molecules will permeate with the coagulant. As a

classical pressure driven process, membrane fouling by the organic material is likely to be significant (Sengupta and Prakash, 2002). However, membrane bioreactors (MBRs) routinely treat waters of 10 g/L concentration of flocculant particle concentration using coarse ultrafiltration (UF) membranes (Verrecht et al., 2010). In contrast to the DD and ED processes, UF costs are more closely linked to permeate volume than ion concentration (Audinos, 1983). For the relatively highly concentrated ionic solutions involved in coagulant recovery, this would be expected to prove highly advantageous.

Many studies have shown the benefit of diffusion dialysis for acid recovery from electroplating waste liquors (Xu et al., 2009; Luo et al., 2011), including >70% yields from nickel electroplating waste (Xu and Yang, 2004). Such a technology is directly relevant to coagulant recovery since it can be used to offset net acid usage and waste generation (two principal drivers of implementing such a process). The economics of combining upstream acid elution of the coagulant with its recovery using each of the three different membrane separation technologies is considered and compared with costs associated with conventional reagent procurement and waste disposal to sewer.

3.2 MATERIALS AND METHODS

3.2.1 Operating Costs Model

The economic analysis was based on data for a large WTW, treating 200 MLD and generating approximately 100,000 wet tonnes per year of sludge. Published membrane performance data on DD of metal coagulants (Prakash and Sengupta, 2003) was used to determine costs. In the case of UF and ED, no empirically-derived performance data is available for coagulant recovery; conservative performance estimates from published data on relevant applications were used, coupled with standard design calculations. Costs for chemical reagents (acids and coagulants) and disposal were derived from data supplied by UK water utilities and public domain information sources.

Key data included the area-specific rate of trans-membrane diffusion for dialysis, the cell pair resistivity figures and current efficiency for ED, and the permeate flux and energy demand for UF (Table 11). These factors all impact on membrane area requirement, which is also influenced by the percentage conversion per unit time in the case of dialysis. While caution should be exercised when basing a full-scale economic model on lab-derived Donnan data, if intramembrane transport is the rate-limiting step (Prakash et al, 2004), such scaling is justifiable.

Table 11: A summary of the OPEX model components, the key inputs and associated limitations.

Model OPEX Components	Economic Model Inputs	Potential Limitations
Fresh coagulant cost as pure metal	<ul style="list-style-type: none"> Coagulant bulk cost Coagulant bulk concentration Metal recovery percentages 	<ul style="list-style-type: none"> Market fluctuations Different performance at full-scale to lab-scale data
Solubilisation acid	<ul style="list-style-type: none"> Empirical acid : M^{3+} extraction molar ratio Sulfuric acid bulk concentration Sulfuric acid bulk cost 	<ul style="list-style-type: none"> Variable sludge buffering capacity; mass transfer issues Market fluctuations
DD Recovery acid	<ul style="list-style-type: none"> Empirical acid : M^{3+} DD molar ratio Sulfuric acid bulk concentration Sulfuric acid bulk cost 	<ul style="list-style-type: none"> Variable membrane selectivity Market fluctuations
UF Electricity	<ul style="list-style-type: none"> UF specific energy demand per flow Metal content per volume flow Electricity unit cost 	<ul style="list-style-type: none"> Fouling decreasing energy efficiency Market fluctuations
ED Electricity	<ul style="list-style-type: none"> Current efficiency Stack resistivity Faradaic current requirement Electricity unit cost 	<ul style="list-style-type: none"> Fouling induced resistance Non-coagulant ion transport Market fluctuations
Polishing adsorbent	<ul style="list-style-type: none"> Empirical DOC : M^{3+} membrane leakage ratio GAC K value for DOC adsorption GAC cost per weight 	<ul style="list-style-type: none"> Higher DOC carryover at full-scale Poor adsorption at low pHs Market fluctuations
Metal recovery membranes	<ul style="list-style-type: none"> Specific membrane M^{3+} flux M^{3+} flow rate in sludge Membrane cost per unit area 	<ul style="list-style-type: none"> Different performance at full-scale to lab-scale data Market fluctuations
Acid recovery membranes	<ul style="list-style-type: none"> Specific membrane acid flux Acid production rate in acidic residuals Membrane cost per unit area 	<ul style="list-style-type: none"> Reduced performance due to high DOC content Different performance at full-scale to lab-scale data Market fluctuations
Neutralisation and disposal	<ul style="list-style-type: none"> Acid amount in unrecovered residuals Molar ratio of lime : acid for neutralisation Cost of lime Mass of neutralised sludge (at 25% dry solids) Cost of landfill per mass of inert waste 	<ul style="list-style-type: none"> Market fluctuations Ease of thickening Changes due to legislation

The model was developed based on published acid:metal ratio data, as determined for target dissolved metal concentration, required for solubilisation. These ratios were well above the stoichiometric acid dose to ensure the buffering capacity of the sludge was overcome. As the pH and alkalinity content of raw water is subject to variability, the solubilisation acid requirements will vary between different sludges. All OPEX data were normalised against the mass of recovered coagulant as pure metal (i.e. as Al for aluminium or Fe for ferric). Membrane costs were converted to OPEX by assuming an appropriate membrane life based on conservative estimates from similar studies (Choi et al., 2003).

All capital costs, as well as labour, maintenance and transport, were excluded from the analysis. Such elements are highly dependent on site location, management and existing assets and are difficult to generalize. The storage of large volumes of sulfuric acid on-site would require particular consideration in relation to health and safety. The costs of storing acid on-site may be partially offset by also using it to facilitate acid dosing of raw water to enhance coagulation. In the case of the ED analysis, the cost and life of the membranes (Table 12) were taken from published literature and adjusted for inflation (Choi et al., 2003). Previously reported acidified sludge feed concentrations (Prakash and Sengupta, 2003) were used in conjunction with the ED parameters to determine the optimum current density with respect to OPEX (Figure 6), yielding a current density of 25 A/m². It was assumed that the equivalent concentration of extracted acid was the same as that of the extracted coagulant, effectively doubling the current required to recover a given amount of metal. Pumping costs were ignored, since the flow of acidified residuals is small: a 200 MLD WTW generates 50 m³d⁻¹ of acidified residuals.

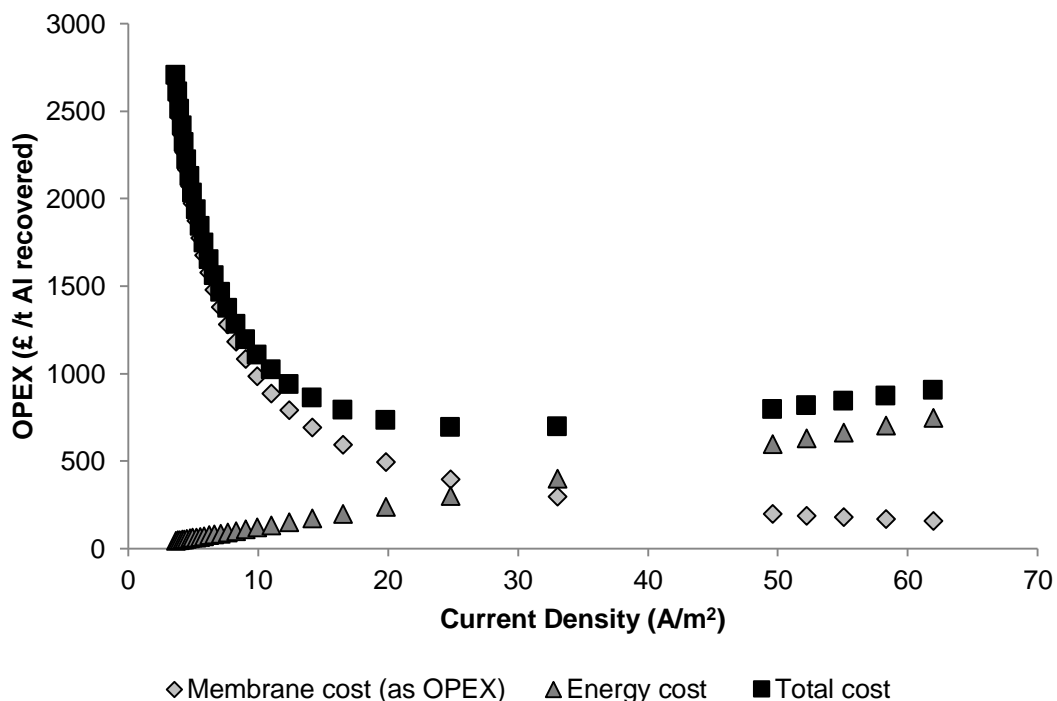


Figure 6: OPEX optimisation for electrodialytic recovery of aluminium from acidified waterworks sludge

UF OPEX data are based on operating parameters for MBR treatment of heavily loaded industrial wastewaters, and are outlined in Table 11. These parameters are based on wastewater MBR mixed liquors of high fouling potential, such as may be generated from landfill leachate or pharmaceutical wastewaters (Judd and Judd, 2010). It was assumed that a crossflow sidestream MBR would be used, providing a flux of 150 L/m²/h at a specific energy demand of 2 kWh/m³ permeate product. The table includes the OPEX for a downstream granular activated carbon (GAC) column, required for adsorbing lower molecular weight organics likely to permeate the UK membrane. The GAC media was assumed to require annual thermochemical regeneration based on the extent of DOC breakthrough shown in previous studies (Prakash and Sengupta, 2003). The actual GAC K value may differ from the assumed value due to the low pH at which adsorption would take place. However, the magnitude of this component is relatively small, so such errors will have a minimal impact on the overall OPEX.

Published acid recovery rates and yields (Xu and Yang, 2004; Xu et al., 2009) were used for the diffusion dialysis through anion exchange membranes has been shown to recover more than 70% of sulfuric acid from acidified electroplating metal liquors at full-scale. The unit cost of these anion exchange membranes was assumed to be the same as those used in ED (Choi et al., 2003). This is justifiable as the same chemical resistance and performance will be required.

Table 12: Summary of main assumptions and inputs to economic model

Parameter	Unit	Value	Reference
Ferric (13.5% as Fe)	£/t	85	1
Alum (4.24% as Al)	£/t	95	1
Sulfuric acid (96%)	£/t	100	1
Coagulant recovery efficiency	%	70	Prakash and Sengupta 2003
Acid recovery efficiency	%	70	Xu and Yang, 2004
ED/acid recovery membranes	£/m ²	120	Choi et al., 2003
Diffusion dialysis SO ₄ ²⁻ transfer rate	Eq/m ² /d	165	Xu et al., 2009
Membrane life, DD	y	5	2
NOM adsorption on GAC, K value	mg/g	20	Karanfil et al., 1999
GAC cost	£/t	3000	1
UF cost	£/m ²	150	3
UF flux	L/m ² /h	150	3
UF specific energy demand	kWh/m ³	2	3
UF metal recovery	%	90	3
Landfill fee (inert waste)	£/t	56	HMSO, 2010
Lime cost	£/t	70	1
Nafion 117 DD membrane cost	£/m ²	530	DuPont
DD M ³⁺ transfer rate	eq/m ² /d	26	Prakash and Sengupta, 2003
Acid extraction dose (DD)	M ³⁺ : H ₂ SO ₄ (mols)	1.8	Jimenez et al., 2007
DD acid dose	M ³⁺ : H ₂ SO ₄ (mols)	1.5	Prakash and Sengupta, 2003
WTW treatment capacity	MLD	200	1
WTW sludge production	t/y	100,000	1
Electricity cost	£/kWh	0.082	EU Energy, 2011
ED current efficiency	%	30	assumption
Membrane lifetime (UF & ED)	y	3	3
Acid extraction (UF & ED)	M ³⁺ : H ₂ SO ₄ (mols)	2.5	Jimenez et al., 2007

¹ Values provided by UK water utilities and chemical suppliers.

² On account of zero trans-membrane pressure and no apparent fouling at bench-scale (Prakash and Sengupta, 2003).

³ Values based on cross-flow MBR treating poor quality industrial wastewaters (Judd and Judd, 2010)

A residual waste common to all coagulant recovery processes is an acidic, coagulant-depleted waste stream. This low-volume stream could be sufficiently diluted by higher volume neutral streams and disposed to the sewer at insignificant cost. A more conservative assumption would be neutralisation with lime, forming a sludge to be disposed at landfill following thickening. Both possibilities were considered in this model, producing profoundly different outcomes with reference to overall process cost benefit. The same issue of sludge neutralisation requirement was cited as a motivation for developing acid recovery from electroplating waste liquors (Xu and Yang, 2004), and this would appear to apply equally to coagulant recovery.

3.3 RESULTS AND DISCUSSION

The output data from the cost model (Table 12) provide an indication of the relative costs of each process component, as well as relative overall costs for each of the seven process options for the two coagulant chemicals. A sensitivity analysis was then conducted to provide the percentage change in overall cost when individual model inputs were changed by 10%, thereby identifying the most cost-sensitive parameters. The five most sensitive parameters and scenarios that would likely trigger their occurrence have been highlighted (Table 13). Accordingly, key factors influencing OPEX for coagulant recovery comprised:

- *Metal coagulant yield.* Assuming all other parameters remain constant, changing the yield of metal will predictably have the greatest effect on overall costs. In reality, greater yields require greater membrane contact time, electrical energy demand and chemicals. Since production rates diminish as yields approach unity, increasing yield may be impracticable or uneconomical beyond a certain point.
- *Acid recovery yield and net usage.* Figure 7 shows a clear distinction in overall costs between processes incorporating acid recovery and those that do not. This is due to a combination of reduced net acid usage as

well as reduced neutralisation requirement and subsequent landfill costs. These make the overall process economics unfavourable when compared to conventional practice. The costs of neutralisation and disposal are more than double those of acid use for metal solubilisation; such costs do not appear to have been considered in previous studies (King et al., 1975; Prakash and Sengupta, 2003)

- *Landfill costs.* If the assumption is made that waste cannot be disposed to sewers and must instead go to landfill, the gate fee becomes a significant cost factor. With UK landfill taxes almost doubling from £56 per tonne in 2011 to £80 in 2014 (HMSO, 2010), this factor is likely to become increasingly important.
- *Acid costs (solubilisation and DD).* Both the amount of acid used and its unit cost significantly influence OPEX.
- *Virgin coagulant costs.* At current coagulant prices, the equivalent cost of alum to ferric is 3 times greater, and thus its recovery is more economically competitive than that for ferric. Compared with conventional procurement and disposal; ED and UF with acid recovery offer equal and reduced OPEX respectively, in comparison to conventional alum dosing. In the case of ferric, only UF with acid recovery offers potentially lower costs. The price difference between fresh coagulant and the materials required for their recovery is obviously key to the future economic viability of coagulant recovery technologies generally.
- *Cost to performance ratio of the ion exchange membranes (where applicable).* The key stage of selective coagulant recovery is the transfer of metal ions across a cation exchange membrane. The rate at which this occurs and the cost per unit membrane area are both key to successful operation. Although resilient, the Nafion 117 membranes have relatively slow metal transfer rates and therefore require large areas of expensive membrane (currently £530/m²). This is a well-documented limitation of DD (Tor et al., 2004; Strathmann, 2010). With acid recovery employed,

cation exchange membranes are by far the biggest OPEX component. Identification of alternative membranes that offer better transfer per cost could drastically improve the economics of the process. Membrane costs are significant for ED but they are less than a third of those used for DD. For the lower-cost membranes employed in UF, the issue of cost to performance is less critical.

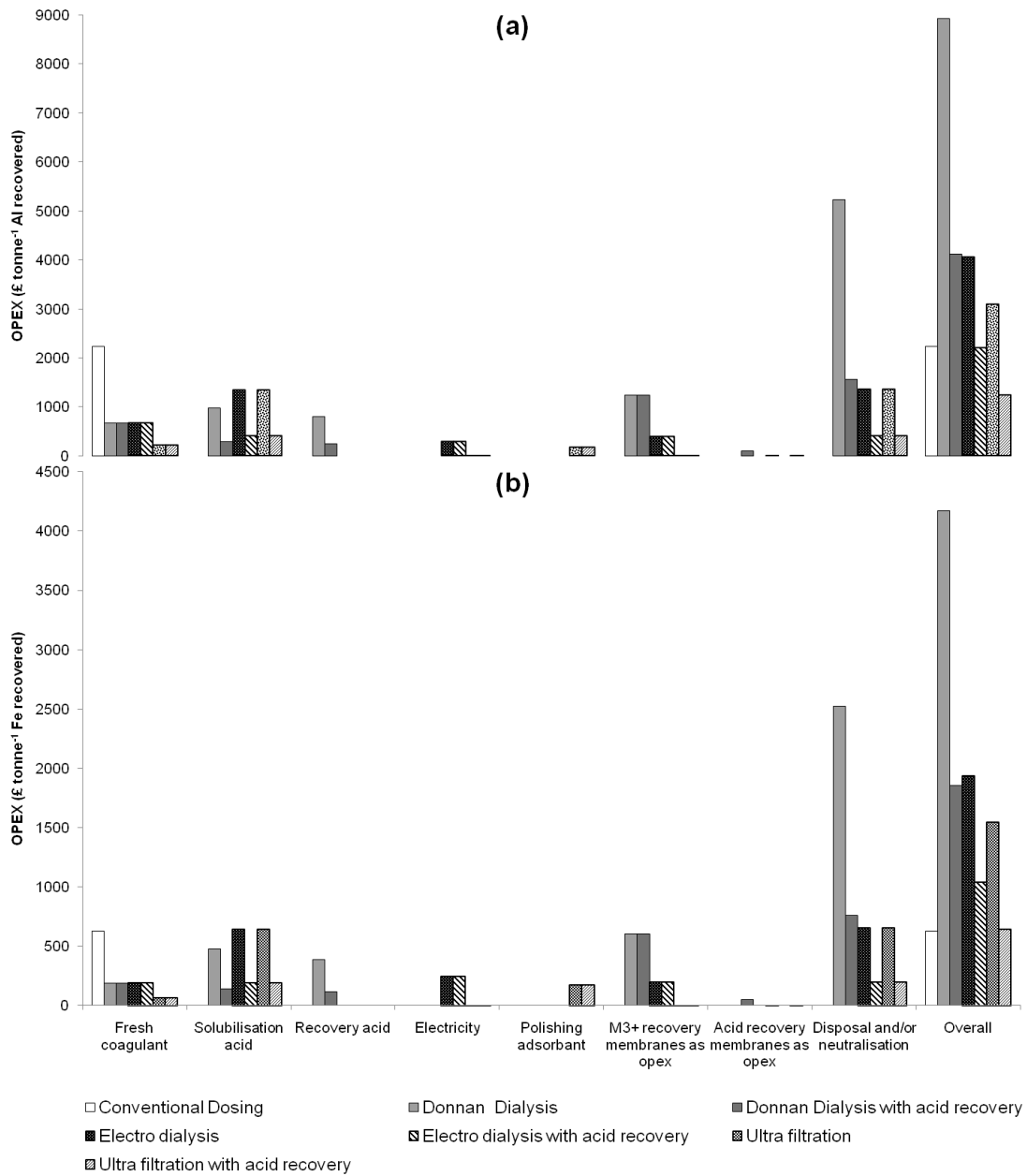


Figure 7: Summary of component OPEX of alum (a) and ferric (b) coagulant recovery.

Table 13: Sensitivity Analysis

Parameter	Possible scenario to instigate a change in parameter value	Range of changes to overall OPEX (%) when parameter is changed by 10%
Metal recovery yield	Improved membrane performance; longer recovery time	7-18
Net acid use/acid recovery yield	Improved acid recovery performance; improved metal recovery yields; reduced sludge buffering capacity; reduced Donnan co-transport of other metals	3-16
Landfill cost	Government legislation and market forces	3-5
Coagulant/acid costs	Coagulant type used, market forces, supplier relations and contract status	1-4
DD membranes	Market forces; competition from other uses (hydrogen fuel cells), reduced manufacturing costs due to higher demand and development	1-3

An additional factor affecting potential cost reductions offered by coagulant recovery is the existing sludge management strategy at the treatment works. Where possible, waterworks sludges are discharged to sewers where they provide benefit through phosphate immobilisation. However, the principle driver for disposal to sewer is to obviate sludge dewatering, transport and disposal to landfill - and so avoid the associated costs. The true costs of sludge treatment and disposal are thus passed onto the wastewater treatment works.

If disposal to sewers is acceptable, in other words the cost of disposing the acidic waste from coagulant recovery is considered to be zero, the impact on overall OPEX significantly changes (Figure 8).

Under these circumstances the benefit gained from acid recovery is reduced but still offers savings. The overall costs of UF and ED with acid recovery are

considerably reduced, while DD approaches parity in comparison to existing coagulant use.

This study is limited to the OPEX of coagulant recovery. When unit cost savings are scaled-up to a 200 MLD site, annual OPEX can be reduced from £1.3m to £0.6m if UF recovery of alum is implemented. After deductions for labour and maintenance, the savings can be used to return the capital investment. The payback period will vary with the original level of investment required and is beyond the scope of this study.

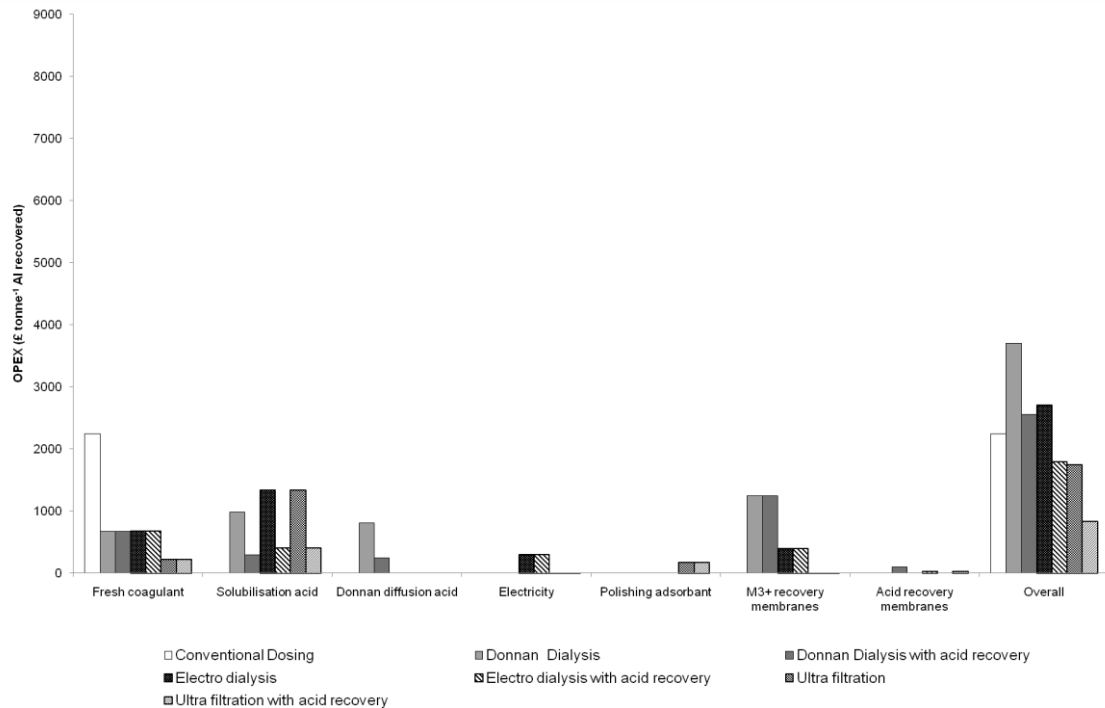


Figure 8: The operating costs of alum recovery if acidified waste streams can be disposed of directly to the sewer.

3.4 CONCLUSIONS

An economic analysis has been conducted, evaluating the operating costs of three selective coagulant recovery technologies. Outcomes of the analysis indicate that the economic viability of coagulant recovery is dependent on a number of external prices, performance criteria and process practices. The overall OPEX is approximately halved when acid recovery is used (as a result of reduced acid use and waste disposal), making its integration alongside any coagulant recovery system mandatory.

Further economic advantages can be gained if an alternative disposal route for the acidic waste stream (or the neutralised sludge formed after lime treatment) can be identified. All of the recovery processes would become more favoured under these conditions, with UF and ED offering significant reductions in OPEX.

The current low value of ferric coagulants makes selective recovery of this coagulant uncompetitive, with only UF providing costs comparable to existing practice. Increases in coagulant costs coupled with non-economic benefits may expand the feasibility of coagulant recovery to include ferric as well as alum.

Yields of coagulant and acid recovered (i.e. the process efficiency) are key to process economics, as would be expected. Higher coagulant recovery yields imply reduced acid consumption per unit weight of coagulant, as well as reducing waste and decreasing demand for supplementary fresh coagulant. Despite the greater membrane area contact time demanded for DD, the savings made from greater yields outweigh the extra cost incurred. It is most efficient to drive recovery processes as close to completion as possible, or in the case of ED, until conductivity drops below an acceptable level.

UF offers a simple and promising method for coagulant recovery. Whilst fouling may reduce the flux, it is likely to be less technically challenging to implement fouling amelioration methods than overcome constraints identified with other technological solutions. On the other hand, low molecular weight organic molecules permeating the membrane and contaminating the product would require removal, most likely with activated carbon, and the viability of adsorptive removal at low pH levels is currently unknown. Whilst economic analysis would suggest ED is a low OPEX option, the unknown factors (fouling, scaling and selectivity) are conspicuous and could significantly impair operation and escalate costs. As with UF, ED remains unproven in this role without further experimental investigation.

Of the three technologies considered here, DD is the best understood and the most rigorously tested for this duty. While the overall OPEX is less favourable than for the other two technologies, the potential for improvement is the most significant, specifically through implementing acid recovery, identifying waste disposal routes, and improving membrane performance and cost. However, UF is potentially the simplest of the three processes considered, with the selectivity and permeability of the membrane being critical to the process efficacy.

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CHAPTER 4

REUSE OF RECOVERED COAGULANTS IN WATER TREATMENT: AN INVESTIGATION ON THE EFFECT COAGULANT PURITY HAS ON TREATMENT PERFORMANCE

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4 REUSE OF RECOVERED COAGULANTS IN WATER TREATMENT: AN INVESTIGATION ON THE EFFECT COAGULANT PURITY HAS ON TREATMENT PERFORMANCE

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ABSTRACT

Coagulant recovery offers many potential benefits to water treatment, by reducing chemical demand and waste production. The key obstacle to successful implementation is achieving the same levels of treatment quality and process economics as commercial coagulants.

This study has evaluated the selectivity of pressure-filtration in the role of a low-cost coagulant recovery technology from waterworks sludge. The treatment performance of the purified recovered coagulant was directly compared to fresh and raw recovered coagulants. Dissolved organic compound and turbidity removal by recovered coagulants was close to that of commercial coagulants, indicating that coagulant can be successfully recovered and regenerated by acidifying waterworks sludge. However, performance was less consistent, with a much narrower optimum charge neutralisation window and 10-30% worse removal performance under optimum conditions. This inferior performance was particularly evident for recovered ferric coagulants. The impact of this was confirmed by measuring trihalomethane formation potential (THM-FP) and residual metals concentrations, showing 30-300% higher THM-FPs when recovered coagulants were used.

This study confirms that pressure-filtration can be operated on an economically viable basis, in terms of mass flux and fouling. However, the selectivity currently

falls short of the purity required for potable treatment, due to incomplete rejection of sludge contaminants.

4.1 INTRODUCTION

Coagulation is a widely used process in the treatment of surface water. Commonly, ferric and alum salts are dosed into raw water to neutralise the surface charge of contaminants and destabilise them. This allows the formation of larger floc particles and thus more effective removal of contaminants from the water. However, the sheer scale of water treatment requires vast quantities of coagulant chemicals and subsequently produces large volumes of waste sludge. The UK water treatment industry alone consumes more than 325,000 tonnes of coagulants (Henderson et al., 2009) and produces more than 182,000 dry tonnes waterworks sludge each year (Pan et al., 2004) giving an annual cost of £41m and £8.1m, respectively for chemical purchase and disposal of the waste (adjusted for inflation to 2012 prices; UKWIR, 1999). The opportunity to reduce these growing costs has driven research towards finding a viable means of recycling coagulants.

To this end, progress has been made in finding lower cost and more sustainable disposal routes for waterworks sludge (Babatunde and Zhao, 2007). However, coagulant demand shows little sign of declining, due to increasing world populations and climate change making drinking water sources more unpredictable and of poorer quality (Hurst et al., 2004; Delpla et al., 2009). Accordingly, the UK Water Industry Research body has highlighted cost-effective recovery of metal coagulants as a key step towards minimising chemical usage in water treatment (UKWIR, 2007). In the context of public health and the stringent regulations required for drinking water quality, the users of any recycled coagulants must ensure their use does not lead to contaminant carryover or detriment to treatment performance. In the UK and US, the primary contaminant of concern is the addition of dissolved organic carbon (DOC) as a precursor to disinfection by-products (DBPs), as well as heavy metals and pathogens (USEPA, 2009; DWI, 2010). A number of selective ion-exchange-based recovery technologies (particularly Donnan cation-exchange membranes) have been reported to achieve similar levels of purity to that of commercial coagulants (Petruzzelli et al., 2000; Prakash et al., 2003). However,

the materials required have been predicted to be prohibitively expensive for full-scale implementation under current economic conditions, with unit area costs for Donnan membranes more than three times greater than pressure-filtration membranes (Keeley et al., 2012).

Conventional pressure-filtration processes should provide a lower cost method of selectively recovering coagulant and have already demonstrated their resilience and affordability in full-scale water and wastewater treatment processes (Keeley et al., 2012). Central to the success of pressure filtration in this role is balancing the rejection of predominantly organic contaminants and maintaining treated water quality with high yields and fluxes of coagulant metals. Previous research has gone some way towards resolving these issues but only gives a limited insight into the impact of recovered coagulant on treated water quality and has focussed only on alum coagulants (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005). In this study, a spectrum of polymeric membranes was compared in terms of their readiness to permeate alum and ferric coagulants, while rejecting organic compounds and pathogens present in the acidified waterworks sludge. Coagulant treatment performance of the purest permeate was then compared with commercial coagulants and unfiltered, acidified waterworks sludge.

