Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1043954

57 (2016) 10948–10957
May

Taylor & Francis
Taylor & Francis Group

Evaluating the suitability of synthetic organic polymers to replace iron salts in the purification of humic and sediment-rich runoff

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Received 24 November 2014; Accepted 30 March 2015

ABSTRACT

Peat extraction runoff water requires chemical treatment to remove organic matter and phosphorus. In Finland, ferric sulphate (FS) is normally used as coagulant agent, but significant variations in runoff water quality and the lack of optimisation of process parameters has led to increased acidity, metal and sulphate concentrations in the purified water. The use of synthetic organic polymers as an alternative to the commonly applied metal salt coagulant is suggested to better cope with typical variations in runoff water quality. This study evaluated the suitability of two synthetic organic polymers (polyDADMAC and polyAmine) for the purification of humic and sediment-rich diffuse runoff by comparing their performance to the normally applied iron-based coagulant. FS was found to require up to fourfold higher dosages but achieved higher overall purification levels than the organic polymers. In particular, removal of organic matter was substantially higher when FS was used. Of the two synthetic organic products, polyDADMAC achieved slightly better purification rates and required lower effective dosages than polyAmine. Low water temperature (2˚C) had a detrimental effect on the performance of all coagulants, especially regarding removal of suspended solids. Decreasing the initial water pH (6.5–4.5) resulted in a substantial decrease in the coagulant dosages required to achieve acceptable purification levels. Although FS presented higher overall removal efficiency, the synthetic organic polymers performed satisfactorily and can potentially replace metal salts as primary coagulants in the treatment of humic and sediment-rich water.

Keywords: Coagulation; Ferric sulphate; Humic substances; Organic polymers; Settling; Temperature

1. Introduction

Diffuse pollution from land uses such as agriculture, forestry and mining is a significant issue in many regions of the world. Large land areas in Finland, Ireland, Estonia, Canada and Russia are exploited for peat extraction mainly for energy and growth medium purposes. Drainage of peatlands and other peat extraction activities result in increased sediment and nutrient transport [1–3] with harmful impacts on

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recreation, migratory fish and biodiversity [4,5]. In Finland, the peat extraction industry is obliged to purify the runoff discharging from extraction sites. Chemical treatment is considered one of the best available technologies [6] for the purification of the typically humic and sediment-rich water [1,2,7]. Metal salts of iron (sulphate as counter-ion) are normally used as coagulant agents. However, the lack of optimisation and adaptation of this treatment method to the specific conditions found in the purification of non-point source pollution, which include variation in runoff water quality, temperature and discharge, has led to significant fluctuations in purification efficiency and to increased acidity, metal and sulphate concentration in the purified water [7]. There is therefore a need for alternative coagulants that can better cope with these conditions, thus enabling the optimisation of the treatment performance and a decrease in the environmental impacts associated with the normally applied metal salt coagulants.

Synthetic organic polymers have been used for decades in the treatment of water and wastewater as flocculants and sludge dewatering aids chemicals [8–10]. Although their use as primary coagulants is not widespread, it is expected to grow as the technology for their production advances and tailor-made products with varying molecular weights (MW), charge densities (CD) and lower residual monomer are produced [10,11]. Organic polymers have been found to require lower dosages than metal salt coagulants and to produce less sludge with better dewatering characteristics [11–13]. Floc re-growth, after breakage caused by initial turbulent mixing, has been found to be almost fully reversible with cationic polymers while mostly irreversible when metal salt coagulants are applied [14]. Furthermore, the addition of organic coagulants does not consume alkalinity eliminating the need for pH adjustments of the purified water [9,10]. Some concerns have arisen regarding the toxicity of synthetic polymers and their impacts on human health [15] and on the aquatic ecosystem [16]. However, the toxicity of these products has mostly been associated with residual concentrations of non-reacted monomers and other contaminants which might be present in the final product [15] and are strictly limited by worldwide legislation.

