Solids management in freshwater-recirculating aquaculture systems: Effectivity of inorganic and organic coagulants and the impact of operating parameters

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Abstract

Coagulants are widely used for solids (uneaten food, faeces, etc.) management in recirculating aquaculture systems (RAS), but no recent research has been performed on the effectiveness of different coagulants in treatment of aquaculture sludge. This study examined the effectivity of selected inorganic (polyaluminium chloride, PAC) and organic products (polyamine- and starch-based) as coagulant agents for solids management in RAS. Reductions in residual concentrations of total phosphorus (tot-P), phosphate-phosphorus (PO_4-P), suspended solids (SS) total nitrogen (tot-N), nitrate-nitrogen (NO_3-N), ammonium-nitrogen (NH_4-N), aluminium (Al) and chemical oxygen demand (COD) in reject water were determined. The effect of process parameters (coagulant type, dose, mixing and sedimentation time) on sludge treatment was also evaluated. The PAC products tested were most effective at concentrating pollutants (Tot-P, PO_4-P, SS, COD) in RAS sludge into the solid phase. The organic products tested, especially a high-molecular-weight polyamine product (pAmine1), achieved good performance and can be considered a valid alternative to inorganic salts. At optimum dose, PAC (dose 32 mg/L) and pAmine1 (dose 15 mg/L) removed, respectively, 99.4% and 82.8% of turbidity, 98.2%

and 65.4% of PO_4-P and 97.7% and 73.6% of SS. The mixing time applied in flocculation and the time allowed for sedimentation had significant effects on coagulant performance, with the organic coagulants being most affected. Flocculation times of 5-15 min and sedimentation times of 15-60 min showed good results and can be used as a starting point in process optimisation with both inorganic and organic coagulants. The use of coagulants for treatment of RAS sludge enhances flock formation and improves particle settling characteristics, substantially decreasing nutrient, organics and solids concentration in reject water.

Keywords: *coagulation, organic polymers, metal salts, aquaculture sludge*

1. Introduction

In recirculating aquaculture systems (RAS) used on fish or shellfish farms, water is continuously recycled between the culture tanks and water treatment systems (filters, biofilters, screens, etc.) to maintain good water quality conditions for the stock (Martins et al., 2010; Rijn, 2013; Heldbo and Meyer, 2016). The implementation of strict environmental legislation, e.g. in northern Europe, to minimise pollution from hatcheries and aquaculture plants has promoted rapid technological development of RAS (Martins et al., 2010; Bregnballe, 2015). Such systems are frequently referred to as 'environmentally friendly', due to e.g. lower water requirements, lower nutrient and carbon discharge, better hygiene and disease management, better biological pollution control (with no escapees) etc. (Martins et al., 2010; Rijn, 2013; Bregnballe, 2015; Heldbo and Meyer, 2016). However, RAS cannot eliminate effluent and waste discharge completely. Particulate matter, such as fish faeces, uneaten food, bioflocs (from biofilters used in for breakdown of ammonia and organic matter) etc. must be separated from the recirculating water (Badiola et al., 2012; Bregnballe, 2015). These particles are usually removed from the culture tanks via sedimentation and filtration, to form what is known as sludge (diluted mixture of solids and water from e.g. filter backwash, culture tank cleaning etc.).

In general, RAS sludge has low solids content (<2%) but can fluctuate in volume due to changes in feeding and cleaning regime (Mirzoyan et al., 2008). Most of the nutrients present in the sludge are in particulate form, but dissolved phosphorus (P), nitrogen (N) and organic matter are also contained in the water. As direct disposal of sludge is costly (high water content), dewatering (thickening of solids and treatment of reject water) is normally applied. Dewatering of the sludge is mostly carried out by settling of solids in basins or ponds and solids capture using e.g. geotextile bags, membranes or mechanical filters. These methods are often used in combination with addition of coagulation/flocculation chemicals to enable high retention of solids and high removal of P from the supernatant (reject water) (Martins et al., 2010; Rijn, 2013). As P is one of the main nutrients contributing to eutrophication of surface water bodies receiving effluent from aquaculture systems, its removal is important for the environmental credentials of RAS. Solids management and effective treatment of the reject water are considered important challenges to be overcome regarding the cost-effectiveness and sustainability of RAS (Midilli et al., 2012).

Although the use of coagulant agents is widespread in RAS units, the only available studies on the effectiveness of different coagulants in RAS date back more than a decade (e.g. Ebeling et al., 2003; 2004; Rishel and Ebeling, 2006). Rapid developments in the water treatment chemicals sector over the past decade have resulted in commercial availability of a wide range of inorganic and organic coagulants that have been proven to be more effective in terms of P and solids removal and have less effect on the water treated (Bratby, 2016). Controlled hydrolysis of iron (Fe)- and aluminium (Al)-based coagulants (tested by e.g. Ebeling et al., 2003, 2004) led to the development of pre-hydrolysed products such as polyaluminium chloride (PAC), which have been found to work more efficiently than their hydrolysing counterparts. For example, they are more effective over a wider pH range and are less sensitive to changes in operating parameters (mixing etc.), temperature, characteristics of the raw water etc. (Yu et al., 2015; Wei et al., 2015; Sillanpää et al., 2018).

Use of synthetic (Rishel and Ebeling, 2006; Guerdat; 2013) and (semi)-natural (Rishel and Ebeling, 2006) organic polymers in RAS has been investigated in a few studies, mostly as a flocculant aid (aiming at improving particle aggregation) added together with a metal salt coagulant. In municipal water and wastewater treatment, organic coagulants (synthetic and natural) have been found to require lower doses than metal salt coagulants and to produce less sludge with better dewatering characteristics (Heiderscheidt et al., 2016; Hameed et al., 2018; Xue et al., 2019). Moreover, natural organic polymers (produced or extracted from animal or plant tissues or microorganisms) have additional benefits such as non-toxicity and high biodegradability (Oladoja, 2015; Xue et al., 2019). Another important aspect is that inorganic Al- or Fe-based metal salt coagulants react with P, precipitating it as stable Al- or Fe-phosphates, thus lowering plant nutrient availability in the dewatered solids (Kirchmann et al., 2017). Therefore, use of organic coagulants, especially natural products (e.g. starch-based), can potentially result in higher nutrient availability in the solids fraction, increasing its fertiliser potential.

The main aim of this study was to assess the effectivity of selected inorganic (PAC) and organic products (polyamine (pAmine)- and starch-based) as coagulant agents for solids management in RAS. A second aim was to identify the effect of process parameters applied in the chemical treatment unit on solids retention and P removal. To achieve these goals, a novel systematic approach was devised and experimental work was performed to answer the following research questions: Can organic polymers effectively replace metal salts as coagulants agents in RAS solid management units? and What is the effect of process parameters, such as coagulant type and dose, residence time in the treatment unit and mixing regime, on the treatment efficiency achieved by metal salts and organic coagulants?

