Organic polyelectrolytes as the sole precipitation agent in municipal wastewater treatment

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Abstract

In municipal wastewater treatment, inorganic coagulants (IC), e.g. polyaluminium chloride (PAC), are normally used to remove pollutants such as dissolved and particulate nutrients, in a process called coagulation/flocculation. However, IC use has been linked to issues e.g. in effluent water post-treatment, sludge management and disposal (IC increase sludge volume and metal concentrations in sludge), etc., raising uncertainties about their overall cost-efficiency and environmental benefits. In this study, the suitability of organic coagulants (OC) as sole precipitation agents to replace IC (PAC) was investigated. A total of 10 synthetic (i.e. polyDADMACs and polyamines) and semi-natural (chitosan, starch, and tannin-based) OC products were tested in treatment of samples from primary sedimentation and secondary sedimentation stages of municipal wastewater treatment, and their performance was compared with that of PAC. The study was conducted using the jar test methodology. The coagulants were tested for their ability to remove target pollutants (e.g. BOD_7, COD, SS, tot-P, PO_4-P, tot-N) and form rapidly settling flocs. In general, higher (up to 60%) coagulant doses were needed in treatment of secondary wastewater samples than primary samples. In comparison with the OC doses required for effective treatment, the PAC doses were higher (up to 80%). In treatment of secondary wastewater samples, OC with high molecular weight (MW) and high charge density (CD) (e.g. pAmine1) achieved best removal of target pollutants (e.g. 72% SS, 87% PO_4-P, 88% BOD_7), followed by PAC. In treatment of primary wastewater, PAC performed best (removing e.g. 96% SS, 96% PO_4-P), closely followed by chitosan and polyamine products. Based on these results, polyamine products with high MW and (very) high CDs have the potential to act as the sole precipitation agent in both primary and secondary stages of municipal wastewater treatment. Further research is needed to determine the effect of residual coagulant on downstream water and sludge treatment processes (e.g. activated sludge process, sludge dewatering, etc.).

Keywords: Coagulation, sewage, semi-natural coagulants, synthetic polymers, municipal wastewater

1. Introduction

Municipal wastewater is composed mainly of suspended and dissolved solids, nutrients, pathogens, metals and other organic and inorganic impurities (Lee et al., 2014). The presence of these contaminants in water poses a threat to humans and the environment, due to the potential risks from e.g. disease-causing microorganisms, accumulated heavy metals in receiving ecosystems, eutrophication of water bodies, etc. (Drinnan, 2001). Thus, reduction, if not complete elimination, of these pollutants is necessary before wastewater is released into receiving water bodies. Conventional wastewater treatment plants predominantly employ coagulation-flocculation followed by solid-liquid separation (e.g. sedimentation) processes in the treatment chain. The aim is effective reduction in concentrations of impurities such as organic contaminants (measured as biochemical oxygen demand, BOD), chemical oxygen demand (COD), suspended solids (SS) and nutrients (phosphorus, P) (Bratby, 2016).

In general, inorganic coagulants (IC), mostly metal salts of aluminium (Al) and iron (Fe), are used in the coagulation process, as they are cheap, easily controlled and well-studied (Bratby, 2016). Metal salt coagulants dissociate into positively charged metal ions, so they have high charge neutralisation potential (Bratby, 2016). Controlled hydrolysis of Fe- and Al-based coagulants 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, less sensitive to changes in temperature and the nature of the raw water, etc. (Jiang and Wang, 2009; Wei et al., 2015, Sillanpää et al., 2018).

Although IC are effective, there are several disadvantages associated with their use. These include production of large sludge volumes that incur high management and disposal costs, high alkalinity consumption which might increase the need for pH adjustment chemicals, and high residual Al or Fe concentrations in the treated water, leading to detrimental effects on downstream purification processes (Liu et al., 2011; Chen et al., 2012) and receiving ecosystems (WWAP, 2017). Use of IC can also restrict the use of sludge as a soil amendment, as Al- or Fe based-coagulants are known to react with P, precipitating it as stable metal phosphates and thus lowering its availability for plant uptake (Krogstad et al., 2005; Kirchmann et al., 2017). This decreases the fertiliser potential of the resulting sludge.

Organic coagulants (OC), particularly synthetic OCs, are widely used in water and wastewater treatment. However, they are primarily used as flocculants and act as a 'bridge' for coagulated particles formed by IC. Addition of OC produces stronger and larger flocs, increasing settling rates and improving solid-liquid separation (Gregory and Bolto, 2007, Sillanpää et al., 2018). Use of OC as the sole precipitation agent in municipal wastewater treatment is rare, mostly due to their relatively high cost and their perceived inability to remove dissolved contaminants such as dissolved organic carbon (DOC) and phosphate P (PO_4-P). However, with advances in the technology for producing synthetic organic polymers, costs have decreased and tailor-made products with varying molecular weight (MW) and charge density (CD) are being produced (Gregory and Bolto, 2007; Bratby 2016). Another type of OC, (semi)-natural polymers, which can be produced or extracted from animals, plant tissues or microorganisms (e.g. chitosan, tannin-based products, etc.), has received significant attention recently, as these OCs are reported to have lower toxicity and higher biodegradability than synthetic OC (Renault et al., 2009; Sánchez-Martín et al., 2010; Oladoja, 2015; Heiderscheidt et al., 2016b; Liu et al., 2017).

Good performance of commercially available OCs as the sole precipitation agent for wastewater purification has been reported in laboratory-based studies (Nozaic et al., 2001; Razali et al., 2011; Heiderscheidt et al., 2016a). The few studies conducted to date in full-scale wastewater treatment plants (WWTPs) have found that OC can achieve the required pollutant removal and that, when costs of transport, sludge management, etc. are taken into consideration, they can also be cost-effective (Nozaic et al., 2001). However, the suitability of OC as the sole precipitation agent in primary and secondary sedimentation stages of municipal wastewater treatment has not been studied previously. Thus, there is a clear need for investigations regarding the potential of OC as the sole coagulant in municipal wastewater treatment and the effectiveness of (semi)-natural products.

This study investigated the applicability of OC as the sole precipitation agent in primary and secondary sedimentation stages of municipal wastewater treatment. The novelty of the work lies in the use of real wastewater samples and testing of a range of OC, both synthetic (e.g. polydiallyldimethylammonium chloride (polyDADMAC) and epichlorohydrin-dimethylamine (polyamines)) and semi-natural (chitosan, starch, and tannin-based products), in comparison with a normally used IC (PAC). The coagulants were tested under laboratory conditions for their capacity to remove e.g. BOD_7, COD, SS, total P (tot-P), orthophosphate (PO_4-P) and total nitrogen (tot-N), and their ability to form rapidly settling flocs.

2. MATERIALS AND METHODS

Experimental work was conducted using the jar test methodology, in two phases. Phase 1 involved determination of coagulant optimum dosage range and purification efficiency in treatment of wastewater samples collected prior to the secondary clarifier (20 ± 2 °C). A total of 11 products were tested, 10 OC (polyDADMACs, polyamines, chitosan, starch, and tannin-based products) and one IC

(PAC). Phase 2 involved determination of coagulant optimum dosage range and purification efficiency in treatment of wastewater samples collected prior to the primary clarifier (20 ± 2 °C). Five products were tested in Phase 2, four OC (two synthetic and two semi-natural, based on performance in phase 1) and one IC (PAC).

2.1 Wastewater sampling

Real wastewater samples were collected from Taskila WWTP (Oulu, Finland) between February and April 2019. Samples for secondary sedimentation tests (sampling point 1) were collected from the last cell of the activated sludge unit (before the membrane bioreactor (MBR)). Sampling point 1 was located in the outflow of the activated sludge process, prior to membrane separation. The MBR line had just been implemented in the WWTP and during the sampling period, no coagulants were added before membrane separation. This enabled the use of activated sludge without residual coagulant contamination from sludge recirculation. For the primary sedimentation tests (sampling point 2), samples were collected after the pre-screening unit before the primary clarifier (Fig. 1), also avoiding coagulant contamination from preliminary treatment stages.