4.2 MATERIALS AND METHODOLOGY

4.2.1 Pressure filtration of acidified sludges

Unthickened and thickened sludges were taken from three water treatment works (WTW) in the UK, with a range of raw water characteristics and two coagulant types (Supporting Information: Figure 12; Table 17). Raw water from the three treatment works was fractionated using Amberlite XAD-7HP and XAD-4 ion exchange resins (Rohm & Haas, PA, USA), providing three organic fractions of hydrophobic, transphilic and hydrophilic) using published methods (Goslan et al., 2002).

The upland reservoir WTW treats peaty, acidic water containing largely hydrophobic compounds (with mean DOC composition of: 68% hydrophobic (HPO), 9% transphilic (TPI), 23% hydrophilic (HPI)) using ferric sulfate. The ferric sulfate-treated lowland reservoir water had a more hydrophilic character (37% HPO, 17% TPI, 47% HPI), high levels of alkalinity at ~140 mg/L as CaCO₃ (Autin et al., 2012). The lowland river source had an intermediate organic character (48% HPO, 13% TPI, 39% HPI), more prone to variation in organic composition than the reservoir samples and treated using aluminium sulfate. Sludge pH was measured using a Jenway 3520 pH meter and a VWR 662-1761 conductivity probe. A 250 ml sample was filtered using Whatman 1.2 µm GF-C filters and dried at 105°C for 24 hours to determine dissolved solids concentration.

To fully dissolve the metals, concentrated H₂SO₄ (>95%, analytical reagent grade, Sigma-Aldrich Ltd, Gillingham, UK) was added to 20 L containers of sludge to acidify to pH 2: a value reported as being sufficient to solubilise the majority of coagulant salts in the sludge (Keeley et al., 2014). The containers were manually agitated then left for one hour to equilibrate, and the process was repeated until a stable pH of 2 was obtained. The acidified sludges were left to settle for at least 24 hours before decanting the supernatant for use as the feed in ultrafiltration (UF) experiments.

A cross-flow membrane cell was fabricated from polyvinyl chloride (Model Products, Bedford, UK), based on a previously-reported design (Kwon et al., 2000). It was sealed with Viton O-rings and gaskets and had an available membrane surface area of 0.007 m² (channel dimensions: 1 mm high, 50 mm wide and 140 mm long). The cell was fed and pressurised from a 5 L high density polyethylene vessel containing 2.7 L of acidified sludge by a Liquiflo 45-series magnetically-coupled variable speed gear pump (Michael Smith Engineers, Woking UK).

Various flat sheet membranes were selected on the basis of nominal molecular weight cut-offs (MWCO) and required pH and temperature tolerance (Sterlitech Corporation, Kent, WA, USA; Figure 9). Membranes were prepared by rinsing

with deionised water from the feed side at ambient pressure. Membrane integrity was assessed by conducting clean water permeability and pressure hold testing at 414 kPa before and after the permeate tests.

Coagulant and Organic Compound Passage Through a Range of Ultra and Nano Filtration Membrane Pore Sizes

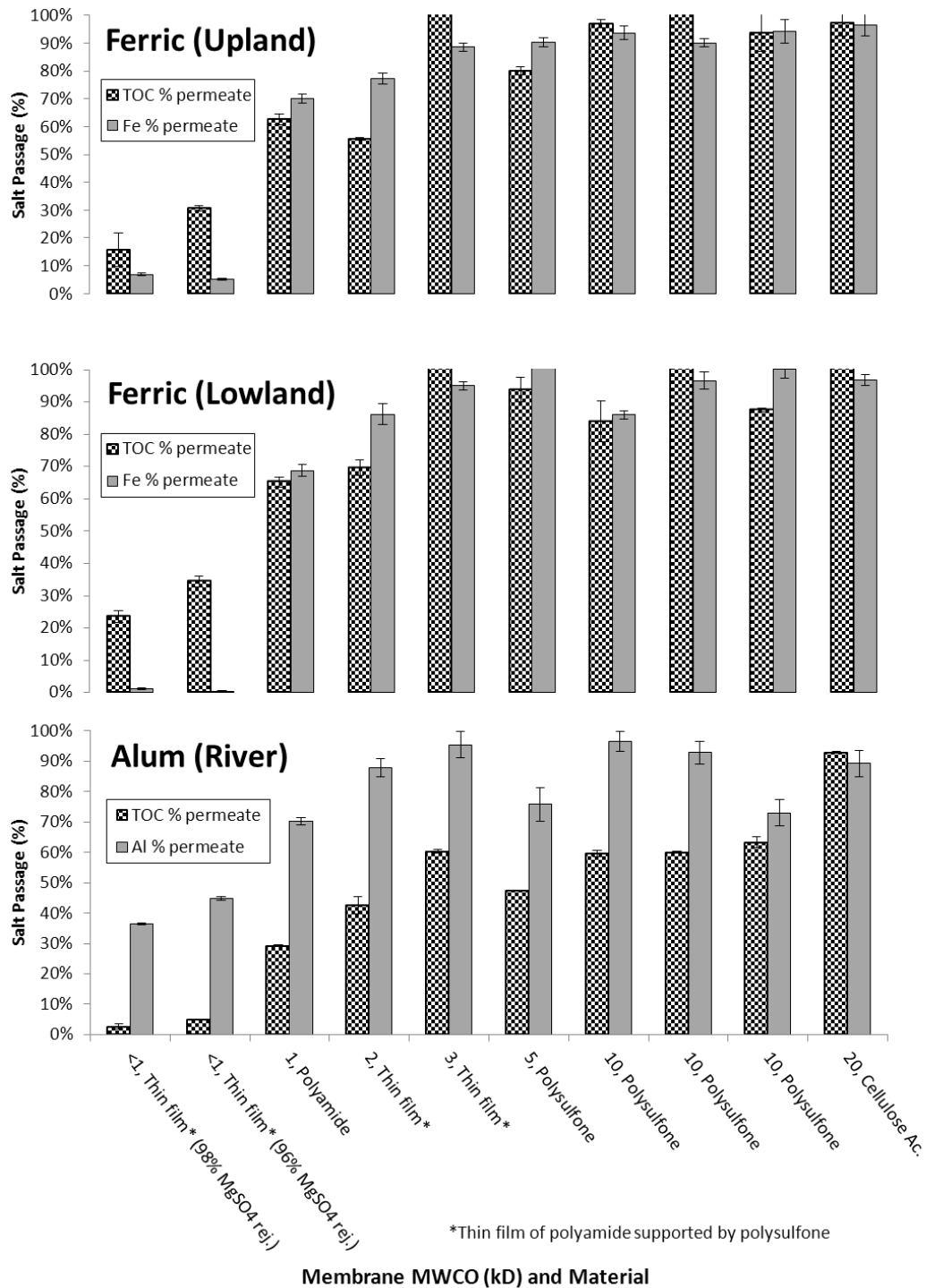


Figure 9: Coagulant and organic compound passage through a range of ultra and nano filtration membrane pore sizes

To determine the degree of separation of the coagulant metals and DOC, the acidified sludge supernatant was fed and recirculated at a cross-flow velocity of 4 m/s (Reynolds number 2350) and at transmembrane pressures (TMPs) between 276 and 414 kPa. Permeate and feed solutions were sampled in triplicate and were stored at 5°C prior to chemical analysis.

The feed and permeate samples were diluted using a 0.01 M solution of analytical grade HCl (Fisher Scientific, Loughborough, UK). The diluted samples were filtered using 1.2 µm GF/C filters and analysed for DOC (as non-purgeable organic carbon in the range 0-20 mg/L) using a Shimadzu TOC-V analyser. Samples were prepared for metals analysis using a 0.01 M solution of trace metal grade nitric acid (Fisher Scientific, Loughborough, UK). Fe and Al samples were diluted and analysed for absorption using an A Analyst 800 atomic absorption spectrometer in the range 0-5 mg/L for Fe and 0-20 mg/L for Al (PerkinElmer, Cambridge, UK). Fresh coagulants were sampled from the same treatment works and jar test doses calculated using the metal concentrations provided by suppliers' data sheets (4% w/v as Al for alum and 13% w/v as Fe for ferric).

4.2.2 Jar testing using recovered coagulants

Jar tests were used to determine recovered coagulant treatment efficacy in terms of the treated water zeta potential values. Tests were conducted using a Phipps & Bird PB-700 jar tester, programmed to mix 1 L of raw water for 1 minute at 200 rpm (after which coagulant is dosed and pH is adjusted); 1.5 minutes at 200 rpm; 5 minutes at 50 rpm and 1 minute at 50 rpm. The pH was adjusted using HCl and NaOH (0.1 M, reagent grade, Fisher Scientific, Loughborough, UK).

Treated water, extracted by syringe, was analysed for zeta potential using a Malvern Zetasizer, and for residual Cu, Pb, Ni, Cd, Cr, Mn and Al using ICP-MS, residual Fe using flame-AAS, turbidity using a Hach 2100N Turbidimeter and THM formation potential using a method (Parsons et al., 2004) modified

from the standard methods (APHA, 1992). Treated water samples were analysed for acrylamide at Severn Trent Water's Quality Assurance laboratories, using high performance liquid chromatography, and DOC and UV₂₅₄ absorbance were also measured.

4.3 RESULTS AND DISCUSSION

4.3.1 Ultrafiltration

The salt passage results (Figure 9) indicate a correlation with MWCO, with values below 5 kD necessitating polyamide-coated polysulfone membranes for organics rejection. At a similar MWCO, the change in membrane composition led to higher levels of permeation for alum coagulants than with uncoated polysulfone membranes but the dominant factor for permeation was MWCO. Coagulant readily permeated through membranes of nominal MWCOs of 1 kD or more, giving recoveries above 70%. In all but two cases for alum coagulant, MWCOs of 3 kD or more allowed recoveries of ~90%. MWCOs <1 kD, in the nanofiltration range, significantly reduced Al recovery and rejected almost all of the higher MW Fe salt.

For the alum sludge, DOC permeation followed a similar pattern to that of the coagulant metal but at lower levels. This is because a large amount of DOC has a higher molecular weight (MW) distribution, with the distribution peak for most NOM sources exceeding 1.5 kD (Schafer, 2001), thereby showing the potential for separation and purification of recovered coagulant (with MWs of <700 g/mol for even the most hydrated alum or ferric sulfates). However, it should be noted that while less abundant, the lower MW organic compounds will still be able to permeate through all but the lowest membrane MWCOs.

Separation between ferric and DOC was less defined, with % permeation actually higher for DOC than Fe for many of the membranes studied. Ferric sludges from both lowland and upland sources gave consistently greater DOC permeation than for the alum samples, suggesting that differing organic

character is not the cause. The noted difference may arise from differing charge density and subsequent organo-metallic complex strength and size: ferric and alum are both trivalent but the molar mass of Fe is nearly double that of Al. Differences in organo-metallic bond strength have been documented, with stability values for high-MW organic acid complexes nearly twice as high for ferric than aluminium ions: $\log K$ of 5.42 for Al^{3+} and 8.00 for Fe^{3+} (van Hees, 2000). The combined effects of a low pH of 2 and ligand-interactions with metals, particularly ferric, would neutralise the surface charge rejection between the membrane pores and the DOC. This would account for the reduced DOC rejection from ferric sludge than would be expected from the nominal membrane MWCO, DOC rejection performance from the alum sludge, and typical raw water DOC peak size distribution. With concentration ratios between 2:1 and 50:1 of coagulant metals to DOC in the permeate, it is likely that the majority of permeating organics compounds will be chemically associated with the coagulant metals, along with lower MW, unbound organic compounds. The organic compounds that were retained by the UF membrane were hydrophobic, higher MW aromatic compounds that were less strongly bound to the permeating coagulant metals. This corresponds with an observable colour change of the recovered coagulants from dark brown to a straw-colour, before and after permeation.

The difference in alum and ferric recoveries contrasts with the results for the selective recovery of ferric and alum coagulants using Donnan dialysis (a process largely dependent on charge) where recovery rates and quality were similarly high for these trivalent metals (Prakash and Sengupta, 2003). The difference in Fe/Al-organic complex strength is less significant due to the much greater strength of the Donnan membrane sulfonic acid bonds with metals: the pK_a for sulfonic acid is several orders of magnitude greater than the carboxylic acid groups found in humic acid (Bordwell, 2011). The separation data for alum is comparable with previous investigations using UF membranes of 10 kD MWCO (Lindsey and Tongkasame, 1975), but the same degree of organic rejection at higher MWCO (>10 kD) could not be replicated (Ulmert and Sarner,

2005). Source waters described as “very dark in colour” suggest this may be due to higher-MW hydrophobic organic compounds that were more readily rejected by UF in the previous study.

To be viable at full-scale, coagulant recovery must balance high metal yields with DOC rejection. Of the membranes examined in this study, a cut-off of 2 kD appeared to best achieve these aims, with optimal separation providing 87% Al salt passage with 58% DOC rejection from alum sludge and 78-87% Fe salt passage with 30-44% DOC rejection from ferric sludge. This membrane MWCO was used as the basis for subsequent studies of permeate quality and the impact on treated water quality.

The overall process efficacy of the UF coagulant recovery system is a function of salt passage percentage and the volume percentage that can be recovered through the UF and acidification stages. A number of other studies have reported optimal recovery to occur between pH values of 2-4 (Keeley et al., 2014). A pH of 2 was thus selected as the target value for coagulant solubilisation, giving 86-95% solubilisation of total coagulant metal and comparable to results from previous studies (Lindsey and Tongkasame, 1975; Parsons and Daniels, 1999).

Percentage metal permeation by concentration was at least 80% for the 2 kD MWCO membrane, with volume recoveries of 80% consistently achieved. The overall coagulant recovery efficiency was thus ~60%. At full-scale, the shortfall in recovered coagulant would demand supplementation by fresh coagulant to maintain the correct dose into the main treatment stream. Whilst such efficiency losses and acid demand reduce the economic gains required of the process (UKWIR, 2007), a 3:2 recovered:fresh coagulant blend would significantly reduce contaminant accumulation in the recovered coagulant. This would then help secure treated water quality in terms of DBPs and metals, which have been shown to be potential issues for more efficient coagulant recovery systems (Xu et al., 2009).

The rate of coagulant recovery was considered for sludge feeds of differing thicknesses (0.12-3.4% dry solids) and coagulant concentrations (100-2450 mg/L as M^{3+}). For each site, the thickened sludge feed permitted significantly greater coagulant metal mass fluxes (averaging up to 13 g. M^{3+} /m²/h, compared to average values as low as 1 g. M^{3+} /m²/h for unthickened sludge) with flux values normalised against temperature, pressure and system hydrodynamics. The decrease in flux over time, by as much as 75%, due to fouling was more apparent for thickened sludges than for the unthickened sludge values which remained within 20% of the initial value.

For both thickened and unthickened sludges, diminishing fluxes were restored close to their original values by relaxation of the membrane, allowing surface fouling to dissolve in the acidic feed solution for approximately one hour. A linear relationship was evident between feed coagulant concentration and mass flux of permeate for feed concentrations below 1 g/L M^{3+} , giving a 12 g/m²/h faster yield per 1g/L increase of feed concentration (Supporting Information: Figure 13). Thicker sludges showed a continued increase in flux with feed concentrations of 1.7 and 2.5 g/L M^{3+} but at approximately half the rate of increase (7 g/m²/h per additional 1 g/L in the feed). This is in agreement with an earlier study that revealed gel-polarisation to be the principal controlling factor for mass flux; increased TMP had little effect on coagulant permeation under the conditions investigated (Lindsey and Tongkasame, 1975).

Increasing solute concentration initially increases the diffusion gradient across the membrane and hence the solute flux. At higher concentrations the membrane surface becomes saturated and gel-polarisation occurs, limiting solute transport through the membrane. Operationally, this would mean that thicker sludges improve recovery efficiency, provided the use of polyacrylamide thickening polymers and their resulting monomers have no detrimental effect on recovered coagulant quality or membrane integrity. Analysis of water treated using recovered coagulant from thickened sludge showed no associated carryover of acrylamide when compared to water treated with fresh coagulant, with levels below the limit of detection in all cases (<0.02 µg/L).

The aim of measuring flux was to ascertain the suitability for larger scale operation of UF in this role. A previous study favourably compared the operating costs of UF with other coagulant management options but this was on the basis of an assumed mass flux that was 10-fold faster than that found in this work (Keeley et al., 2012). Although significantly different, the concentrated nature of the sludge stream only requires a small membrane area, making the overall operating costs quite insensitive to changes in these parameters. Therefore, the reported cost savings offered by UF remain valid. The recovery rates using UF presented in this study are comparable with the other successful membrane-based coagulant recovery technology, Donnan dialysis. For feed concentrations of 2500 and 1670 mg/L Al respectively after 24 hours of operation, Donnan dialysis recovered 10 g Al/m²/h (Prakash and Sengupta, 2003) compared to 8 g Al/m²/h achieved using a 2 kD MWCO UF membrane. UF achieves this at a third of the unit area cost of Donnan ion exchange membranes. Donnan membranes, however, offer greater organic matter rejection than UF membranes while selectively recovering coagulant metals (Figure 9). It should be noted that because the presence of DOC is not an existing issue for industrially produced fresh coagulants, there is no direct regulation of it in coagulants themselves but only for their impact. Thus a subsequent test was conducted to determine the impact of the DOC content on coagulant performance, and thus the requirement for separation of coagulant metals from sludge DOC.

4.3.2 Recovered coagulant performance

It was hypothesised that when recovered coagulants are reused at correct doses and pH values for effective charge neutralisation, a portion of the carried over DOC will again be removed by the coagulant in the flocs, along with raw water DOC. If sufficiently removed, this could allow more economic, less selective recovery processes to be used without detriment to treatment quality. To test this, residual levels of DOC and turbidity were measured for fresh, unfiltered and ultrafiltered recovered coagulants for three water types:

hydrophobic DOC-rich upland reservoir, hydrophilic DOC-rich lowland reservoir with high alkalinity, and lowland water from a flashy river with less stable organic content (Supporting Information: Figure 12).

In addition to the varying character of the raw waters, it was also considered important to appraise impacts of sludge quality on that of the recovered coagulant and so ultimate treated water quality. Differences in the effectiveness of UF in purifying recovered coagulants of different types have been discussed in terms of salt passage percentage (Figure 9). However, the solids concentration (Supporting Information: Table 17), which is highly variable due to differing thickening operation (between 4.5 g/L and 33.7 g/L dissolved solids in the unfiltered acidified sludge), may also have an effect on performance.

Residual turbidity after coagulation showed that in all cases optimal removal occurred when charge neutralisation was achieved with reference to particle surface charge measured as zeta charge. This occurred within zeta potentials of -5 to 0 mV (Supporting Information: Figure 14, Figure 15, Figure 16), where particle repulsion was minimal, allowing aggregation into stable flocs and thus effective turbidity removal. This range is in agreement with previous coagulation trials using fresh coagulants (Sharp et al., 2006). In all cases, coagulants were capable of treating water to 1 NTU or less and removed 60-70% of raw water turbidity for the river and upland reservoir waters. Turbidity removal for the lowland sample was less effective but raw water levels were already <1 NTU.

Average treated water turbidity values showed fresh coagulant to provide the lowest residual turbidity for the three water types examined, with average optimal values of 0.27-0.40 NTU (Figure 10). UF-purified recovered alum almost matched the turbidity residual of fresh coagulant (0.29 and 0.24 NTU, respectively), with unfiltered coagulant performing significantly worse with a residual of 1.0 NTU. This is perhaps due to the higher concentration of colloidal solids in the less pure alum (33.7 and 26.6 g/L dissolved solids respectively for the unfiltered and ultrafiltered recovered alum) combined with the relatively high degree of UF purification for the recovered alum with 87% Al permeate, 58% DOC rejection (Figure 9). The recovered ferric coagulants of varying purity were

less effective, probably reflecting the reduced purification attained by the UF treatment (Figure 9). For both water types, the ultrafiltered recovered ferric gave turbidity residuals within 0.2 NTU of fresh coagulants. The unfiltered coagulants performed worse still but only by 0.15 NTU or less (Figure 10).

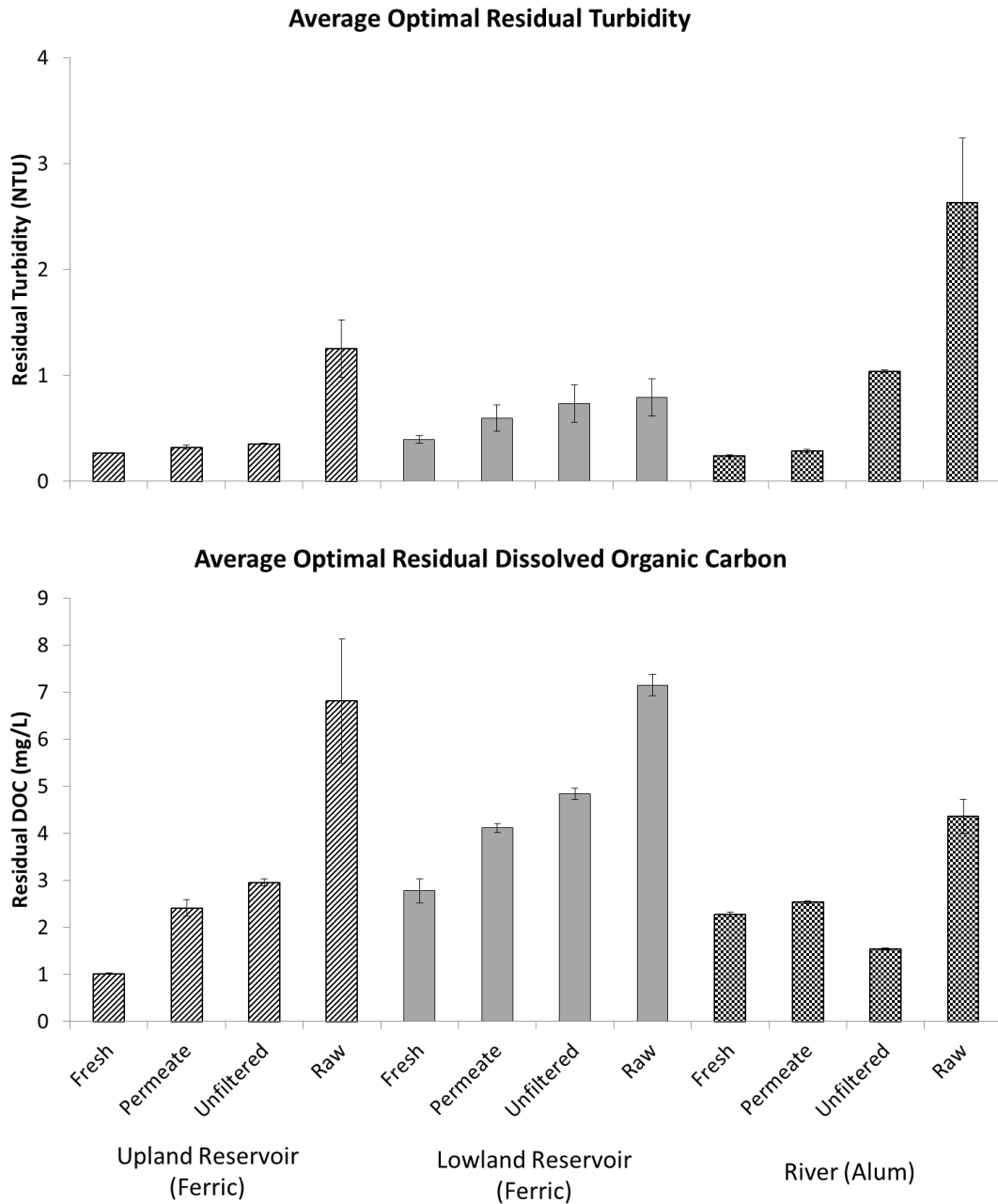


Figure 10: Residual turbidity and DOC levels for the three source waters investigated, with various coagulant types, based on the averages of the lowest three values.

Once optimised, jar tests with ferric coagulants gave a very clear trend between coagulant purity and residual DOC. Both upland and lowland waters had incrementally higher residuals for filtered and unfiltered recovered coagulants than with fresh coagulant (Supporting Information: Figure 10; Figure 17, Figure 18, Figure 19). Recovered ferric was active and able to remove 30-65% of DOC from raw water, although this compared poorly with the 60-85% removal achieved with the fresh coagulants. A significant amount of carried-over DOC can be removed alongside raw water DOC by the recovered coagulant. However, DOC in the recovered coagulant appeared to impair treatment efficacy by reducing coagulant availability to neutralise the negative surface charge of raw water contaminants. This is evidenced by ~30% lower M^{3+} :carried-over DOC ratios for unfiltered coagulants (Table 14). The impact of raw water organic character also significantly influenced treatment. The hydrophobic-rich upland water (Supporting Information: Figure 12) permitted effective DOC removal by coagulation, with >55% removal even by the unfiltered recovered ferric. In contrast, the hydrophilic character of the lowland sample was less treatable, with the fresh ferric only achieving 55% removal and unfiltered ferric removing <30%.

The optimal DOC removal performance for the alum coagulants follows a similar trend between the fresh and ultrafiltered coagulant but, in contrast to the ferric coagulants, the lowest residual was achieved with the unfiltered recovered coagulant: the 1.5 mg/L DOC residual was almost 1 mg/L lower than of the fresh coagulant (Figure 10). The M^{3+} :DOC ratio alone does not explain this difference. It could be that the alum availability is sufficiently high for optimal charge neutralisation, even in its impure state. When differing the M^{3+} :DOC is normalised to equivalent cationic charge:DOC to take into account the different charge density of Fe and Al (based on the assumption that all coagulants are solely available in their trivalent state, following oxidation by sulfuric acid and that carried-over DOC- M^{3+} interactions are consistent between all coagulants), it suggests that the unfiltered alum is almost as available as the filtered upland ferric sample, with ratios of 0.25 and 0.29, respectively (Table 14). It is

suspected that the unfiltered alum, containing a higher pre-treated DOC total, can produce a lower residual DOC than both the fresh and filtered alum due to higher dissolved solids (33.7 g/L compared to 25.9 g/L for the ultrafiltered reagent) acting as floc nucleation sites when they form their hydroxide coagulation products.

Table 14: A mass balance for DOC loadings and removals, when coagulants of differing purities are dosed.

Source, coagulant	Coagulant state	Coagulant dose			Carried-over and dosed	Raw Water	Pre-treatment total	Post-treatment residual	Total removed	M ³⁺ : carried over-DOC mg/L:mg/L ratio	M ³⁺ : carried over-DOC meq:mg/L ratio	Total DOC removed /meq coagulant
		Coagulation pH	M ³⁺ (mg/L)	meq /L*								
Upland reservoir, ferric	Fresh	4.7	26.8	1.4	0	6.8	6.8	1.1	5.7	n/a	n/a	4.0
	Filtered	4.1	28.8	1.5	5.1	6.8	11.9	2.5	9.4	5.6	0.29	6.1
	Unfiltered	4.1	7.6	0.4	1.8	6.8	8.6	3.1	5.5	4.2	0.22	13.4
Lowland reservoir, ferric	Fresh	4.9	20	1.1	0	7.1	7.1	3.1	4.1	n/a	n/a	3.8
	Filtered	4.5	20	1.1	2.9	7.1	10.0	4.3	5.8	6.9	0.38	5.4
	Unfiltered	5.5	16	0.9	2.9	7.1	10.0	5.0	5.0	5.5	0.31	5.9
River, alum	Fresh	5.2	9.5	1.1	0	4.4	4.4	2.4	2.0	n/a	n/a	1.9
	Filtered	3.9	7.6	0.8	1.6	4.4	6.0	2.6	3.3	4.8	0.50	3.9
	Unfiltered	4.5	13.2	1.5	5.9	4.4	10.3	1.6	8.7	2.2	0.25	5.9

*Calculated, assuming solely trivalent speciation of coagulant metals (following oxidation by sulfuric acid, for the recovered coagulants).

When replicate jar tests were conducted several months later with freshly sampled water from the same WTWs, using pH values and doses determined to be optimal from previous experiments, less effective DOC removal was attained for the unfiltered alum coagulant with the residual increasing from 1.5 to 3.2 mg/L (Figure 11). This may be partly due the seasonal variability of the source water (Supporting Information: Figure 12). Examination of the zeta potential for these replicates showed that they were on average 3 mV lower than the target value that had been achieved with the same alum dose and pH before. This highlights the increased operational complexity and unreliability of using recovered coagulants that require greater process control to treat water with constantly varying quality.