2. MATERIALS AND METHODS

All laboratory work was conducted at the Laukaa RAS fish farm at the Natural Resources Institute Finland (Luke, Pulkkinen et al., 2018). The work was performed in two phases. In Phase 1, the selected coagulants were evaluated for their ability to induce coagulation and subsequent solid/liquid separation. Five coagulants were selected for testing, based on the literature (e.g. Ebeling et al., 2004, 2005; Rishel and Ebeling, 2006; Guerdat et al., 2013), previous studies by our research group (Heiderscheidt et al., 2016) and commercial availability. In Phase 2, the effect of chemical treatment process parameters on performance of the best-performing organic and inorganic coagulants from phase 1 was investigated. A full 2^4 factorial design (four factors each, at two levels) and two 2^3 factorial designs (three factors each, at two levels to which centre points were added) were used in the experiments. The factors evaluated and the levels (low, high and centre points) were selected based on the findings from Phase 1 and on results from previous studies (e.g. Ebeling et al., 2004, 2005; Rishel and Ebeling, 2006).

2.1 Sampling and quality of sludge tested

The sludge used in the experiments came from a newly constructed pilot RAS unit at Laukaa fish farm. The unit consists of four 5-m^3 aluminium fish tanks followed by sludge cones (FREA Aquaculture Solutions, Denmark), two drum filters (60 µm, Hydrotech HDF801, Veolia, France), four 1.5 m^3 fixed-bed bioreactors (700 m^2 m^{-3} Saddle-Chips, KSK Aqua, Denmark), two 2.25 m^2 degassing zones, two 0.74 m^3 pump sumps and two low-head oxygenators (FREA Aquaculture Solutions, Denmark). Sludge is collected from the drum filters (water level-based backwash), the sludge cones (daily flushing) and the backwash from the fixed-bed bioreactors. These are conducted to a storage tank outside the RAS loop. Treatment of the sludge (coagulant addition followed by sedimentation) occurs in batch mode, which is controlled by the sludge level in the storage tank. During the experiments, the fish tanks contained rainbow trout (*Oncorhynchus mykiss*, average weight 1.9 kg) and European whitefish (*Coregonus lavaretus*, average weight 0.7 kg) and the total feeding rate was approximately 6 kg d^{-1} (Circuit Red and Circuit Silver, Raisioaqua).

Sampling of sludge in the storage tank was conducted daily during the experimental period. The sludge was mixed with a wooden stick before sampling and a pump was used to extract sludge from the storage tank and transfer it to a 30-L container, which was transported to the in-house laboratory located in an adjacent building. The storage container was mixed well before samples were extracted for jar-tests. The characteristics of the sludge (raw and after treatment; Table 1) were evaluated in the following analyses carried out by an outsourced certified laboratory (using SFS-EN and ISO standard methods): biochemical oxygen demand (BOD_7), total phosphorus (tot-P), total nitrogen (tot-N), total aluminium (Al) and total solids (TS). The characteristics of the reject (supernatant) water samples collected after treatment (blank and treated by coagulants) were evaluated by the following analyses carried out by an outsourced certified laboratory: chemical oxygen demand (COD), tot-P, phosphate-phosphorus (PO_4-P), tot-N, nitrate-nitrogen (NO_3-N), ammonium-nitrogen (NH_4-N), Al and suspended solids (SS). In addition, reject water samples were analysed at the in-house laboratory for: SS (GFC; SFS-EN 872:2005); turbidity (EN 27027:1994; Hach 2100 Q turbidity meter), pH, electric conductivity (EC) (ISO 9963-1:1994 and SFS-EN 13037:1994; Hach Lange TitraLab AT1000) and PO_4-P (Hach Lange HT 200S and Hach Lange DR 3900).

Table 1. Characteristics of sludge collected from the recirculating aquaculture system (RAS) unit at Laukaa fish farm during the experiments (n = number of samples analysed)

Water quality parameter	Value or Mean ± std. dev.
COD* (mg/L)	74
Tot-P* (mg/L)	7.6
PO_4-P (mg/L)	5.45 ± 1.86 (n = 6)
Tot-N* (mg/L)	8.6
NO_3-N* (mg/L)	2.6
NH_4-N' (mg/L)	0.18
Tot Al* (mg/L)	0.78
SS (mg/L)	201 ± 68.5 (n = 3)
Turbidity (FNU)	315 ± 59.24 (n = 5)
pH†	7.0 -7.5 (n =5)
EC (mS/m)	39.66 ± 1.43 (n =5)

*Value obtained from one sample. For abbreviations see text.
†Range.

2.2 Experimental procedure

Five coagulants were tested, two inorganic pre-hydrolysed metal salts of aluminium (polyaluminium chlorides (PAC1, PAC2) with different properties), two synthetic organic polymers (polyamines pAmine1 and pAmine2 with different molecular weight (MW)) and one semi-natural starch-based polymer (Table 2). Jar-test equipment was used (Kemira Kemwater Flocculator 2000) to simulate a batch type of continuously stirred tank reactor (CSTR), followed by sedimentation (Fig. S2 in Supplementary Material (SM)). Stock solutions (e.g. 20 mg/mL) of the coagulants were prepared based on the density of the respective products and de-ionised water (Table 2).

Table 2. Characteristics of the five coagulants tested (coagulant samples supplied by Kemira Oyj)

Metal salt, inorganic coagulants				
Product	Density (g/cm^3)	Al_2O_3 content	Concentration	Abbreviation
Polyaluminium chloride	1.39	17.6%	40%	PAC1
Polyaluminium chloride	1.31	14.2%	40%	PAC2

Organic coagulants						
Product	Density (g/cm^3)	Concentration	Molecular weight	Charge	Charge density (meq/g)	Abbreviation
Polyamine	1.20	40%	High	Cationic	8.1	pAmine1
Polyamine	1.18	50%	Low	Cationic	7.2	pAmine2
Starch		Powder	High	Cationic	4.3	Starch

2.2.1 Phase 1: Suitability of different coagulants

For determination of the working dosage range of the coagulants, increasing doses of each coagulant were added to 1-L sludge samples placed in the glass beakers of the jar-test equipment. Fast (200 rpm for 30 s) or slow (40 rpm for 5 min) mixing was applied, followed by sedimentation (30 min). Supernatant water samples (reject water, ~300 mL) were then extracted from the jars treated with each coagulant dose and from jars where blank runs were conducted (sludge submitted to similar mixing and sedimentation conditions, without addition of coagulant) and analysed for turbidity, PO_4-P (cuvette tests) and pH. The optimum dose of each coagulant was identified as the dose that achieved, simultaneously, the lowest residual turbidity and PO_4-P concentration. Reported doses refer to the active coagulant dose, where the water content of commercial products was deducted. To evaluate the purification efficiency achieved by different coagulants, sludge samples were treated (2 replicates) with the optimum dose and supernatant samples were sent to a certified laboratory for water quality analysis (COD, tot-P, PO_4-P, tot-N, NO_3-N, NH_4-N, Al and SS), in addition to the in-house measurements. Due to the nature of the flocs formed, less than 400 mL of supernatant water could be extracted from 1-L jars. Therefore, a decision was made to combine supernatant water from the two replicates of the same treatment for SS analysis.