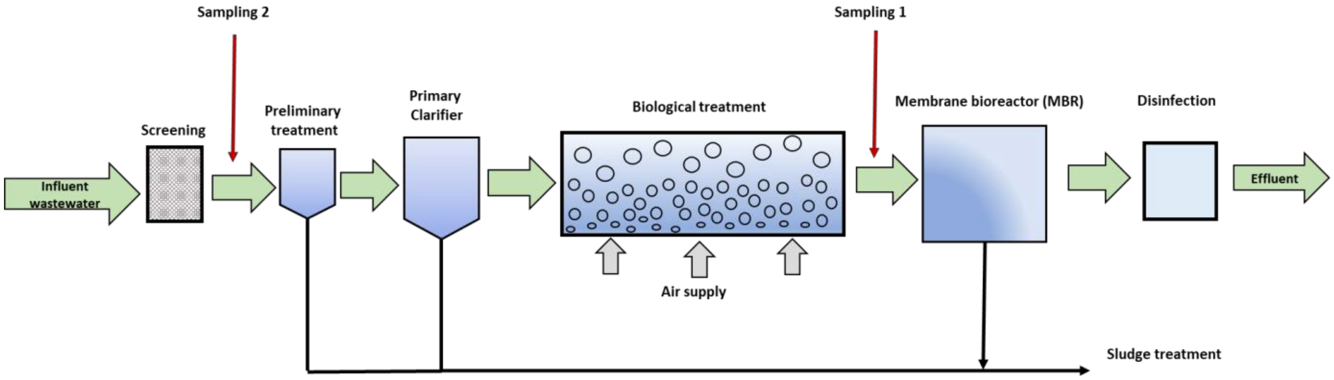

Fig. 1. Sampling points at Taskila wastewater treatment plant (WWTP). Sampling 1 = prior to secondary clarifier, sampling 2 = prior to primary clarifier).

The characteristics of the collected samples were initially assessed using parameters determined upon sample collection (e.g. pH, temperature, dissolved oxygen (DO) and mixed liquor suspended solids

(MLSS)) (Table 1). The samples were later also assessed in water quality analyses conducted in an external laboratory (Section 2.4, Table 3). Secondary wastewater samples (pumped into 30-L containers) were placed in a 5-10°C cold-room and aerated intermittently (45 min on, 15 min off) for ≥12 hours to ensure DO levels were within 1-3 mg/L before the coagulation experiments. Primary wastewater samples (transferred into 40-L containers) were placed in cold storage (5-10°C) and stirred (paddle mixer) continuously (100 rpm) throughout the experimental period.

Table 1. Characteristics of wastewater samples upon collection and the coagulants tested on each type of sample (see Table 2 for coagulant characteristics). MLSS = mixed liquor suspended solids, DO = dissolved oxygen.

	Sample	**Date**	**MLSS (mg/L)**	**pH**	**DO (mg/L)**	**Temperature (°C)**	**Chemical Tested**
Secondary Wastewater	1	13.02.19	11310	6.80	5.3	9.8	PAC
	2	14.02.19	10240	6.83	7.5	9.6	pAmine1
	3	21.02.19	5820	6.93	9.6	9.6	pDMAC1
	4	22.02.19	5310	7.01	11.1	9.3	Tannin
	5	26.02.19	4500	7.02	10.8	9.8	pDMAC2
	6	27.02.19	4310	6.98	9.2	9.8	pAmine2
	7	07.03.19	5750	6.85	6.1	8.9	Starch
	8	08.03.19	6130	6.84	7.6	9.1	pAmine3
	9	13.03.19	7130	6.82	5.6	9.8	pDMAC3
	10	14.03.19	6980	6.81	7.8	9.9	Chitosan
	11	14.03.19	6980	6.81	7.8	9.9	pDMAC4
Primary Wastewater	1	03.04.19	---	7.54	---	7.0	PAC
	2	08.04.19	---	7.65	---	7.1	pAmine1
	3	09.04.19	---	7.41	---	8.0	Starch
	4	11.04.19	---	7.87	---	7.4	pAmine3
	5	12.04.19	---	7.74	---	7.3	Chitosan

2.2 Characteristics of coagulants tested

Coagulants were evaluated for their ability to induce coagulation and subsequent solid/liquid separation. The coagulants were selected based on a literature review (e.g. Bolto, 1995; Bolto and Gregory, 2007; Renault et al., 2009; Razali et al., 2011; Oladoja, 2015; Liu et al., 2017, Sillanpää et al., 2018), previous research at our department (Heiderscheidt et al., 2016a), commercial availability and prevalence of use in water and wastewater treatment. Of the 11 coagulants tested, one was an inorganic pre-hydrolysed metal salt of aluminium (PAC) and 10 were synthetic or semi-natural polymers of varying MW and CD. These included polyDADMACs and polyamine synthetic polymers and semi-natural polymers based on starch, chitosan and tannin products. The characteristics of the products tested are listed in Table 2.

2.3 Experimental procedure

Laboratory experiments were carried out using the jar test methodology and Kemira Kemwater Flocculator 2000 (six programmable paddle stirrer) equipment. Suitable mixing conditions were identified in preliminary tests conducted on secondary wastewater samples using PAC as coagulant. In these preliminary tests, supernatant water was drawn from 1-L samples subjected to different mixing parameters after addition of PAC and constant sedimentation time (60 min) and analysed for turbidity (nephelometric turbidity units, NTU). Based on the settling behaviour of the wastewater (lowest turbidity values in supernatant samples), the following mixing conditions were used during phases 1 and 2 of the experiment for all coagulants: 200 rpm for 30 s (fast mixing) and 40 rpm for 5 min (slow mixing), followed by 60 min of sedimentation.

Table 2. Characteristics of coagulants tested.

Metal Salt Inorganic Coagulant (IC)

Product	Density (g/cm^3)	Concentration	Char (
Polyaluminium chloride	1.34	42%	

Synthetic Organic Coagulants (OC)

Product	Density (g/cm^3)	Concentration	Relative molecular weight	Charge	Char (
PolyDADMAC	1.09	40%	Very high	Very high cationic	
PolyDADMAC	1.08	50%	Very high	High cationic	
PolyDADMAC	1.05	22%	High	Very high cationic	
PolyDADMAC	1.05	22%	Medium	High cationic	
Polyamine	1.20	40%	High	Very high cationic	
Polyamine	1.14	50%	Medium	Very High cationic	
Polyamine	1.18	50%	Low	Very high cationic	

Semi-natural Organic Coagulants (OC)

Product	Concentration	Relative molecular weight	Charge	Char (
Starch	100%	High	High cationic	
Chitosan	100%	Low	High cationic	
Tannin	100%	Very Low	Low cationic	

*Measured at in-house laboratory facilities.

To maintain more constant conditions, the pH of collected samples was adjusted to between 6.40-6.70 prior to the tests, using hydrochloric acid solution (1M HCl). Stock solutions (e.g. 20 mg/mL) of the coagulants were prepared using the respective specific density of different products and deionised water. The stock solution for the chitosan-based product was prepared by dissolving it in deionized water and 1% acetic acid (due to its insolubility in non-acidic media) (Table 3). For determination of coagulant dose required, increasing doses of coagulant were added to 1-L wastewater samples (primary and secondary) in glass jars. Fast and slow mixing was applied, followed by sedimentation. Supernatant water samples were extracted from the jars (after sedimentation) containing each coagulant dose and from jars with blanks (wastewater subjected to similar mixing conditions, without addition of coagulant) and analysed for turbidity. The optimum dose was identified as the dose that attained the lowest residual turbidity values for each product tested. In addition, charge quantity (CQ, μeq/L) and colour analysis (mg Pt/L) were performed in all samples. Standard methods and equipment were used: turbidity (EN 27027:1994; Hatch Ratio/XR Turbidity meter), pH (SFS-EN 13037:1994; WTW Universal meter), colour (ISO 7887:1994; Lovibond Nessleriser Daylight 2000) and SS (SFS-EN 872:2005; Class fibre filter Whatman GF/C). Charge quantity analysis was carried out using the Mütek particle charge detector PCD 03 PH (Mütek Analytic GmbH, Germany) following the manufacturer's instructions. The measurement is based on the streaming current principle where samples are titrated with a titrant of opposite charge until the point of zero charge is reached. The titrant volume consumed to neutralize the charge of the samples is used to calculate the charge density (Mütek Instruction Manual 2000; Leiviskä, 2010)

Supernatant samples (two replicates) extracted from jars treated with the optimum dose of each coagulant were sent to a certified laboratory. Purification efficiency was assessed based on the residual concentration (determined by standardised SFS and ISO analytical methods) of: biochemical oxygen demand (BOD_7): SFS-EN 1899-1:1998, chemical oxygen demand (COD): ISO 15705:2002, total phosphorus (tot-P): SFS-EN ISO 15681-2:2005, orthophosphate (PO_4-P): SFS-EN ISO 15681-

2:2005, total nitrogen (tot-N): SFS-EN ISO 11905-1:1998, total aluminium (tot-Al): SFS-EN ISO 15587-2:2002,11885:2009, and total iron (tot-Fe): SFS-EN ISO 15587-2:2002,11885:2009. Sludge volume was determined after 60 min sedimentation time in tests with secondary wastewater samples, via direct reading from the markings on the glass jars. The settling characteristics of flocs formed (optimum dose of three best-performing coagulants) in the treatment of primary wastewater samples were evaluated using the methodology described by Bratby (2006). Turbidity measurements were conducted on 30-mL supernatant samples collected at 2, 4, 6, 8, 16, 32 and 60 min during the sedimentation period.