This work is a novel attempt to investigate the capabilities of synthetic organic polymers as primary coagulants in the purification of natural waters where sedimentation is the chosen solid–liquid separation process. The aim was to evaluate under laboratory conditions the suitability of selected synthetic organic polymers for the purification of humic and sediment-rich diffuse runoff by comparing their performance with that of the commonly applied metal salt coagulant ferric sulphate (FS). The destabilization of humic substances by cationic polymers is believed to be the result of reactions between positively charged segments of the polymer chain with negatively charged carboxylic and phenolic groups on the humic acid molecules [11,17–19]. Several studies reported improved removal of dissolved organic matter and suspended solids (SS) by polymers with high CD [8,19–21]. Low-to-medium MW products were also found to present better performance in the destabilization of humic substances [10,12,22]. Based on reported findings and recommendation from the organic products supplier, two commercially available synthetic organic polymers with high CD and low-to-medium MW were selected: poly(diallyldimethyl) ammonium chloride (polyDADMAC) and epichlorohydrin-dimethylamine copolymer (polyAmine). Specific objectives were to evaluate the dosage requirements of the selected coagulants and to determine their ability to form flocs with good sedimentation characteristics as well as their capability to remove concerning substances such as organic matter, nutrients and SS. Further objectives were to investigate the influence of the water pH and temperature on the coagulants performance.

2. Materials and methods

Humic and sediment-rich runoff water was used and experimental procedures based on jar test methodology were designed to investigate the suitability of the synthetic organic polymers (polyDADMAC and polyAmine) and FS as primary coagulants. The following aspects were evaluated: (1) Dosage requirement of the coagulants, purification efficiency and settling characteristics of flocs formed at 20°C with initial runoff water pH 6.5; (2) the influence of low water temperature (2°C) on purification efficiency and settling with initial runoff water pH 6.5; and (3) the influence of runoff water pH (4.5, 5.5, and 6.5) on dosage requirements and purification efficiency at 20°C.

2.1. Characteristics of the water and tested coagulants

Runoff water was collected in 35-L containers from Kurkisuo, one of Vapo Oy's peat extraction sites in Suonenjoki, Finland, and stored at 5–10°C for the six-week testing period. Water quality analyses were performed in each container as taken into use, in order to assure accurate initial conditions and to evaluate possible changes in water quality during the storage period. The analyses performed were as follows: total organic carbon (TOC), colour, SS, turbidity, total phosphorus (tot-P), phosphate phosphorus (PO_4-P), total nitrogen (tot-N), total iron (Fe), total aluminium (Al) and pH. The water quality characteristics of collected samples (Table 1) were typical of peat extraction runoff water [2,7]. Water quality monitoring data from 10 peat extraction sites, collected over a 2–8 years monitoring period with either biweekly or monthly recordings, were provided by Vapo Oy and used in the evaluation of the collected water samples and the results. Analysis of monitoring data from Kurkisuo site revealed dissolved organic carbon (DOC) and UV absorbance (254 nm) values which resulted in specific UV absorbance (SUVA = UV_{254}/DOC) around 3 (L/mg-m). According to Matilainen et al. [23], this indicates the presence of DOC composed of a mixture of hydrophobic and hydrophilic aquatic humics with varying MW.

Three commercial quality coagulants (Kemira Oyj, Kemwater) were tested, the normally applied metal salt coagulant FS and two selected synthetic organic polymers with high relative cationic charge (medium MW polyDADMAC and low MW polyAmine) (Table 2). Epichlorohydrin-dimethylamine is a polyAmine-type polymer formed by the step-reaction synthesis of 2-hydroxi-3-dimethylaminopropyl, a monomer formed by the reaction of epichlorohydrin and dimethylamine. The process tends to produce a linear rather than a branch chain or cross-linked quaternary ammonium polymer of low-to-medium MW [10]. The manufacturing of poly(diallyldimethyl) ammonium chloride (normally referred to as polyDADMAC) involves two sequential steps: the formation of the monomer and its polymerizsation. The monomer is usually formed by a reaction of a stoichiometric mixture of allyl chloride with dimethylamine in an aqueous solution. Free-radical polymerisation of the obtained monomer results in a polymer with low-to-medium MW containing five-membered pyrrolidinium units [10]. The coagulants were dosed at 10 mg/L (product) stock solution freshly prepared every two test days.