The settling characteristics of sorbent particles was evaluated in separate tests following the methodology outlined in Bratby (2016). Jar-test experiments were performed following the procedure described previously, with the modification that 30-mL samples were collected at constant jar depth (8 cm from the bottom) at pre-determined intervals during sedimentation. Turbidity measurements were performed on the collected samples, as an indicator of the concentration of particles in suspension. Sampling collection times were: -1 min (1 min before mixing was stopped) and at 1, 2, 3, 4, 6, 8, 11, 14, 17 and 25 min of sedimentation (2 replicates).

2.2.2 Phase 2: Effect of process parameters

In Phase 2, experiments were carried out, using the same jar-test equipment and procedures as described for Phase 1, on the two best-performing coagulants from Phase 1 (PAC1 and pAmine1). The optimum dose identified for each coagulant was added to jars containing 1 L of sludge. After mixing and sedimentation, supernatant water was extracted and analysed. The effect of four process parameters on the resulting reject water quality was investigated. These factors (parameters) were coagulant type (A), coagulant dose (B), slow mixing (flocculation) time (C) and sedimentation time (D) (Table 3). Low and high levels of individual factors and centre points were selected based on Phase 1 results and previous studies (Table 3). The settling characteristics of sorbent particles for all treatment combinations were also evaluated (1 replicate), following the methodology outlined previously (Phase 1).

In statistical analysis of the factorial designs, the effect of changes in the levels of factors A, B, C and D on the response variables was evaluated. The effect of a factor is defined as the change in the response variable caused by a change in the level of that factor, averaged over the levels of the other factors. When a factor effect depends on the level of one or more other factors, an interaction effect is said to occur (Montgomery, 2006). The selected response variables were the residual concentrations of PO_4-P, SS and turbidity in the treated samples. The magnitude and direction of the factor effects and their interactions were determined using an orthogonal contrast approach (Montgomery, 2006; Heiderscheidt et al., 2016). The significance of observed effects was evaluated by ANOVA (performed using MiniTab 19 software). The treatment combinations corresponding to the experimental runs performed are presented in standard order or Yate's order (Yates, 1937) as: (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, abcd, where a treatment code containing the lower-case letter for a factor (a, b, c or d) signifies application of the high level of that factor, while absence of the letter signifies application of the low level. For example, in the treatment 'ab', factors A and B are at their high levels. The notation (1) is used to describe a treatment combination where all factors are applied at a low level (Montgomery, 2006). The effects of individual factors or of interactions between factors are, by convention, indicated with the capital letter corresponding to the factors, e.g. the effect of factor A (coagulant type) is represented by the letter A, the interaction effect between factor A (coagulant type) and factor B (dose) is denoted AB and so forth. Centre points were used to evaluate the linearity of the observed effects for factors B, C and D (Table 3).

Table 3. Factors evaluated and selected high, low and centre point values ('optimum' refers to the individual optimum dose identified for each coagulant during Phase 1)

Parameter	**Factor**	**Level**		
		Low	**High**	**Centre point**
Coagulant (type)	A	PAC†	Organic	
Dose (mg/L)	B	Optimum - 50%	Optimum + 50%	Optimum
Slow mixing time (min)	C	5	15	10
Sedimentation time (min)	D	15	60	30

†Polyaluminium chloride.

3. RESULTS

3.1 Required coagulant dose and purification efficiency (Phase 1)

Residual concentration of contaminants in the supernatant (reject) water decreased with increasing dose of all coagulants tested until the optimum dose was reached (Fig. 1). The decreases in turbidity and PO_4-P were significantly greater in samples treated with the PAC products than in samples treated with the pAmine and Starch products (Fig. 1). The optimum dose (lowest residual concentrations of turbidity and PO_4-P achieved) was found to be: PAC1 32 mg/L, PAC2 28 mg/L, pAmine1 and pAmine2 15 mg/L, and Starch 15 mg/L. It is important to note that the optimum dose identified for the PAC products around twice as high as that for the organic products. However, both PAC products achieved better removal of turbidity and PO_4-P than the organic coagulants at doses as low as 10 mg/L (Fig. 1).

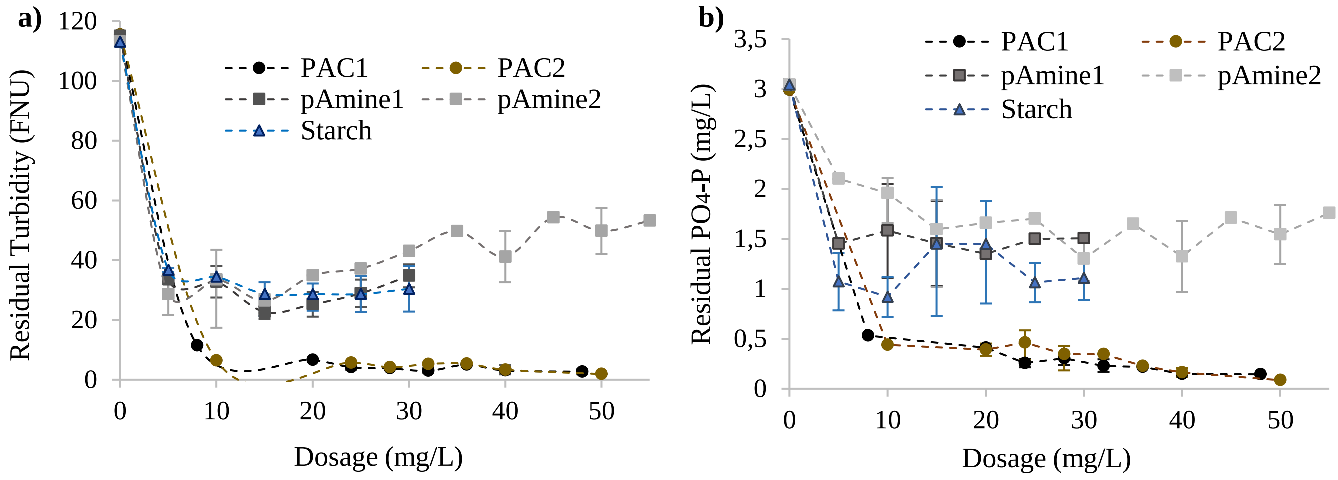

Figure 1. Decrease in (a) residual turbidity and (b) residual phosphate-phosphorus (PO_4-P) in supernatant (reject water) following treatment of sludge from a recirculating aquaculture system (RAS) with increasing dose of the five coagulants tested (see Table 2 for details).