2.4 Quality of wastewater samples tested

Samples extracted from blanks of experimental runs were sent to a certified laboratory for water quality analysis (BOD_7, COD, tot-P, PO_4-P, tot-N, tot-Fe, tot-Al) and were also tested using in-house laboratory facilities (pH, electrical conductivity (EC), turbidity, colour, SS, CQ,).

Table 3. Water quality characteristics of blank samples (average ± standard deviation).

Water Quality Parameters	**Secondary wastewater (mean ± std. dev.) (n=11)**	**Primary wastewater (mean ± std. dev.) (n=5)**
BOD_7 (mg/L)	68 ± 54	143 ± 129
COD (mg/L)	301 ± 105	360 ± 193
tot-P (mg/L)	1.95 ± 0.50	3.70 ± 0.68
PO_4-P (mg/L)	0.76 ± 0.55	2.84 ± 0.72
tot-N (mg/L)	74 ± 8	53 ± 5
tot Fe (mg/L)	4.33 ± 3.29	7.50 ± 1.75
tot Al (mg/L)	0.82 ± 0.42	0.40 ± 0.18
SS (mg/L)	35.91 ± 13.79	64.73 ± 15.17
Turbidity (NTU)	34.46 ± 9.44	74.82 ± 12.75
Colour (mg Pt/L)	---	315 ± 30
pH	6.85 ± 0.18	7.52 ± 0.04
Sludge Volume (ml)	572 ± 152	40 ± 9
EC (µS/cm)	1290 ± 55	905 ± 101

2.5 Data analysis

The rank-based nonparametric statistical analysis Kruskal-Wallis H test (confidence interval 90%, $p \leq 0.1$) followed by the post-hoc Dunn test and Bonferroni correction (IBM SPSS Statistics 26.0) was used to test the hypothesis of equality of samples median for both the quality of the wastewater samples tested (blank) and the removal of target pollutants achieved by different coagulants (PAC, pAmine1, pAmine3, Starch and Chitosan). In addition, clustering based on a Principal Component's analysis following Ward's method for Eucleadian distance was used to determine similarities in wastewater quality between blank samples and removal rates achieved by different coagulants (RStudio software). Analysis regarding wastewater quality were conducted based on turbidity (Kruskal-Wallis H test), BOD_7, tot-P, PO_4-P and tot-N (cluster analysis) concentrations found in blank samples while analysis related to treatment efficiency was done based on removal of turbidity, BOD_7, tot-P, tot-N (Kruskal-Wallis H test) and PO_4-P (cluster analysis). Removal efficiency was calculated using Equation (1).

$$Ref = 100 * \frac{Ci - Cf}{Ci} (\%) \quad (1)$$

where: R_{ef} = removal efficiency (%), C_i = initial concentration of contaminant (mg/L) and C_f = final concentration of contaminant (mg/L).

3. RESULTS

The effectiveness of the different OC products as sole precipitation agent for purification of municipal wastewater was compared with that of PAC. Coagulant doses are reported as active dose (water content of products was disregarded). The quality of the supernatant water extracted from samples treated with the optimum dose of each coagulant was compared with that of their respective blank samples in terms of pollutant concentrations (BOD_7, COD, SS, tot-N, tot-P, PO_4-P).

3.1. Coagulant dose required for treatment of secondary wastewater samples (Phase 1)

In the dosage requirement tests, an increasing dose of all coagulants resulted in a reduction in residual turbidity in the supernatant water until an optimum dose was reached. Doses higher than the optimum caused increased turbidity in the supernatant water. In general, OC required substantially lower doses than PAC for effective turbidity removal, regardless of the initial turbidity of the wastewater samples

(Fig. 2). Among the OC tested, products with (very) high CD and high MW required lower doses than products with lower CD and MW. The PAC product tested achieved its lowest residual turbidity values, of about 12 NTU, at a dose of 120 mg/L. A high-MW polyDADMAC product (pDMAC3) required a dose of only 15.4 mg/L to achieve similar residual turbidity (Fig. 2a). The optimum dose identified for pAmine1 was 20 mg/L, which removed as much turbidity (71%) as PAC at 120 mg/L (Fig. 2b). Among all products tested, including IC and OC, chitosan (50 mg/L) achieved the highest overall turbidity removal (~80%) and produced supernatant water with the lowest residual turbidity values (~7 NTU).

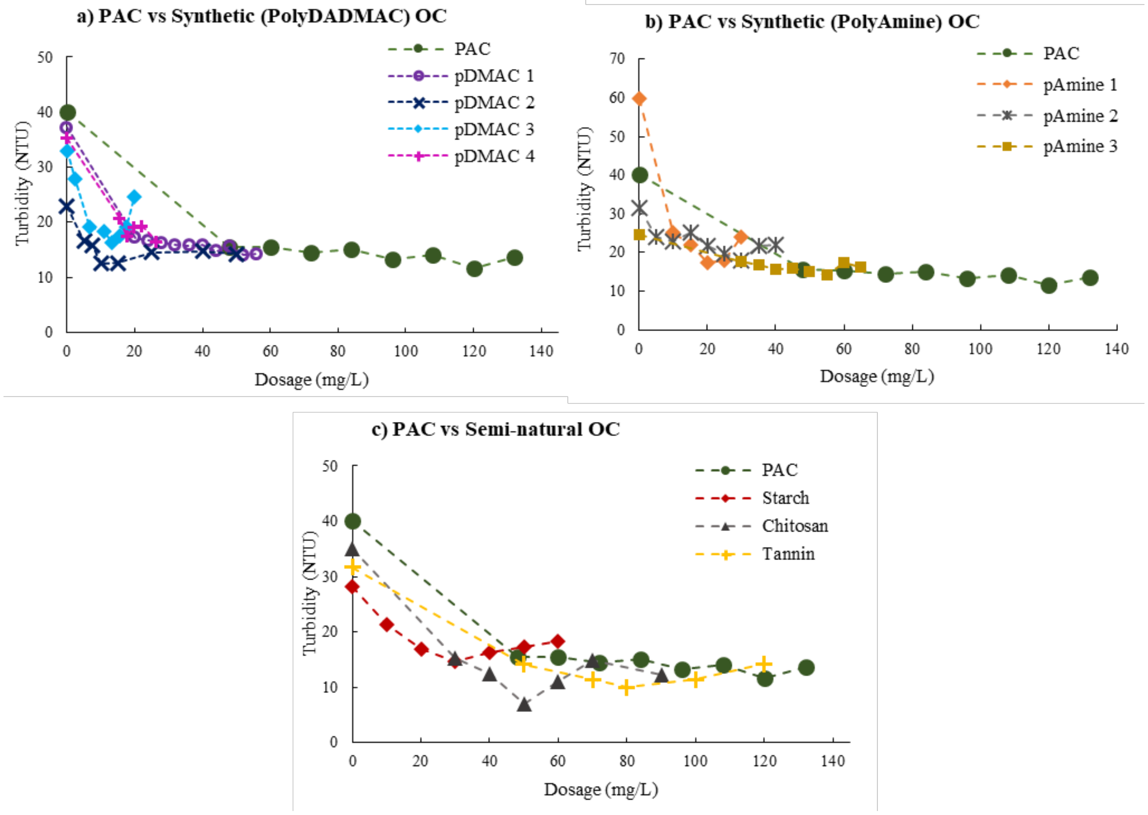

Fig. 2. Turbidity (NTU) of secondary wastewater samples treated with increasing doses (mg/L) of inorganic coagulant (IC) and organic coagulant (OC). Turbidity at 0 dose (mg/L) refers to the turbidity of blank samples.