Table 1
Water quality characteristics (number of analyses $n = 11$, std. dev. = standard deviation)

Water quality parameters	Mean ± std. dev.
TOC (mg/L)	30.7 ± 0.9
Colour (mg Pt/L)	396 ± 12.1
SS (mg/L)	20.8 ± 5.2
Turbidity (NTU)	50.5 ± 4.9
Tot-P (μg/L)	74.7 ± 4.6
PO_4-P (μg/L)	44.2 ± 5.9
Tot-N (mg/L)	2.2 ± 0.4
Fe (mg/L)	6.7 ± 0.5
Al (mg/L)	0.9 ± 0.2
pH	6.2–6.7 (range)

2.2. Experimental procedure

Jar tests were performed using the six (1-L) jar programmable paddle stirrer equipment Flocculator 2000 (Kemira Kemwater). Previously identified optimum mixing parameters [7] were applied: 300 rpm for 10 s followed by 50 rpm for 25 min and 30 min of sedimentation. For the evaluation of dosage requirements and purification efficiency (20 ± 2˚C), increasing dosages of coagulant were added sequentially to 1-L samples. The purification efficiency achieved by the coagulants was first monitored and evaluated at the in-house laboratory by measuring colour, turbidity, pH and temperature (3 replicates). Standard methods and equipment used were the following: turbidity (EN 27027:1994; Hach Ratio/XR Turbidity meter), colour (ISO 7887:1994; Lovibond Nessleriser Daylight 2000) and pH (SFS-EN 13037:1994; WTW Universal meter). Dosages which provided the best removal of colour and turbidity were identified as the coagulants optimum dosages and are reported as mg of product per litre of water. For the evaluation of purification efficiency, samples of the water purified with the optimum coagulants dosages (3 replicates) were sent to a certified laboratory for further analyses of TOC, tot-P, PO_4-P, tot-N, Fe, Al and SS, using standardised SFS and ISO analytical methods. The settling characteristics of flocs formed at 20 (±2)˚C were evaluated according to the method outlined in Bratby [9]. Turbidity measurements were performed on 30-mL samples collected at constant jar depth (8 cm from the bottom) and at pre-determined time intervals (1, 2, 3, 4, 6, 8, 11, 13, 17, and 25 min) during the sedimentation phase (2 replicates). The influence of temperature on the purification process was investigated by transferring the jar test equipment to a temperature controlled (2 ± 2˚C) insulated water tank. The aforementioned procedures for the evaluation of purification efficiency and settling characteristics were then performed (2 replicates). For investigations of the influence of pH on the purification process, the initial pH of the water was decreased from the averaged 6.5 to 5.5 and 4.5 sequentially via the addition of stock solution of sulphuric acid (0.5 M). Dosage requirements and purification efficiency at each pH were then determined according to previously described methodology (1 replicate).