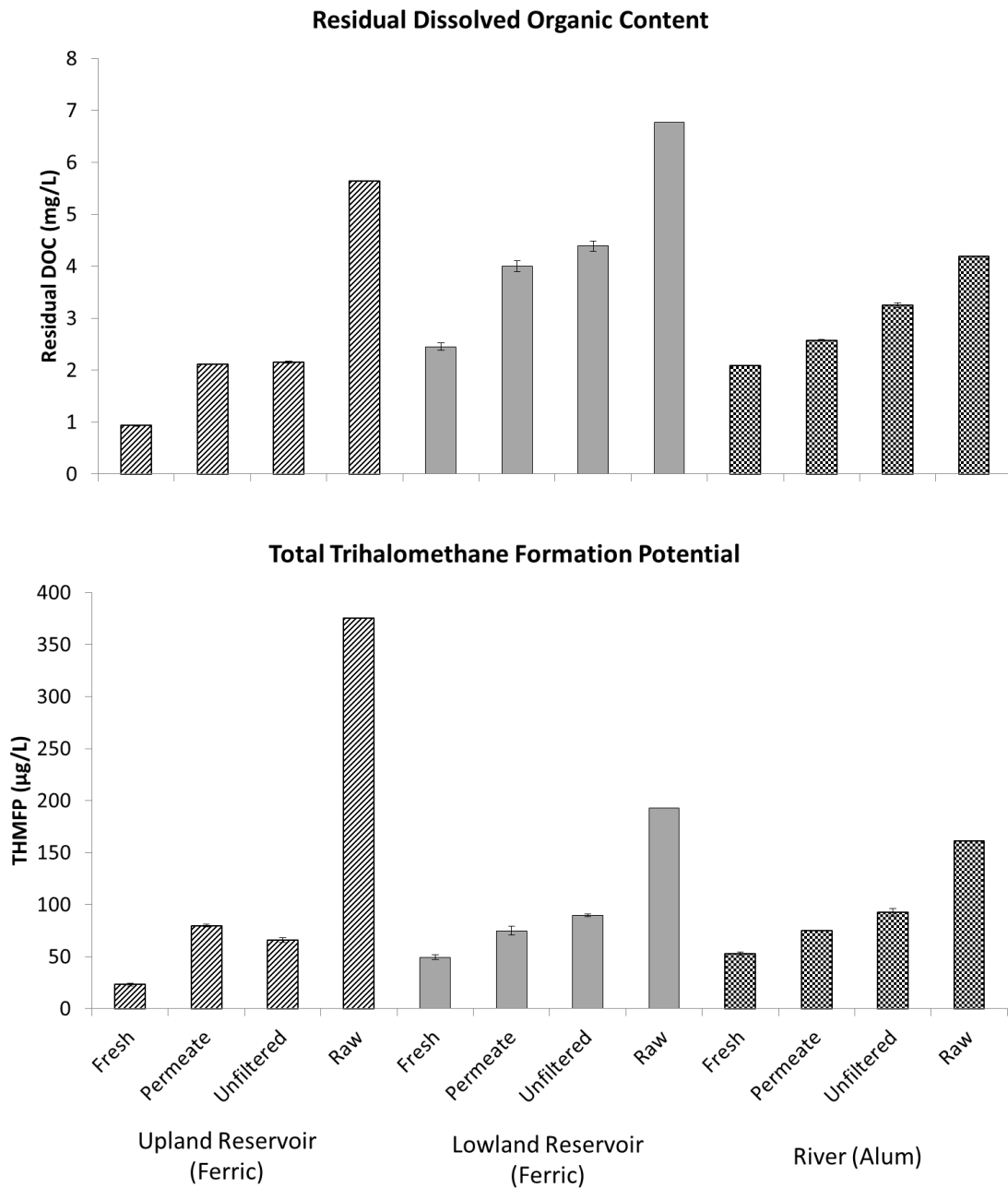


Figure 11: Trihalomethane formation potential and corresponding DOC levels for different coagulant purities and source water types.

The aim of DOC removal is to minimise the production of DBPs, of which trihalomethanes (THMs) and haloacetic acids have been of most concern to regulators and are used as indicators for total DBPs (WHO, 2011). Because the source and fate of DOC are more complex when recovered coagulants are used, determining the THM formation potential (THM-FP) is a critical step

towards understanding the impact of recovered coagulants on this regulated water quality issue. THM-FP represents the maximum possible amount of THMs DOC-containing water can produce, and is measured after adding Cl_2 in excess for a prolonged contact time to ensure THM formation approaches completion as a worst case (Parsons et al., 2004). For each water type, there was a strong correlation between residual DOC after treatment and THM-FP (R^2 s= 0.83-0.89). This relationship did not transcend across all of the water types due to differences in the organic compound speciation, giving a weaker correlation of $R^2=0.55$ when samples were grouped together. Waters containing mostly hydrophobic DOC are likely to form more THMs due to their higher reactivity (Goslan et al., 2002). In terms of reactivity with chlorine, the correlations for individual water suggests there is no significant difference in the residual organic character and its reactivity caused by the process of acidification and UF in comparison to conventionally treated water (Figure 11).

Waters treated with recovered coagulants had higher THM-FPs than those treated with fresh reagent (66-93 $\mu\text{g/L}$ compared to 23-53 $\mu\text{g/L}$), reflecting the higher DOC residuals (Figure 11). Water treated using ultrafiltered recovered coagulants had THM-FP levels of 75-80 $\mu\text{g/L}$ and would fall just within the regulatory limits of 80 and 100 $\mu\text{g/L}$ for THMs set out by US and UK regulations (USEPA, 2009; DWI, 2010). Unfiltered coagulants gave higher levels of THMs, as high as 93 $\mu\text{g/L}$ and would run a risk of exceeding these regulatory limits, particularly for less effectively treated hydrophilic-rich waters. Previous investigations have never evaluated the impact recovered coagulants have on DOC removal or DBP production, although the low levels of DOC in the Donnan-purified coagulant (1 mg/L DOC per 1,600 mg/L Al) would suggest a superior performance (Prakash and Sengupta, 2003).

Future legislation on DBPs will become more rigorous: in 2010 an amendment was made by the Drinking Water Inspectorate to its Water Supply Regulations, stating that English and Welsh water companies must “design, operate and maintain the disinfection process so as to keep disinfection byproducts as low as possible” (DWI, 2010). Recovered coagulants will only satisfy such stringent

regulatory philosophies when they can consistently match or better commercial coagulant quality. In the context of these regulations, the advantage of the relatively low recovery efficiencies discussed earlier is the necessity of supplementing recovered coagulants with fresh, thus reducing DBP-precursor loadings in the treated water relative to the recovered coagulant dose.

Another key water quality issue that coagulant recovery may impact is the concentration of regulated metals. ICP analysis has shown that recovered coagulants (both ultrafiltered and raw) increased the concentration in treated water for many of these but in most cases they remained well below the regulatory limits (Table 15). Pb and Ni regulatory limits were breached in two separate samples for ultrafiltered recovered coagulant but not in the unfiltered sludge feed. The most likely source of these loadings is from the corrosion of stainless steel and brass alloy fittings used in the crossflow cell pump and pressure gauges. This would also account for the significantly higher levels of Cu in the permeate than in the raw acidified sludge (Table 16).

Mn concentrations consistently breached the UK's regulatory limit of 50 µg/L but are less of a concern as most water treatment plant flowsheets for these types of water sources usually have specific Mn contactors downstream of coagulation-clarification-filtration, for removal of Mn and other metals. High Fe residuals for the lowland ferric samples were probably caused by seasonal changes in raw water quality increasing the required ferric doses for charge neutralisation, when jar tests were repeated for metals analysis. This was evidenced by lower zeta potential values than derived from the same dose during the optimisation experiments. As UF was chosen to allow for coagulant metal recovery, rejection of these other metal contaminants cannot be expected. Unfiltered recovered coagulant, uncontaminated by corroded brass and steel, shows similar residual metal concentrations to fresh coagulants and would pass both European coagulant standards (Table 16) as well as treated water regulations (Table 15).

Table 15: Treated water residual metal concentrations

	Cu		Pb		Ni		Cd		Cr		Mn		Al		Fe			
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.		
Upland ferric fresh	0	0	0	0	13	2	0	0	0	0	278	10	0	0	0.0	0.0		
Upland ferric permeate	760	49	19	2	16	1	0	0	4	1	87	3	1	0	0.3	0.1		
Upland ferric unfiltered	0	1	0	0	6	0	0	0	0	0	346	3	0	0	1.1	0.2		
Lowland ferric fresh	0	0	0	0	6	0	0	0	0	0	142	9	0	0	0.1	0.1		
Lowland ferric permeate	52	2	0	0	6	0	0	0	0	1	286	10	0	0	11.7	1.1		
Lowland ferric unfiltered	0	0	0	0	5	0	0	0	0	1	305	10	0	0	12.2	1.2		
River alum fresh	0	0	0	0	0	0	0	0	0	0	3	1	0	0	0.0	0.0		
River alum permeate	102	2	4	0	23	0	0	0	3	0	90	2	2	0	0.0	0.0		
River alum unfiltered	0	0	0	0	0	0	0	0	6	1	40	3	0	0	0.0	0.0		
Upland ferric raw	0	-	0	-	1	-	0	-	0	-	2	-	0	-	0.1	-		
Lowland ferric raw	0	-	0	-	0	-	0	-	9	-	0	-	0	-	0.0	-		
River alum raw	0	-	0	-	0	-	0	-	10	-	0	-	0	-	0.0	-		
DWI (2010) limits	2000		10		20		5		50		50		200		0.2			
USEPA (2009) limits	1300 (1000)		15		-		5		100		(50)		(50-200)		(0.3)			
Units															µg/L		mg/L	

Table 16: Recovered coagulant metal impurities normalised to coagulant dose, in relation to European Standards EN 888:2004 and EN 878:2004 for type 3 ferric chloride and aluminium sulfate to be used for treatment of water for human consumption [28], [29].

	Cu	Pb	Ni	Cd	Cr	Mn	Fe	Al
Maximum addition µg/g Fe	-	0.40	0.50	0.005	0.50	-	-	-
Upland ferric permeate	24.3	1.13	0.43	0.003	0.43	4	210	-
Upland ferric feed	0.1	0.21	0.09	0.003	0.07	3	221	-
Lowland ferric permeate	11.8	0.52	0.64	0.003	0.45	18	133	-
Lowland ferric feed	0.1	0.00	0.35	0.002	0.07	15	195	-
Maximum addition µg/g Al	-	0.80	1.00	0.010	1.00	-	-	-
River alum permeate	3.3	0.39	0.54	0.010	0.56	17	-	209
River alum feed	0.3	0.05	0.10	0.010	0.04	17	-	234
Units	µg/g Fe or Al						mg/L	

In Europe, the reuse of water treatment chemicals must be placed in the context of a robust regulatory environment that puts water quality and public health above all else (EU, 1998). However, water is treated on vast scales and must use relatively inexpensive methods to ensure economic viability. It was hoped that UF could undercut the costs of ion-exchange based recovery methods, while maintaining quality levels to satisfy regulations. This study shows that UF can be used to selectively recover coagulants both economically and with sufficient activity to be reused. While the recovered coagulants have approached the removal performance of fresh equivalents, performance has been less reproducible and has been undeniably inferior for many regulated parameters (Figure 10 and Figure 11), although this is partially mitigated by UF purification.

Other studies have used adsorption, ion exchange, precipitation and filtration to further purify UF permeate (Ulmert and Sarner, 2005). Additional purification stages risk offsetting the already fragile process economics but may become viable if coagulant prices rise (Henderson et al., 2009). Sufficiently monitoring and certifying recovered quality to satisfy water treatment chemical standards would be a further operational challenge to consider. The combination of water quality regulations, operational complexity and cost all combine to make a sizeable barrier to the marginal benefits ultrafiltered recovered coagulants offer at current prices. However, this is subject to change, as historic price fluctuations have demonstrated (Henderson et al., 2009). An alternative application for recycled coagulants is for phosphorus removal in wastewater treatment which would allow the coagulant activity to be exploited without risking public health and regulatory breaches due to DOC carryover. This would allow recovered coagulant purification to be less intensive and costly, while still reducing the demand for coagulants and sludge disposal capacity (Parsons and Daniels, 1999) and thus offer a viable area for coagulant reuse.

4.4 CONCLUSIONS

This study has demonstrated the constraints on the efficacy of UF for coagulant recycling in potable treatment. Membrane performance in terms of flux and metal permeation for the 2 kD MWCO was in-line with expectations and would support the proposed operational expenditure (OPEX) savings suggested in a previous study. Using thickened in preference to unthickened sludge gave higher coagulant mass flux rates and would appear to be more economical. A significant percentage of DOC was rejected but levels of residual DOC and metals were far from the quality levels required by coagulant regulatory standards. Analysis of the impact these impurities had on actual treatment performance demonstrated that, in spite of the significantly higher loadings of DOC added with the recovered coagulant (in comparison to fresh coagulants), similar levels of treatment could be achieved provided they were dosed under optimum conditions. Marked treatment differences were revealed when recovered coagulants were dosed outside these optimum conditions and would represent a major operational challenge were they to be used at full-scale.

While MWCOs of <1kD have shown the potential of recovering alum with a lower level of DOC contamination, in practice this would not be viable. Due to the comparatively low value of coagulants in relation to the cost of acidification and UF operation, salt passage efficiencies of <50% would be operationally unacceptable, leaving higher-yielding, less selective UF as the only technically feasible option. When the lack of selectivity by UF for coagulant ions is viewed in the context of stringent potable regulations, for both actual treatment chemicals and treated water quality, it is clear that UF-based coagulant recovery cannot reliably meet the requirements in this role, at a practical level of recovery efficiency, despite potentially reducing net chemical costs. It would be more appropriate to reuse waterworks coagulants in wastewater treatment, where organic content is less closely regulated.

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SUPPORTING INFORMATION

Resin Column Fractionation of Natural Organic Matter in The Three Source Waters Investigated

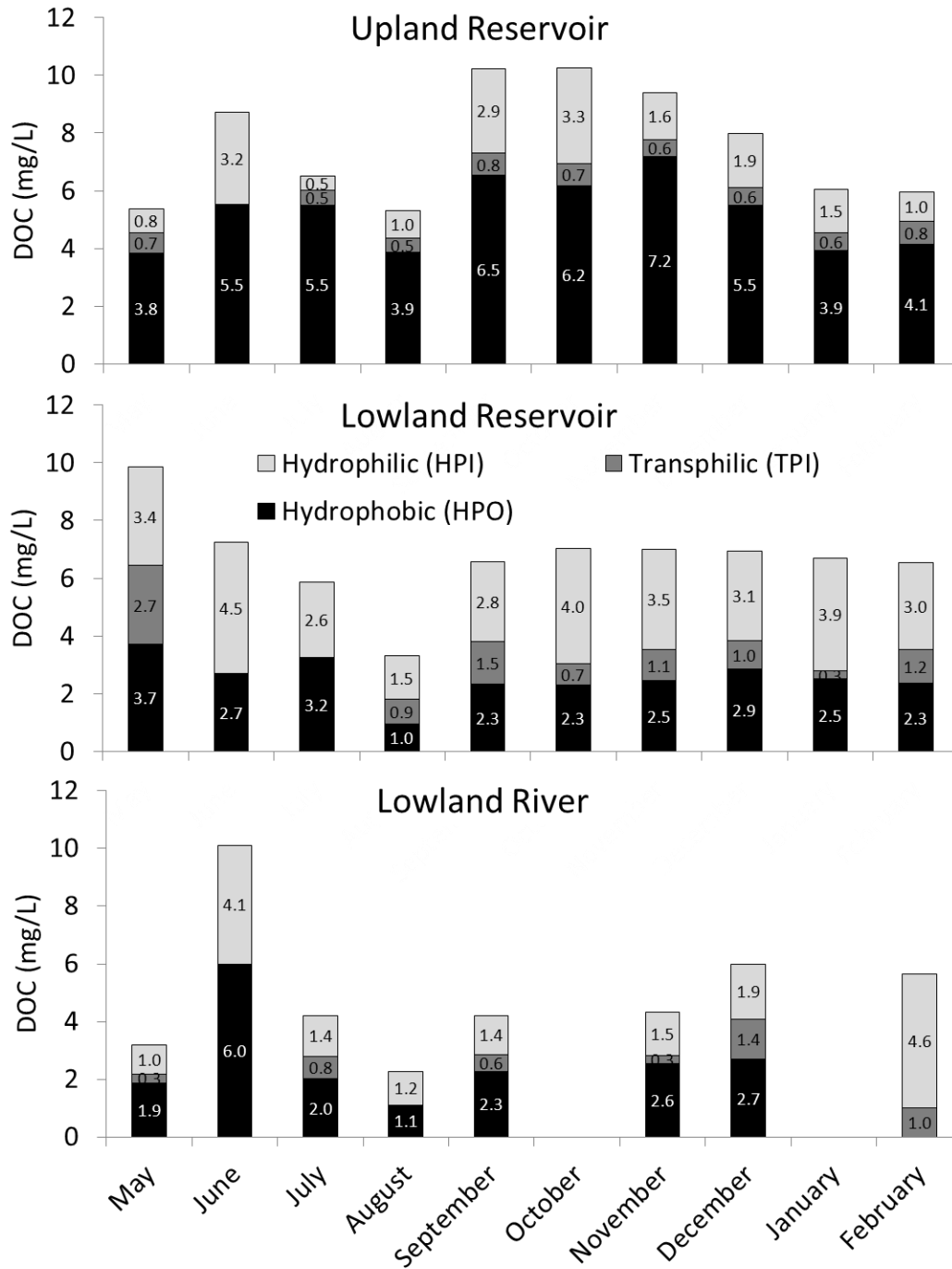


Figure 12: Variation in raw water character for the three sites sampled and investigated.

Table 17: Details of sludge character

Site location	Source water type	Coagulant dosed	Dissolved unthickened; acidified sludge (%)	solids: thickened	Sludge at sample point	pH
Derbyshire	Upland reservoir	Ferric sulfate	0.12; 0.45		4.5	
Warwickshire	Lowland reservoir	Ferric sulfate	0.27; 0.55		7.3	
Worcestershire	Lowland river	Aluminium sulfate	0.22; 3.4		6.5	

Mass Flux vs. Feed Coagulant Concentration for a 2kD Polymeric Membrane

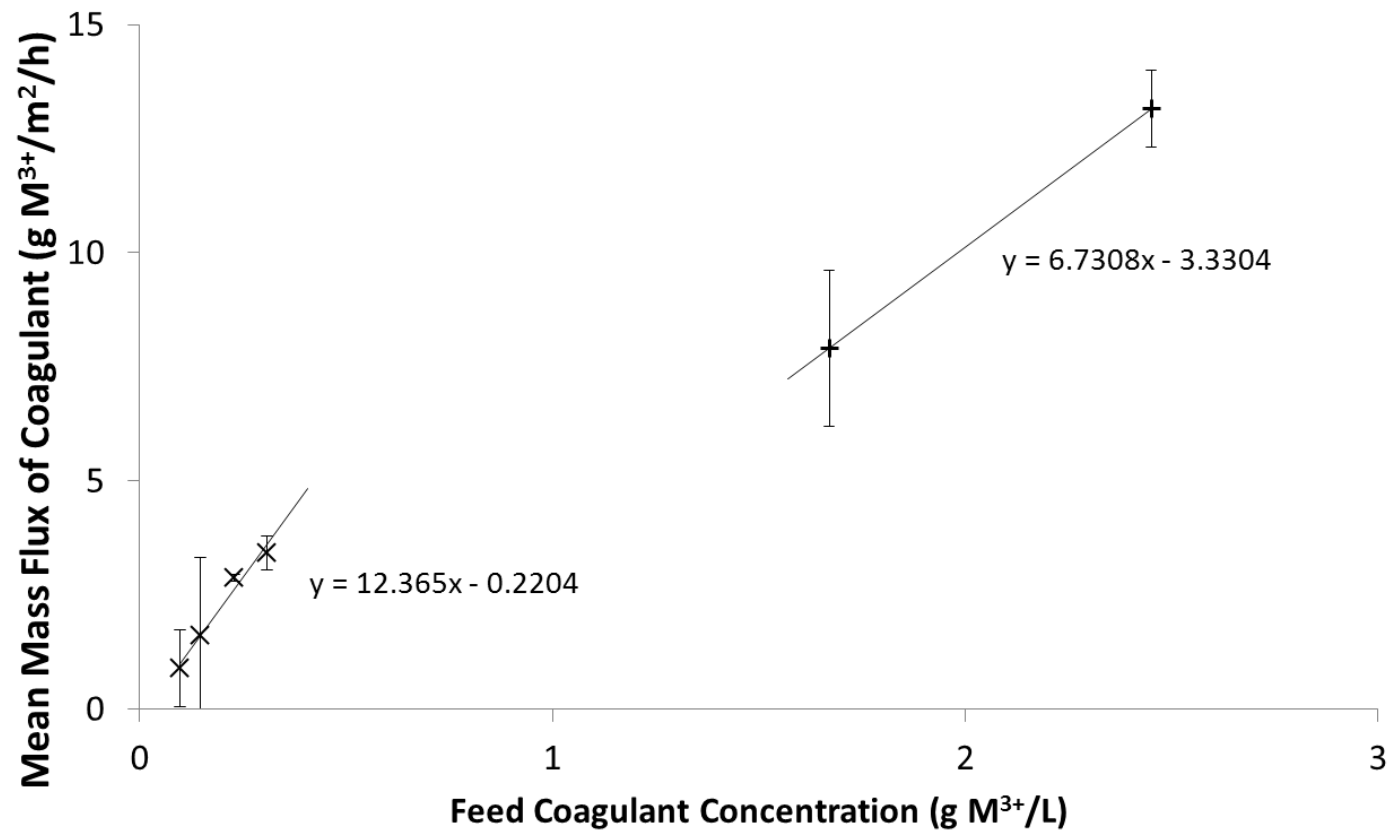


Figure 13: The effect of coagulant feed concentration on permeate mass flux for a 2 kD MWCO polymeric membrane

Upland Reservoir: Turbidity Residuals with Filtered, Unfiltered and Fresh Ferric

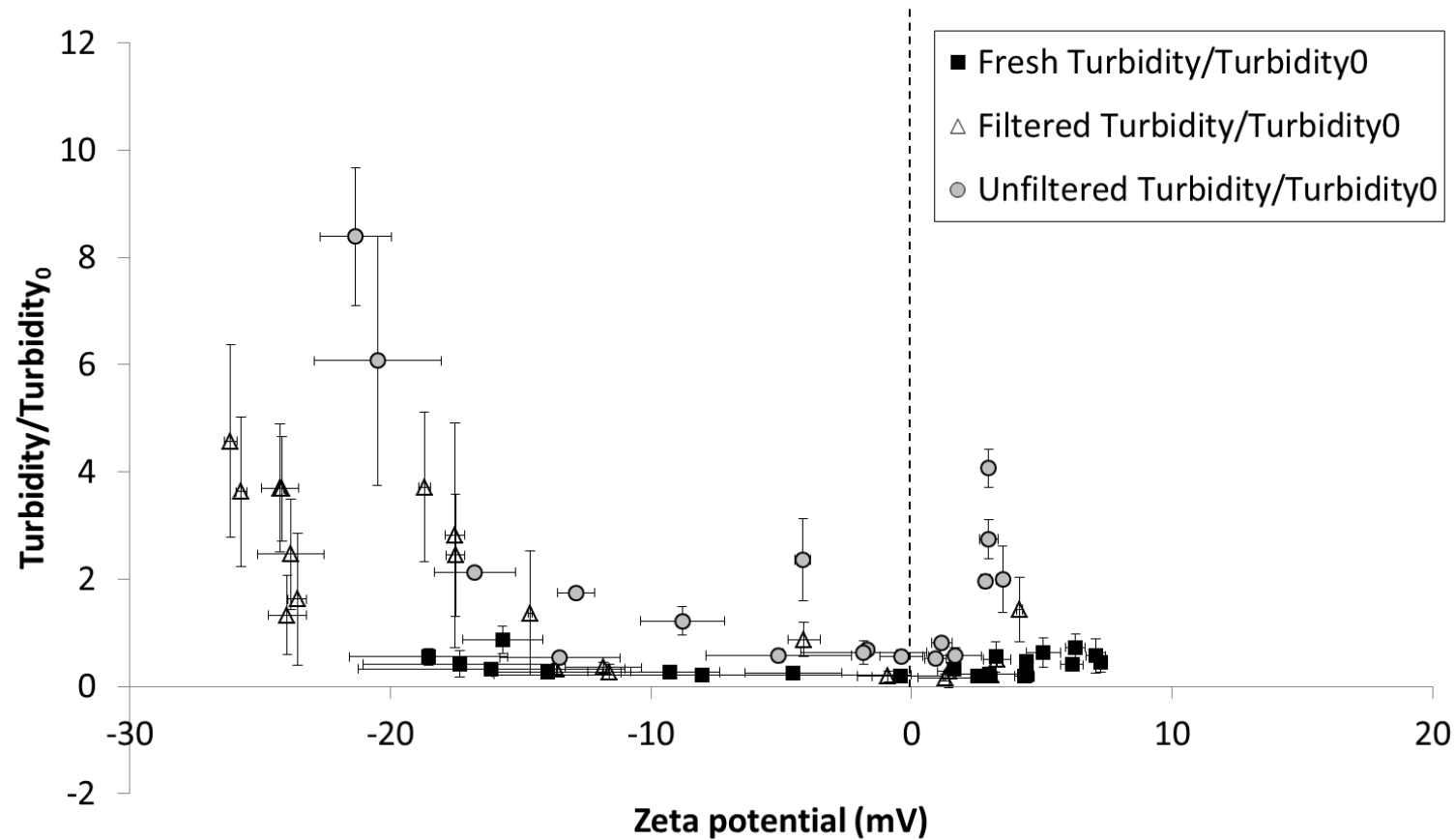


Figure 14: Upland reservoir turbidity residuals when treated with ferric coagulants

Lowland Reservoir: Turbidity Residuals with Filtered, Unfiltered and Fresh Ferric

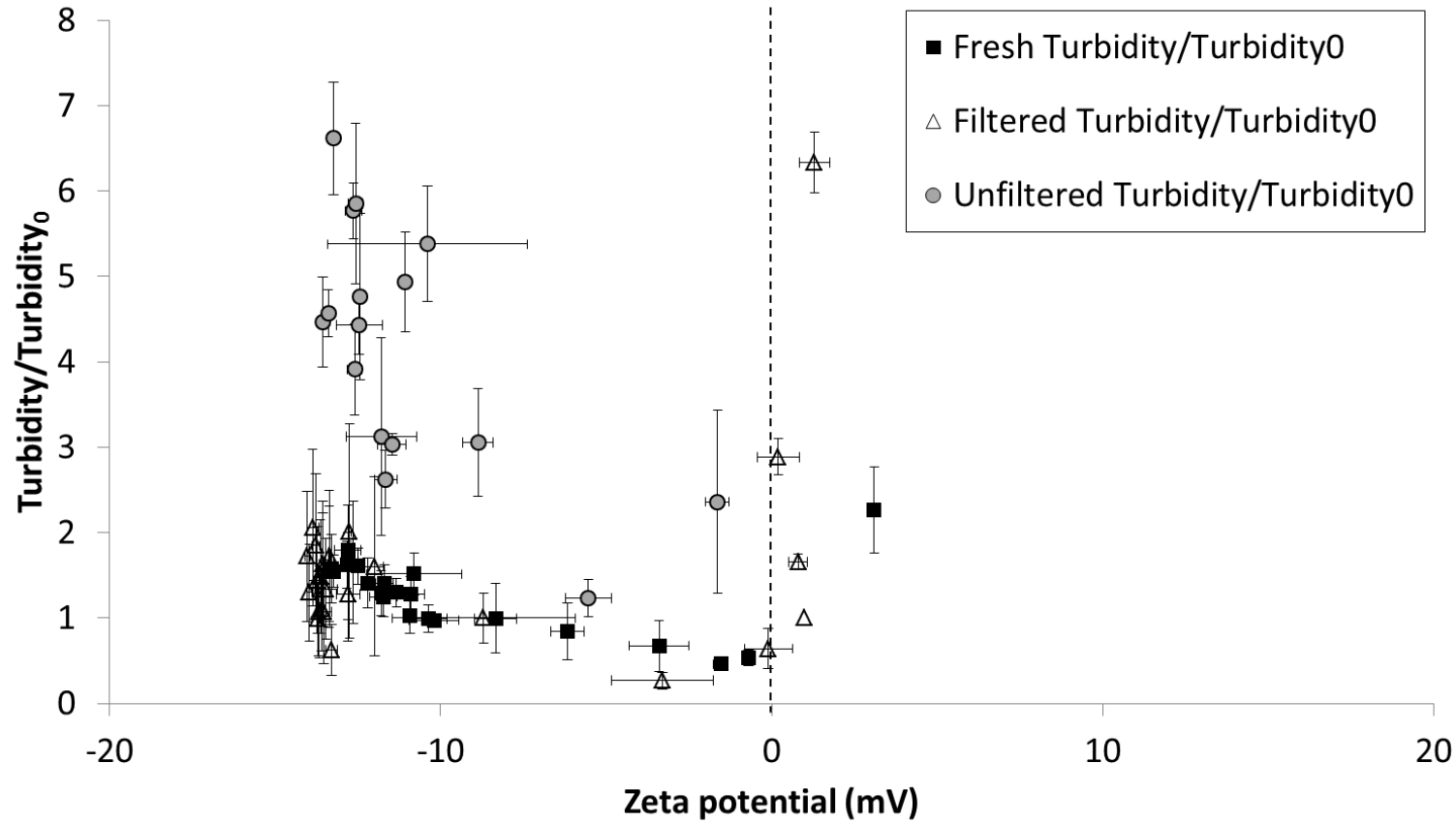


Figure 15: Lowland reservoir turbidity residuals when treated with ferric coagulants