3.2. Purification efficiency in treatment of secondary wastewater samples (Phase 1)

Purification efficiency (removal of target pollutants) achieved by the optimum dose of the coagulants was evaluated. The quality of the wastewater (blank) samples varied significantly (Table S1a, Supplementary Material) during the test period (e.g. turbidity, Kruskal Wallis $p = 0.047$) which made a straight comparison among coagulant performances challenging. However, pair-wise comparison and cluster analysis (Table S1b and Fig. S1, Supplementary Material) showed that the quality of wastewater samples treated by e.g. pAmine3 and Starch (turbidity, Kruskal-Wallis $p = 0.409$) as well as samples treated by PAC and pAmine1 (turbidity, Kruskal-Wallis $p = 0.546$) were not significantly different.

In general, residual contaminant concentrations found in samples treated with OC were comparable to those found in samples treated with PAC (Fig. 3). Among the coagulants tested, pAmine1 achieved higher overall removal efficiencies than PAC for all target contaminants, but particularly BOD_7, COD, tot-P, PO_4-P, tot-N and SS. Regarding organic matter removal, samples treated with the high-MW OC (pDMAC3, pAmine1, and Starch) showed lower residual concentrations of BOD_7 than samples treated with PAC. These were followed by the very high-MW OCs (pDMAC1 and pDMAC2) (Fig. 3a). On the other hand, COD removal by OC was slightly lower than that achieved by PAC (Fig. 3b). Treatment with chitosan produced supernatant water with substantially higher BOD_7 and COD concentrations than those found in the blank samples (Fig. 3b). The lowest concentrations of SS were found in samples treated with the high-MW pAmine1 and the low-MW pAmine3 (Fig. 3c). In terms of removal efficiency, the highest removal of SS was achieved by pAmine1 (72%), followed by pAmine3 (58%) and the tannin-based semi-natural polymer (56%). The removal of SS achieved by different coagulants followed similar patterns to the turbidity removal efficiency observed during dosage requirement tests (Fig. 2), except for the semi-natural products. The optimum dose of chitosan achieved high turbidity removal (Fig. 2c), but wastewater samples were found to contain substantial amounts of SS after purification tests (Fig. 3c).

The synthetic OC, pDMAC1 (very high MW) and pAmine1 (high MW), attained the highest removal efficiencies of tot-P and PO4-P. In addition, samples treated with these two synthetic OC and the tannin-based semi-natural polymer (low MW) showed the lowest residual PO4-P and tot-P concentrations (Figs. 3d and 3e). As expected, removal of tot-N was lower than that of other target contaminants. The products pDMAC1 and chitosan achieved the highest tot-N removal rates, 18%, and 9%, respectively. It is important to note that samples treated with pDMAC2 and pDMAC3 contained higher tot-N concentrations than those found in the blank samples (Fig. 3f).

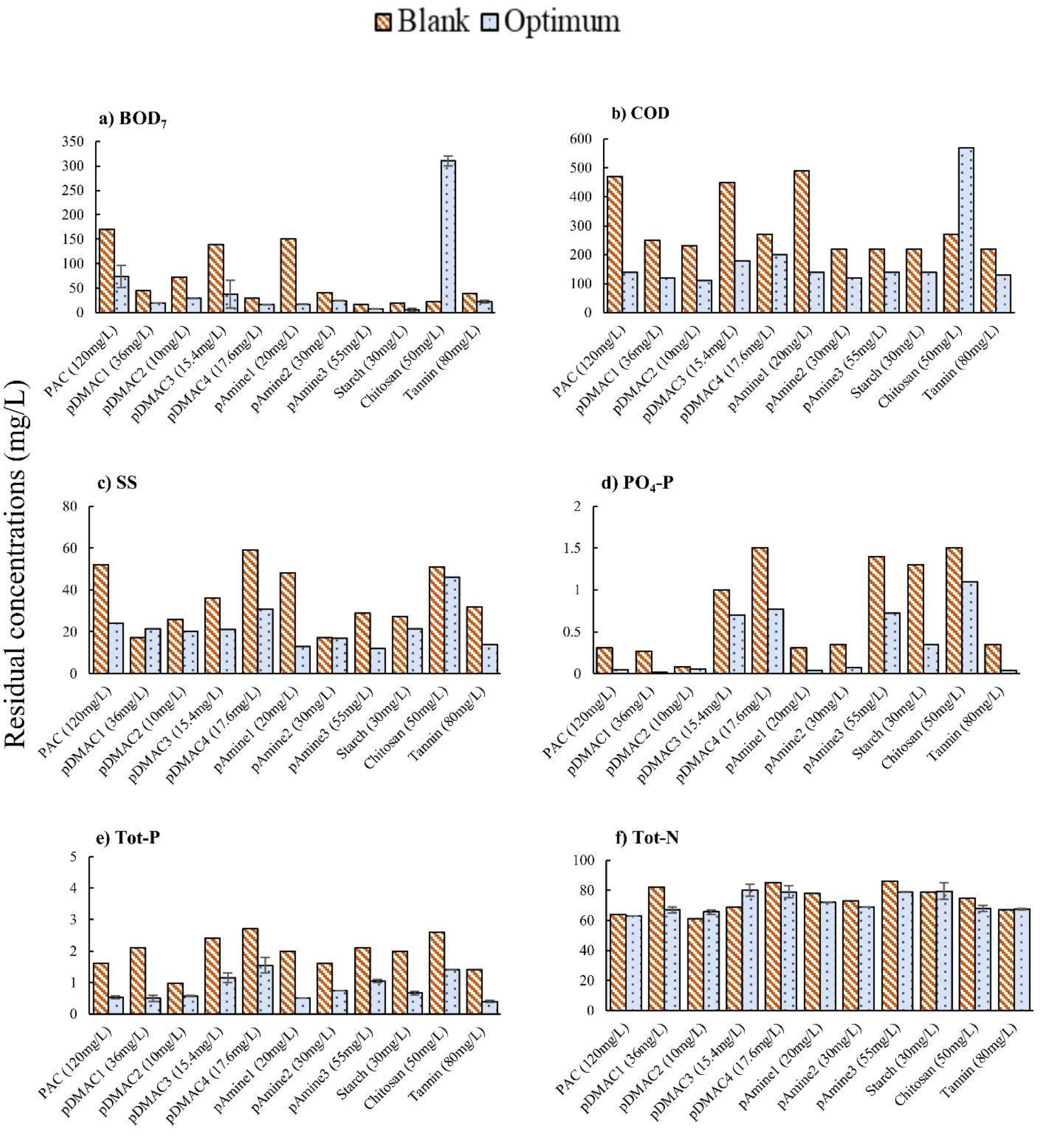

Fig. 3. Residual concentrations (mg/L) of target contaminants in blank and treated (optimum doses) secondary wastewater samples. Error bars represent maximum and minimum values obtained from experimental replicates.

3.3. Sludge volume produced during secondary wastewater sample treatment

The amount of sludge produced due to addition of coagulant is an important parameter when assessing their cost-efficiency. The volume of sludge generated by the coagulants tested in comparison with the blank samples (mixing and sedimentation but no coagulant addition) increased or decreased for different products (Fig. 4). Organic polymers with high MW and high CD produced lower sludge volumes (~25% lower) than those observed in blank samples. Among the coagulants tested, pAmine1 obtained the highest reduction in sludge volume, followed by starch and pDMAC3, with 28%, 25% and 20% decrease in volume, respectively, when compared to their blank samples. In contrast, treatment with pDMAC1 caused a 10% increase in sludge volume and addition of PAC did not appear to affect the volume of sludge produced (Fig. 4).