Table 2
Characteristics of coagulants

Chemical type	Molecular weight	Dry solids	Charge density
PolyDADMAC (liquid)	200,000 g/mol	20%	6 meq/g (dry solids)
PolyAmine (liquid)	10,000 g/mol	50%	7 meq/g (dry solids)
	Density	% $Fe_2(SO_4)_3$	Active substance
Ferric sulphate [$Fe_2(SO_4)_3 \cdot nH_2O$] (liquid)	1,550 kg/m3	42%	2.1 mol/kg

3. Results and discussion

3.1. Dosage requirements

The optimum coagulant dosages identified were: FS 200 mg/L, polyDADMAC 80 mg/L and polyAmine 50 mg/L. The pH of samples treated with organic polymers remained mostly constant around 6.5 (Fig. 1(a) and (b)), whereas the pH of samples treated with high dosages of FS decreased substantially, to values below four (Fig. 1(c)). Based on the percentage of dry solids of the organic products (Table 2), the effective dosages of the polymers were polyDADMAC 16 mg/L and polyAmine 25 mg/L. Therefore, polyDADMAC presented a more efficient coagulation performance, requiring a significantly lower effective dosage than polyAmine to achieve satisfactory removal of colour and turbidity.

For a simplified cost evaluation analysis, the dosage as mg/L of product was considered. The polyAmine product is slightly more expensive than the polyDADMAC and both organic polymers cost around 10 times more than FS. In a straight comparison, despite the three- to fourfold lower dosage required by the organic polymers, treatment using these products would still be substantially more expensive. However, if the related costs of product transport, pH adjustment, equipment and energy requirements as well as sludge handling are taken into consideration, the cost effectiveness of the organic polymers can increase significantly with savings of up to 25% reported [12].

An important issue regarding the chemical purification process is the environmental impacts of the residual concentrations of the added coagulants and their effect on water quality. The high FS dosage required resulted in purified water with pH around 4 and a residual iron concentration of between 1.2 and 1.5 mg/L. High iron concentrations (>1 mg/L) and acidic conditions have been found to have a significant impact on the structure and function of aquatic ecosystems [24]. Our evaluation of water quality monitoring data from peat extraction sites showed that 75–100% of added sulphate is released in the purified water. For a dosage of 200 mg/L $Fe_2(SO_4)_3$, between 45 and 60 mg/L of sulphate are potentially released into downstream water bodies. Elevated sulphate concentrations are known to increase the mobilisation of nutrients from sediments and increase the risk of eutrophication of surface waters [25]. Further research is required to determine the residual concentrations resulting from the use of synthetic organic polymers as primary coagulants and their potential impact on the environment. Existing studies mention low residual concentrations resulting from the low dosages required when polymers are used as flocculant aid chemicals [16].

The formation of insoluble hydrolysis products by metal salt coagulants is mostly responsible for their

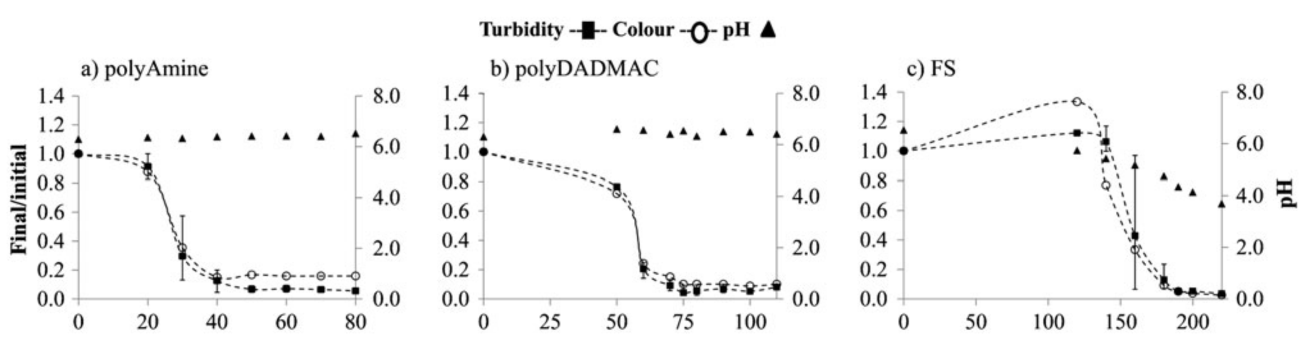

Fig. 1. Removal of turbidity and colour (normalised as final/initial values) with increasing dosages of coagulants and the resulting water pH (variation in turbidity shown as error bars) at 20˚C and initial water pH 6.5.