River: Turbidity Residuals with Filtered, Unfiltered and Fresh Alum

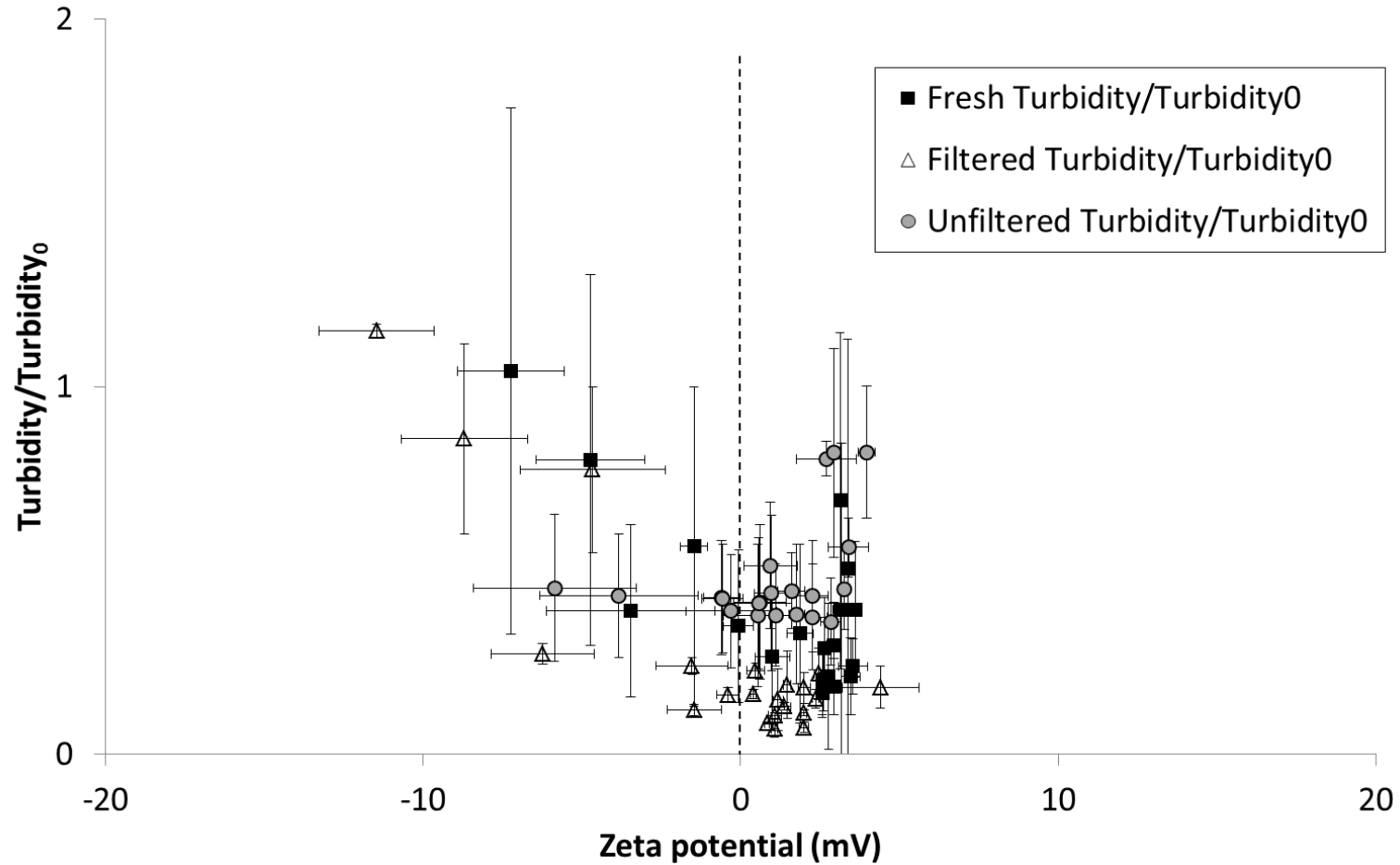


Figure 16: River turbidity residuals when treated with alum coagulants

Upland Reservoir: DOC Residuals with Filtered, Unfiltered and Fresh Ferric

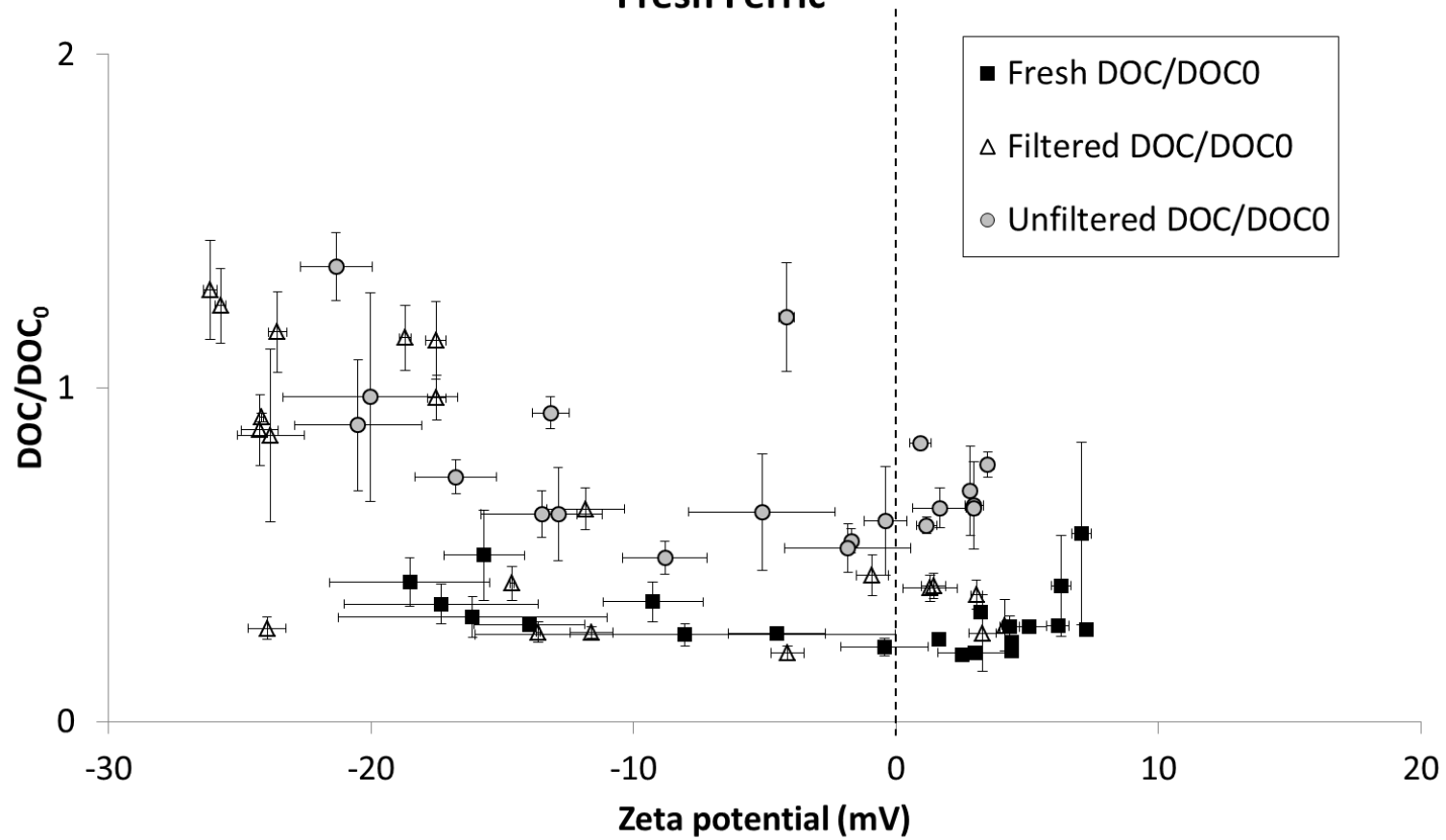


Figure 17: Upland reservoir DOC residuals when treated with ferric coagulants

Lowland Reservoir: DOC Residuals with Filtered, Unfiltered and Fresh Ferric

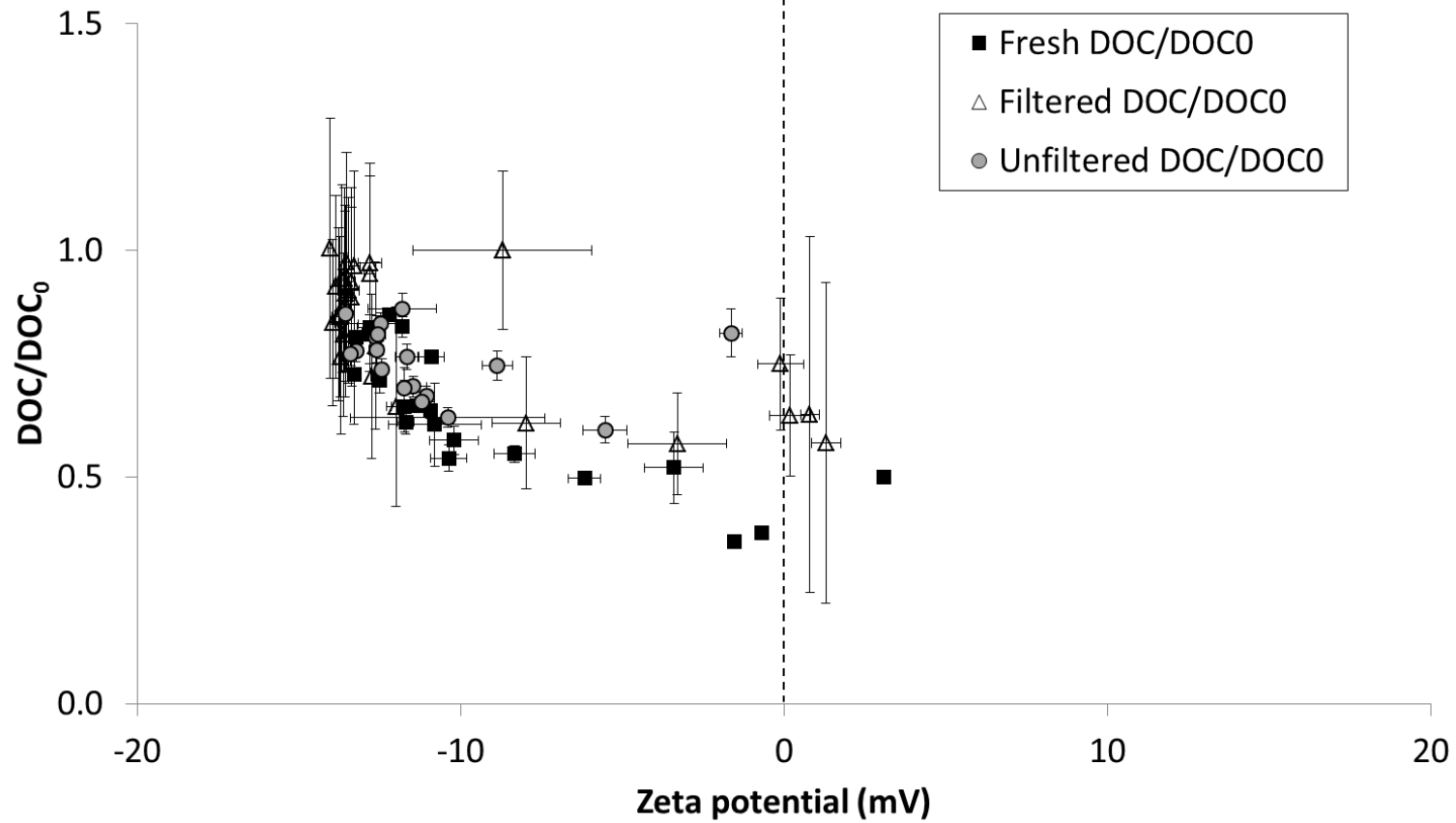


Figure 18: Lowland reservoir DOC residuals when treated with ferric coagulants

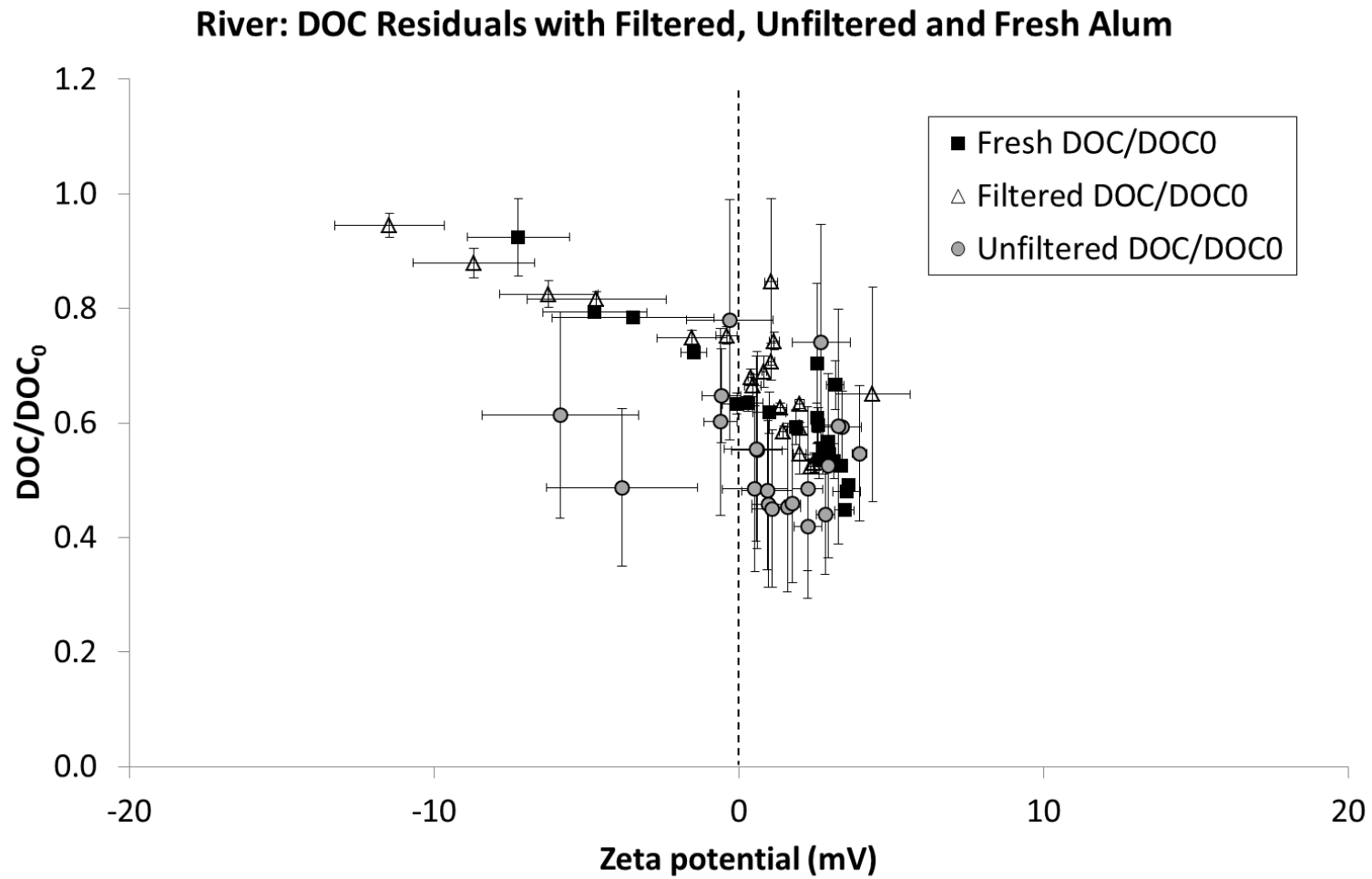


Figure 19: River reservoir DOC residuals when treated with alum coagulants

CHAPTER 5

PERFORMANCE AND ECONOMIC POTENTIAL OF THE REUSE OF WATERWORKS FERRIC SLUDGE FOR PHOSPHORUS REMOVAL FROM WASTEWATER

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5 PERFORMANCE AND ECONOMIC POTENTIAL OF THE REUSE OF WATERWORKS FERRIC SLUDGE FOR PHOSPHORUS REMOVAL FROM WASTEWATER

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ABSTRACT

This study investigated the application of ferric sludge from a drinking water treatment plant for phosphorus removal from primary wastewater. The treatment performance and whole life cost (WLC) of various sludge reuse configurations have been considered in relation to fresh ferric sulfate (FFS).

Unacidified sludge showed 53% of the phosphorus removal efficiency of FFS, at a dose of 20 mg/L as Fe and a contact time of 90 minutes. A longer contact time of 8 hours 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. FFS P removal performance was matched by pre-filtering the acidified ferric sludge using a 2kD ultrafiltration membrane. Analysis of the removal of P showed that rapid phosphate precipitation accounted for >65% of removal with FFS. However, for the acidified sludges a slower adsorption mechanism dominated; this was accelerated relative to unacidified sludge, by a lower pH.

Economic 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 50 miles for reuse in wastewater treatment. A maximum inter-site distance was determined to be 150 miles 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 sludge.

5.1 INTRODUCTION

Coagulation-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) at a cost of £41m. This generates >182,000 tonnes of waste sludge (WTR; Pan et al., 2004), demanding ~£8.1m for its disposal (UKWIR, 1999).

Wastewater treatment works (WWTW) also require more 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 than 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 potentially alleviate these problems (Babatunde and Zhao, 2007). P removal from wastewater by WTRs is already widespread as disposal of WTRs to sewer is convenient and frugal (Walsh, 2009) as it avoids WTR dewatering, haulage and disposal fees. However, this is limited by sewer access (<30% in the UK; UKWIR, 1999; Walsh, 2009).

Reuse of acid-recovered coagulants from WTRs has already been considered in potable treatment and is capable of reducing coagulant demand and waste production. However, acidification is non-selective and its carryover of organic compounds would elevate formation of disinfection byproducts if used in potable treatment (Keeley et al., 2014a). Numerous purification methods have been documented but none adequately combine selectivity with feasible costs (Keeley et al., 2014b).

Reusing recovered coagulants in wastewater treatment can provide similar advantages as reuse in potable treatment but is less sensitive to 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; Jimenez et al., 2007). 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 whole life cost (WLC) of several WTR reuse approaches with conventional chemical P removal.

Ferric coagulants typically remove 95-96% of P after 90 minutes and M³⁺: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 sulfate or chloride salts rapidly hydrolyse, forming metal hydroxides and, when P is present, metal phosphates. Optimal mixing (average G values >100 s⁻¹; Szabo et al., 2008) and a pH <9 (Garlarneau et al., 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 hours) 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 (<4x10⁻¹⁵ cm²s⁻¹; Makris et al., 2004) to bind to Fe sites, displacing hydroxide groups (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 WTR and chemically similar ferric hydroxide media can match the performance of FFS (fresh ferric sulfate) 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 WTR by acidification to pH 2 can increase the chemical efficiency of P removal by facilitating precipitation pathways (Parsons and Daniels, 1999; Jimenez 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). 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.

5.2 METHODOLOGY

5.2.1 Analysis of Treatment Performance

Jar tests were used to replicate chemical treatment of primary wastewater and examine removal performance and treated water quality. Various forms of WTR and commercial grade FFS (measured as 20% Fe) were used. Screened, municipal wastewater was collected daily from a 2000 population equivalent WWTW (Cranfield, UK).

Dewatered sludge cake (14% dry solids; DS) was taken from a 120-180 MLD WTW treating upland water (Derbyshire, UK) using ferric sulfate coagulant. Sludge cake (1g, wet) was dissolved in 1L of 0.1M 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 (1g/L), titrated against dilute sulfuric acid.

Recovered coagulant (RC) solutions were prepared as 2.8% DS in deionised water. Acidified sludge was prepared by mixing a measured amount of concentrated sulfuric acid, until the required pH was held. Ultrafiltered, acidified sludge was filtered through a 2 kD molecular weight cut off (MWCO) polyethersulfone membrane (Sterlitech Corporation, Kent, WA, USA), using apparatus previously described (Keeley et al., 2014b).

Fe Dose. Tests were conducted at Fe doses of 0- 50 mg/L, using a Phipps & Bird PB-700 jar tester. This mixed cylindrical beakers containing 1 L of wastewater for 1 minute at 200 rpm ($G = 128 \text{ s}^{-1}$), followed by 30 rpm ($G = 7.4 \text{ s}^{-1}$) for 15 minutes, and a 30 minute unmixed settlement stage. Average velocity gradients 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. Residual Fe was analysed using AAS, as well as pH and turbidity.

Examination of P Removal Mechanisms. Using an adaptation of a previous method (Szabo, 2008), jar tests were run with a 90 second mix (200 rpm) and a 60 minute mix (30 rpm). Samples were taken 2 and 60 minutes after dosing with 20 mg/L Fe. These were immediately syringe filtered (0.45 μm , nylon) and analysed for soluble P. This process was repeated with prehydrolysed coagulants (adjusted to pH 7, prior to dosing) to discriminate between P removal mechanisms.

Coagulant pH. Sludges and coagulants were diluted to equal volumes using deionised water and pH adjusted using sulfuric acid. These were dosed at equal Fe concentrations.

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 minutes. Prolonged mixing for 2, 4, 8 and 24

hours at 100 rpm ($G = 43 \text{ s}^{-1}$) 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 hour/km; Gutierrez et al., 2010).

Rapid Mix Intensity. This was studied to simulate ideal and non-ideal mixing conditions as may be experienced in the field: at 20, 60, 140 and 300 rpm (5, 21, 72 and 250 s^{-1} , respectively), followed by 30 minutes flocculation at 30 rpm.

Selected treated waters were analysed further: alkalinity consumption was measured by titration to pH 4.5 against 0.02M HCl, using a pH meter; Zeta potential and floc size were measured using a Malvern Zetasizer and Mastersizer.

5.2.2 Cost Modelling

A case study was used to investigate the WLC of different WTR and P removal strategies. 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, 50 miles 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, 20 miles away.
- A WWTW requiring $\leq 9,000 \text{ t/y}$ of 13% Fe commercial ferric sulfate, 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; Supporting Information: 5.4.4 Components of the cost model). 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/m²/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 (Supporting Information: 5.4.4 Components of the cost model), plus an additional: 10% for piping; 5% for groundworks; 20% for electrical and controls; and 35% for engineering, legal and administration (McGivney and Kawamura, 2008).

Chemical demand operational expenditure (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 (Supporting Information: 5.4.4 Components of the cost model).

5.3 RESULTS AND DISCUSSION

5.3.1 Chemical Factors

For acidified RC and FFS, increasing Fe dose up to 20 mg/L significantly improved P removal (up to 2.1:1 molar ratio of Fe:P, Figure 20D) 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 acidified sludge 84%; acidified sludge, 64%; and just 16% with raw cake. These are 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 molar 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.

The differing physical and chemical properties of the recovered coagulants can explain the varied performance. The high percentage P removal at lower Fe:P ratios of 2.1:1 observed with acidified sludges suggests a similar P removal mechanism to FFS (Thistleton, 2002). Comparatively inferior removal with unfiltered, acidified sludge is due to interference from organic compounds binding to Fe (Wang, 2012). The high proportion of insoluble Fe (55%) that was unavailable for P removal by precipitation would also restrict the contact area available for adsorption. This also accounts for the poorer performance of unacidified sludge, with >99% Fe insoluble, precipitation cannot occur and the surface area for adsorption will depend on particle size (Supporting Information: 5.4.2 Supplementary analysis of particle size).

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

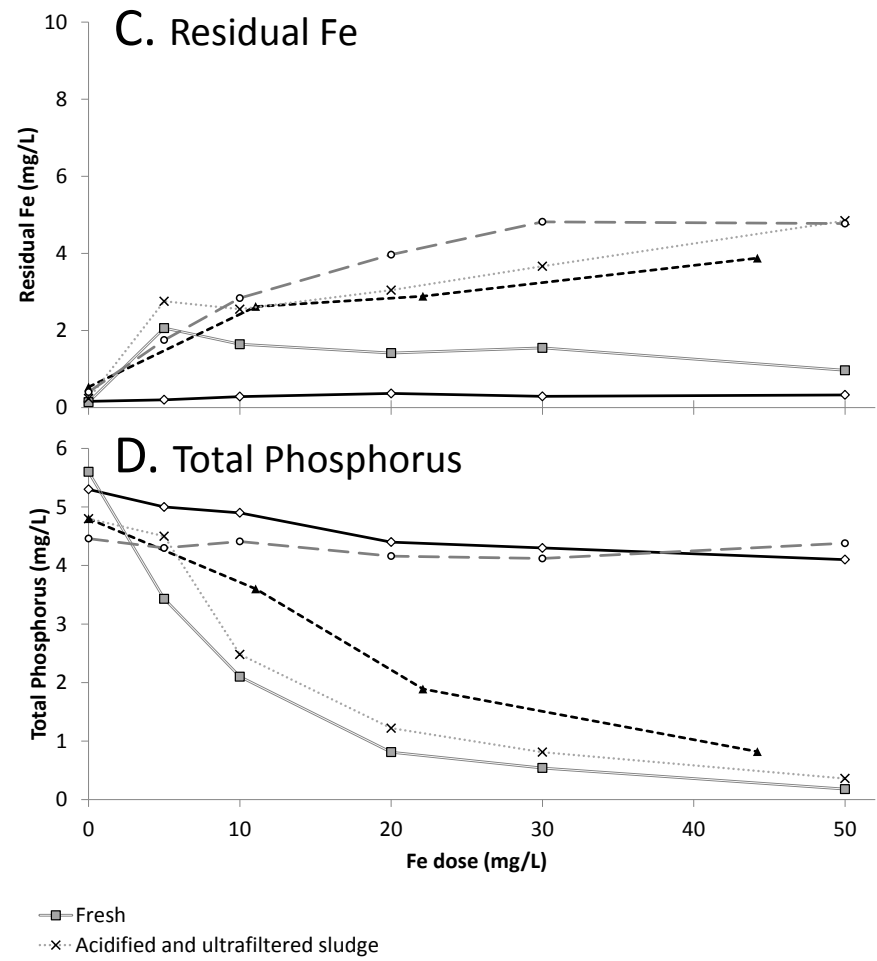
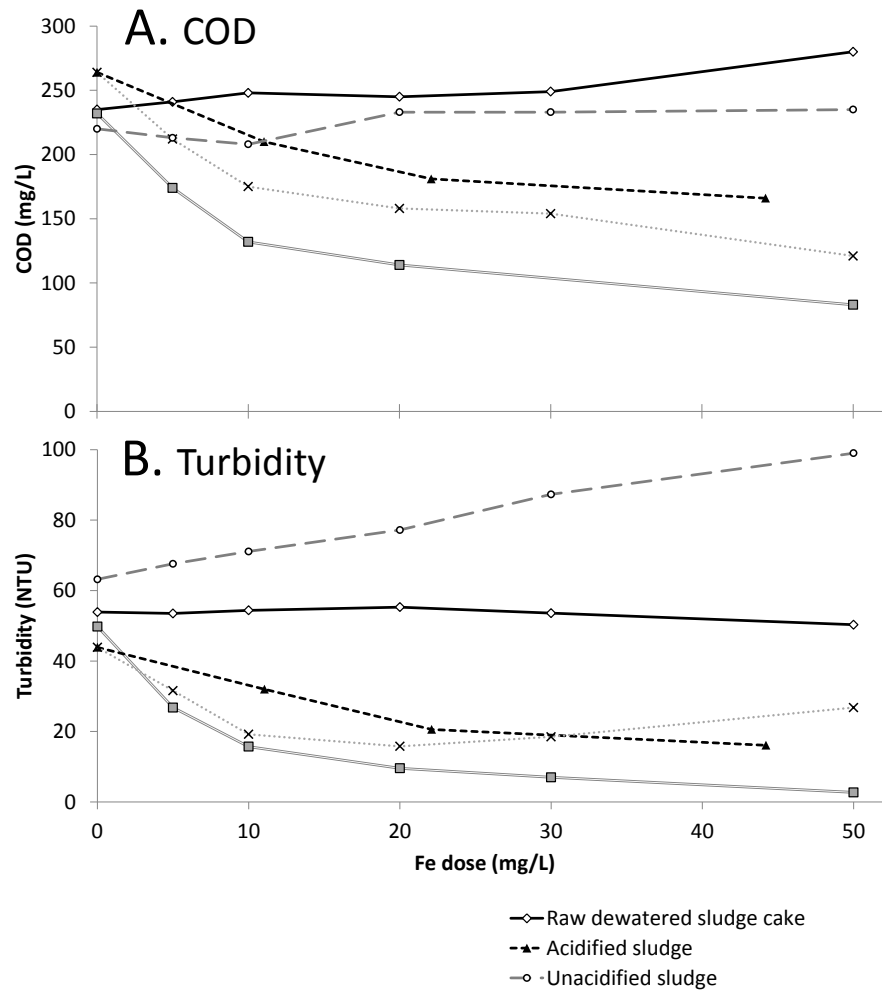


Figure 20: Residual COD, turbidity, residual Fe and total phosphorus after varying doses of coagulants.

While ferric coagulants are effective at P removal, they can consume wastewater alkalinity and elevate residual Fe concentrations. At Fe doses of ≤ 20 mg/L, residual Fe was maintained < 3 mg/L for all tested coagulant sludges, with FFS yielding a residual of 1.4 mg/L. These would exceed the European *Environmental Quality Standard* final effluent discharge limit of 1 mg/L as total Fe, themselves (Environment Agency, 2007) but further physical separation by downstream settlement (Parsons and Daniels, 2003) and filtration would mitigate this. Further experiments under the same conditions gave Fe residuals of < 1 mg/L for all RCs but ultrafiltered, suggesting the higher values were due to the short experimental settling time of 30 minutes in comparison to ~ 2 hours at full-scale (Tchobanoglous et al., 2003).

For acidified sludges, Fe doses of 20 to 50 mg/L led to a rapid rise in Fe residuals at a rate of 0.05 mg/L residual per additional mg/L Fe dosed, to a maximum of 5 mg/L (Figure 20). Conversely, for FFS, higher doses led to a slight decrease in residual Fe, due to the greater charge neutralisation of FFS than the less pure RCs. Compared to a raw water zeta potential of -14.6 mV, FFS neutralised particle surface charge to -10.7 mV, while the RCs were less effective, giving end values of -12.8 to -14.0 mV. The more stable (more negatively charged) waters correlated with higher residual Fe and turbidity (Figure 20) as Fe-DOC complexes were less inclined to aggregate and be removed through settlement. Sweep flocculation explains the lower Fe residual for the highest dose of FFS.

From an initial pH value of 7.8 and at 20 mg/L Fe, all coagulants maintained an end pH within < 0.6 units. Alkalinity titrations with treated wastewater against dilute HCl gave final alkalinities of 416, 428, 340 and 456 mg/L as CaCO_3 , for FFS, acidified, ultrafiltered and raw cake coagulants, respectively, compared to an undosed blank value of 524 mg/L. These all left sufficient alkalinity for subsequent nitrification, based on the requirement of 7 mg CaCO_3 per g of $\text{NH}_4^+\text{-N}$ (Liu and Wang, 2012) and the measured total nitrogen (48 mg/L ± 4).