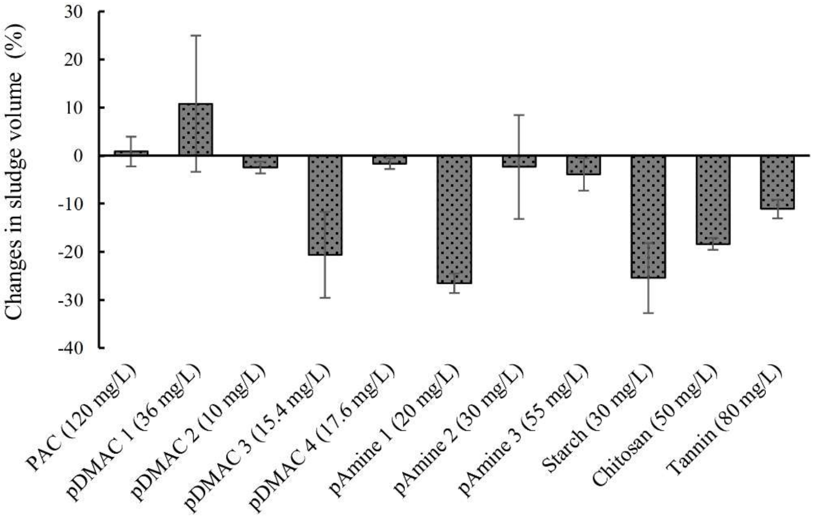

Fig. 4. Change in sludge volume for each coagulant (optimum dose) compared with blank samples in the treatment of secondary wastewater. Error bars represent maximum and minimum values obtained from experimental replicates.

3.4. Coagulant dose required for treatment of primary wastewater samples (Phase 2)

Dosage requirement tests for the treatment of primary wastewater samples were conducted using five coagulants: PAC, pAmine1, pAmine3, starch, and chitosan (Fig. 5). As observed during tests with the secondary wastewater samples, addition of increasing coagulant doses decreased the turbidity of the supernatant water until an optimum dose was reached. Doses higher than the optimum caused an increase in the supernatant water turbidity, particularly when OC were used (Fig. 5). In general, PAC required a higher optimum dose (48 mg/L) than pAmine (10-35 mg/L) or semi-natural OC (7.5-10 mg/L). On the other hand, the residual turbidity measured in samples treated with the optimum dose of PAC was evidently lower than that measured in samples treated with all other products except chitosan.

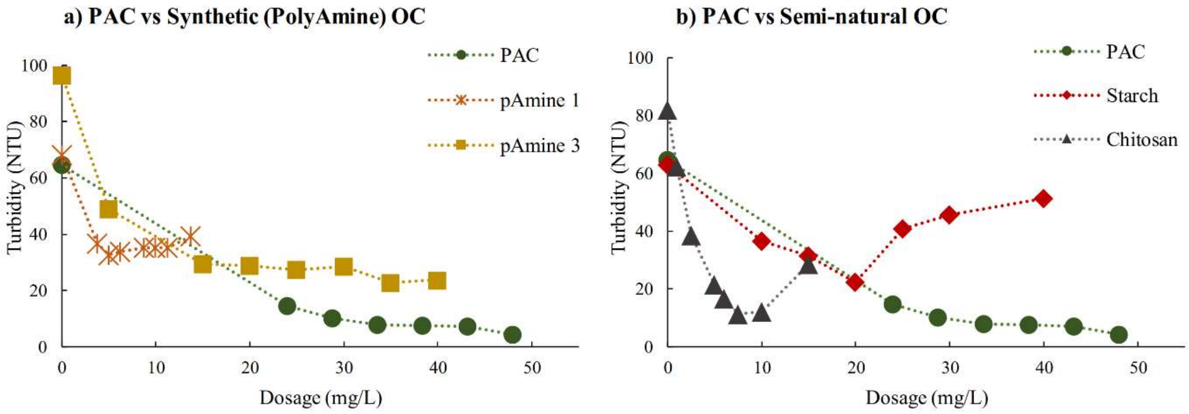

Fig. 5. Residual turbidity (NTU) with an increasing dose (mg/L) of polyaluminium chloride (PAC) and different synthetic and semi-natural organic coagulants (OC) in treatment of primary wastewater samples. Turbidity at 0 dose (mg/L) refers to the turbidity of blank samples.

3.5. Purification efficiency in the treatment of primary wastewater samples (Phase 2)

According to the statistical analysis performed, water quality varied significantly (Table S1a, Supplementary Material) among primary wastewater (blank) samples (turbidity, Kruskal Wallis, $p = 0.068$). In particular, the organic matter and SS concentrations found in blank samples treated with

PAC were substantially lower than those measured in blank samples by other products (Fig. 6). Pair-wise comparison and cluster analysis (Table S1c and Fig. S2, Supplementary Material) showed that, samples treated by PAC and Starch (turbidity, Kruskal-Wallis, p = 0.509) and by Chitosan and pAmine1 (turbidity, Kruskal-Wallis, p = 0.509) were not significantly different.

In general, residual contaminant concentrations were lower in samples treated with PAC. However, the performance of the five OC tested was to some extent comparable to that of PAC (Figs. 6c-6e). Lower residual BOD_7 and COD concentrations were found in samples treated with pAmine1 than in samples treated with PAC (Fig. 6a and 6b). Semi-natural polymers (e.g. chitosan), performed as well as PAC in removing PO_4-P. Samples treated with chitosan contained about 10% higher tot-N concentration than the blank samples, while other products had little or negligible effects on the tot-N concentration of the water (Fig. 6f).

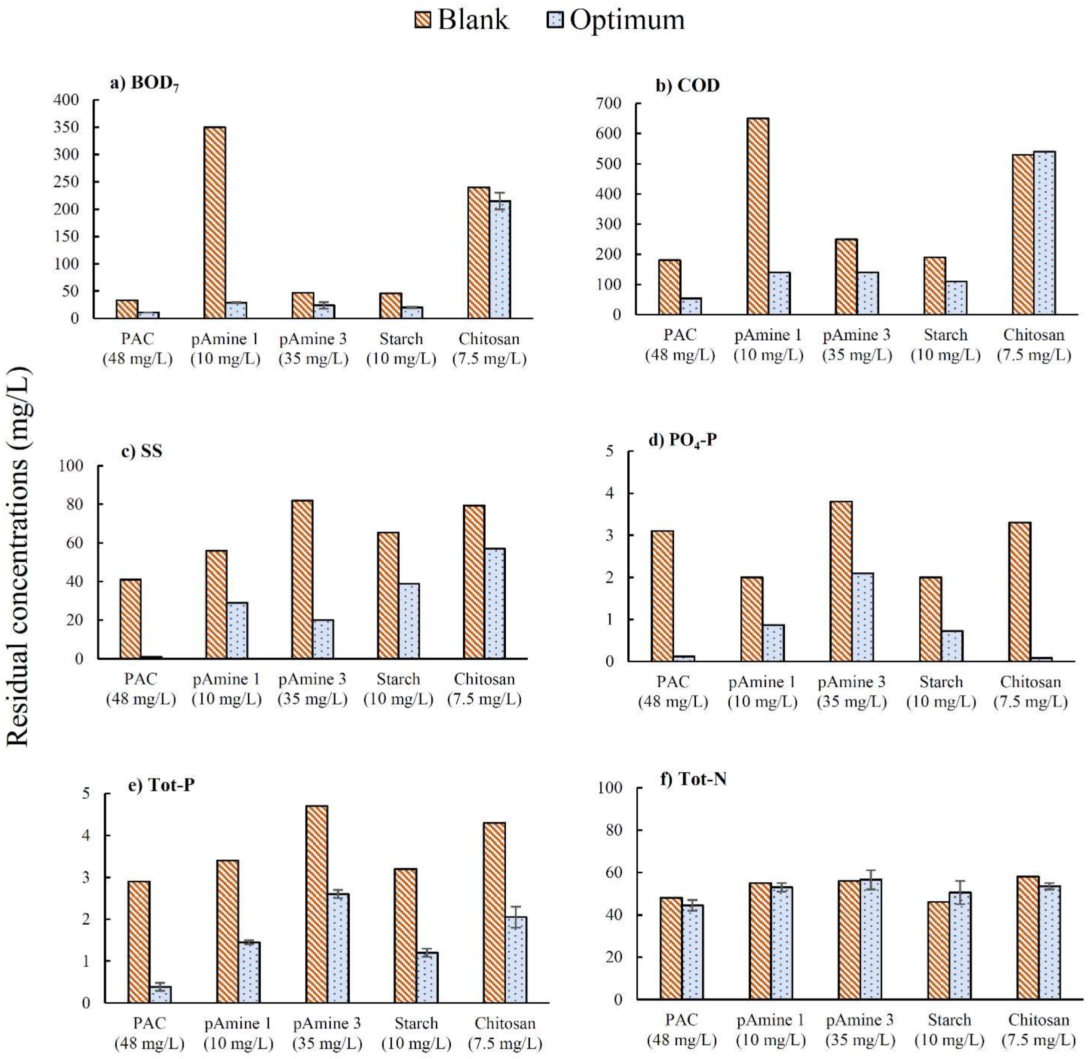

Fig. 6. Residual concentrations (mg/L) of target contaminants (see Table 3) in blank and treated (optimum doses) primary wastewater samples. Error bars represent maximum and minimum values of experimental replicates.