higher (up to 50%) sludge formation when compared to organic polymers [8,9,12]. Turbidity measurements performed in samples taken during the last minute of the flocculation process (end of mixing) showed that turbidity values increased from the average 50 NTU in untreated samples to values around 90 NTU in samples treated with FS and 70 NTU in samples treated with the synthetic organic polymers. The higher turbidity values observed in samples treated with FS can, in this context, be linked to higher particle concentration and therefore higher sludge formation. Sludge characteristics depend not only on the quality of the water being treated but also on the type and dosage of coagulant applied [8,9]. Generally, due to the quality of the water, sludge produced by the purification of peat extraction runoff has characteristics which are more similar to the sludge produced in potable water production than in sewage treatment. Polymer-based sludge has been found to present better flocculation and dewatering characteristics and to be more viscous than sludge formed by metal salt coagulants [9,12]. Sludge disposal is considered a financial and environmental burden; in an effort to reduce its impacts several re-use, recycling and recovery methods (e.g. utilisation as soil amendment material, recovering of coagulant, etc.) have been suggested for metal salt derived sludge [26]. Nevertheless, more information is needed regarding the toxicity and the re-use, recycle and recovery possibilities of sludge formed by synthetic polymers as primary coagulants.

3.2. Purification efficiency

FS achieved higher overall purification efficiency than the synthetic organic coagulants, with the removal of TOC being especially high when FS was applied (Fig. 2). An increase in tot-N residual concentration was consistently found in samples treated with polyAmine, which might be due to its lower molecular weight and consequently higher solubility. Although the overall removal efficiencies achieved by the organic coagulants were lower than those achieved by FS, the results obtained were mostly inside the load reduction levels expected from the chemical purification of peat extraction runoff (SS 30–90%; tot-N 30–60%; tot-P 75–95%) [6].

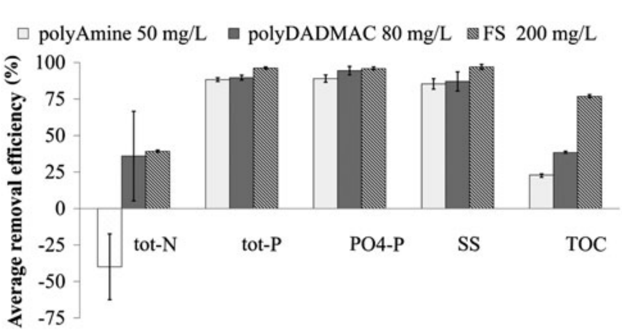

Fig. 2. Average removal efficiency (including maximum and minimum values of experiment replicates presented as error bars) achieved by the optimum dosages of coagulants at 20˚C and initial water pH 6.5.

In the purification of acidic and mostly humic waters, charge neutralisation/precipitation is believed to be the dominant coagulation mechanism in the reactions of both metal salt and organic coagulants [20–23,27]. The higher overall purification efficiency achieved by FS can be attributed to its higher charge neutralisation capacity [27]. Furthermore, it is believed that the formation of insoluble hydrolysis products by metal salt coagulants improve the coagulation/flocculation process by increasing the number of particles in suspension and thus improving coagulation kinetics [22,28]. This being especially beneficial for natural waters with relatively low turbidity. Our results agree with findings of previous studies in which metal salt coagulants achieved higher removal of organic matter than organic polymers at acidic pH levels [8,27]. Regarding the difference between the performances of the organic polymers, the higher removal efficiencies achieved by polyDADMAC can to some extent be attributed to its higher MW, which might have facilitated the occurrence of electrostatic patch and bridging coagulation in addition to the dominant charge neutralisation mechanism [10,21].