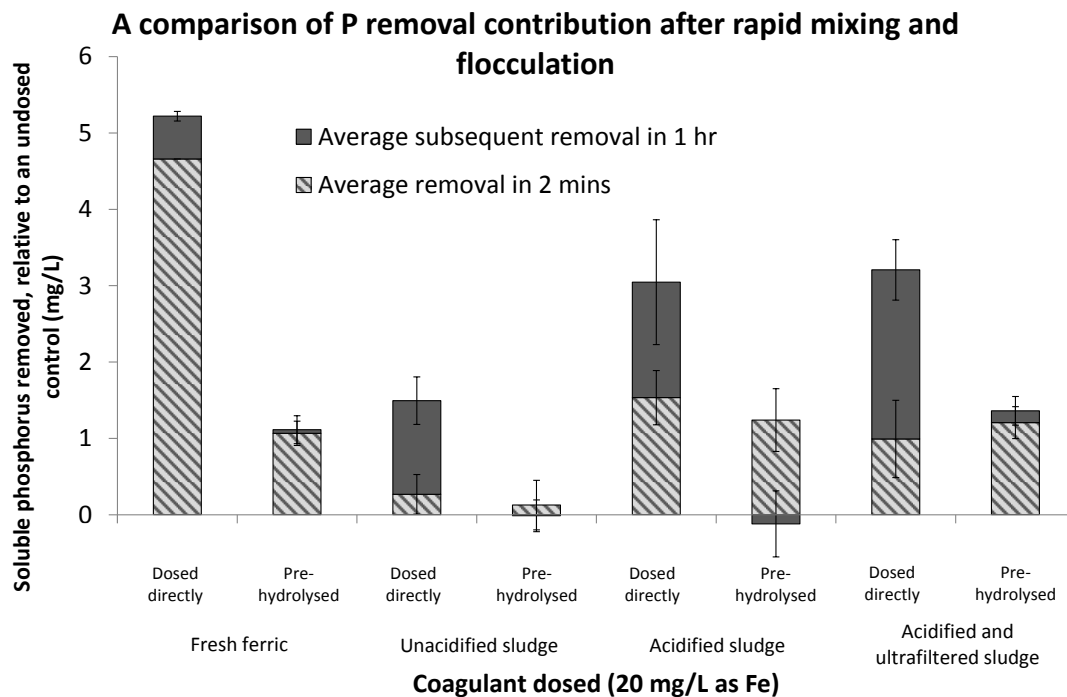


Figure 21: A comparison of soluble phosphorus removal contributions at two minutes and one hour.

To discriminate the P removal mechanisms used by RCs, removals after two minutes were compared to those after one hour. Removal was stopped at the time of sampling by filtration, so only soluble P (P_{sol}) removal can be discussed (measured as $71\% \pm 7\%$ of TP for the raw water). FFS achieved 90% of overall P_{sol} removal within two minutes of dosing (Figure 21). Formation of ferric-phosphate precipitates was the main removal route, due to the high stoichiometric efficiency (~ 225 mg P/g Fe in 2 minutes) which was achieved much faster than for adsorption, which is typically <30 mg P/g Fe per hour (Parsons and Daniels, 1999). This was confirmed when FFS was hydrolysed prior to dosing, such that P removal via precipitation could not occur. While some P removal still occurred, through adsorption onto the preformed ferric hydroxide (Smith et al., 2008), 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 one hour with FFS. This confirmed the predominance of the precipitation mechanism giving $>65\%$ of overall P_{sol} removal.

The RCs demonstrated slower removal (2 mg/L/h), with a greater proportion of P_{sol} removal achieved after one hour and equal removals to FFS when prehydrolysed (Figure 21). This was expected for the unacidified sludge, which is predominantly ferric hydroxide but surprising for the soluble Fe^{3+} dominated acidified RCs. Inhibition by organic compounds may account for this (Wang et al., 2012) but the ultrafiltered sludge, with a lower organic content, did not show any greater P_{sol} removal at 2 minutes (Figure 21). The additional water in the acidified RCs (>10 times more dilute than FFS) would mediate the hydrolysis of ferric sulfate on addition to the wastewater and impede contact with P_{sol} while precipitation occurred. For the RCs, subsequent removal after one hour gave a greater contribution to overall P_{sol} removal (~50%). This was due to more favourable equilibrium conditions than with FFS, with ineffective precipitation providing higher residual P concentrations to drive adsorption kinetics.

Specific removals of ~160 mg P/g Fe (after one hour) for the acidified sludges are 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 their removal mechanisms. The closest comparative specific removal was for a wastewater treated with fresh ferric chloride under poor mixing conditions (163 mg P/g Fe) where a similar combination of mechanisms occurred (Smith et al., 2008).

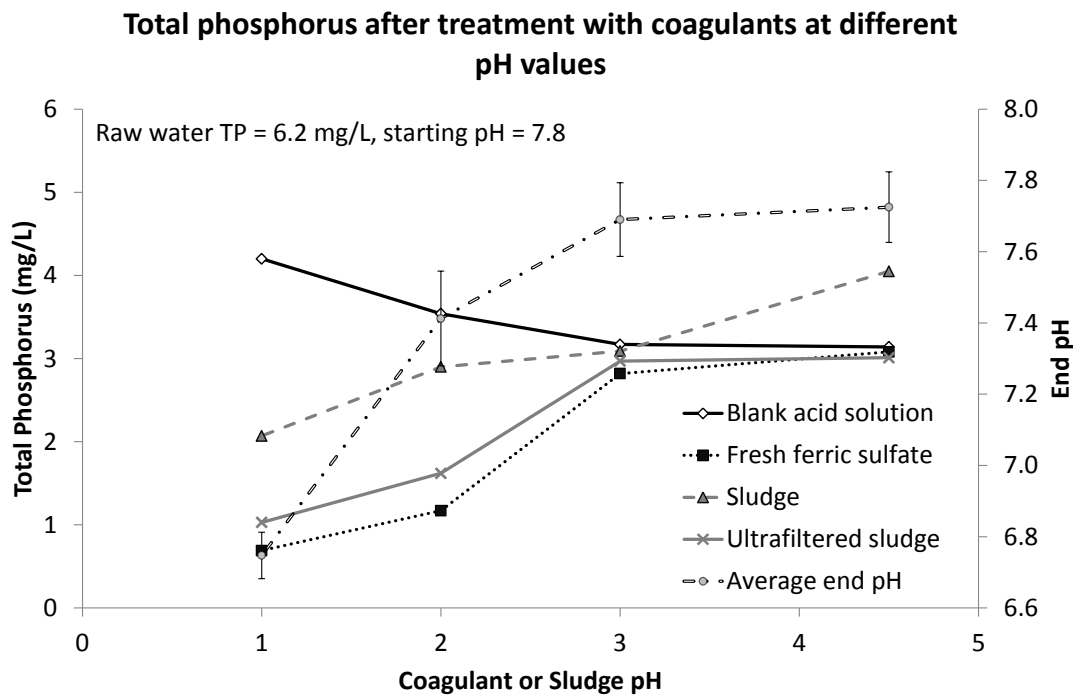


Figure 22: Residual total phosphorus at different coagulant pH values (prior to dosing).

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 pHs (Figure 22; Supporting Information: 5.4.1 Supplementary analysis of sludge pH adjustment and solubilisation). Ultrafiltered sludge closely mimics the performance characteristics of FFS, removing 81% and 74% of P at a sludge pH of 2, respectively. This similarity is due to the exclusion of insoluble Fe and 50% of DOC by the ultrafiltration membrane (Keeley et al., 2014a). When dosed, normalised to total Fe, this ensured similar Fe surface area 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. A pH of 1 enabled even greater P removals but was associated with a significant decrease in average treated water end pH to below 6.8 (Figure 22), 0.5 units below the pH values recommended to ensure sufficient alkalinity for downstream processes. P removal with unfiltered sludge 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 sludge gave consistently 0.5-1.0 mg/L higher Fe residuals than the other coagulants between coagulant pH values of 2 and 4.5. This correlated with the higher residual Fe (Figure 20C) and turbidity (Figure 20B) 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, the stable ferric-organic complexes may remain unreactive and soluble in the acidified sludge (Keeley et al., 2014b).

5.3.2 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 two minutes, 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} (Figure 23) 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 poorly mixed value), while the RCs increased from 0.0-0.5 mg/L, when poorly mixed to $\sim 1.0\text{ mg/L}$ at 75 s^{-1} and above.

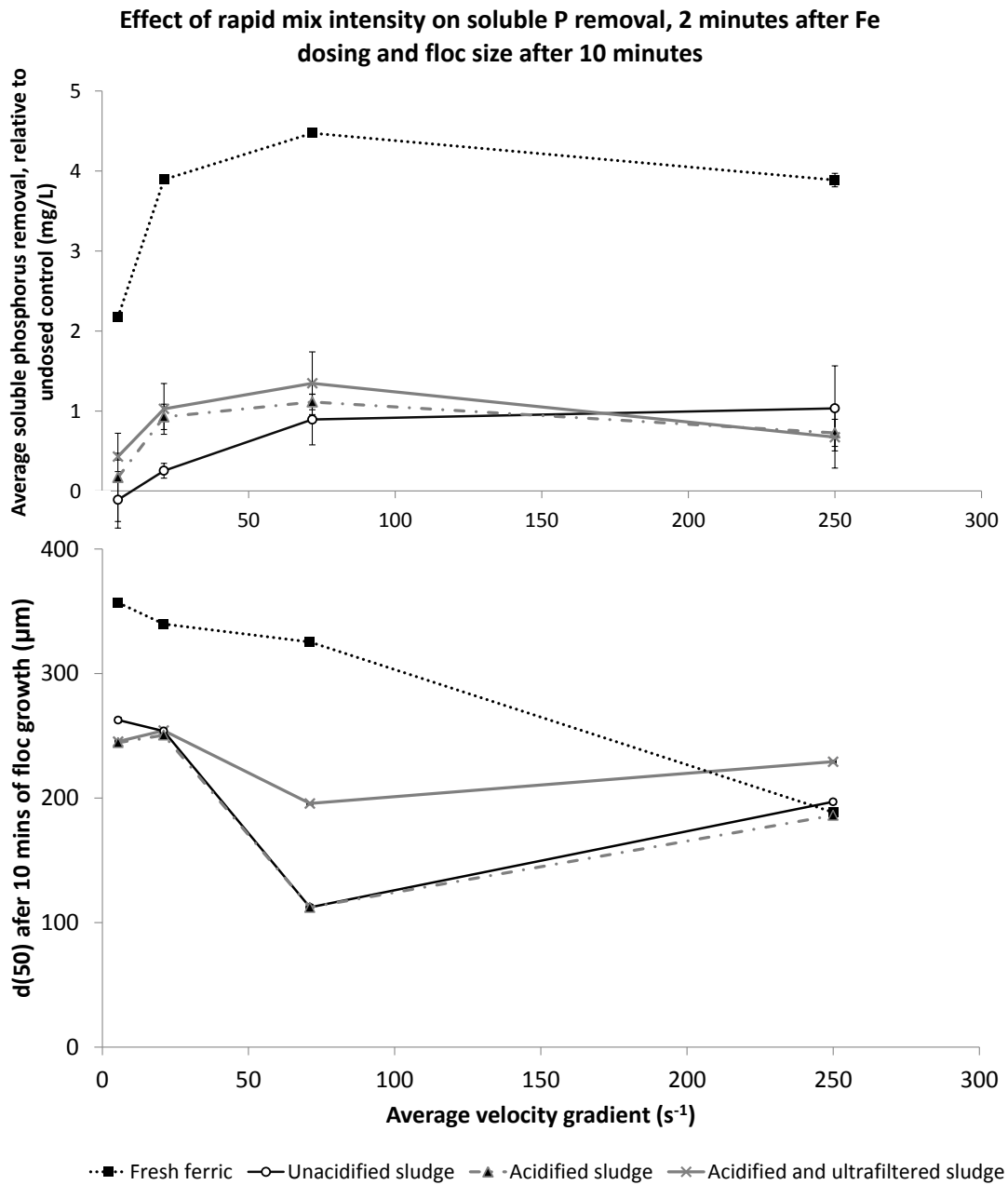


Figure 23: The effect of rapid mix intensity on soluble phosphorus removal and subsequent floc size.

Increased mixing intensity above $75 s^{-1}$ led to a minor decrease in P_{sol} removal and suggests that ferric-phosphate precipitates were resolubilised. To understand this, the effect of mixing intensities on floc size was examined (Figure 23). FFS formed the largest, most stable flocs, with a median size of $330-350 \mu m$ between $5-75 s^{-1}$. RCs generally had smaller floc sizes, with a

maximum median size of 250 μm after poor mixing ($<20\text{ s}^{-1}$). Increased mixing to 75 s^{-1} appeared to impede early-stage floc growth, giving a smaller median size of 100 μm for acidified sludges and 200 μm for unacidified sludge. This is due to the differing proportion of insoluble fractions in the sludge after acidification. Mixing values of 250 s^{-1} led to a decrease in FFS floc size, as there is sufficient energy to break up the ferric-phosphate flocs and corresponds to a minor reduction in P_{sol} removal (Figure 23). However much floc size is a factor in settleability, it is not indicative of preceding P_{sol} adsorption or precipitation until coprecipitation and aggregation develop (Takacs et al., 2006).

The hydraulic retention time in settlement tanks at WWTWs is typically 2 hours, following a flocculation time of typically >30 minutes (Tchobanoglous et al., 2003) and provides sufficient contact time for P adsorption. Extended jar tests at a moderate mixing intensity of 43 s^{-1} gave an insight to the changing rates of P removal over of several hours. All coagulants showed fastest removal rates in the first two hours, with 3.6, 3.1, 2.5 and 1.9 mg/L/h for FFS, ultrafiltered, acidified and unacidified sludges, respectively (Supporting Information: 5.4.3 Supplementary analysis of P removal over extended mixing durations). While FFS and ultrafiltered sludge provided no further removal, acidified and unacidified sludge continued for a further 6 hours, at 0.2 and 0.4 mg/L/h, respectively. After 2 hours, this equated to 82%, 71%, 56% and 52% TP removal with fresh, ultrafiltered, acidified and unacidified sludges, respectively. After 8 hours, all sludges except the dewatered sludge cake achieved P removals within 15% of FFS.

The continued removal contribution from adsorption onto ferric hydroxide highlights the potential to obviate the costs of WTR acidification, provided the treatment stream allows sufficient contact time. A key consideration for determining the optimal ferric-based P 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.

5.3.3 Economic Analysis

The assessment of treatment efficacy and acid demand enables a direct comparison of the economic efficiency of FFS to recovered sludges. Relative to P removal performance of FFS, at a dose of 20 mg/L and 90 minutes of mixing and settlement, unacidified sludge is 53% as efficient; acidified sludge, 88%; and ultrafiltered, 95% (Figure 22). The molar requirement of $\text{H}_2\text{SO}_4:\text{Fe}$ required to acidify sludge to pH to 2 was 2.6:1 (Supporting Information: 5.4.1 Supplementary analysis of sludge pH adjustment and solubilisation). This exceeds the 1.5:1 stoichiometric requirement but compares to empirical values (Parsons and Daniels, 1999).

The lowest 20 year WLC was provided by the transport and dosing of raw acidified sludge to the WWTW (Table 18). This was closely followed by transport and dosing of unacidified sludge. These reuse strategies would halve the 20 year WLC of using FFS with WTR disposal to land (Table 18). Such similarity in WLC shows that the acidification cost is almost equal to the value of improved P removal performance. Longer contact times will improve the P removal performance of unacidified WTR relative to acidified WTR, which would allow further reductions in WLC.

The improved treatment performance of ultrafiltered sludge fails to justify its costs, with its 20 year WLC approaching parity with conventional treatment. Direct connection of the WTW and WWTW sites with a sewer provided the lowest OPEX but this was insufficient to offset the construction capital expenditure (CAPEX) and gave rise to the highest WLC: £5.5m above conventional treatment. However, if sludge was sent to sewers instead of land, the significant OPEX of WTR 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 (Supporting Information: 5.4.5 Outcomes of sensitivity analysis). Acid and the monetary value of inferior P removal of RCs, relative to

FFS are 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 sludge by 16%. A 50% increase in FFS prices would increase unacidified sludge WLC by 28%. 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: 150 miles for acidified and unacidified; 80 miles for ultrafiltration; and 10 miles for a connecting sewer (Supporting Information: 5.4.5 Outcomes of sensitivity analysis). Shorter distances would significantly improve the processes' WLC.

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 WTR disposal, whilst better protecting the aquatic environment through more extensive nutrient removal.

Table 18: Whole life cost estimations for five possible sludge management/phosphorus removal strategies

	Component cost (£)	Basis of cost	Ref.	Fresh ferric for WWTW, with WTW sludge disposed to land	Raw sludge	Acidified sludge	Ultrafiltered	Direct connection	
CAPEX* (£)	Sludge reception	80,000	based on dewatered sludge conveyor		-	80,000	80,000	-	
	Acidification	350,000	5 L acid /min	1	-	-	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	
	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	
<i>Value of TP removal (based on performance relative to fresh) - Not directly included in OPEX total -</i>									
	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 H2SO4		-	-	80,000	80,000	-
	Transport	0.15	£/tonne/mile 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 (2g/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	

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

5.4 CONCLUSIONS

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

- When sufficiently mixed, raw and acidified WTRs are effective at removing P, with performance within 15% of FFS, at doses of 20 mg/L Fe and 8 hours of mixing.
- While effective at P removal, RCs relied on a greater contribution from the adsorption removal mechanism, in contrast to FFS which was more reliant on precipitation (65% of overall soluble P removal).
- At sludge pH values of ≥ 2 and Fe doses of 20 mg/L, there was sufficient residual alkalinity for nitrification and residual Fe levels were within 1 mg/L of water treated with FFS.
- Reuse of acidified or unacidified sludges 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 to equal conventional practice.
- A sludge-wastewater contact time of ≥ 8 hours can allow unacidified WTR performance to match acidified, making it an important consideration when evaluating their cost benefit.
- Inter-site distance had a significant effect on economic feasibility. A distance of 150 miles more than the current distance for sludge disposal to land brought the WLC of acidified and unacidified sludge reuse on parity with conventional practice.

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SUPPORTING INFORMATION

5.4.1 Supplementary analysis of sludge pH adjustment and solubilisation

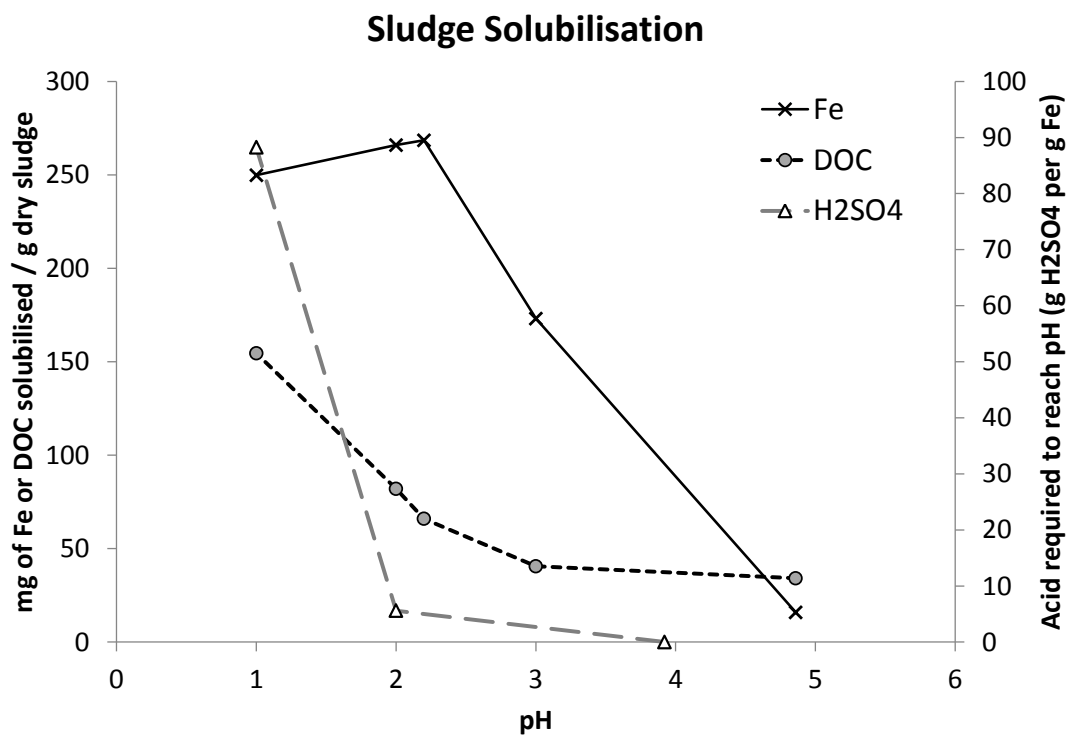


Figure 24: Acid requirement and iron solubilisation for waterworks sludge under excessively dilute conditions (1 g/L wet sludge).

5.4.2 Supplementary analysis of particle size

Method

Acidified and unacidified sludges (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 dosed into jar tests at normalised doses of 20 mg/L Fe.

Discussion

The influence of sludge particle size on Fe distribution and P removal was examined (Figure A). For both acidified and unacidified sludges, Fe was evenly distributed in the mesh-filtered fractions. The key difference was the soluble Fe content, with 2.5 g/L of soluble Fe in the <10 µm acidified fraction and almost none in the unacidified sludge. When normalised doses (20 mg/L as Fe) of these fractions were dosed into wastewater, there was a minor increase in P removal as the soluble fraction dominated the acidified sludge, as more Fe was available for precipitation (Figure 25). Without a soluble fraction, the unacidified sludge fractions P removal diminished as the Fe-containing particle size distribution decreased.

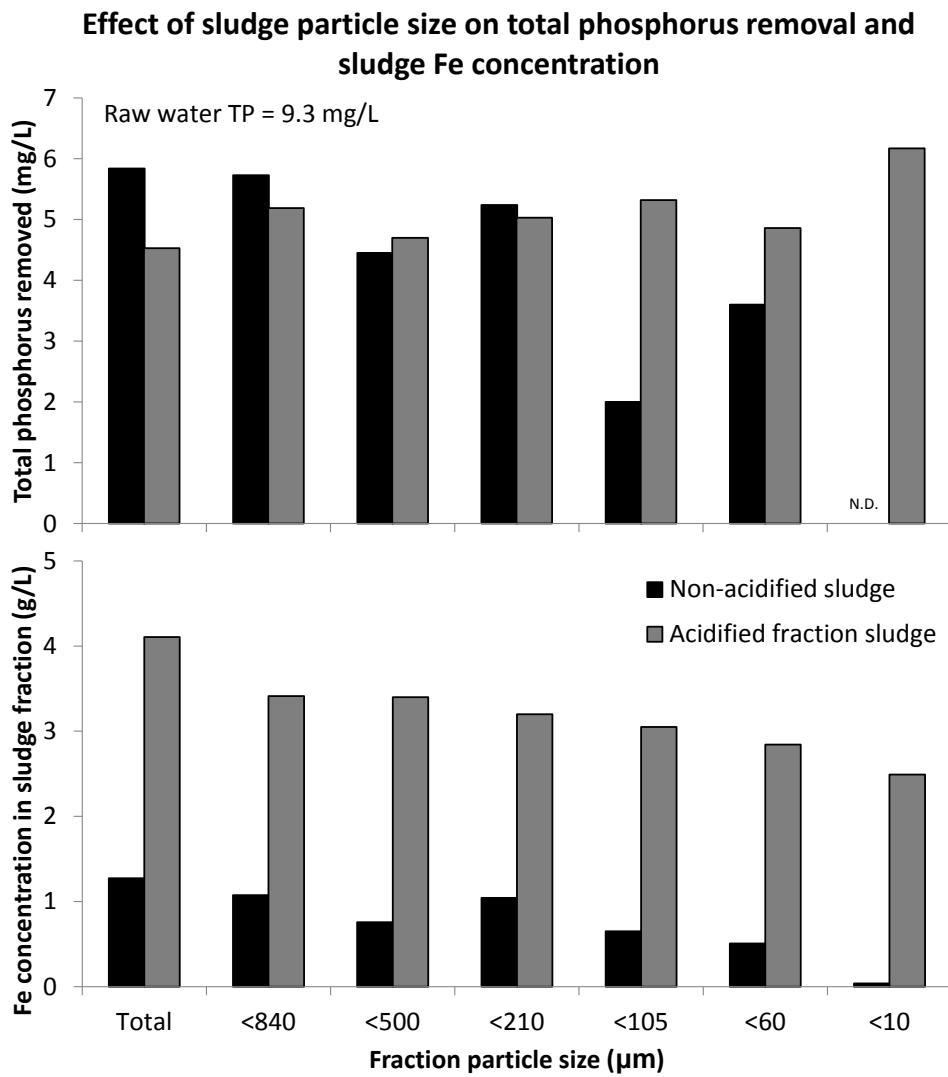


Figure 25: The effect of sludge particle size on iron concentration and total phosphorus removal when dosed equally at 20 mg/L as Fe.

5.4.3 Supplementary analysis of P removal over extended mixing durations

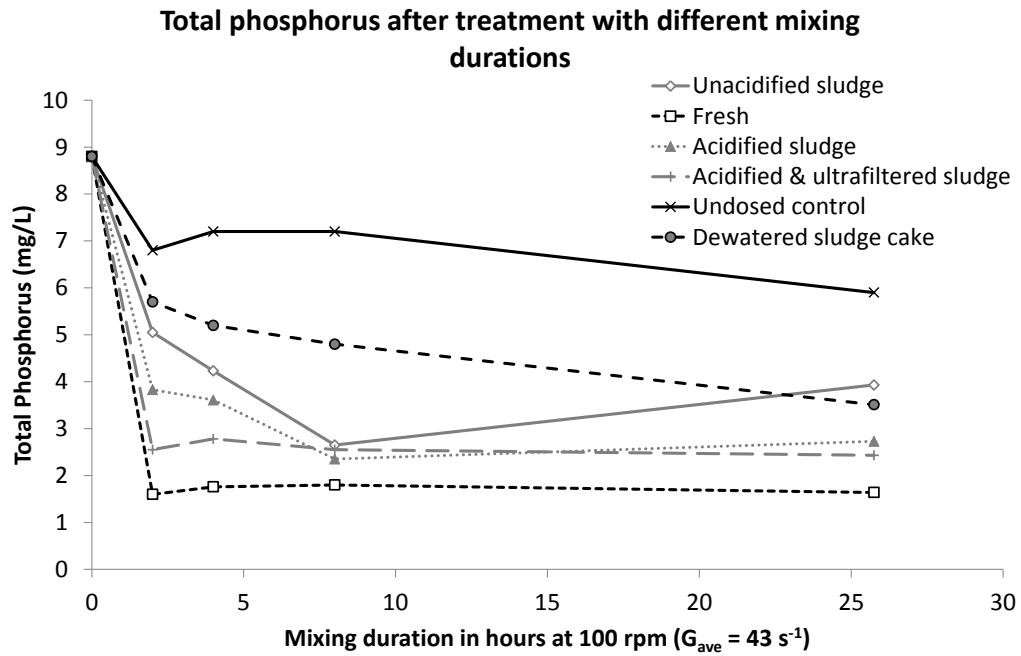


Figure 26: Removal of total phosphorus by ferric sludges over longer contact times (used to calculate removal rates).

5.4.4 Components of the cost model

As eluded to in Cost Modelling 5.2.2

$$WLC = C + \sum_{i=1}^n O_n + (O_{n-1} \times R_{inf})$$

Equation 2: Whole life cost determination

(Where C = total construction costs; O = annual OPEX; R_{inf} = annual rate of inflation, 3%; n = asset operational life in years; McGivney and Kawamura, 2008)

$$C = 667445 + 1078Q + 0.0716Q^2$$

Equation 3: Sludge reception and handling CAPEX

(Based on a filter press; where C = CAPEX in 2008 USD; Q = sludge volume flow in US gallons per hour; McGivney and Kawamura, 2008)

$$C = 26395 + 32.6Q$$

Equation 4: Sludge acidification CAPEX

(Where C = CAPEX in 2008 USD; Q = flow of concentrated sulfuric acid dosed in US gallons per day; McGivney and Kawamura, 2008)

$$C = 34153Q^{0.319}$$

**Equation 5: Ferric coagulant dosing
CAPEX**

(Where C = CAPEX in 2008 USD; Q = flow of ferric coagulant dosed in US gallons per day; McGivney and Kawamura, 2008)

$$C = 33269 + 7.0814V$$

**Equation 6: Rapid mix basin (G=900)
CAPEX**

(Where C = CAPEX in 2008 USD; V = basin volume in US gallons; McGivney and Kawamura, 2008)

$$C = 15.212Q^{0.7271}$$

**Equation 7: Ultrafiltration facility
CAPEX**

(Where C = CAPEX in 2008 USD; Q = millions of US gallons per day; McGivney and Kawamura, 2008)

$$O = 0.13D + 2.7$$

Equation 8: Transport OPEX

(Where O = OPEX in 2013 GBP; D = inter-site distance in miles, validated using quotes from commercial hauliers for values between 50 and 110 miles; Road Haulage Association, 2013)

5.4.5 Outcomes of sensitivity analysis

Table 19: Sensitivity analysis for component costs (results with <5% change have been omitted)

Parameter changed (+50%)		Fresh ferric	Raw sludge	Acidified sludge	Ultrafiltered	Direct connection	
Base: 20 year WLC (£)		13,650,000	7,510,000	6,930,000	11,630,000	19,120,000	
Percentage of base WLC	CAPEX* (£)	Sludge reception / pipeline	-	-	-	-	139%
		Acidification	-	-	-	-	-
		Ultrafiltration	-	-	-	109%	-
		Ferric dosing system	-	-	-	-	-
	OPEX (£)	Fresh ferric cost	133%	128%	108%	-	110%
		Acid cost	-	-	116%	109%	-
		Inter site distance	-	116%	117%	110%	-
		UF electricity cost	-	-	-	113%	-
		Disposal to land cost	111%	-	-	-	-

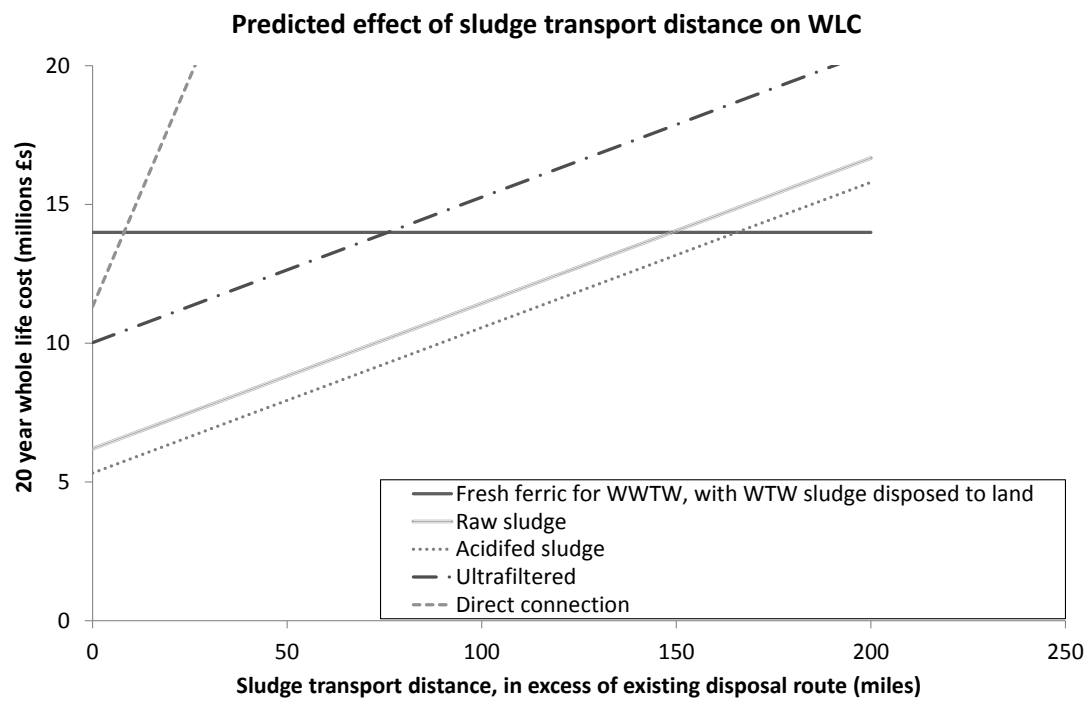


Figure 27: The effect of excess sludge transport distance, beyond the current disposal route, on the whole life cost of sludge reuse in wastewater treatment.