3.6. Settling characteristics of flocs formed

The ability of coagulants to form readily settleable flocs that sedimented over the selected residence time was evaluated. Three coagulants were selected according to turbidity test results from dosage requirement experiments: PAC (48 mg/L), pAmine3 (35 mg/L) and chitosan (7.5 mg/L). In comparison with the blank sample, addition of all three coagulants improved the settling characteristics of particles in suspension (Fig. 7). It was evident that, as the sedimentation period progressed, the turbidity of samples to which coagulant was applied decreased at a faster rate than that of the blank sample. In addition, the final turbidity of the supernatant water at the end of the sedimentation period was much lower in coagulant-treated samples. Lowest turbidity residuals were achieved within 20 mins of sedimentation for all coagulants, and a further increase in sedimentation time had little or no effect in clarification of the supernatant water by IC or OC products (Fig. 7). Of the products tested, PAC and chitosan achieved faster settling rates and better supernatant water clarification than pAmine3.

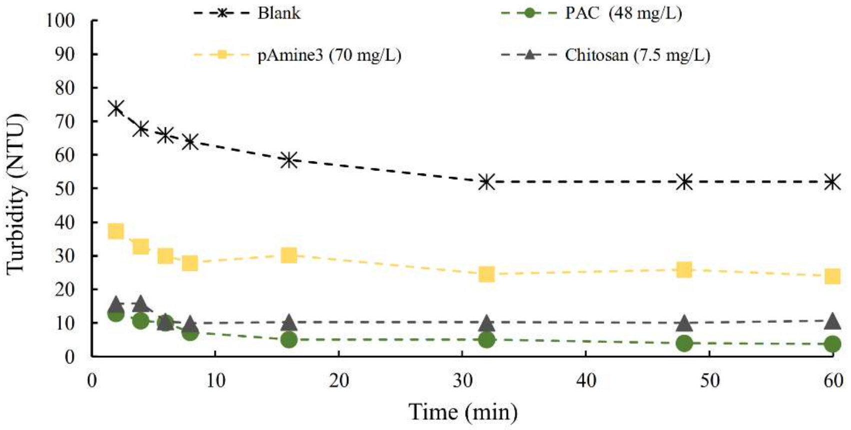

Fig. 7. Settling characteristics of flocs formed by the addition of coagulant in comparison with the blank sample during treatment of primary wastewater samples.

4. DISCUSSION

The quality of the wastewater samples collected prior to secondary and primary clarifiers in a municipal WWTP differed markedly. For instance, the amount of particulate matter and P in secondary samples was about half that in primary samples (Table 3). While most of the P in primary samples was in PO_4-P form (~70%), particulate-P was the dominant form in secondary samples (~60%). During tests, it was also observed that the particulate matter in primary samples was mostly composed of smaller particle sizes than the particulate matter in secondary wastewater samples. In addition, the pH of primary and secondary wastewater samples differed (mean 7.7 and 6.8, respectively). As the coagulant dose required for treatment and purification effectivity is directly dependent on the amount and type of contaminants in the water (Bolto and Gregory, 2007; Bratby, 2016), treatment efficiency and coagulant dose required in purification of primary and secondary samples differed substantially (Fig. 3 and Fig. 6). Moreover, there were significant variations in water quality between samples from the same treatment stage (secondary, Kruskal Wallis $p = 0.047$ and primary, Kruskal Wallis $p = 0.068$) (Table 3). Purification efficiency and dosage requirements of different products were affected by water quality characteristics of the samples treated, hampering direct comparison of the performance of different products tested.

In general, it was observed that dosage requirements of coagulants were up to 60% higher in treatment of secondary samples compared with primary samples (Fig. 2 and Fig. 5). This is in line with existing reports that higher particle concentrations lead to lower coagulant dosage requirement for effective treatment and that smaller particles have a higher tendency to coagulate than larger particles. Thus, suspensions containing a large proportion of smaller particles (as in primary samples in our study) normally require lower doses of coagulant to achieve maximum solids removal (Bratby, 2016; Sun et al., 2019). Optimum doses identified for OC were substantially lower than that identified for the IC product tested (PAC). Higher dosage requirements of IC compared with OC have been reported previously (Nozaic et al., 2001; Heiderscheidt et al., 2016a; Tetteh and Rathilal, 2019). Based on results obtained with the synthetic OC tested, dosage requirements for OC generally decreased with increasing MW, as also reported by Bolto et al. (1999, 2001) and Wilts et al., 2018.

In terms of purification efficiency, some of the OC produced treated samples with low contaminant concentrations and their performance was similar to that of PAC. As reported previously by Bolto et al. (2001), OC with (very) high MW and CD (e.g. pAmine1 and pDMAC1) were found to produce the lowest residual concentrations of organic matter (BOD_7 and COD) in treatment of both secondary and primary wastewater samples. These two OC products also achieved similar or better removal of SS, PO_4-P, and tot-P than PAC. As reported previously (Wang et al., 2005; Yang, 2012;

Ramasahayam et al., 2014), IC was better in removing P from primary wastewater samples, where PO_4 was the dominant form of phosphorus. This is attributable to the fact that PO_4-P, a strong anion, competes with coordinating ligands (e.g. hydroxyl ions) to form a stable bond with polymeric hydrolysis products of PAC (Duan and Gregory, 2003). Therefore, a higher number of PO_4-P ions in the solution induces higher affinity to Al ions, which then form precipitates that are removed from suspension via sedimentation. Conversely, in the purification of secondary samples, OC with (very) high MW and very high CD worked best in removal of PO_4-P. This is most likely due to the low ionic strength (due to low PO_4-P concentration) of the samples, enabling repulsion between strongly charged segments of the organic polymer molecules. These molecules adopt an expanded coil configuration, allowing for a larger area of contact between the polymer and PO_4-P ions and result in higher removal efficiency (Bolto and Gregory, 2007; Bratby, 2016).

Overall, low removal of N from wastewater samples was achieved by all coagulants tested, with some OC (e.g. pDMAC2, pDMAC1, starch) actually increasing the tot-N concentrations in the samples (Table 4). This was due to the presence of residual coagulant in the treated samples, as OC contain quaternary amine groups in their structure (Bolto and Gregory, 2007; Sánchez-Martín et al., 2010; Heiderscheidt et al., 2016a; Heiderscheidt et al., 2016b).

In order to further strengthen the evaluation of the coagulant performance, statistical analysis of data regarding removal rates achieved by the different coagulants was conducted (Tables S2a-b, and S3a-b and Figs. S3-S4, Supplementary Material). Removal efficiency was used instead of contaminant residual concentrations to minimise the effect of variations in wastewater quality on the analysis performed. In the treatment of secondary wastewater samples, removal of turbidity and tot-P were found to differ substantially (Kruskal Wallis p = 0.012, 0.080 consecutively) among the coagulants while removal rates of BOD_7 and tot-N were not significantly different (Kruskal Wallis p = 0.120, 0.130 consecutively). During the treatment of primary wastewater samples, removal rates of turbidity, BOD_7 and tot-P by the coagulants PAC, pAmine1, pAmine3, Starch and Chitosan were significantly different (Kruskal Wallis $p = 0.009$, 0.080, 0.093 consecutively) while variations in the removal of tot-N among the coagulants was statistically negligible (Kruskal Wallis $p = 0.567$).