Residual concentrations of target contaminants in the supernatant samples from treatments using the optimum dose of the coagulants are shown in Figure 2. In general, the PAC products achieved higher purification efficiency than the pAmine and Starch products. The PAC1 and PAC2 coagulants were particularly efficient in the removal of Tot-P (94% and 91%, respectively) and PO_4-P (91% and 89%, respectively) (Fig. 2a). Overall, PAC1 performed slightly better than PAC2, with samples treated by PAC1 showing the lowest Tot-P, PO_4-P, COD, SS, NO_3-N and Al concentrations (Fig. 2). Among the organic products, pAmine1 was the best-performing coagulant, achieving similar removal of COD and SS to that achieved by PAC1 and PAC2 (Fig. 2b, 2c). An increase in Tot-N and NO_3-N concentrations was consistently found for treated reject water samples compared with blanks (Fig. 2d). Increase in NO_3-N concentration might be due to improved nitrification condition provided to samples during treatment (additional handling/aeration steps). While the observed increase in Tot-N concentrations (more evident, although not substantial, in samples treated by PAC coagulants) is most likely due to impurities contained in the commercial inorganic products. Although the overall removal efficiencies achieved by the organic coagulants were lower than those achieved by the PAC products, the results obtained by pAmine1 can be considered satisfactory (SS 93%, tot-P 63%, PO_4-P 35%), with the added benefit of low residual Al concentration in treated samples (Fig. 2f).

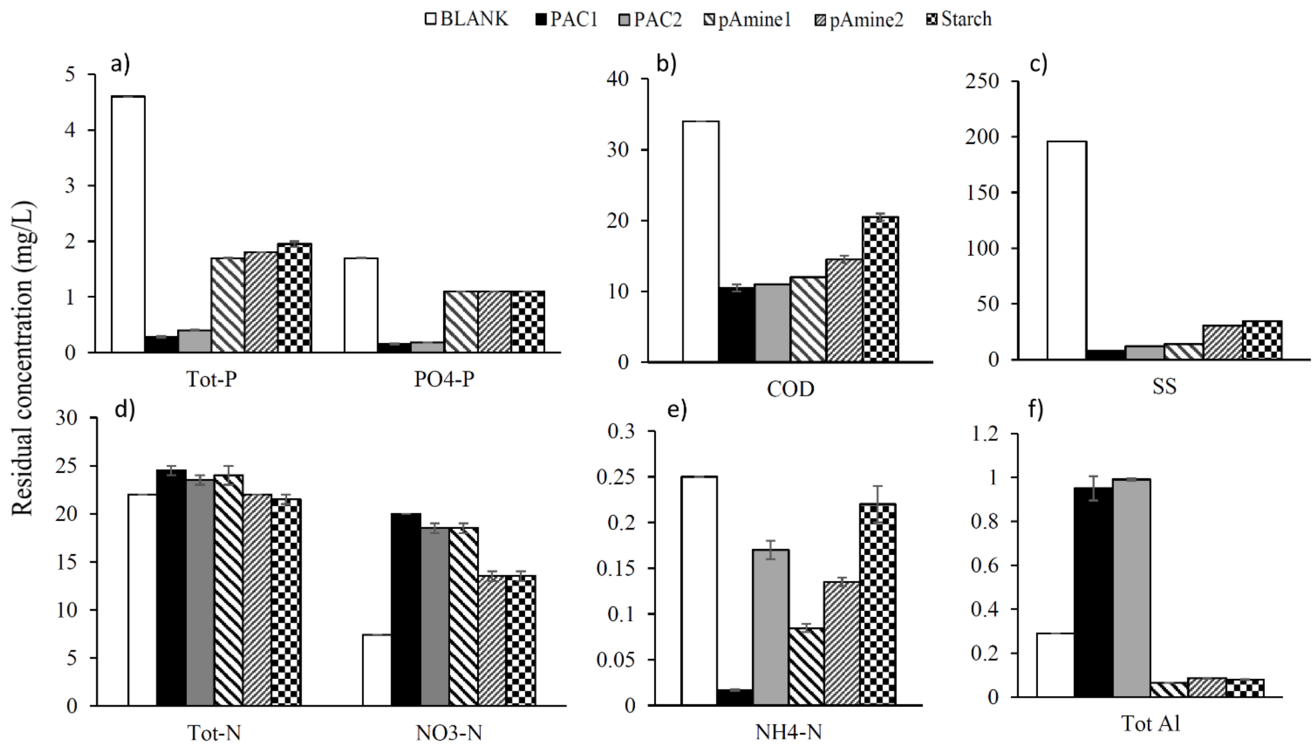

Figure 2. Residual concentration of (a) total phosphorus (Tot-P) and phosphate-phosphorus (PO_4-P), (b) chemical oxygen demand (COD), (c) suspended solids (SS), (d) total nitrogen (Tot-N) and nitrate-nitrogen (NO_3-N), (e) ammonium-nitrogen (NH_4-N) and (f) aluminium (Al) in reject water samples following treatment of sludge from a recirculating aquaculture system (RAS) with different coagulants (for details, see Table 2). BLANK samples were submitted to mixing and sedimentation but did not receive coagulant.

Settling properties of flocs formed on addition of different coagulants

The settling characteristics of flocs formed following addition of PAC1 and PAC2 differed from those formed following addition of pAmine1 (Fig. 3). PAC1 and PAC 2 displayed the fastest sedimentation rates in the initial, and most important, stage of the sedimentation process (Fig. 3). Both products reached turbidity values <20 NFU within 5 minutes of sedimentation, with further decreases in turbidity after 8 minutes of sedimentation being negligible. Settling velocity of PAC1 flocs was particularly high, as the sample turbidity after PAC1 addition was over 130 NFU. For the organic pAmine1 product, the final water turbidity was >34 NFU.

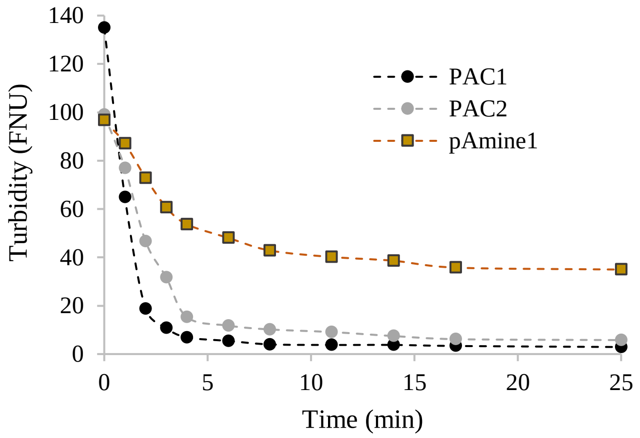

Figure 3. Settling rate (decrease in supernatant water turbidity with sedimentation time) of flocs formed by addition of the optimum doses of the PAC1, PAC2 and pAmine1 coagulants to sludge from a recirculating aquaculture system (RAS).