CHAPTER 6

MAKING COAGULANT RECOVERY WORK FOR DRINKING WATER TREATMENT

IN PREPARATION FOR: *The Journal of Hazardous Materials*

6 MAKING COAGULANT RECOVERY WORK FOR DRINKING WATER TREATMENT

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ABSTRACT

Coagulant recovery from waterworks sludge has the potential to significantly reduce the operational costs water utilities pay for waste disposal and chemical procurement. Stringent drinking water regulations necessitate purification of any recovered metals before they can be safely reused and while many separation technologies have proven effective in this role, none have successfully matched commercial coagulant treatment performance at full-scale.

This study has examined the individual and successive separation performance of a number of novel and existing ferric coagulant recovery purification technologies, in an attempt to match fresh coagulant purity. The novel approach of alkali extraction of dissolved organic compounds (DOC) from waterworks sludge, prior to acidic solubilisation of ferric coagulants, demonstrated similar selectivity performance (874 mg/L Fe; 61 mg/L DOC) to more established separation by size: ultrafiltration (1285 mg/L Fe; 91 mg/L DOC). Cation exchange Donnan membranes were also examined and while they were the most selective individual process (2555 mg/L Fe; 29 mg/L DOC), the low pH of the recovered ferric solution impaired treatment performance.

Experiments using a carbon adsorbent as a polishing stage showed that powdered activated carbon (PAC) was superior to powdered graphite, in terms of specific DOC adsorption capacity. When used in tandem with ultrafiltration or alkali pre-treatment, a PAC dose of 80 mg/mg DOC reduced recovered ferric DOC contamination to <1 mg/L with no significant Fe uptake. The treatment performance of the purified recovered coagulants was compared to fresh ferric sulfate coagulant on the basis of key water quality parameters. Several PAC-

polished recovered coagulants matched or bettered fresh ferric coagulant performance in terms of DOC and turbidity removal, and showed the potential to reduce disinfection byproducts and regulated metals to similarly low levels as their fresh counterparts.

6.1 INTRODUCTION

Coagulation-flocculation is a key process in potable water treatment. While effective, the sheer scale of its operation accounts for ~5% of water treatment works' operational costs, from a combination of coagulant and pH adjustment chemical costs, as well as disposal of the resulting sludge, also known as water treatment residuals (WTR) (Niquette et al., 2004). Within the UK water treatment industry, annual coagulant consumption exceeds 325,000 tonnes (Henderson et al., 2009) and WTR production exceeds 182,000 tonnes (Pan et al., 2004), costing £41m and £8.1m, respectively (adjusted to current prices) (UKWIR, 1999). The problem is reflected globally, with annual waterworks sludge production exceeding 6.6m tonnes in the US (Walsh, 2009) and 300,000 tonnes in Japan (Fujiwara, 2011).

Coagulant recovery (CR) provides the opportunity to reduce these costs by regenerating and reusing the coagulant metals in the WTRs. This is usually achieved through acidification, with most studies reporting total coagulant metal solubilisation at pH 2 (Keeley et al., 2014a). However, organic compounds within the sludge have similar pH-solubility (Prakash and Sengupta, 2003), contaminating the acidified recovered coagulant (RC) with dissolved organic compounds (DOC). If these are dosed into the potable treatment stream, the levels of residual DOC will be higher at the final chlorination stage. These higher levels of disinfection byproduct precursors will elevate the levels of harmful (World Health Organization, 2000) and regulated (USEPA, 2009; DWI, 2010) halogenated organic compounds in the final treated water. To protect public health and to abide water quality regulations, reuse of RCs must be

preceded by a purification stage that removes organic and monitored metal contaminants.

Conventional membranes (Keeley et al., 2014), adsorbents (Lindsey and Tongkasame, 1975), chemical precipitation (Ulmert and Sarner, 2005) and ion exchange (Prakash and Sengupta, 2003) have been tested in this role but have failed to provide adequate removal of organic contaminants or provide 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 set out by a UK's Water Industry Research council white paper (UKWIR, 2007).

This study aims to provide a benchmark for the purity and treatment performance of various recovered ferric sulfate coagulants, 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 (Figure 28) in an attempt to improve RC quality, particularly in terms of minimising DOC contamination, which has never been documented as being below 3.5 mg/L for RCs (Prakash and Sengupta, 2003).

6.2 METHODOLOGY

6.2.1 Coagulant recovery and purification

Dewatered WTR cake (measured as 14% dry solids, of which ~25% Fe) was collected from a 120-180 MLD WTW treating upland water with ferric sulfate coagulant (Derbyshire, UK). Slurries containing 1 kg of sludge cake in 10 L of deionised water were mixed for 24 hours at 60 rpm using a rotary paddle mixer and were used as the basis for coagulant recovery extractions using acid or alkali.

An alkali pre-treatment stage was investigated by adjusting the WTR slurry to pH 12 using reagent grade sodium hydroxide pellets and was mixed for 24 hours before being allowed to settle. The soluble phase was set aside for analysis while the insoluble fraction was retained on glass-fibre filters (1.2 μm pore size) and washed using 1 L of deionised water. The solid phase was digested in 1 L of sulfuric acid (5 M) using a magnetic stirrer for 24 hours, before being diluted to 10 L with deionised water. Direct solubilisation with acid was achieved by adding sulfuric acid (18 M) to the WTR slurry, until a pH of 2 was held, and mixing for 24 hours.

Both the alkali pre-treated and direct acid extractions were purified using pressure filtration or extraction through a cation exchange membrane. Pressure filtration through a polyethersulfone membrane with a molecular weight cut-off of 2 kD (Sterlitech Corporation, Kent, WA, USA) was conducted using a flat-sheet cross-flow cell described fully in a previous study (Keeley et al., 2014b). In brief, this comprised a membrane of 0.007 m^2 , with a feed-side Reynolds number of 2350 and transmembrane pressures of 400 kPa. The membrane cell was also adapted for use with a Nafion 115 cation exchange membrane, with the same available membrane area. The feed-side recirculated 2 L of acidified sludge and the strip-side recirculated 1 L of 1 M sulfuric acid, both using 520du Watson-Marlow peristaltic pumps at 30 rpm. Dialysis 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).

A post-treatment adsorption stage was applied to all RCs to further reduce dissolved organic carbon (DOC) concentrations. In addition to powdered activated carbon (PAC; Norit SA Super 94002-8), powdered graphite (PG; Fisher, UK) was also examined as a previous study has suggested it may have a high adsorption capacity for organic acids at pH values ≤ 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 sulfuric acid) were mixed on magnetic stirrers for 48 hours with 25 mL of RC at

pH 2 (UF permeate for the acidified RC sample). The aqueous phase was filtered through 0.45 µm nylon filters (Fisher, UK) before analysis for DOC using a Shimadzu TOC-V analyser and for soluble Fe, using a PerkinElmer atomic absorption spectrometer (AAS). 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 (Figure 28).

RCs were characterised directly in terms of pH, Fe, DOC content, and charge density using a method of visual titration with ortho-toluidine blue indicator against a standardised polyvinylsulfate anionic polymer solution (Kam and Gregory, 1999).

6.2.2 Recovered coagulant treatment performance

Jar tests were used to compare RCs to fresh coagulant in terms of treatment performance. Raw water and fresh ferric sulfate coagulant (FFS; measured as 20% Fe using AAS) were sampled from the same site as the WTRs. A Phipps & Bird PB-700 jar tester was used to mix 1 L of raw water in a cylindrical beaker. Jar tests were conducted at room temperature, following an existing method (Sharp et al., 2006) with a 1.5 min rapid mix at 200 rpm, 15 min flocculation mix at 50 rpm and a 20 min settlement stage. Treated water was analysed for DOC, turbidity, and zeta potential using a Malvern Zetasizer Nano ZS.

A series of jar tests with FFS were used to determine the optimum coagulation 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 (Figure 30). This dose and pH was then used for further jar tests with RCs. DOC, UV absorption at 254 nm (which was then used to calculate specific UV adsorption; SUVA), turbidity, and zeta potential were analysed, in addition to analysis of residual metals (Cu, Pb, Ni, Cd, Cr and Mn) using inductively-coupled plasma spectroscopy, and trihalomethane formation potential (THM-FP) using a method (Parsons et al., 2004) modified from the standard methods (APHA, 1992). Size

exclusion liquid chromatography with detection of UV absorption at 254 nm was also carried out using a Shimadzu VP series chromatogram.

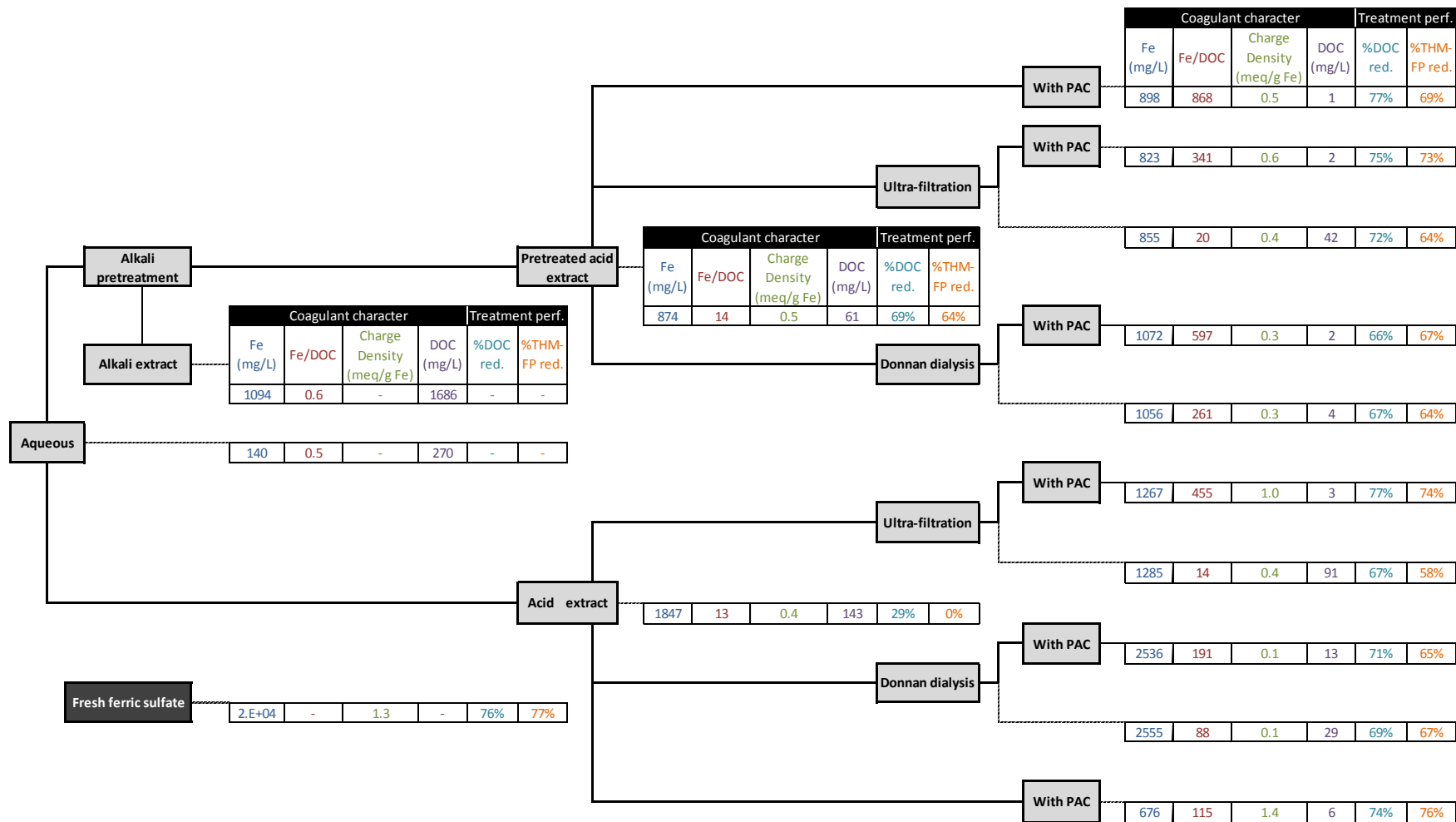


Figure 28: Recovered coagulant experimental processing scheme and sampling points

6.3 RESULTS AND DISCUSSION

6.3.1 Recovered Coagulant Purification: Unit Process Performance

Three coagulant purification unit processes were investigated: 1) alkali extraction of DOC prior to acidification and solubilisation of the retained solids; 2) membrane separation using UF or DD; and 3) DOC adsorption using powdered carbon (Figure 28).

Alkali pre-treatment. Sodium hydroxide is an established chemical for the removal of natural organic compounds in membrane cleaning protocols, via hydrolysis, saponification and dissolution (Porcelli and Judd, 2010). A pH 12 solution of sodium hydroxide was used to extract the bulk of organic compounds from WTRs prior to further treatment, while leaving less soluble iron in a more pure, suspended phase which was subsequently solubilised in sulfuric acid. This process showed selectivity for Fe: an equal mass of WTR produced the same volume of acidified sludge extract with 57% less DOC than simply acidifying (61 mg/L \pm 1.4% compared to 143 mg/L \pm 2.8%; Figure 28). However, only 47% of the Fe extracted by simple acidification was recovered when the alkali pre-treatment stage was incorporated. While solubility profiles would suggest that only negligible amounts of Fe remain in solution at pH 12 (King et al., 1976), greater losses could be attributed to the passage of colloidal iron hydroxide and Fe-DOC particles through the retaining glass-fibre filter. Despite this, the process demonstrated selectivity for Fe, with a slightly higher Fe:DOC ratio of 14.3, compared to 12.9 with simple acidification.

Ultrafiltration. Size exclusion based purification of RCs has been thoroughly investigated in previous studies (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005; Keeley et al., 2014). These studies showed that within a range of <1-20 kD MWCO UF membranes, a 2 kD MWCO gave the optimum balance of DOC rejection and trivalent metal recovery. However, this MWCO still allowed a significant amount of DOC carryover, at 91 mg/L DOC with 1285 mg/L Fe, from a feed containing 143 mg/L DOC and 1287 mg/L Fe (Figure 28). A similar Fe:DOC ratio before (12.9) and after UF (14.1) would suggest a similarly low

level of selectivity by size exclusion as with alkali treatment. 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 weaker interacting Al (Keeley et al., 2014).

Donnan dialysis. This method utilizes a cation exchange membrane to extract coagulant metal ions from an impure acidified sludge, rather than forcing them through a conventional membrane. In doing so, DD avoids the costs of membrane fouling, high transmembrane pressures and energy consumption associated with conventional membrane filtration (Prakash and Sengupta, 2003). In addition, DD has 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 <5mg/L DOC contamination (Prakash and Sengupta, 2003). Similar performance was repeated 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 (Figure 28). The comparatively high yield and more dilute recovery solution are due to a lower 2:1 volume ratio of feed sludge to recovery acid than the ratio of 4:1 used by Prakash and Sengupta (2003). The relative volumes of which affected the distribution of ions across the membrane at the point of Donnan equilibrium.

Further dilution of the Donnan RC solution occurred by osmosis, as 190 mL of water per litre of recovery solution, across the ion exchange membrane, after Donnan equilibrium had been reached (Prakash et al., 2004). This osmosis may also have carried hydrophilic organic compounds and would account, in combination with a thinner, more permeable cation exchange membrane (127 μm for Nafion 115 vs. 183 μm for Nafion 117, as used by Prakash and Sengupta, 2003) for the higher level of DOC carryover observed in this study. This record of osmosis highlights the importance of balancing recovery yield with concentration and purity, through specific dialysis time.

DD of the alkali pre-treated sludge was less effective, with the same volume of sludge yielding 73% Fe at 1072 mg/L but with lower DOC carryover of 4 mg/L.

The lower yield and concentration was due to a feed Fe concentration of less than half that of the solely acidified feed, 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 Na in the RC, following the preceding extraction of organic compounds with sodium hydroxide. These Na⁺ ions would also be extracted through the cation membrane via the same ion exchange mechanism, competing with Fe and allowing the Donnan equilibrium to be reached before as many Fe³⁺ ions had exchanged into the recovery side.

Adsorption of DOC from an Acidic Ferric Sulfate Solution Using Powdered Graphite and Activated Carbon

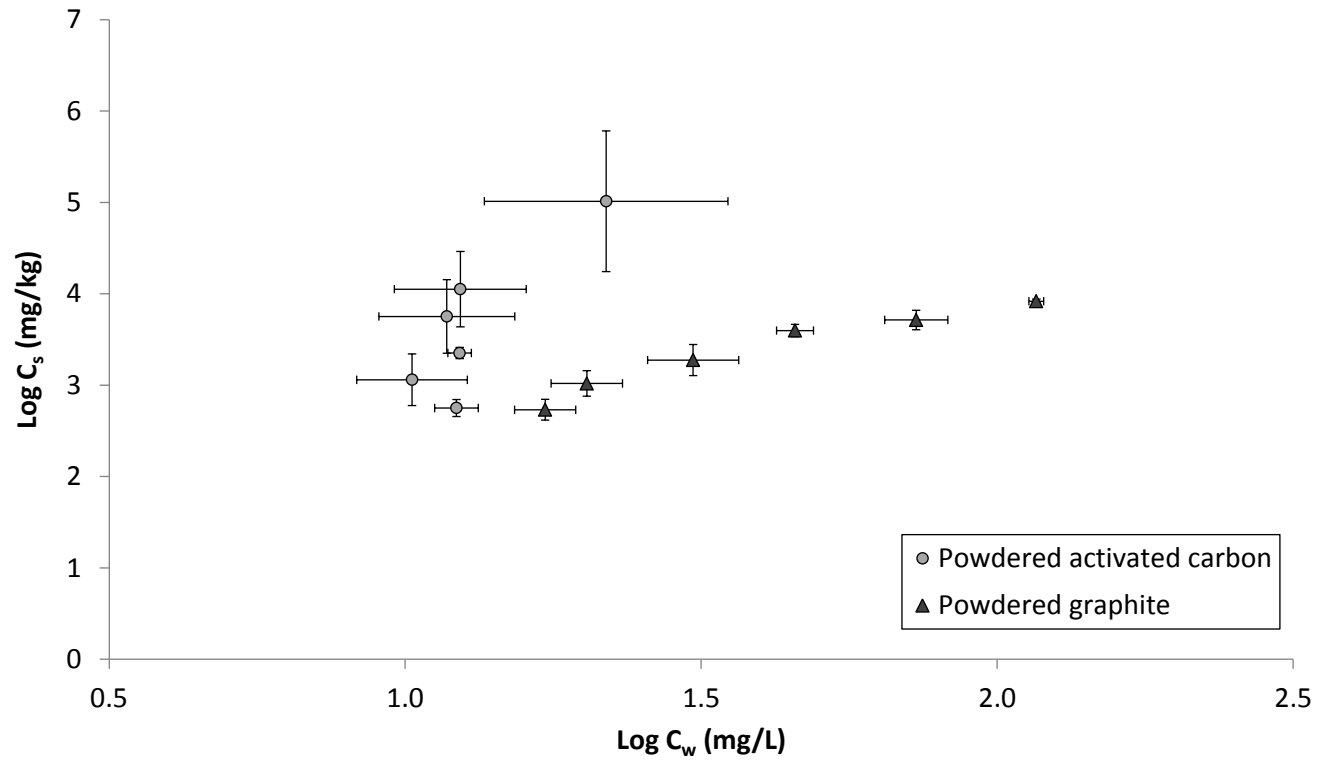


Figure 29: Adsorption of DOC by PAC and powdered graphite at pH 2

Adsorption. Preliminary tests compared the adsorption of DOC by PG and PAC from an ultrafiltered RC sample containing 91 mg/L DOC and 1285 mg/L Fe. Adsorption isotherms at pH 2 showed DOC removals of 90 and 86% by PAC and PG at the highest adsorbent dose of 200 g/L but at lower doses PAC showed higher DOC percentage removals that were between 1.5 and 10 times more than that of PG (Figure 29). This supports the reported success in using granular activated carbon for the removal of DOC from recovered alum sludge (Cornwell et al., 1981) and suggests that the predominantly non-electrostatic driven adsorption that occurs at pH <3 is sufficient for the required DOC removal performance in this role, since the DOC and PAC will be protonated and positively charged at this low pH (Newcombe and Drikas, 1997). This study has focused on achieving the optimum separation of DOC from Fe and not modelling of the adsorption isotherms, but relative gradients of the isotherm plot (Figure 29) indicate that PAC has a greater specific DOC adsorption capacity than PG.

A PAC dose of 10 g/L was selected as higher doses gave only marginal removal improvements: a 100 g/L reduced the DOC residual by only 2 mg/L whilst removing 330 mg/L of Fe. At this dose PAC removed 6 times more DOC than PG. Accordingly, PG was precluded 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. At the highest adsorbent dose of 200 g/L the Fe concentration increased by 10-15%. This was possibly due to incomplete wetting of the PAC prior to adsorption as the volume of wetting water was completely absorbed, indicating the potential for further water absorption from the RC solution.

The isotherms showed that a PAC dose of 80 mg/mg DOC (10 g/L for the UF solutions used in the preliminary isotherm tests) would ensure effective DOC removal from partially purified RCs, without significant uptake and loss of Fe. At these doses, removals of 94-98% were achieved from acidified; alkali pre-treated; and ultrafiltered RCs. DD RCs were less effectively purified by PAC, with DOC removals of 54-56%. This could be partly due to the low starting DOC

concentrations of 4 and 29 mg/L for pre-treated and non-pre-treated DD RC (their differing DOC content due to alkali extraction pre-treatment). Additionally, the DD RCs had significantly lower initial pH of ca.0.5, compared to 1.5-2.8 for other PAC treated RCs. Such a high H⁺ concentration would make DOC and PAC more electropositive, increasing electrostatic repulsion to a point that adsorption is inhibited (Xiao and Pignatello, 2014). The organic character of the residual DOC in DD treated RCs may also negatively affect the ability to be adsorbed: to permeate a cation exchange membrane, they are likely to be hydrophilic, have a low molecular weight, and a low electronegative charge. The final DOC concentrations for PAC-treated RCs were in the range of 1 to 13 mg/L (Figure 28) which is 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 for those that were alkali pre-treated, with and without UF or DD treatment. This indicates that alkali pre-treatment removes DOC of different character to PAC, combining to give a greater overall removal. Alternatively, the alkali pre-treatment may chemically alter the remaining DOC through hydrolysis and saponification (Randtke and Jepsen, 1981; Schafer, 2001), making it move more easily through PAC micro-pores and adsorb more effectively.

Relative separation performance of individual processes. All of the individual processes were capable of recovering Fe at concentrations of 70% or greater than their feeds, except for alkali pre-treatment and direct PAC treatment of acidified sludge, which gave concentrations of only 57% and 35% of their Fe feed. More importantly, in terms of their impact on treated water quality, there was significant DOC rejection from each stage. UF gave the least effective DOC exclusion of 31-36% due to the crossover of molecular weight distributions for DOC and Fe compounds. PAC treatment of DD treated RCs 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 sludge organic compounds leading to carry-over into the recovered solid phase and subsequent organic compound solubilisation upon acidification. Far better DOC rejection was provided by DD (80-93%) and PAC treatment at pH values of 2 and higher initial DOC loadings (90-98%). These data indicate that charge or adsorptive DOC removal is key to ensuring the minimum RC final DOC concentration.

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).

6.3.2 Recovered Coagulant Purification: Treatment Train Performance

The combined performance for a number of CR treatment trains has been evaluated in terms of a number of potential measures for RC quality, as previously proposed by Cornwell (1981): Fe concentration, DOC carryover, and pH; as well as the novel consideration of Fe/DOC ratios and measured charge density. These measures were then compared to coagulant treatment performance and benchmarked against fresh ferric coagulant in a subsequent section (Figure 28).

Fe concentration. For fully acidified and solubilised ferric RCs, soluble Fe concentration could be indicative of an RC's ability to destabilize impurities, via surface charge neutralisation, when it is dosed to raw water. By this measure, DD was the most effective treatment option: DD without alkali pre-treatment and DD followed by PAC polishing gave the highest Fe concentrations of 2555 and 2536 mg/L, respectively. The next highest was the unpurified sludge acid extract with 1847 mg/L. These results highlight the inevitable losses of Fe if alkali pre-treatment or, to a lesser extent, UF stages are incorporated into the RC purification train. The concentrations of Fe recovered using UF and DD are

comparable with previous studies using similar approaches that gave RCs with 3500 mg/L Al with UF (Ulmert and Sarner, 2005) and 5400 mg/L Fe with DD (Prakash and Sengupta, 2003) with feed concentration and volume being key determinants of RC concentration, respectively. 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 because the cost benefit of producing RCs at such a significantly higher concentration remains uncertain, although it would reduce transport volumes and allow centralised processing.

DOC concentration. Because the principal concern of RC use in potable treatment is elevated DBP (disinfection by-product) formation resulting from carried over DOC, another useful measure of CR efficacy is the level of residual DOC in the RCs. Processes using PAC and alkali pre-treatment gave the lowest DOC concentrations with: alkali pre-treatment coupled with PAC post-treatment (1 mg/L); alkali pre-treatment with UF or DD and PAC post-treatment (2 mg/L); and non-pre-treated UF with PAC post-treatment (3 mg/L). This suggests that PAC treatment is integral to reaching the highest purity of RC and confirms the necessity of an activated carbon polishing stage which had previously been proposed by Cornwell et al. (1981). While PAC is effective as polishing stage, it is still dependant on the DOC removal contribution from preceding treatment processes, whether that is alkali pre-treatment, membrane separation or a combination of both. Without these preceding treatments the high DOC load in the RC and thus higher PAC dose relative to Fe, would lead to significantly greater Fe adsorption and higher less complete DOC removal from the RC. Because UF and PAC utilize different mechanisms of DOC removal (size and adsorption, respectively) they will remove different fractions of DOC from RC and maximize overall removals: removal of the larger DOC compounds by UF will reduce the loadings onto the PAC and will prevent clogging of its pores, just as coagulation and filtration prior to GAC is beneficial in main water treatment streams.

Fe/DOC ratios. These ratios enable comparison of the selectivity for a given CR process: if the Fe concentration is higher, smaller volumes of RC will be required for a given dose application and thus less carried over DOC will be added. Because DOC concentrations are proportionately more variable between the CR processes (varying between 1 and 143 mg/L in acidified RCs, compared to Fe varying between 676 and 2555 mg/L) Fe/DOC ratios correlate more closely with DOC concentrations than Fe. Accordingly, the highest Fe/DOC values are for alkali and PAC treated without further membrane treatment (868), and with DD (597), both achieved primarily through extensive DOC rejection. These were followed by UF permeate with PAC post-treatment (455) which had a higher DOC carryover (3 mg/L) but this was offset by a higher Fe concentration yield than the alkali pre-treated RCs, as well as fouling of the PAC pores by larger DOC molecules.

Charge density. The final measure investigated for RC quality was direct measurement of the coagulant metal cationic charge density, determined by titration against an anionic polymer. However, for both FFS and RCs, the measured values were 10-100 times lower than the theoretical equivalence for Fe^{3+} or Fe^{2+} would suggest. It is likely that in all but the most DOC-depleted RCs, the majority of Fe is unavailable or it is unfavourable for it to bind to the anionic polymer, thus excluding their charge from the measurement. The low value of 1.3 meq/g for DOC-free FFS also suggests that the difference in molecular weights between the ~1kD coagulant compound and ~170 kD anionic polymer titrants (Kam and Gregory, 1999) may be less compatible than for the cationic polymers the method was designed to measure. This could allow multiple coagulant cations to bond to a single anionic polymer molecule, leading to an underestimated reading. PAC treated RC without alkali pre-treatment had the highest charge density of the RCs with a value of 1.4 meq/g Fe (Figure 28). This was followed by PAC treated UF permeate without alkali pre-treatment (1.0 meq/g Fe) and the same RC but with alkali pre-treatment (0.6 meq/g Fe). The other RCs had lower values of 0.4-0.6 meq/g Fe, with DD RCs having a

markedly lower range of 0.1-0.3 meq/g, possibly due to their lower pH limiting Fe charge availability.