It is important to emphasize that, while variations in wastewater quality may have affected the coagulants performance to a great extent, the type of coagulant used was an extremely important factor influencing the results obtained. For example, pair-wise comparison and cluster analysis (Table S1b and Fig. S1, Supplementary Material) reveal that the quality of secondary wastewater samples treated by e.g. Chitosan and pAmine1 (Kruskal-Wallis, $p = 0.228$) were not significantly different but the contaminant removal rates achieved by these products varied substantially (tot-P, Kruskal-Wallis, $p = 0.008$) (Table S2b and Fig. S3, Supplementary Material). Similarly, during treatment of primary wastewater samples, pair-wise comparison and cluster analysis (Table S1c and Fig. S2, Supplementary Material) showed that the quality of the samples treated by e.g. PAC and Chitosan (Kruskal-Wallis $p = 0.186$) were not significantly different however, purification efficiency obtained by the two products differed greatly (Kruskal-Wallis, BOD_7 $p = 0.048$ and tot-P $p = 0.047$) (Table S3b and Fig. S4, Supplementary Material)

To enable more direct comparisons of the products tested, the mass (mg) of contaminant removed per unit mass (mg) of coagulant added was determined (Table 4). Overall, high-MW organic polymers with (very) high CD were found to remove a higher mass of contaminants from secondary samples per unit mass of coagulant. The highest mass of SS, tot-P, BOD_7 and COD removed per unit mass of coagulant was achieved by pAmine1, while pDMAC3 achieved similar removal of BOD_7, COD and tot-P per unit mass of coagulant as pAmine1. However, PO_4-P was removed most efficiently by pDMAC4, which is characterised by medium MW. pDMAC1 (very high MW) removed the highest mass of tot-N per unit mass of coagulant, followed by pDMAC4 and pAmine1. In primary wastewater samples, optimum dosage requirement tests showed chitosan to be the best-performing coagulant among the OC tested. However, purification efficiency tests showed that pAmine1 removed greater amounts of some target contaminants (BOD_7 and COD) per unit mass of the coagulant. Due to its high dosage requirement, PAC achieved the lowest contaminant removal per unit mass of coagulant, particularly for BOD_7, tot-P and PO_4-P. In general, high-MW synthetic OC required lower doses than PAC and semi-natural OC to remove a higher mass of target contaminants. Low-MW semi-natural OC showed high removal efficiency per unit mass of coagulant for nutrients (PO_4-P, tot-P, tot-N) and SS.

The coagulants were also tested for their capacity to remove metals (i.e. tot-Al and tot-Fe; Table S4, Supplementary Material). The pAmine1 coagulant achieved the highest ratio of mass of tot-Al and tot-Fe removed per unit mass of coagulant added among all coagulants tested in treatment of secondary wastewater samples. Semi-natural polymers were comparatively better in removing metals from primary wastewater samples, with starch and chitosan achieving the highest mass of tot-Al and tot-Fe removed, respectively, per unit mass of added coagulant.

Table 4. Mass (mg) of contaminant removed per unit mass (mg) of coagulant added in treatment of primary and secondary wastewater samples (best removal values are in bold).

	Coagulants	**Doses (mg/L)**	**SS (mg/mg)**	**Tot-P (mg/mg)**	**PO_4-P (mg/mg)**	**BOD_7 (mg/mg)**	**COD (mg/mg)**	**Tot-N (mg/mg)**
Secondary Wastewater	PAC	120.00	0.23	0.01	0.002	0.80	2.75	0.008
	pDMAC1	36.00	0.11	0.04	0.007	0.69	3.61	**0.417**
	pDMAC2	10.00	0.60	0.04	0.003	**4.35**	**12.00**	-0.507
	pDMAC3	15.40	0.97	**0.08**	0.019	**6.63**	**17.53**	-0.715
	pDMAC4	17.60	**1.59**	**0.07**	**0.041**	0.71	3.98	**0.341**
	pAmine1	20.00	**1.75**	**0.07**	0.014	**6.63**	**17.50**	**0.300**
	pAmine2	30.00	0.01	0.03	0.009	0.55	3.33	0.133
	pAmine3	55.00	0.31	0.02	0.012	0.17	1.45	0.127
	Starch	30.00	0.20	0.04	**0.032**	0.47	2.67	-0.017
	Chitosan	50.00	0.10	0.02	0.008	-5.74	-6.00	0.140
	Tannin	80.00	0.23	0.01	0.004	0.22	1.13	-0.006
Primary Wastewater	PAC	48.00	0.83	0.05	0.06	0.46	2.63	0.07
	pAmine1	10.00	2.70	**0.20**	0.11	**32.10**	**51.00**	0.20
	pAmine3	35.00	1.77	0.06	0.05	0.66	3.14	-0.01
	Starch	10.00	**2.63**	**0.20**	0.13	2.60	**8.00**	-0.45
	Chitosan	7.50	**2.98**	**0.30**	**0.43**	**3.33**	-1.33	**0.60**

The sludge volume produced was monitored during tests with secondary wastewater samples. Treatment with PAC and the (very) high-MW and -CD pDMAC1 increased the sludge volume produced in comparison with blank samples, while high-MW OC (e.g. pDMAC3, pAmine1, starch) produced lower sludge volumes than blank samples (Fig. 4). Higher sludge amount generation by IC can be expected, due to the formation of insoluble hydrolysis products (Bolto and Gregory, 2007; Oladoja, 2016; Zhang et al., 2017; Tetteh and Rathilal, 2019). In comparison with other OC, smaller flocs were observed when pDMAC1 was used. The formation of small flocs from the interaction of high-CD polymer with organic matter under neutral pH conditions has been reported previously (Libecki, 2010; Razali et al., 2011). In those studies, it was linked to charge reversal, which occurs when there is an excess amount of polymer in the solution, causing re-dispersion of particles and leading to poor settling characteristics and higher sludge volume. The possibility of charge reversal appears to be higher with (very)-high MW and (very) high-CD coagulants than with low-MW and low-CD coagulants (Bolto and Gregory, 2007; Razali et al., 2011). However, CQ measurements carried out for all coagulants at optimum dosage showed that charge reversal did not occur during the treatment of samples (Tables S5 and S6, Supplementary Material).

The complex, long-chain structure of organic polyelectrolytes contributes to the high contaminant reduction potential of OC during the coagulation and flocculation stages, since their dominant mechanism is bridging particles previously coagulated by IC in a regular wastewater treatment process. High-MW polyelectrolytes are more effective at bridging, whereas high-CD polyelectrolytes are more effective at destabilisation by charge neutralisation (Bolto and Gregory, 2007; Wilts et al., 2018). Flocs formed through a bridging mechanism are more compact and stronger than those formed through charge neutralisation and electrostatic patch formation, which are the dominant destabilisation mechanisms for metal salt coagulants (IC). Hence, low sludge volume formation is normally observed for such polymers. IC-formed flocs are more prone to breakage and have high sludge production potential, due to the relatively higher optimum dose required and the formation of hydroxide precipitates (Nozaic et al., 2001; Bolto and Gregory, 2007; Oladoja, 2016; Zhang et al., 2017; Tetteh and Rathilal, 2019).

Although sludge volume was effectively reduced by high-MW OC products, sludge settling tests for primary wastewater samples showed that the low-MW semi-natural product chitosan performed as well as the IC product PAC in forming larger, easily settleable flocs (Fig. 7). In addition, the flocs formed in the treatment with chitosan settled within 20 min of sedimentation time and no further decrease in supernatant water turbidity was seen over the remaining 40 min of settling time allowed.

In general, the cost of the organic products (e.g. pAmine1, Starch, etc.) are 2 times higher than the PAC product tested (i.e. Al_2O_3 content > 17%) and 4-5 higher than the more affordable PAC products commonly used (i.e. Al_2O_3 content 12-15%). The lower required dose of the organic products (up to 80%) can partly offset their higher price tag. However, complete cost-benefit analysis should be conducted where e.g. product transport, storage, sludge management and disposal, etc. should be taken into consideration.

4. CONCLUSIONS

The effectiveness of OC (synthetic and semi-natural) with varying MW and CD compared with that of the IC (PAC) conventionally used in removal of target pollutants from real secondary and primary municipal wastewater samples was successfully investigated. Overall, high purification efficiency was achieved by a number of the coagulants tested (e.g. PAC, pAmine1) in treatment of wastewater samples, despite variations in wastewater characteristics upon sample collection. The following conclusions can be drawn:

- Higher (up to 60%) coagulant dose was needed in treatment of secondary wastewater samples compared with primary samples.
- Significantly higher doses of PAC (up to 80%) than of OC were needed for effective treatment.