3.2 Effect of process parameters on purification efficiency (Phase 2)

In general, residual turbidity and PO_4-P and SS concentrations found in purified water samples varied significantly between different treatment combinations. However, a clear pattern emerged where the lowest residual pollutant concentrations were found for samples treated with PAC1 (factor A at low level, i.e. treatment combinations not containing the letter ‘a’). The variation in purification efficiency observed between treatment combinations indicates measurable influences of process parameters on the purification results.

Table 4. Residual concentrations in reject water and removal efficiency of turbidity, phosphate-phosphorus (PO_4-P) and suspended solids (SS) achieved by the different treatment combinations (mean of two replicates ± difference between max and min values, values in bold are the highest removal rates achieved)

	Turbidity		**PO_4-P**		**SS**	
*Treatment combination	Residual (FNU)	Removal (%)	Residual (mg/L)	Removal (%)	Residual (mg/L)	Removal (%)
1	17.00 ± 0.10	92.4	1.465 ± 0.015	71.1	37.5	71.7
a	61.20 ± 1.00	72.6	2.625 ± 0.095	48.2	56.0	57.7
b	1.71 ± 0.16	**99.2**	0.239 ± 0.007	**95.3**	4.0	**97.0**
ab	56.20 ± 1.40	74.8	2.325 ± 0.005	54.1	46.0	65.3
c	11.45 ± 0.25	94.9	1.230 ± 0.030	75.7	16.0	87.9
ac	62.35 ± 1.25	72.0	2.475 ± 0.005	51.2	60.0	54.7
bc	1.22 ± 0.05	**99.5**	0.077 ± 0.005	**98.5**	4.0	**97.0**
abc	48.95 ± 1.15	78.1	2.175 ± 0.015	57.1	43.0	67.6
d	14.60 ± 0.90	93.5	1.360 ± 0.080	73.2	29.0	78.1
ad	60.05 ± 2.25	73.0	2.400 ± 0.060	52.	57.0	57.0
bd	1.76 ± 0.19	**99.2**	0.136 ± 0.007	**97.3**	1.0	**99.3**
abd	40.25 ± 0.75	81.9	1.920 ± 0.030	62.1	32.0	75.8
cd	8.94 ± 0.56	96.0	0.917 ± 0.019	81.9	25.5	80.7
acd	50.05 ± 1.95	77.6	2.245 ± 0.025	55.7	67.0	49.4
bcd	1.40 ± 0.11	**99.4**	0.092 ± 0.006	**98.2**	3.0	**97.7**
abcd	38.30 ± 0.70	82.8	1.755 ± 0.045	65.4	35.0	73.6

*Treatment combinations containing a lower-case letter (a, b, c, d) indicate application of the corresponding factor (A, B, C, D) at the high, while absence of the letter signifies application at the low level. For example, in treatment 'abcd', factors A (coagulant type), B (coagulant dose), C (mixing time) and D (sedimentation time) were at their high level.

Influence of process factors on turbidity, PO_4-P and SS concentrations in treated reject water

Evaluations on the effect of coagulant type (factor A), dose (B), mixing time (C) and sedimentation time (D) on the response variables (residual turbidity, PO_4-P and SS concentrations in the treated reject water) revealed statistically significant factor effects ($p<0.05$) (Table 5). Several interaction effects were also statistically significant, indicating that the effect of individual factors depended on the level of other factors applied during treatment. In particular, the effects of mixing time and sedimentation time were strongly dependent on the level of coagulant type and dose (Table 5).

Table 5. Magnitude (Magn.) of effect of different factors (coagulant type (A), dose (B), mixing time (C), sedimentation time (D)) and factor interactions, and statistical significance of factor effects (confidence interval 95%) on turbidity and residual concentrations of phosphate-phosphorus (PO_4-P) and suspended solids (SS) in treated reject water (response variables). Values in **bold** indicate significance at $p<0.05$

	Turbidity			**PO_4-P**			**SS**		
Factor	Magn. of effect	F statistic	p-value	Magn. of effect	F statistic	p-value	Magn. effect	F statistic	p-value
A	44.9	8183.8	**0.000**	1.6	5929.3	**0.000**	34.5	297.6	**0.037**
B	-12.0	582.6	**0.000**	-0.8	1386.9	**0.000**	-22.5	126.6	0.056
C	-3.8	57.5	**0.000**	-0.2	87.1	**0.000**	-1.1	0.3	0.674
D	-5.6	126.8	**0.000**	-0.2	122.9	**0.000**	-2.1	1.1	0.481
AB	-0.5	1.0	0.325	0.4	315.1	**0.000**	1.5	0.6	0.590
AC	-0.7	2.3	0.152	0.0	2.7	0.122	4.6	5.4	0.260
AD	-4.4	79.4	**0.000**	-0.1	23.1	**0.000**	-1.4	0.5	0.617
BC	1.3	6.4	**0.024**	0.1	8.2	**0.012**	1.6	0.7	0.566
BD	-1.0	4.1	0.062	0.0	0.1	0.807	-4.4	4.8	0.273
CD	-0.7	2.2	0.163	0.0	0.5	0.505	4.0	4.0	0.295
ABC	-1.3	7.3	**0.017**	-0.1	9.0	**0.009**	-5.1	6.6	0.237
ABD	-2.3	21.2	**0.000**	-0.1	18.9	**0.001**	-3.1	2.4	0.362
ACD	-0.7	2.2	0.160	0.0	0.2	0.670	-1.0	0.3	0.705
BCD	2.1	17.7	**0.001**	0.0	3.9	0.069	-2.0	1.0	0.500
ABCD	2.0	16.7	**0.001**	0.0	4.4	0.055	2.0	-*	-*

*Analysis conducted ignoring the high-order ABCD interaction since there was only one replicate for SS.

Regarding the magnitude and direction of factor effects, a plot of the main factor effects further clarified the results obtained (Fig. 4). Factor A (coagulant type) had the greatest influence on residual turbidity, PO_4-P and SS concentrations (44.0, 1.6 and 34.5, respectively). The observed effects were in the positive direction, meaning that when factor A varied from low to high level (coagulant type changed from PAC1 to pAmine1), pollutant concentrations (turbidity, PO_4-P or SS) increased in treated reject water (Table 5, Fig. 4). On the other hand, the effect of factor B (dose) was negative (-12, -0.8 and -22.5 for turbidity, PO_4-P and SS respectively), with lower pollutant concentrations found when higher coagulant doses were applied (Table 5, Fig. 4).