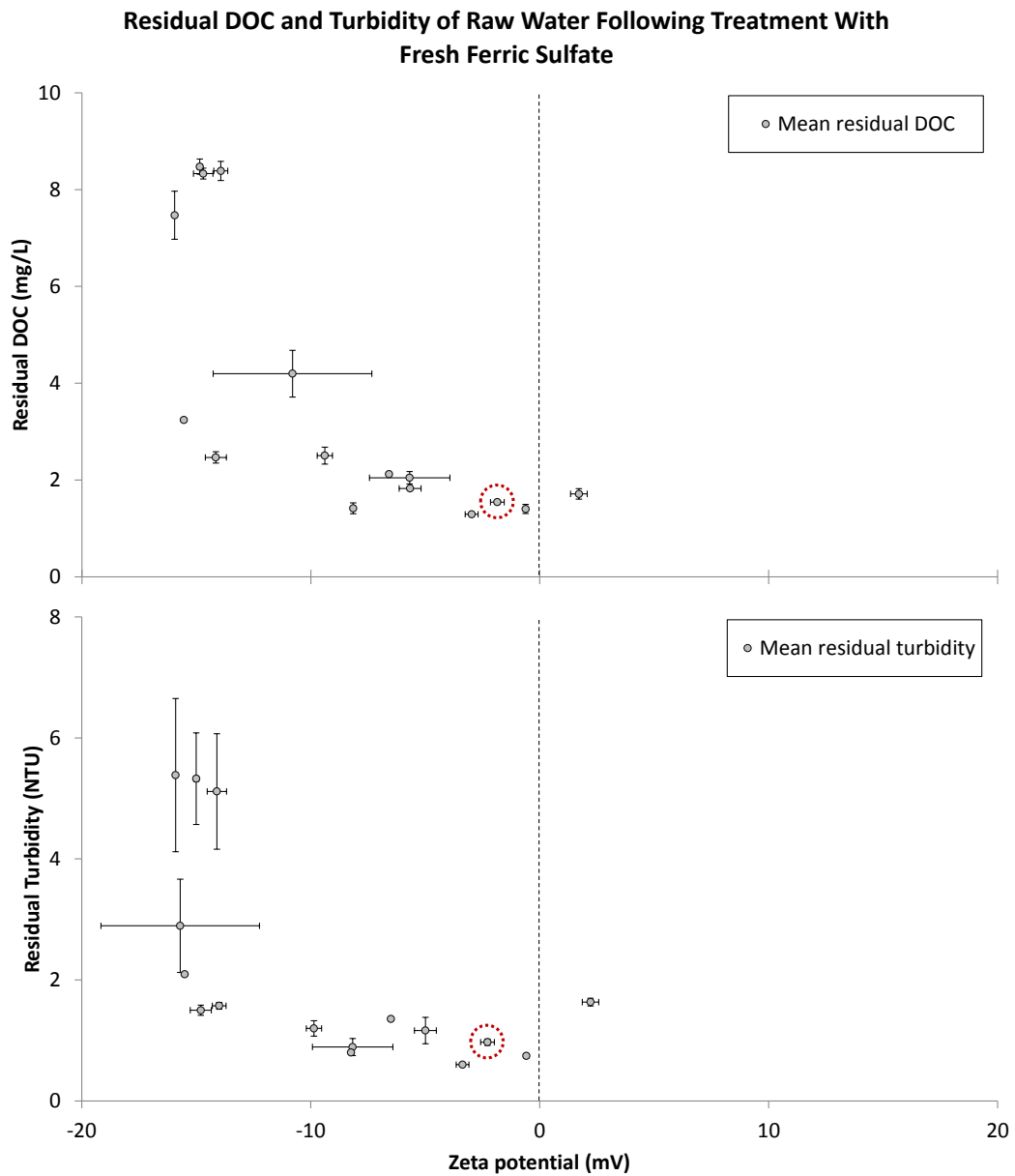


Figure 30: Coagulation optimisation for DOC and turbidity removal using fresh ferric sulfate. The circled data point indicates the dose selected for subsequent tests (24 mg/L Fe).

6.3.3 Recovered Coagulant Treatment Performance

While the aforementioned data may provide a useful comparison between RCs, DOC and turbidity removal performance, as well as residual metals and THM-FP, remain the fundamental criteria for validating measures of RC quality.

Using FFS, a conservative coagulant dose of 24 mg/L as Fe and pH of 4.5 were selected from well within the optimum zeta potential zone and optimum DOC and turbidity removals (Figure 30). This was to ensure that coagulant performance was only affected 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 with RCs.

RC treatment performance, in terms of DOC and THM-FP reductions, as well as residual turbidity and Fe in treated water, was plotted against RC Fe, DOC, Fe/DOC and charge density to identify which RC characteristics most affected treatment performance (Figure 31). For all purified RCs, DOC removal with RCs was within 10% of FFS performance and marginally better for non-DD RCs with carried-over DOC levels <3 mg/L (Figure 32). THM-FP reduction was within 18% of FFS for all RCs but crucially, always inferior to FFS; and residual turbidity was equal or 50% less than when treated with FFS. Residual Fe was more variable, with generally higher concentrations than with FFS but in some cases, including the best DOC removing RCs, the residual Fe concentrations were approximately equal to those treated with FFS. Unpurified, acidified RC gave very different performance, providing only 30% DOC removal, no THM-FP reduction and elevating turbidity and residual Fe to levels ca. 10 times that of the raw water. This is due to its unique nature compared to the other RCs: having a significant DOC concentration (143 mg/L) with an additional 100 mg/L of suspended organic compounds that was absent in the other RCs (total organic carbon was measured as 242 mg/L).

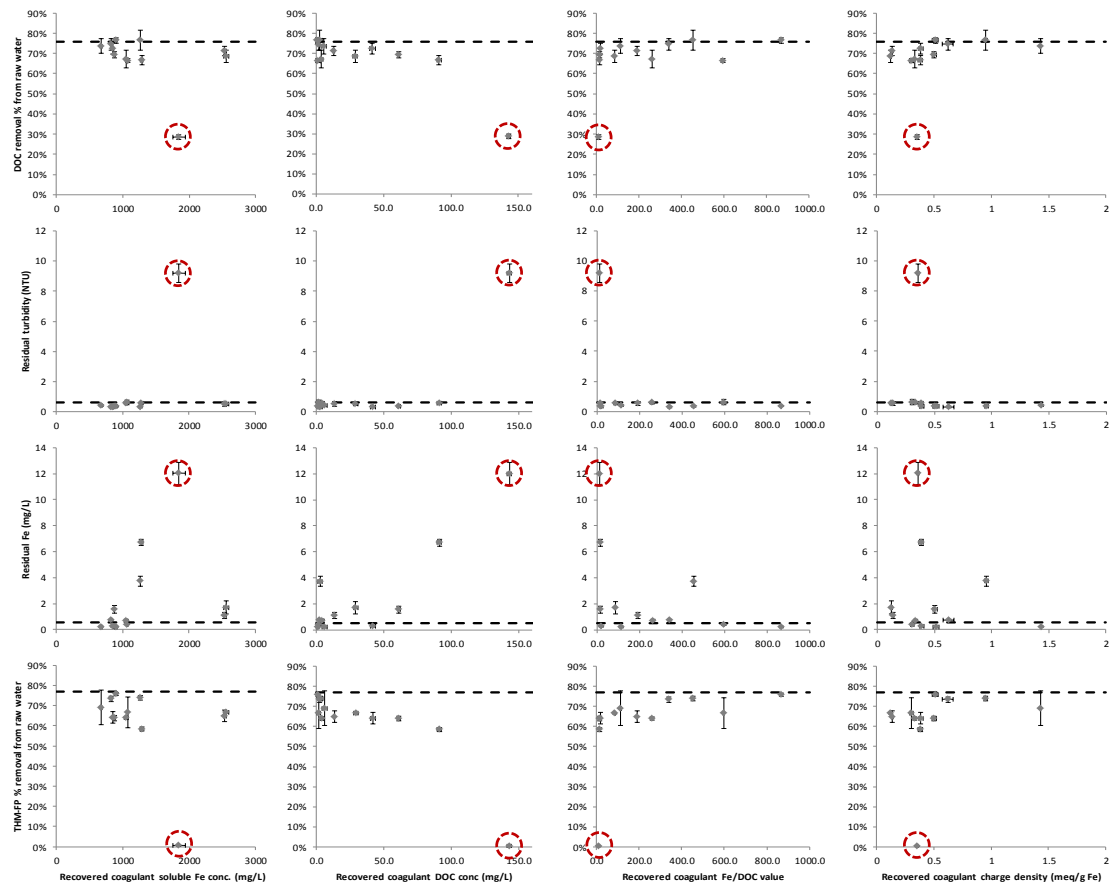


Figure 31: Recovered coagulant treatment performance in terms of DOC, turbidity, Fe residual and THM-FP for four potential measures of RC quality. The dashed horizontal line indicates performance of fresh ferric sulfate under the same dose and conditions. Outlying data points for unpurified RC are circled and were excluded from subsequent correlation plots.

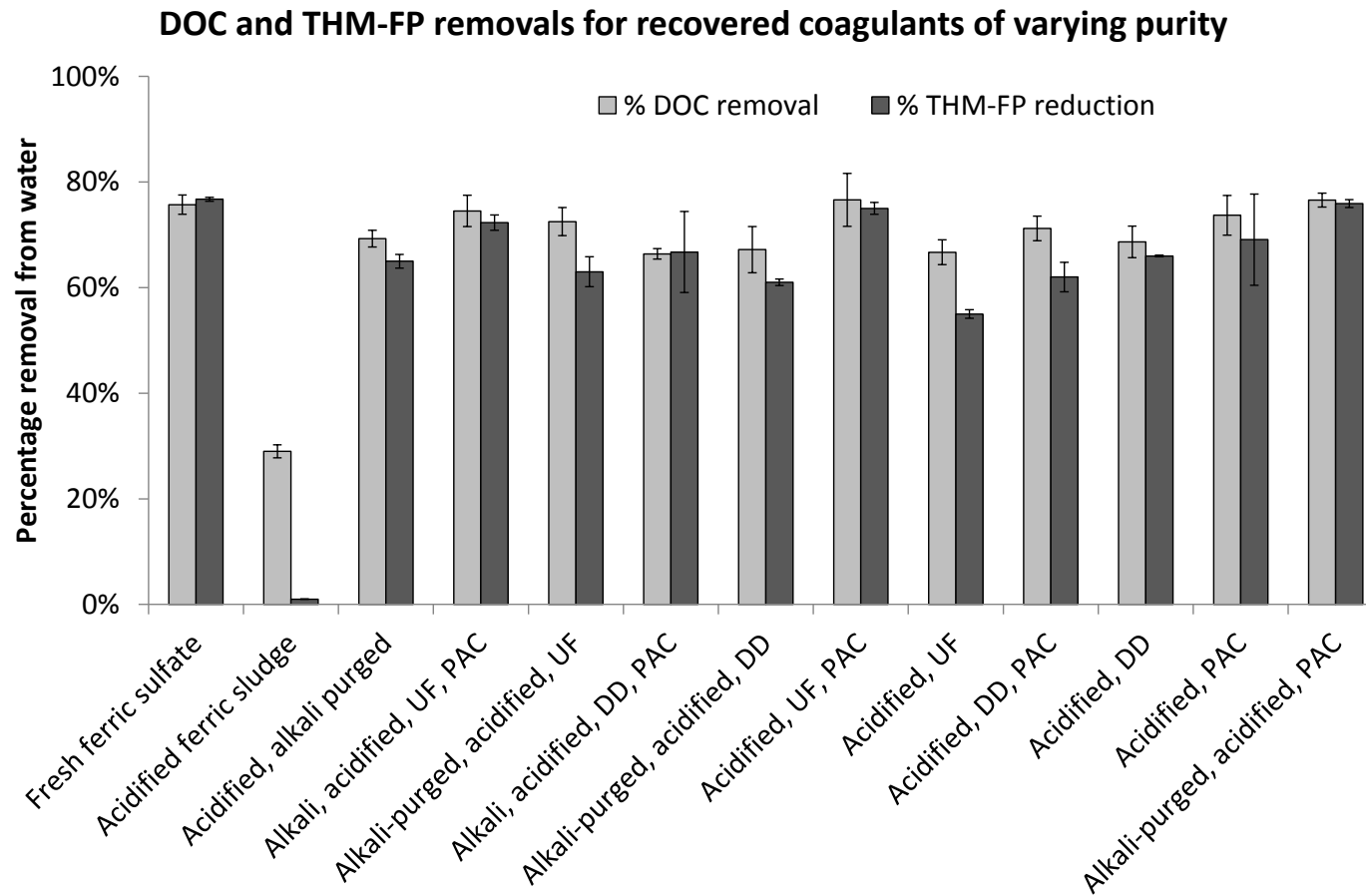


Figure 32: Mean percentage removals of DOC and THM-FP for recovered coagulants of differing purity

With the impure RC excluded due to its differing character, the remaining RCs' performance did not appear to be solely dependent on a single RC parameter (Figure 31). The data was analysed using linear, power, logarithmic, exponential and second order polynomial for least-squares regression correlations, with maximum R^2 values selected for each (Supporting Information: Figure 34). Correlations were poor for many of the relationships ($R^2 < 0.40$) but some stronger correlations were also observed. The concentration of residual Fe was dependant on coagulant Fe and DOC concentrations (polynomial R^2 values of 0.70 and 0.50, respectively), suggesting that a high DOC concentration would increase soluble Fe levels by stabilising it in solution. The relationship with Fe concentration would indicate that intermediate concentrations lead to the highest residual. This may reflect the onset of sweep flocculation at higher concentrations or the contribution of other factors such as RC pH.

The dependence of DOC removal and residual turbidity on charge density gave R^2 polynomial correlations of 0.50 and 0.40, respectively. These indicate that a charge density between 0.5 and 1.0 meq/g gave the best removal performance. For these RCs, the charge density and purity was sufficient to achieve charge neutralisation of raw water contaminants. In addition, the low level of DOC contamination in these RCs that contributed to their slightly reduced charge density, would also provide nucleation sites to seed floc formation and aid turbidity and DOC removal, in a similar way to ballasted-floc technologies (Desjardins et al., 2002). In effect, the small amounts of carried over DOC within the RCs could be acting as coagulant-aid polymers, helping flocs aggregate and capture lower molecular weight DOC fractions (Zhao et al., 2013). Reductions of THM-FP had power correlations with RC DOC concentrations and Fe/DOC values (R^2 values of 0.64 and 0.58, respectively). These highlight the sensitivity of THM-FP removal on RC purity, with FFS THM-FP removal performance only being matched when RC DOC decreased below 5 mg/L and at Fe/DOC ratios above 350 (Figure 31).

Although no single measure of RC quality can fully predict the treatment performance of RCs, the CR processes which produce RCs with the best treatment performance can still be identified. The greatest DOC removals were achieved by non-DD PAC-treated coagulants, which gave removal percentages of 74-77%: equal to FFS. The other purified RCs gave removals of 65-73%, with solely acidified RC giving only 29% removal, due to its high carried-over DOC content and low availability of free Fe ions to neutralise the surface charge of DOC in the raw water. The inferior performance of DD RCs, despite low levels of carried-over DOC and correction to pH 4.5 upon dosing to the water, suggests that the low pH (~0.5, which is similar to FFS), the required volume (more than 10 times that of FFS, for the same Fe dose) of the final Fe-containing strip solution and the time taken for pH correction to be fully mixed can combine to partially inhibit coagulation. This then allowed slightly higher amounts of DOC and turbidity to remain in solution than RC purity alone would suggest (Figure 28). For the DD RCs the molar requirement of NaOH to maintain a coagulation pH of 4.5 was 150 times the number of Fe mols added to achieve a 24 mg/L Fe dose. 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 exceed the UK's national limit of 200 mg/L (DWI, 2010). Acid recovery, which has already been proposed to improve the chemical efficiency of the feed side of the DD CR process (Schneider, 2013), may be able to reduce the acidity of the DD RC product and thus the requirement for NaOH to achieve the pH window for coagulation.

Reductions in THM-FP followed a similar pattern to DOC, suggesting that the RCs removed DOC of the similar reactivity (Figure 32). Based on previously determined DOC reactivity (Keeley et al., 2014b) and actual DOC residuals, coagulants that reduced THM-FP by ~75% would 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 were: FFS (THM-FP reduction: 77%); alkali pre-treated with PAC polishing (76%); UF with PAC polishing (75%); and alkali pre-treated with UF and PAC (72%). The other

RCs gave THM-FP reductions of 55-69%, with the unpurified acidified RC providing no reduction.

The purest RCs appear able to match the THM precursor removal performance of commercial FFS and may allow their use at full-scale to be reconsidered. Furthermore, because THM-FP is a measure of the maximum possible THM levels, it is important to remember that under more realistic conditions, with intermediate treatments (such as GAC or advanced oxidation) and less complete chlorination, the actual THM levels would be lower. Repeated analysis of THM-FP is required to ensure this performance is repeatable given the seasonal and geographical variation in natural organic material character (Parsons et al., 2004), as well as the added complexity of an RC system.

HPSEC was used to further investigate if the use of RCs affected the DOC character (in terms of the size distribution of UV absorbing fraction). Relative to the raw water chromatogram profile, all non-DD RCs removed the faster eluting, larger organic compounds most effectively (Figure 33), leaving a residual that eluted between 10-12 minutes, just as with FFS. Such similarity would confirm that these RCs have been successfully regenerated and recovered and employ the same removal mechanism of DOC from raw water as FFS. The higher ionic strength following treatment with the more acidic DD RCs (and subsequent pH adjustment following dosing) appeared to increase the elution time of the DOC residual in the treated water. This could be due to increased charge interaction with the size exclusion column media; increased natural organic linearity, due to shielding of the organic molecules by the higher aqueous ionic charge (Schafer, 2001); or by hydrolysis and saponification of organic molecules, on addition of alkali during pre-treatment or to reach a coagulation pH of 4.5. The occurrence of either of these mechanisms would help explain the poorer DOC removal performance than the high purity of DD RCs would suggest.

UV absorbance size exclusion chromatograms for waters treated with recovered ferric coagulants with varying purity

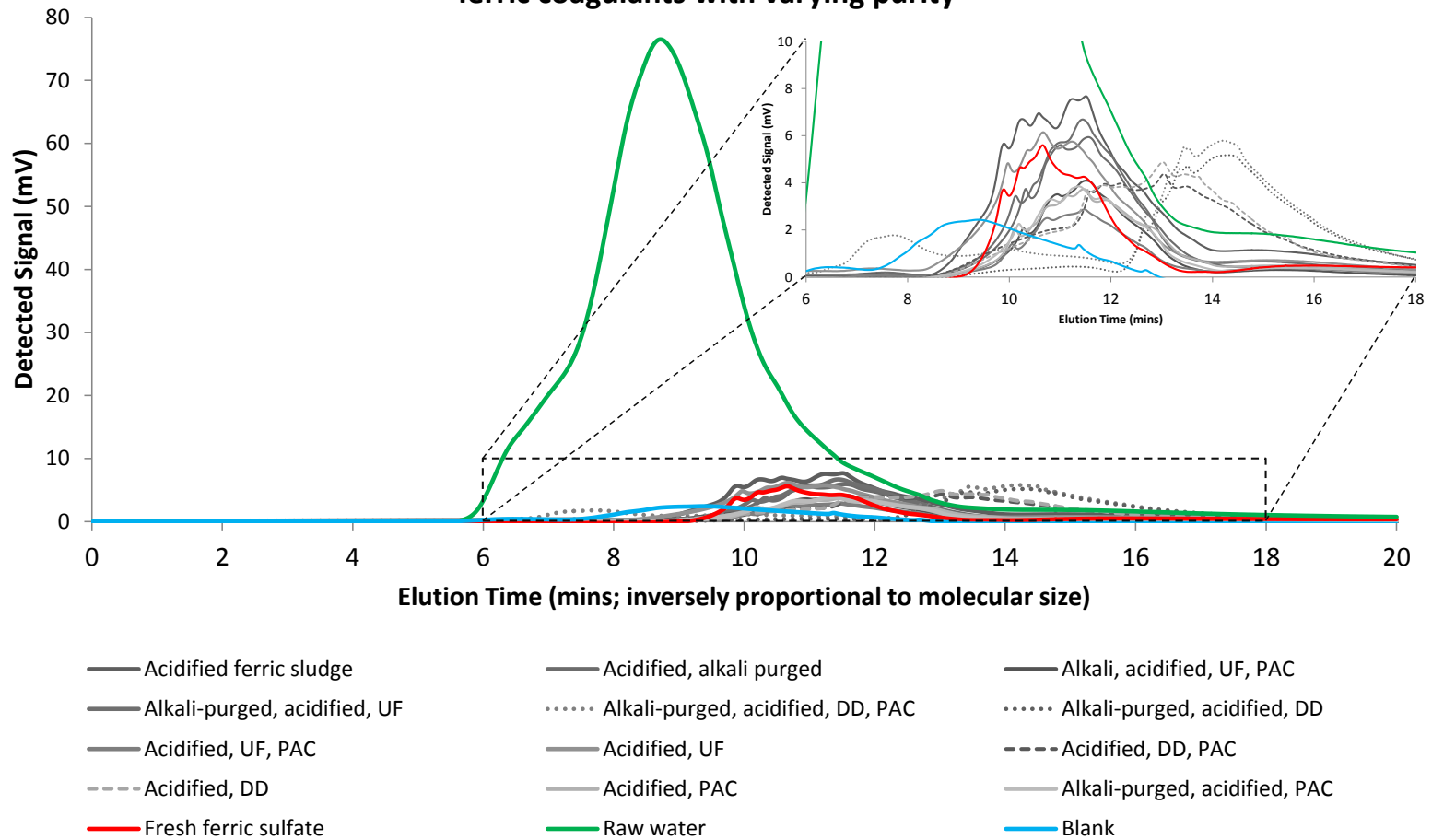


Figure 33: Size exclusion chromatograms for waters treated with recovered coagulants of varying purity

Analysis of trace metals in water treated by all RCs satisfied Cu, Pb, Cd and Cr limits for the US and UK (Table 20). Ni limits were exceeded for all UF treated waters, which when viewed alongside elevated Cu and Pb, may have been caused by corrosion of the brass pressure gauge fittings used in the UF cell. Mn levels were elevated above that for FFS treated water for all RCs except alkali pre-treated. All treated waters (including FFS) would require Mn removal following coagulation using downstream Mn removal processes to meet the regulatory limit of 50 µg/L. However, this treatment stage is often present because commercial ferric coagulants are permitted to contain Mn in concentrations up to 2% w/v (European Standards EN 890:2004). Any backwash return streams from the Mn contactors should be excluded from WTRs that are used for CR, as their inclusion in the recycle would lead to Mn accumulation (Tomono, 1977). Similarly, Fe levels would exceed the regulatory limits of 200 and 300 µg/L, (DWI, 2010; USEPA, 2009, respectively) but these would be removed by the same Mn removal process. The claim made that DD is selective for trivalent Fe and Al metals (Prakash and Sengupta, 2003) cannot be supported by the levels of residual metals in the waters treated in this study.

Table 20: Residual metal content for waters treated with recovered coagulants of varying purity

	Cu	Pb	Ni	Cd	Cr	Mn	Fe
	Value (SD)	Value (SD)	Value (SD)	Value (SD)	Value (SD)	Value (SD)	Value (SD)
Fresh ferric sulfate	2 (1)	-	8 (3)	0.0 (0.01)	0.9 (0.5)	89 (3)	0.22 (0.0)
Acidified ferric sludge	3 (1)	-	6 (1)	0.1 (0.00)	0.9 (0.2)	188 (1)	12.01 (1.8)
Acidified, alkali purged	2 (0)	-	3 (1)	0.1 (0.00)	0.5 (0.1)	74 (3)	1.57 (0.6)
Alkali, acidified, UF, PAC	174 (5)	1 (0.1)	24 (1)	0.1 (0.01)	1.1 (0.1)	82 (2)	0.75 (0.1)
Alkali-purged, acidified, UF	136 (1)	1 (0.0)	19 (0)	0.0 (0.00)	0.9 (0.2)	60 (1)	0.26 (0.1)
Alkali, acidified, DD, PAC	6 (2)	1 (0.1)	6 (0)	0.1 (0.00)	1.2 (0.1)	84 (2)	0.39 (0.0)
Alkali-purged, acidified, DD	6 (2)	-	6 (0)	0.1 (0.01)	1.1 (0.3)	87 (2)	0.69 (0.2)
Acidified, UF, PAC	215 (11)	-	31 (0)	0.1 (0.00)	1.0 (0.1)	150 (4)	3.74 (0.8)
Acidified, UF	240 (9)	0 (1.1)	30 (1)	0.1 (0.00)	1.4 (0.1)	138 (4)	6.72 (0.5)
Acidified, DD, PAC	4 (2)	-	5 (0)	0.1 (0.01)	1.0 (0.2)	148 (5)	1.10 (0.5)
Acidified, DD	4 (1)	-	5 (0)	0.1 (0.01)	0.9 (0.2)	152 (4)	1.70 (1.0)
Acidified, PAC	4 (0)	-	15 (0)	0.3 (0.02)	0.8 (0.1)	582 (3)	0.23 (0.1)
Alkali-purged, acidified, PAC	3 (1)	-	6 (0)	0.1 (0.01)	0.7 (0.1)	105 (5)	0.23 (0.1)
Raw water	1 (0)	-	1 (0)	0.0 (0.00)	1.2 (0.0)	6 (1)	0.46 (0.1)
Units	µg/L						mg/L
<i>DWI 2009 limit</i>	<i>2000</i>	<i>10</i>	<i>20</i>	<i>5</i>	<i>50</i>	<i>50</i>	<i>0.20</i>
<i>USEPA 2010 limit [denotes non-enforceable guidelines]</i>	<i>1300 [1000]</i>	<i>15</i>	<i>-</i>	<i>5</i>	<i>100</i>	<i>50</i>	<i>[0.30]</i>

6.4 CONCLUSIONS

This study has investigated the selectivity of a number of new CR processes and the performance of resulting RCs in comparison to FFS. PAC outperformed PG and a dose of 80 mg PAC /mg DOC consistently reduced RC DOC levels to <15 mg/L (and <6 mg/L for RC with pH values >1) with a minimal loss of Fe. When used in conjunction with alkali pre-treatment or UF, PAC-treated RCs provided DOC and turbidity removal performance on raw water, which was equal to or greater than FFS. UK and US parametric limits for residual metals levels and THMs were sufficiently satisfied by the purest RCs (with some requiring downstream removal of Mn and Fe), as was the UK's regulatory obligation to minimize DBP formation, by matching the THM precursors removal of commercial FFS. This demonstrates that simple, multistage RC purification technologies can meet the needs of potable treatment quality.

Extraction through DD membranes showed the highest selectivity for Fe and rejection of DOC in a single process, corroborating previous research (Prakash and Sengupta, 2003). However, this investigation also found that the potentially high ratio of acidity to Fe in the resulting RC created a high alkali requirement to achieve the normal coagulation pH window for DOC removal (Qin et al., 2006) and could be detrimental to treated water quality and process economics. In this respect, while a certain acidity (ca. pH 2) is beneficial to RC performance and a requirement of more extensive Fe solubilisation, excessive acid content could be seen as an unwanted contaminant.

The heterogenic nature of organic and inorganic contaminants within raw RC creates a matrix from which the recovery of a sufficiently pure Fe RC 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 and Fe recovery. Therefore, the use of both in the same CR purification train would be of marginal value. Instead, one of these treatments (or DD, if its acidity can be reduced) could be used in tandem with a PAC polishing stage. This would reduce the DOC loadings the PAC is exposed to. This would then minimize the

required dose of PAC and its adsorption of Fe, maximizing final Fe/DOC, charge density and treatment performance.

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SUPPORTING INFORMATION

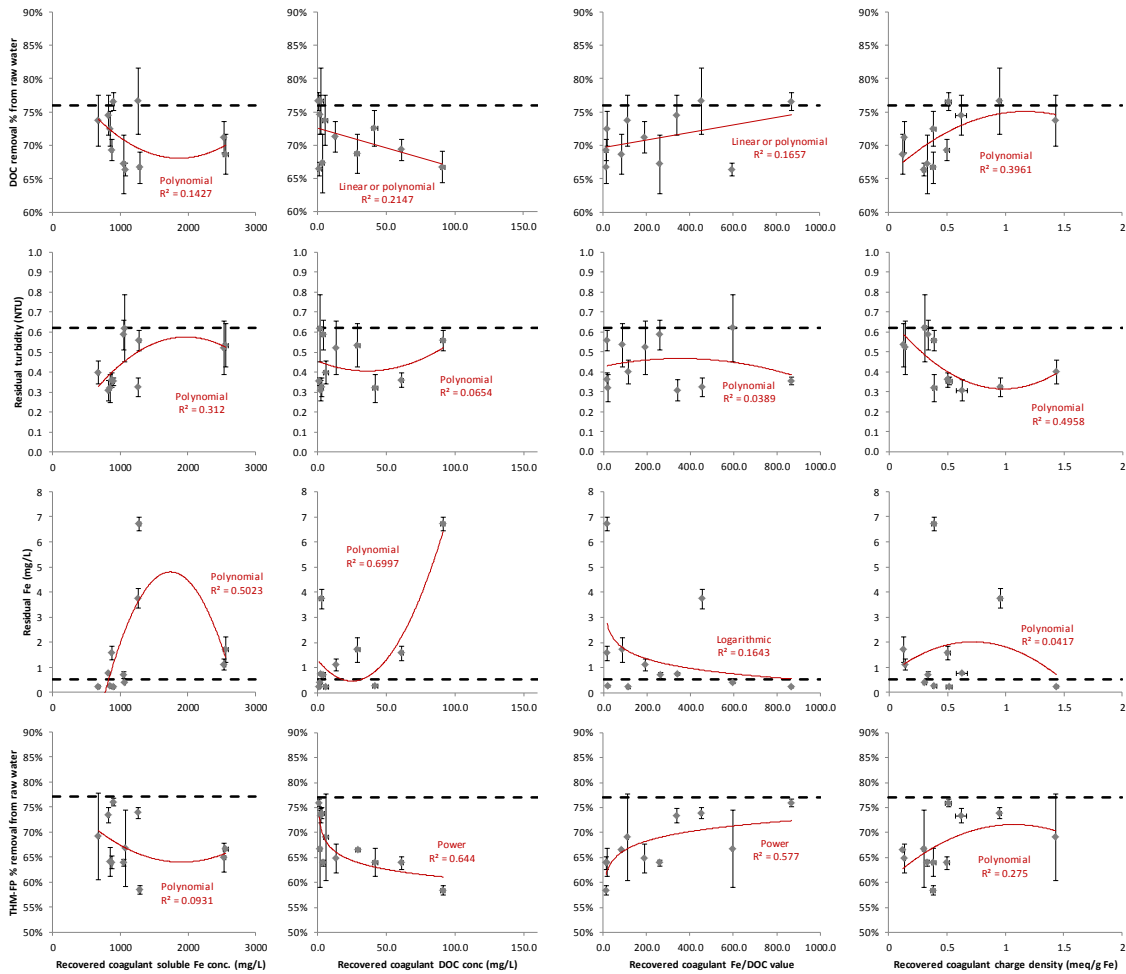


Figure 34: Optimum regression correlations between RC parameters and treatment performance.