- In treatment of secondary wastewater samples, high-MW and high-CD OC (e.g. pAmine1) achieved best removal of target pollutants (e.g. SS, PO_4-P, BOD_7), followed by PAC.
- High-MW and (very) high-CD OC (e.g. pAmine1, PDMAC3, starch) reduced the volume of sludge produced compared with blank samples and samples treated with PAC.
- In treatment of primary wastewater, PAC was the best performing coagulant, closely followed by chitosan and pAmine1.
- The OC pAmine1 achieved high mass (mg) removal of target pollutants (SS, tot-P, PO_4-P, BOD_7, COD) per unit mass (mg) of coagulant added and was among the best-performing of the coagulants tested. For example, in treatment of secondary wastewater samples, 1.75 and 0.23 mg of SS, 0.07 and 0.01 mg of PO_4-P and 6.63 and 0.80 mg of BOD_7 were removed per mg of pAmine1 and PAC, respectively.

Based on the results obtained, polyamine products with high MW and (very) high CDs have the potential to act as the sole precipitation agent in both primary and secondary stages of municipal wastewater treatment. Further research is needed on the effect of residual coagulant on downstream water and sludge treatment processes (e.g. activated sludge process, sludge dewatering, etc.).

ACKNOWLEDGMENTS

This study was part of the project *"Nutrient availability and losses, and risks of micropollutant contamination from land spreading of chemically precipitated sewage sludge"*, which is funded by Maa- ja vesitekniikan tuki ry. and other stakeholders (Pohjois-Suomen Vesivaliokunta, Lakeuden Keskuspuhdistamo, Finnish Water Utilities Development Fund and Finnish Foundation for Technology Promotion (TES)). The authors would like to acknowledge the support received from Oulun Vesi and personnel at the Water, Energy, and Environmental Engineering Research Unit at the University of Oulu, particularly laboratory technician Tuomo Reinikka. In addition, the authors would like to thank Clyde Blanco (Ghent University) for the guidance received on the statistical analysis methods used.

REFERENCES

Bolto, B., 1995. Soluble polymers in water purification. *Progress in Polymer Science*, 20 (6).

Bolto, B., Abbt-Braun, G., Dixon, D., Eldridge, R., Frimmel, F., Hesse, S., King, S. and Toifl, M., 1999. Experimental evaluation of cationic polyelectrolytes for removing natural organic matter from water. *Water Science and Technology*, 40(9).

Bolto, B., Dixon, D., Eldridge, R. & King, S. 2001. Cationic polymer and clay or metal oxide combinations for natural organic matter removal. *Water Research*, 35 (11).

Bolto, B. and Gregory, J., 2007. Organic polyelectrolytes in water treatment. *Water Research,* 41(11).

Bratby, J., 2006. *Coagulation and flocculation in water and wastewater treatment*. 2nd ed. London: IWA Publishing.

Bratby, J., 2016. *Coagulation and flocculation in water and wastewater treatment*. 3rd ed. London: IWA publishing.

Chen, S., Zamudio Cañas, E. M., Zhang, Y., Zhu, Z. & He, Q. 2012. Impact of substrate overloading on archaeal populations in anaerobic digestion of animal waste. *Journal of Applied Microbiology*, 113(6).

Drinnan, J., 2001. Wastewater sources and types. N. Whiting ed. *Water and Wastewater Treatment.* New York: CRC Press, pp. 127-131.

Duan, J., Gregory, J., 2003. Coagulation by hydrolysing metal salts. *Advances in Colloid and Interface Science*, 100, pp. 475-502.

Heiderscheidt, E., Leiviska, T., Ronkanen, A.-K. and Kløve, B., 2016a. Evaluating the suitability of synthetic organic polymers to replace iron salts in the purification of humic and sediment-rich runoff. *Desalination and Water Treatment,* 57.

Heiderscheidt, E., Leiviska, T. and Kløve, B., 2016b. Coagulation of humic waters for diffused pollution control and the influence of coagulant type on DOC fractions removed. *Journal of Environmental Management*, 181.

Jiang, J. and Wang, H. 2009. Comparative Coagulant Demand of Polyferric Chloride and Ferric Chloride for Removal of Humic Acid. *Separation Science and Technology*, 44 (2).

Kirchmann, H., Börjesson, G., Kättarer, T. and Cohen, Y., 2017. From agricultural use of sewage sludge to nutrient extraction: A soil science outlook. *Ambio,* 464.

Krogstad, T., Sogn, T., Asdal, Å. and Saebo, A., 2005. Influence of chemically and biologically stabilized sewage sludge on plant-available phosphorous in soil. *Ecological Engineering,* 25.

Lee, C. S., Robinson, J. and Chong, M. F., 2014. A review on the application of flocculants in wastewater treatment. *Process Safety and Environmental Protection,* 92.

Leiviska, T., 2009. Charge quantity. *Coagulation and size fractionation studies on pulp and paper mill process and wastewater streams*. Oulu University Press 2009, pp. 34-35.

Libecki, B. 2010. The effectiveness of humic acid coagulation with the use of cationic polyacrylamides. *Water Science and Technology*, 61(6).

Liu, Y., Shi, H., Li, W., Hou, Y., He. M., 2011. Inhibition of chemical dose in biological phosphorus and nitrogen removal in simultaneous chemical precipitation for phosphorus removal. *Bioresource Technology*, 102.

Liu, Z., Wei, H., Li, A. and Hu, Y., 2017. Evaluation of structural effects on the flocculation performance of a co-graft starch-based flocculant. *Water Research,* 118.

Nozaic, D. J., Freese, S. D. and Thompson, P., 2001. Longterm experience in the use of polymeric coagulants at Umgeni water. *Water Science and Technology: Water Supply,* 1(1).

Oladoja, N., 2015. Headway on natural polymeric coagulants in water and wastewater treatment operations. *Journal of Water Process Engineering,* 541.

Oladoja, N. A., 2016. Advances in the quest for substitute for synthetic organic polyelectrolytes as coagulant aid in water and wastewater treatment operations. *Sustainable Chemistry and Pharmacy,* 3.

Ramasahayam, S., Guzman, L., Gunawan, G. and Viswanathan, T., 2014. A comprehensive review of phosphorus removal technologies and processes. *Journal of Macromolecular Science,* 51(6).

Razali, M., Ahmad, Z. and Ariffin, A., 2011. Treatment of pulp and paper mill wastewater with various molecular weight of polyDADMAC induced flocculation. *Chemical Engineering Journal,* 166.

Renault, F., Sancey, B., Badot, P. & Crini, G. 2009. Chitosan for coagulation/flocculation processes - An eco-friendly approach. *European Polymer Journal*, 45(5).

Sánchez-Martín, J., Beltrán-Heredia, J. and Solera-Hernández, C., 2010. Surface water and wastewater treatment using a new tannin-based coagulant. Pilot plant trials. *Journal of Environmental Managemen*t, 91(10).

Sillanpää, M., Ncibi, MC, Matilainen, A. and Vepsäläinen, M. 2018. Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review. *Chemosphere*, 190.

Sun, H., Jiao, R., Xu, H., An, G. & Wang, D. 2019. The influence of particle size and concentration combined with pH on coagulation mechanisms. *Journal of Environmental Sciences*, 82.

Tetteh, E. K. and Rathilal, S., 2019. Application of organic coagulants in water and wastewater treatment. *Organic Polymers.* Durban: IntechOpen.

Wang, Y. et al., 2005. Optimization of phosphorus removal from secondary effluent using simplex method in Tianjin. *Journal of Hazard Matter,* 121(1-3).

WWAP (United Nations World Water Assessment Programme), 2017. The United Nations World Water Development Report 2017. *Wastewater: The untapped resource.*

Wei, N. et al., 2015. Coagulation behaviour of polyaluminium chloride: Effects of pH and coagulant dosage. *Chinese Journal of Chemical Engineering,* Volume 23.

Wilts, E. M., Herzberger, J. & Long, T. E. 2018. Addressing water scarcity: Cationic polyelectrolytes in water treatment and purification. *Polymer International*, 67(7).

Yang, K., 2012. Using coagulants polyaluminium chloride and aluminum sulfate to optimize phosphorus and turbidity removal from secondary effluent. *International Journal of Digital Content Technology and its Applications,* 6(17).

Zhang, Z., Wang, J., Liu, D., Li, J., Wang, X., Song, B., Yue, B., Zhao, K. and Song, Y., 2017. Hydrolysis of polyaluminium chloride prior to coagulation: Effects on coagulation behavior and implications for improving coagulation performance. *Journal of Environmental Sciences*, 57.