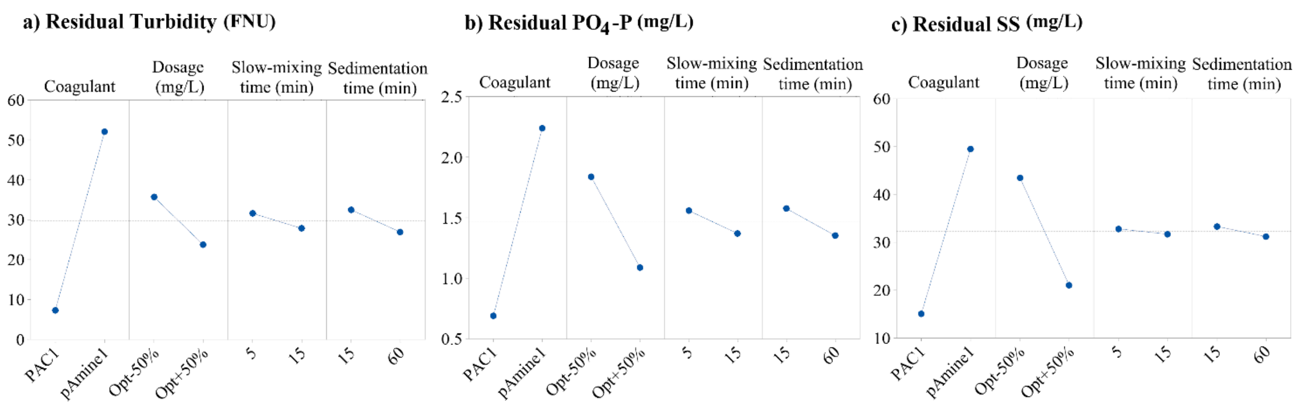

Figure 4. Plots showing the effects of the factors coagulant type, dose, mixing time and sedimentation time on the response variables (a) turbidity, (b) phosphate-phosphorus (PO_4-P) and (c) suspended solids (SS) residual concentrations in reject water.

Based on the two 2^3 factorial analysis (factors B, C and D, each at two levels to which centre points were added) conducted for PAC1 and pAmine1, the effect of the factors on SS residual concentration was not statistically relevant, especially when coagulant pAmine1 was used (Table 6). Application of the high levels of factors B, C and D (i.e. higher dose, longer mixing time and longer sedimentation time) resulted in lower turbidity, PO_4-P and SS concentrations in reject water following treatment by both PAC1 and pAmine1 coagulants, i.e. the main factor effect was negative (Table 6). Overall, coagulant dose (B) exerted the largest influence on residual turbidity and PO_4-P concentrations for both coagulants, although the influence was more accentuated when PAC1 was used (Table 6). Coagulant dose was also influential for removal of SS when PAC1 was the coagulant used (Table 6).

It is important fact to be noted that the effect of factors B, C and D on residual pollutant concentrations in reject water was significant, but not linear (Fig. 5). Curvature was found to be statistically significant ($p<0.05$) for both PAC1 and pAmine1 and to have a negative coefficient (concave curve). Plots of main factor effects and the curvature caused by the centre points further clarified the results obtained for PAC1 (Fig. 5a-c) and pAmine1 (Fig. 5d-f).

Table 6. Magnitude (Magn.) and significance of factor effect (confidence interval 95%) for the response variables (turbidity and residual concentrations of PO_4-P and SS in reject water) in 2^3 factorial analysis where coagulant type (A) was kept constant and dose (B), mixing time (C) and sedimentation time (D) were varied between two levels (high, low). Centre points were included to evaluate the linearity of the factor effect, which is represented by the curvature. Values in **bold** are significant at p<0.05.

	Turbidity				**PO_4-P**				**SS**			
PAC1	Magn. of effect	F statistic	p-value	Coefficient	Magn. of effect	F statistic	p-value	Coefficient	Magn. of effect	F statistic	p-value	Coefficient
B	-11.5	1483.7	**0.000**	-5.7	-1.1	1533.3	**0.000**	-0.6	-24	219.43	**0.005**	-12.0
C	-3.0	102.4	**0.000**	-1.5	-0.2	61.1	**0.000**	-0.1	-5.8	12.6	0.071	-2.9
D	-1.2	15.4	**0.004**	-0.6	-0.1	20.0	**0.002**	-0.1	-0.8	0.21	0.689	-0.4
BC	2.6	75.6	**0.000**	1.3	0.1	17.4	**0.002**	0.1	6.8	17.36	0.053	3.4
BD	1.3	18.7	**0.002**	0.6	0.1	8.5	**0.017**	0.0	-1.3	0.6	0.521	-0.6
CD	0.0	0.0	0.987	0.0	0.0	0.6	0.447	-0.0	5.0	9.52	0.091	2.5
BCD	0.1	0.0	0.847	0.0	0.0815	8.3	**0.018**	0.0	-4.0	6.1	0.132	-2.0
Curvature		157.6	**0.000**	-5.1		124.25	**0.000**	-0.4		33.66	**0.028**	-9.0
	Turbidity				**PO_4-P**				**SS**			
pAmine1	Magn. of effect	F statistic	p-value	Coefficient	Magn. of effect	F statistic	p-value	Coefficient	Magn. of effect	F statistic	p-value	Coefficient
B	-12.5	113.3	**0.000**	-6.2	-0.4	53.1	**0.000**	-0.2	-21.0	9.1	0.094	-10.5
C	-4.5	14.8	**0.004**	-2.3	-0.2	8.3	**0.018**	-0.1	3.6	0.3	0.665	1.8
D	-10.0	72.8	**0.000**	-5.0	-0.3	35.3	**0.000**	-0.2	-3.6	0.3	0.665	-1.8
BC	-0.1	0.0	0.942	-0.0	0.0	0.0	0.964	0.0	-3.6	0.3	0.665	-1.8
BD	-3.3	7.9	**0.021**	-1.6	-0.1	3.0	0.120	-0.1	-7.6	1.2	0.394	-3.8
CD	-1.5	1.6	0.244	-0.7	0.0	0.0	0.928	0.0	3.0	0.2	0.708	1.5
BCD	4.1	12.3	**0.007**	2.1	0.0	0.0	0.964	0.0	0.0	0.0	1.000	0.0
Curvature		185.9	**0.000**	-21.7		37.1	**0.000**	-0.4		10.0	0.088	-21.0