CHAPTER 7

DISCUSSION – IMPLEMENTING COAGULANT RECOVERY IN THE WATER INDUSTRY

7 DISCUSSION – IMPLEMENTING COAGULANT RECOVERY IN THE WATER INDUSTRY

7.1 INTRODUCTION

The preceding chapters have thoroughly examined the separation of coagulant metals from dissolved organic compounds (DOC), using a number of different approaches. Of these, ultrafiltration (UF) combined with powdered activated carbon (PAC) resulted in the greatest overall selectivity for coagulant metals. The recovered coagulant (RC) products were capable of matching or bettering fresh coagulant performance in terms of turbidity and disinfection byproduct precursor (DBP) removal. In addition, impure RCs showed similar treatment efficacy to their commercial counterparts in the role of phosphorus removal from primary wastewater (WW). On the basis of these results and in the context of the many coagulant (Chapter 2) and sludge (Babatunde and Zhao, 2007) reuse options available, the following two options are proposed as potentially viable implementation strategies for recovering the value of waterworks sludge:

- Selective and more costly recovery of a higher value coagulant for recycling in potable treatment. While highest in economic and regulatory risk, this option could most closely approach net zero chemical treatment (Chapters 1 and 4). There are several technically viable candidates but UF (Chapter 4) coupled with PAC polishing (Chapter 6) was identified as the optimum balance of performance and process economics.
- Transport and unselective recovery prior to dosing into wastewater, primarily for enhanced P removal (Chapter 5). This approach would not alleviate coagulant demand in potable treatment directly but would reduce competing demand from WW treatment and provide an alternative disposal route for waterworks sludge (Chapter 1). The less stringent quality requirements for wastewater treatment alleviate many of

the risks and resulting process costs that would apply to CR in potable treatment (Chapter 5).

These two approaches can co-exist: alum coagulants were more effectively separated from DOC using UF membranes than ferric (Figure 9) making them more suitable for coagulant recovery (CR) in potable treatment. In contrast, the lower toxicity of ferric coagulants makes them more suitable for WW treatment as there are more lenient predicted no-effect concentrations in final effluents for Fe residuals (16 µg/L, long-term in fresh water) than for Al (0.05 µg/L, long-term in fresh water; Environment Agency, 2007a,b). However, due to the more widespread use of ferric coagulants in the UK's water treatment industry, it is likely that ferric reuse would be in both potable and WW treatment, hence the focus on ferric coagulants in Chapter 6.

The following sections will describe how these two CR approaches can be implemented at full-scale. Key factors that may influence process performance and economics will be identified, with a particular focus on ways in which scientific principles and development can be used to optimise them.

7.2 DESIGN AND COST OF COAGULANT RECOVERY IN POTABLE TREATMENT

To allow the whole life costs of a full-scale potable CR system to be estimated, the capital expenditure (CAPEX) and operational expenditure (OPEX) were scaled on the basis of a 150 MLD site using approximately 1 tonne of alum coagulant as Al per day (equivalent to a 7.5 mg/L dose as Al, a dose that is within the typical dose range; Jarvis et al., 2012). This scale of works was chosen as it was similar to two of the sites that sludge samples were taken and being so large, it would benefit from any available economies of scale. The recovery process would incorporate three main stages: acidification, UF and polishing. These stages are presented alongside their percentage volume recoveries (which roughly equate to Al loadings) in Figure 35. This highlights the overall Al recovery efficiency of 67% and thus the requirement for 33% of total Al as a fresh alum supplement.

The economic implications of the lab-scale experiments have been estimated using a combination of published cost equations (McGivney and Kawamura, 2008), empirical values (Chapters 3-6) and commodity costs from British water companies. The relevant values that were determined experimentally have been noted adjacent to the CAPEX and OPEX items (Table 21 and Table 22, respectively). The CAPEX and OPEX totals were collated and processed using Severn Trent Water's proprietary cost benefit analysis tool. This gave an evaluation of viability against current practices in terms of the years required until the project would yield a return on its investment. The same methodology was repeated for the reuse of waterworks sludge in WW treatment.

A potable CR system attempts to create a controlled, closed loop around the coagulation-flocculation-settlement stages of the main treatment stream (Figure 35). Particularly when considering the sizing and costs of the recovery system CAPEX, it is important to remember that the recovery stream is 400 to 500 times more concentrated than the main stream, with Al dosed at ~7.5 mg/L and acidified thickened sludge containing ~3000 mg/L Al, similar to the

concentrations achieved in Chapter 4, following an acid dose of 2.6:1 mols of sulfuric acid to aluminium that was required to reach a pH of 2.

Sizing of the largest capital asset, the UF plant, was based on the 0.3 MLD flow of acidified sludge that a 150 MLD works would generate, coupled with the average flux of 15 L/m²/h determined in Chapter 4. This flux was 10 times lower than the original prediction used in the OPEX evaluation Chapter 3 but was partially offset by the actual specific energy demand being 10 times lower than the originally predicted value of 2 kW/h, due to the relatively low transmembrane pressure of 400 kPa that was eventually used (Chapter 4).

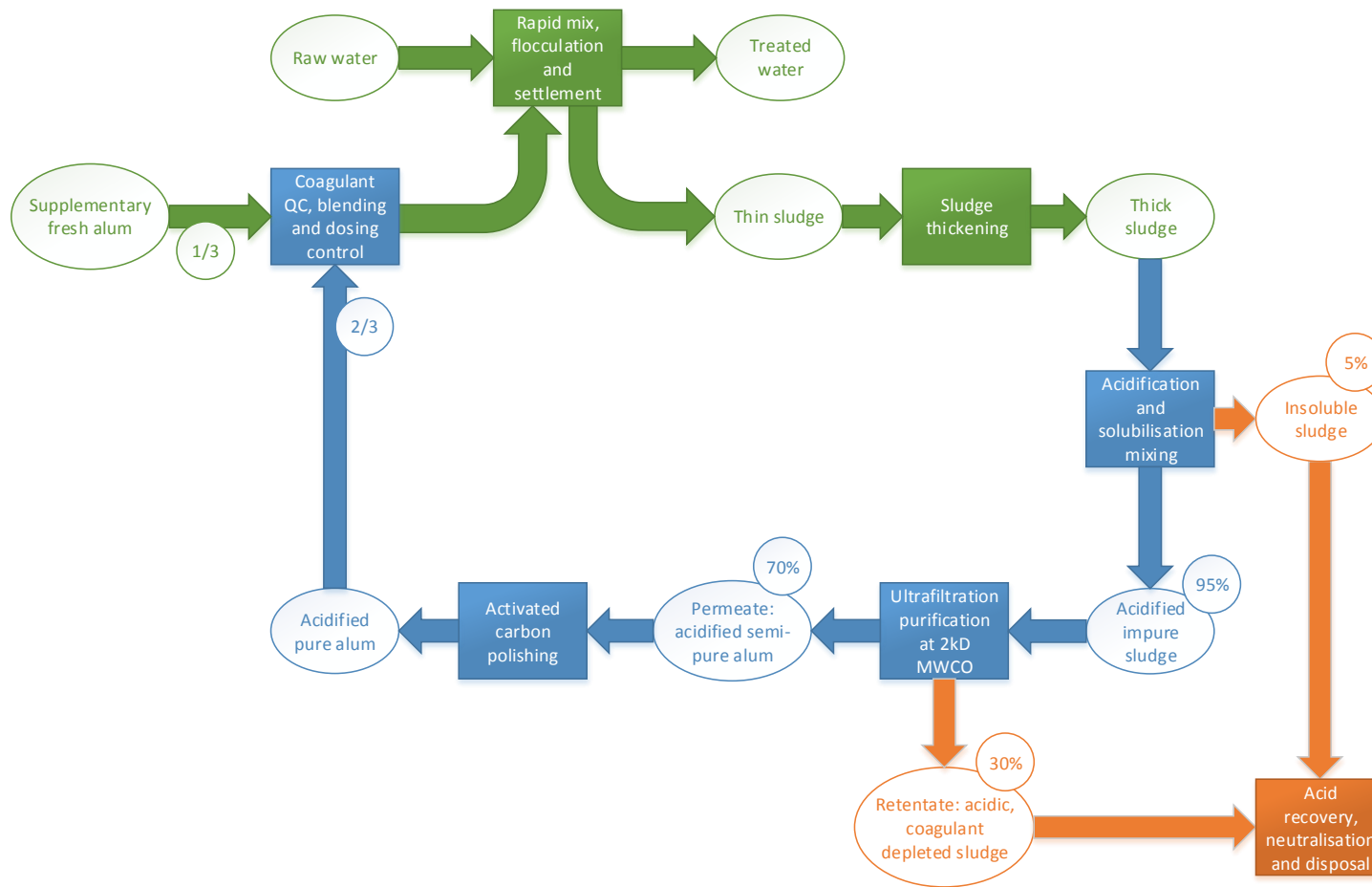


Figure 35: A process diagram for an alum coagulant recovery system within drinking water treatment (percentage volume efficiencies in parenthesis)

Table 21: Capital costs of alum recovery in drinking water treatment

<u>Unit construction costs</u>		<u>Comments</u>
Acid dosing and storage	£70,000	Sized on 2.6:1 molar ratio of H ₂ SO ₄ to Al required to reach pH 2 (Ch. 5)
Mixing tank for waterworks sludge acidification	£42,000	Sized on 3 g/L Al
Ultrafiltration system	£1,000,000	Sized on 15 L/m ² /h and 3 g/L Al (Ch. 4)
Activated carbon polishing stage	£420,000	Sized on 10 g/L PAC and 67% of Al recovery after UF fed with 3 g/L Al. (Ch. 4&6)
Retentate and insoluble waste neutralisation	£127,000	Sized on the lime req. to neutralise 33% volume RC loss (37 kg/d)
<u>Subtotal construction cost</u>	£1,659,000	
Yard piping 10%	£165,900	
Site work landscaping 5%	£82,950	
Site electrical and controls 20%	£331,800	
<u>Total construction cost</u>	£2,240,000	
Engineering, legal and administrative costs 35%	£784,000	
Total project cost	£3,025,000	

Table 22: Annual operating costs of alum recovery in drinking water treatment

<u>Unit operational costs</u>		<u>Comments</u>
Reductions in commercial alum dosed	-£550,000	Based on 67% overall CR efficiency and equal mg/mg treatment performance to commercial alum
Reductions in sludge volumes for transport and disposal	-£107,200	Based on 67% reduction in thickened sludge volume and the disposal route described in Ch. 5
Sulfuric acid for solubilisation	£130,000	Based on a 2.6:1 molar ratio of H ₂ SO ₄ to Al required to reach pH 2 (Ch. 5)
Lime for neutralisation of acidic residuals, prior to disposal (14 t/y)	£1,400	Based on the lime req. to neutralise 33% volume RC loss at pH 2 (37 kg/d)
Electricity	£3,000	Based on a UF flow of 0.3 MLD; 400 kPa transmembrane pressure; 70% pump efficiency; 0.082 £/kWh (Ch. 3).
Clean in place chemicals for membranes	£5,000	Nominal estimate
PAC	£800,000	Based on a 10 g/L dose (Ch. 6) and a unit cost of £1000/tonne (Alibaba, 2014)
Staff-training and additional man-hours	£10,000	Nominal estimate
Total annual OPEX (negative means savings)		£293,000

While the total project capital cost of £3m (Table 21) is a significant investment, the viability of CR is most sensitive to the balance of OPEX savings and costs (Table 22). With the exception of PAC costs, these seem reasonable: when PAC is excluded, the net OPEX savings would allow the project to pay back its investment after 11 years. However, at a cost of £800,000/y, a 10 g/L PAC dose nullifies any savings made from CR and makes the project unviable. With this in mind, a second examination of the removal efficiency at lower PAC doses (Chapter 6) reveals that changing from a 10 g/L to 1 g/L PAC dose would only reduce the removal of DOC from RC from 97% to 82% and would give a payback period of 12 years. In the case of the UF purified RC considered here, this would elevate RC DOC levels from 3 mg/L to 16 mg/L, which is still comparable to the upper boundary of 17 mg/L for Donnan dialysis (Prakash and Sengupta, 2003) and may still match fresh coagulant treatment performance (Chapter 6). The critical annual PAC cost that allows the project to pay back within 25 years is £280,000, which equates to a dose of 3.5 g/L at the prices and volumes considered in this assessment. Substituting PAC with a lower cost fixed-media bed configuration with granular activated carbon may allow further savings, whilst ensuring a high purity recovered coagulant.

The other aspects of this potable CR process scheme offer few opportunities to further reduce costs: 1) UF pore size has been optimised (Chapter 4) and more porous membranes did not appear to significantly reduce the pressure requirement or increase the flux but did worsen the rejection of DOC; 2) acid requirements have also been optimised and while some sources have suggested that slightly higher pHs than 2 can achieve the same solubility (Parsons and Daniels, 1999) this would only realise a marginal reduction in acid and associated cost. Chapter 3 identified that greater reductions in net acid use could be achieved by using a membrane acid recovery system (Schneider, 2013) offering ~70% recovery but the value would be partly diminished by recovery costs and increased dilution after repeated cycles.

The factor that can affect CR the most is the cost of commercial coagulants and less directly, the availability of other alternative treatment technologies. As

discussed previously (Chapter 2), coagulants are commodity chemicals with relatively low value and collectively, water treatment chemical prices rises have been below the average for industry as a whole (Bureau of Labor Statistics, 2008). Competition for coagulant production chemicals is dependent on global economic growth, which up until its peak in 2008 increased coagulant prices and threatened the security of their supply (Henderson et al., 2009). The subsequent economic slow-down has eased this and recent discussions with British water companies' procurement teams have suggested that coagulant prices have stabilised since. However, when the global economy recovers, the strain on coagulant production and supply may return or exceed its pre-recession levels. The need for coagulants to meet tighter P removal consents throughout the world (Chapter 5) will apply pressure to the coagulant market from the demand side, potentially exacerbating scarcity and price rises. Such a scenario would make CR more economically competitive and may allow higher purity separation (assuming the other costs of CR remain stable or rise at slower rates than commercial coagulants). This price shift could also be induced artificially by opting to use higher value coagulants such as Zr and Ti tetrachlorides, which can be recovered more competitively (Jarvis et al., 2012; Hussain et al., 2014).

While the low cost of fresh coagulants is a constraint that may change to benefit CR over time, the greatest risk and barrier to implementation is water quality. This thesis has advanced the understanding of how RC purity affects treated water quality in terms of DBP precursor removals and residual metals. After the disappointing outlook the results of Chapter 4 gave, the higher purity RCs produced in Chapter 6 appear to perform equally as well as fresh coagulants. However, raw water character is highly variable across seasons and locations (Chapter 4), making further, larger scale investigations necessary to ensure that RC performance is as consistent and controllable as fresh coagulants. It is also important to consider the inconsistent application of coagulation science on-site: operators err on the side of caution, or suppress coagulation pH, through coagulant overdosing. Implementation of CR would add further complexity and

risk which would need to be managed at every level from site operations to water quality regulators.

The risks of potable CR could be investigated at pilot scale by recovering a portion of sludge and dosing the RC to a single, isolated coagulation-flocculation-settlement stream. The treated water quality could then be analysed and compared to the control streams, before an additional treatment stage (such as nanofiltration) that would act as a contingency to any problems with RC treatment. This additional treatment and the dilution with the other streams would protect the final water quality and allow the progression of CR understanding. Water utilities may be able to share the risk of such a trial by collaborating with other potential stakeholders such as coagulant manufacturers and water treatment solutions providers.

Potable CR has a large number of challenges arising from the requirement for high purity and the costs associated with achieving it. In contrast, CR in WW offers many of the same benefits with fewer risks and is a more immediate candidate for larger scale testing. Potable CR may be able to benefit from the lessons learned from WW CR, which would better prepare it for its own scale-up when the economic and regulatory risks are deemed acceptable.

7.3 DESIGN AND COSTS OF COAGULANT RECOVERY IN WASTEWATER TREATMENT

The whole life cost of reusing waterworks sludge in WW treatment has previously been assessed and explained in detail in Chapter 5. Here the two most promising options: acidified and non-acidified are reassessed to allow direct comparison to reuse in potable treatment (Figure 36). Because acidified sludge gave near equal cost benefit to unacidified sludge, both have been included for this comparison with potable CR. The distance for transportation between water and WW works is an influential factor on the WLC for this operation and a distance of 50 miles was selected as a likely inter-site distance for comparison (Chapter 5).

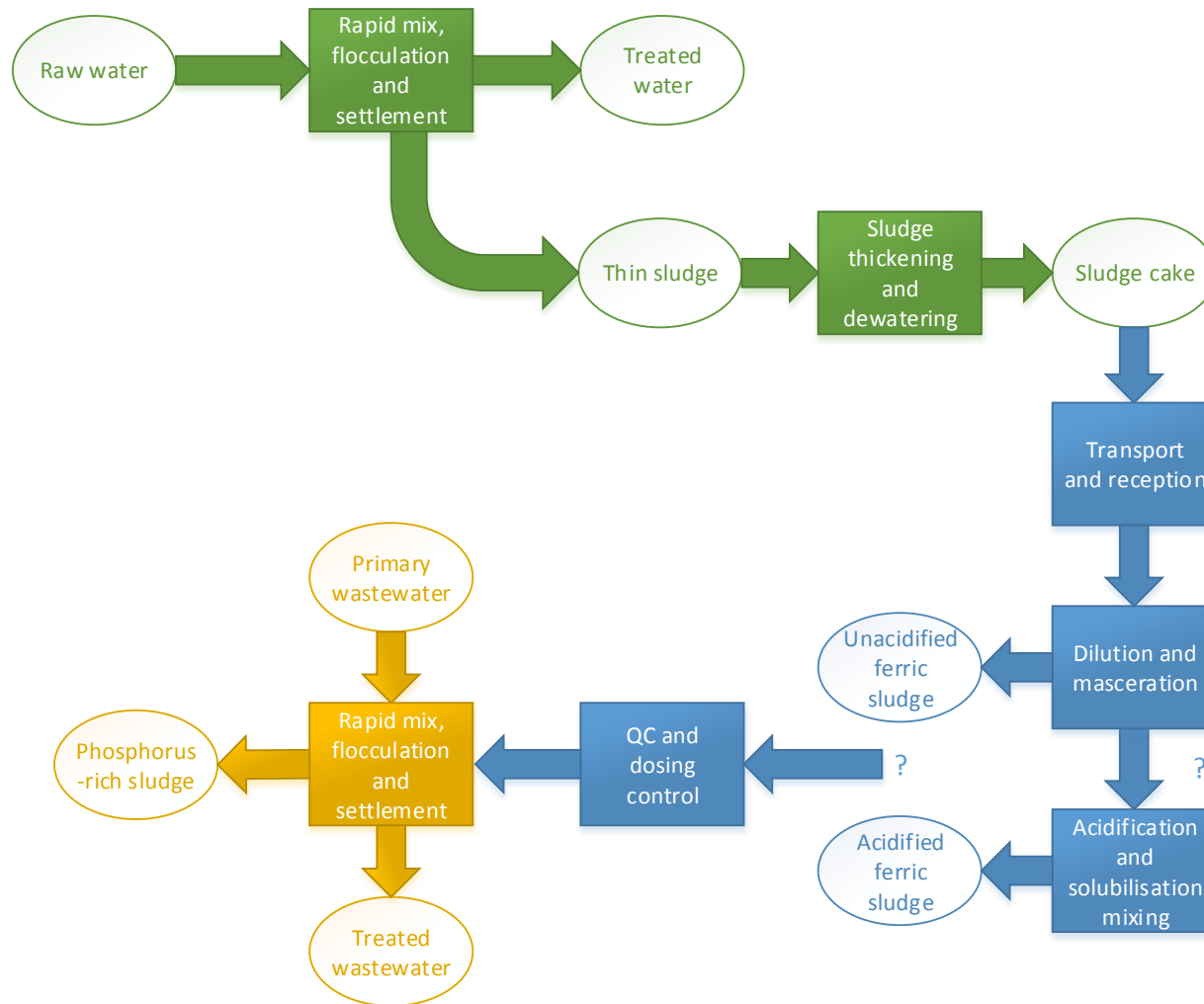


Figure 36: A process diagram for a coagulant recovery system in wastewater treatment

Table 23: Capital costs of alum recovery in drinking water treatment (*taken from Chapter 5)

	With acid dosing	Without acid dosing
<u>Total project cost*</u>	£770,000	£420,000

Table 24: Operational costs of ferric recovery in wastewater treatment

Reductions in commercial ferric dosed	-£290,000	-£180,000
Sulfuric acid for solubilisation	£80,000	-
Reduction in transport cost if transported 50 miles and not disposed to land	-£70,000	
Electricity	£10,000	
Staff-training and additional man-hours	£10,000	
Total annual OPEX (negative means savings)	-£260,000	-£230,000

Many of the challenges of coagulant purification and the subsequent creation of waste streams in potable CR are avoided in WW by dosing the sludge into the treatment stream in its entirety, whether acidified or unacidified and these are reflected in the lower CAPEX and OPEX (Table 23 and Table 24). Insoluble fractions will impact the cost of WW sludge handling but this would be incorporated within existing capital assets and any additional OPEX will enjoy the economies of scale that a standalone residual treatment system would not. While inferior in terms of P removal, non-acidified sludge has the added advantage of not requiring any chemicals to enable its reuse (i.e. acid), thus fulfilling the concept of green chemistry more closely. This is reflected by its

shorter payback period of just 6 years, with acidified sludge giving a payback after 7 years. The slightly inferior WLC for acidified is partly offset by the greater control over P removal that acidification provides in contrast to unacidified sludge, which is reliant on the availability for longer contact times, of up to 8 hours (Chapter 5). Concerns regarding a detrimental impact of waterworks sludge on downstream WW and sludge quality should be monitored but have been shown to be within acceptable boundaries, in terms of alkalinity (Chapter 5) and metals (Elliott et al., 1990).

The main limitations of waterworks sludge reuse in WW treatment are: the logistical restrictions of transporting sludge, which will require careful site selection; no consideration of nutrient recovery, which is expected to gather momentum particularly in response to phosphate scarcity (Cordell et al., 2009); and that the reuse is singular and thus not a true closed loop. Previous studies have shown that coagulant salts can be recovered from WW sludge using acid (Jimenez et al., 2007) but this introduces the same problematic requirements faced in potable CR: acid demand for regeneration, purification and the costs that these two processes carry. In addition, acidification of WW sludge would compromise downstream energy recovery and production of marketable biosolids from digested sludge, which are significant income streams for water utilities.

Accordingly, reuse of waterworks sludge in WW treatment offers a useful efficiency and cost saving alternative to using fresh coagulants to meet tightening P consents. However, in the long-term, primarily biological technologies that better satisfy chemical, energy and nutrient recovery agendas will become more preferential options (Daigger, 2009). The economic and performance analyses presented in this thesis indicate that the optimal long-term reuse strategy for waterworks sludge is within drinking water treatment, provided the quality and economic risks are managed appropriately, through continued progression of our understanding of the underlying science. This progression will be best advanced through larger-scale and longer-term trials and a pro-active sharing of risk among as many stakeholders as possible.

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CHAPTER 8

CONCLUSIONS AND FURTHER WORK

8 CONCLUSIONS AND FURTHER WORK

8.1 CONCLUSIONS

This thesis has considered and prioritised a range of reuse options for coagulant metals contained within waterworks sludge. It has advanced the scientific understanding of their propensity to be separated from organic and inorganic compounds by size, solubility and charge discrimination. It has also assessed the impact recovered coagulants (RCs) have on water chemistry, in the context of raw surface water and primary wastewater (WW) treatment. From this, the following conclusions can be made:

1. Ultrafiltration (UF) purified recovered ferric and alum coagulants gave equal or near-equal raw water treatment performance as their fresh counterparts, in terms of dissolved organic compound (DOC) and turbidity removal. The required transmembrane pressures (276-414 kPa) were shown to be within operationally viable ranges. Fluxes appeared more dependent on feed volume than concentration (between 0-2500 mg/L M^{3+}) and caused the fastest M^{3+} mass fluxes to be achieved with thickened sludges, as opposed to unthickened.
2. Incomplete discrimination of DOC from trivalent metals across a range of UF molecular weight cut-offs and membrane materials (<1-20 kD) indicates that the two compounds exist as stable complexes, with overlapping or homogenous molecular weight ranges. Separation using adsorption onto powdered activated carbon (PAC) or powdered graphite (PG); differing solubility at high pH values; and charge exclusion using cation exchange membranes were more effective at discriminating the characteristics of trivalent metals and DOC.
3. Augmenting UF purification of ferric RCs with a PAC polishing stage or an alkali pre-treatment stage reduced the concentration of DOC

contamination in the RCs to <2 mg/L. These purer RCs gave superior DOC and turbidity removal and equal trihalomethane (THM) precursor removal to fresh ferric sulfate (FFS).

4. Provided suitably corrosion-resistant apparatus are used and downstream removal of Mn and Fe occurred, the use of RCs would not be of detriment to final treated water quality, in terms of monitored metals content. Similarly, acrylamide was never detected in waters treated with RCs.
5. Donnan dialysis provided the greatest separation of Fe and DOC for any single process but imparted high levels of acidity to the RC. When this was dosed without correction it gave treated water pH values below 1. If corrected to pH 4.5 when dosed, the final water exceeded sodium regulatory limits by 7-fold. A review of the literature and economic analysis identified acid recovery as a being key to reducing Donnan dialysis' operational costs; the experimental outcomes of this work suggest that it may also improve the quality of the coagulant product by reducing the RC acid content.
6. The combined constraints of stringent potable quality regulations and the comparatively low cost of conventional coagulant usage make the immediate implementation of coagulant recovery (CR) in drinking water treatment high risk. Accordingly, while it is a lower-value reuse strategy, transportation of waterworks sludge cake up to 150 miles for dosing into WW would be economically beneficial and comparatively low risk. This would help alleviate the increasing demand for coagulants for phosphorus removal, thus helping protect the supply of fresh coagulant for its higher value use in drinking water treatment.

7. Acidification of waterworks sludge prior to dosing to WW facilitated a similar level of P removal as FFS, predominantly using the same rapid precipitation mechanism. Dosing unacidified waterworks sludge removed lower levels of P using a slower, adsorption-dominated mechanism, with an adsorption capacity similar to hydrated ferric oxides. Despite having differing efficiency and mechanisms, economic analysis showed that unacidified and acidified waterworks sludges would give similar whole life costs: approximately half that of implementing a new FFS dosing system.

8. The basic processing requirements and the expansive range of economically viable sludge transport make centralisation of waterworks sludge recovery unnecessary for WW treatment. While more complex, potable CR technologies are highly modular and because surface water treatment works are typically more centralised than WW works, there would be no foreseeable advantage to transporting sludge for potable reuse. Indeed, potable CR has the added benefit of obviating the requirement for costly dewatering processes at sites that currently transport sludge off-site for disposal.

8.2 FURTHER WORK

In the course of this project, several interesting research areas have been identified:

1. Longer-term and larger-scale examination of potable and WW CR technologies, to confirm the observations made at lab-scale. There is also a requirement to develop an automated method of process control that integrates with existing process streams.
2. Acid recovery would allow improved chemical efficiency for all acidification-based CR processes, allowing net chemical-free treatment to be more closely approximated. Recovery of acid from CR waste streams will also reduce waste volumes and the requirement for neutralisation prior to their disposal. Promising work is already under way in this area (Schneider, 2013)
3. Integration of potable CR technologies with higher value coagulants such as Zr (Jarvis et al., 2012) or Ti (Hussain et al., 2014) would be an ideal synergy: recovery costs are likely to be comparable to conventional Fe and Al coagulants but the cost and performance of the Zr or Ti coagulants would increase the benefit of recycling.
4. The water industry should also look beyond its own operations to identify waste streams that may provide a suitable source of coagulant metal ions, acid or alkali. It is hoped that such progressive thinking will provide alternative coagulant sources that are as beneficial as anaerobic codigestion of imported waste has been to WW treatment's income stream.

5. A dialogue must be initiated with potable water quality regulators with regard to the requirements for RC quality. Existing water treatment chemical regulations do not recognize or differentiate RCs and create a barrier to the possible advantages of CR. A more pragmatic, case-by-case assessment of the risks posed by changes to water quality (i.e. coagulant recycling) could offer the same level of protection for public health and would be more conducive to innovation in drinking water treatment.

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