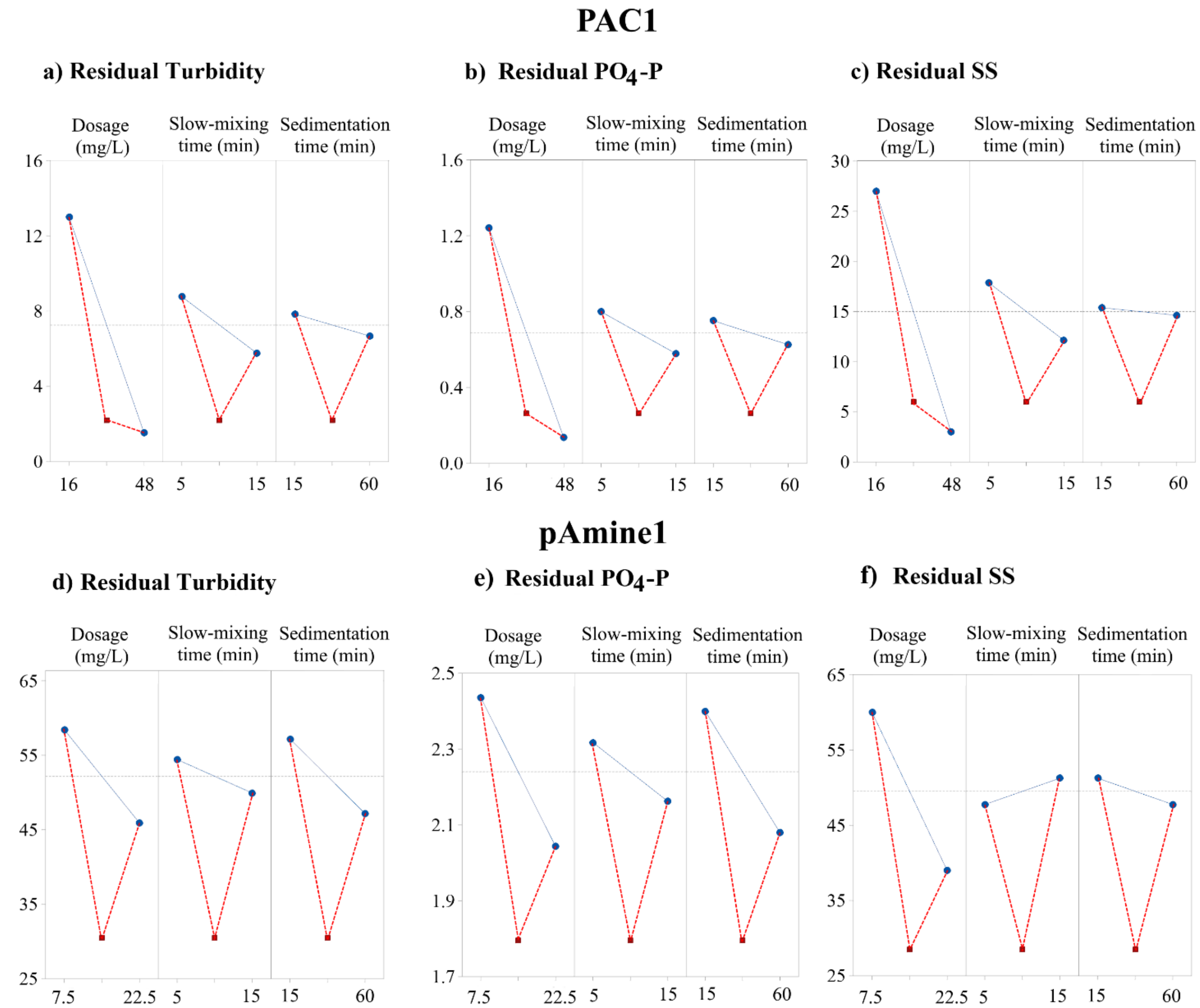

Figure 5. Plot of main factor effects and curvature on the response variables turbidity, phosphate phosphorus (PO_4-P), and suspended solids (SS) in reject water following treatment of recirculating aquaculture system (RAS) sludge with inorganic PAC1 (a, b and c) and organic pAmine1 (d, e and f).

4. DISCUSSION

Coagulation, flocculation and sedimentation processes and the efficiency of the coagulants tested

The performance of the pre-hydrolysed products tested (PAC) was excellent, when compared to results reported by Ebeling et al. (2003) for non-pre-hydrolysed aluminium- and iron-based coagulants in treatment of similar aquaculture sludge. The removal rates of PO_4-P and SS were higher at substantially lower coagulant doses in this study (90-99% with a dose of 30 mg/L) than in Ebeling et al. (2003) (89-93% with a dose of 60-90 mg/L). Our results confirm the generally reported superior performance of pre-hydrolysed metal salts in comparison with hydrolysing products (Wei et al., 2015; Sillanpää et al., 2018). On comparing the efficiency of inorganic and organic coagulants, the PAC products showed better performance, which was to some extent an expected outcome. Coagulants interact with dissolved, colloidal and particulate matter by different mechanisms (e.g. complexing, adsorption, neutralisation, entrapment etc.). In treatment of water containing dissolved organic carbon (DOC), e.g. humic acids (such as the RAS sludge used in this study), charge neutralisation/precipitation reactions are reported to be the dominant coagulation mechanism when effective treatment is achieved (Rojas-Reyna et al., 2010; Sillanpää et al., 2018). As metal salts normally have higher neutralisation capacity than organic polymers (Wei et al., 2009), the efficacy of inorganic metal salt coagulants is higher for this type of water (Heiderscheidt et al., 2016). Although several studies have identified charge neutralisation as an important coagulation mechanism for high-CD polymers (Libecki, 2010, Heiderscheidt et al., 2016), other mechanisms such as electrostatic patch and bridging normally also play a significant role in the coagulation process when organic coagulants are used. Furthermore, it is believed that formation of insoluble hydrolysis products by metal salts improves the coagulation/flocculation process by increasing the number of particles in suspension, leading to improved reaction kinetics and floc aggregation (Yu et al., 2015; Sun et al., 2019). This can to some extent explain the superior sedimentation performance (settling characteristics of flocs formed) observed for the PAC products in this study (Fig. 3).

Influence of process parameters on coagulant performance

In general, analysis of the 2^4 factorial design data showed that type of coagulant (PAC or pAmine1; factor A) exerted the largest influence on the residual pollutant concentrations (turbidity, PO_4-P and SS) measured in the supernatant (reject) water following treatment of RAS sludge, with lower concentrations found in samples treated with PAC1 (Fig. 4). In addition, treatment combinations which had coagulant dose (factor B) at its high level (optimum + 50%) achieved higher removal of target contaminants, although the effect of coagulant dose on SS removal by pAmine1 was found not to be statistically significant (Table 6). According to the output of the statistical analysis of the two 2^3 factorial designs, which examined the effect of the main factors on PAC1 and pAmine1 individually, the two products responded in different ways to changes in process parameters, with the factors having more influence on the performance of pAmine1, although the effect of coagulant dose on SS removal was only significant when PAC1 was used. The significant curvature observed for the effect of mixing time (5 or 15 min; factor C) and sedimentation time (5 or 60 min; factor D) are most likely the result of the effect of the centre point applied for dose, which was the optimum dose identified for each coagulant. Thus, most effective treatment should occur at the centre point. Due to the dominant effect of coagulant dose, it caused the significant curvature seen in the effects of mixing and sedimentation time. The response observed exemplifies quite clearly the principles of the coagulation process, where the coagulant dose needed for effective treatment correlates to the amount (and type) of contaminant substances contained in the substrate. However, as reported here, the relationship between dose and pollutant removal is mostly not linear. Increasing removal rates are normally achieved with increasing coagulant dose until an optimum dose range is reached, while doses higher than the optimum can result in re-entry of particles into suspension (Libecki, 2010, Heiderscheidt et al., 2016), causing lower pollutant removal.

Although the curvature observed for the effects of mixing rate and sedimentation time may be disregarded, these factors had statistically significant effects on the residual turbidity and PO_4-P concentrations found in reject water, as reported in earlier studies (Zhan et al., 2011; Heiderscheidt et al., 2013; Zhang et al., 2013). The lack of statistical significance in the effects of mixing and sedimentation time on SS removal by both coagulants might be due to the fact that only one replicate was used in the analysis (reject water from two replicates was combined to obtain the volume required for SS analysis). However, previous studies have found that slow mixing intensity has a stronger effect on charge-neutralisation coagulation than on sweep flocculation (Zhang et al., 2013), which supports the stronger effect of mixing time on PO_4-P than SS removal in this study (Table 6). Overall, lower contaminant concentrations were found in reject water when longer mixing and sedimentation times were applied in treatment of RAS sludge. However, further tests at optimum coagulant dose are needed to identify the optimum hydraulic parameters to be applied and these will, intrinsically, be coagulant-dependent.

Use of coagulants for solids management in RAS

In this study, the residual turbidity in reject water achieved by the PAC1 product applied at the optimum dose and in optimum process conditions (15 min mixing and 60 min sedimentation) ranged between 1.17 and 1.5 NFU, while the PO_4-P concentration ranged between 0.07 and 1.0 mg/L. For the pAmine1 product under the same process conditions, the residual turbidity ranged between 30 and 39 NFU and the PO_4-P concentration between 1.7 and 2.0 mg/L. While residual turbidity values measured in reject water following treatment of RAS sludge by pAmine1 were high, the values observed when PAC1 was applied were similar to those obtained using other solids management technologies, such as a mechanical filter (0.52-1.55 NTU) (Blidariu et al., 2013), a backwash sand filter (1.52 NTU) (Petrea et al., 2013), a novel biological aerated filter (3.2 NTU) (Zhang et al., 2020) or membrane filtration (0.6 NTU) (Wang et al., 2016). Phosphorus concentrations in the reject water following sludge treatment by both coagulants were lower than those normally reported for other solids management technologies. For example, 1-7 mg/L of Tot-P has been reported for RAS sludge samples treated by a novel biological aeration filter (Zhang et al., 2020) while 3.15-3.36 mg/L has been reported for sludge samples treated by a mechanical filter (Blidariu et al., 2013). Low P concentrations, comparable to those achieved by coagulant utilisation, are typically only reported for membrane technologies (e.g. Sharrer et al., 2007, 2010).

Efficient and stable P removal from sludge can be viewed as an additional advantage of using coagulants in RAS solids management. Use of inorganic coagulants has the dual benefit of high solids and organics removal in addition to high P removal but can lead to high residual concentrations of Al (or Fe depending on the coagulant used) in the reject water. In our experiments, the residual Al concentrations were up to 995 µg/L in samples treated by the PAC products and 85 µg/L in samples treated by the pAmine-based organic coagulants (compared with ~290 µg/L in blank samples). Therefore, re-introduction of reject water from PAC-induced solids thickening into RAS recirculation can result in accumulation of Al in the culture water, which could increase the freshwater intake requirement. Investigations in marine-based systems have shown that even low Al concentrations (4-8 µg/L) can cause physiological responses and reduced growth and survival rate in marine salmon (Kroglund and Finstad, 2003). To avoid such effects, use of pAmine-based organic coagulants in RAS sludge treatment would ensure low residual Al concentrations in the culture water. Another perceived benefit of using organic coagulants is the higher nutrient content and nutrient availability in the solid's product (Kirchmann et al., 2017). This can be considered of critical importance for RAS sustainability and for the goal of zero-waste loops in the wider aquaculture sector. Fish faeces are known to be one of the most nutritious animal wastes (Khiari et al., 2019), and thus have great potential for use as fertiliser or bio-stimulant in agriculture. However, the cost of organic products is 4-5 times that of the inorganic PAC products tested, although the lower required dose of the organic products (50%) can partly offset the higher price of these products. However, complete cost-benefit analysis should be conducted where e.g. cost of product transport, residual solids management, RAS requirements for fresh water, water treatment steps, etc. should be taken into consideration.

5. CONCLUSIONS

Use of a coagulant to treat the sludge removed from recirculating aquaculture systems (RAS) enhances floc formation and improves the settling characteristics of particles, substantially decreasing the nutrient, organics and solids concentrations in the supernatant (reject water). This allows the reject water to be re-introduced into the RAS water treatment chain, potentially decreasing the need for freshwater intake, without increasing the nutrient, organic and solids load on water purification units. Based on the findings of this study the following conclusions can be drawn:

- Of the coagulants tested, inorganic PAC products were the most effective at concentrating the pollutants (Tot-P, PO4-P, SS, COD) contained in RAS sludge into the solid phase, although the organic products, especially pAmine1, achieved good performance and can be considered a valid alternative to the inorganic salts.
- At the optimum dose, PAC1 (32 mg/L) and pAmine1 (15 mg/L) removed, respectively, 99.4% and 82.8% of turbidity, 98.2% and 65.4% of PO_4-P and 97.7% and 73.6% of SS.
- Type and dose of coagulant had the most significant effects on residual concentrations of PO_4-P, turbidity and SS in reject water. Thus, the optimum dose of each coagulant selected must be carefully identified and monitored.
- In coagulant selection, the effect on culture water and water treatment processes, loops and recycling of residual solids arising from recirculation of reject water into the RAS must be considered.
- The mixing rate applied in flocculation and the sedimentation time had a significant effect on coagulant performance, with pAmine1 being the most affected. However, at optimum dose this effect was reduced.
- Overall, flocculation times of 5-15 min and sedimentation times of 15-60 min showed promising results as high solids and phosphorous removal was achieved and can be used as a starting point in process optimisation for both inorganic and organic coagulants.

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