3.3. Settling characteristics of flocs formed

FS displayed the fastest sedimentation rate in the initial and most important stages of the sedimentation process. It reached 60% turbidity removal after 6 min of sedimentation, while both of the organic polymers reached the 60% removal mark at around 8 min (Fig. 3). FS also achieved the best clarification of the supernatant water in the final stages of sedimentation. It required around 15 min to reach 90% turbidity removal, while polyAmine and polyDADMAC required 20–25 min.

The settling characteristics of flocs formed represent the coagulation and flocculation capabilities of the coagulant and its ability to provide flocs that can readily sediment, resulting in clarified supernatant water. The formation of insoluble hydrolysis products when FS is applied and the consequent increase in the number of particles in suspension [22,28] can to some extent explain the superior sedimentation performance observed for the metal salt coagulant. Moreover, it is

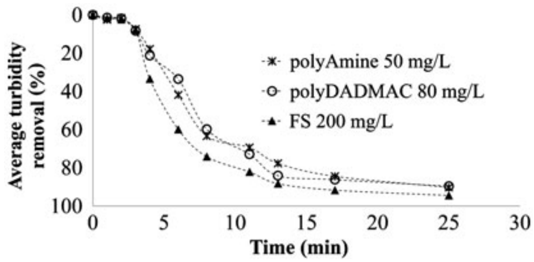

Fig. 3. Settling characteristics (removal of turbidity with time) of flocs formed by the optimum dosage of coagulants at 20˚C and initial pH 6.5.

well known that floc formation and its resulting characteristics are significantly dependent on mixing conditions applied upon and after coagulant addition [29,30]. The mixing parameters used in the present work were taken from a previous study where the optimisation of process parameters for the use of FS in the purification of peat extraction runoff was performed [7]. Therefore, the mixing conditions applied to some extent favoured FS performance. Optimisation of mixing parameters to the specific requirements of the organic polymers is suggested. This could result in flocs with improved settling characteristics and an overall improvement in the polymers performance. The settling rates achieved by the organic polymers were nevertheless satisfactory, and would enable good clarification results if the recommended design parameters for sedimentation units, such as surface load of 0.2 m/h, are applied [6].

3.4. *Influence of temperature on purification efficiency and settling characteristics*

Modifying the experiment conditions by reducing the water temperature to 2 (±2)˚C had an overall negative effect on the purification efficiency achieved (Fig. 4). The most significant difference was observed in the removal of SS by all coagulants. The removal of SS at 2˚C was greatly decreased (by up to 20%) compared with the removal observed at 20˚C. On the other hand, the residual concentration of tot-N in the treated samples decreased at low temperatures. This was particularly significant for samples treated with polyAmine (Fig. 4(a)). The removal of TOC was mostly not affected by low water temperature.

The negative influence of temperature on SS removal was confirmed by the observed impact of low temperature on the settling characteristics of the flocs formed. At 2˚C, FS required around 65% longer sedimentation time to reach 60% (10 min) and 90% (25 min) turbidity removals (Fig. 5(c)). Both polyAmine and polyDADMAC required around 17 min to reach 60% turbidity removal, which was more than double the time required at 20˚C (Fig. 5(a) and (b)). After 25 min of sedimentation, they achieved a turbidity removal of 80%.

Low temperatures are known to affect coagulation and flocculation by altering coagulant solubility, increasing water viscosity and hindering charge neutralisation reactions and, especially, the subsequent particle aggregation process [31,32]. The low influence of temperature in the removal of dissolved substances (Fig. 4) agrees with previous findings that the most significant influence of low temperatures occurs during the flocculation and sedimentation stages of the purification process [31,32], resulting in a significant impact on the removal of SS. The apparent improvement in removal of tot-N at low temperatures might be connected to the lower solubility of organic coagulants. To our knowledge, the influence of temperature on the coagulation mechanisms of organic polymers has not been studied in detail. According to our results, based solely on the removal efficiencies

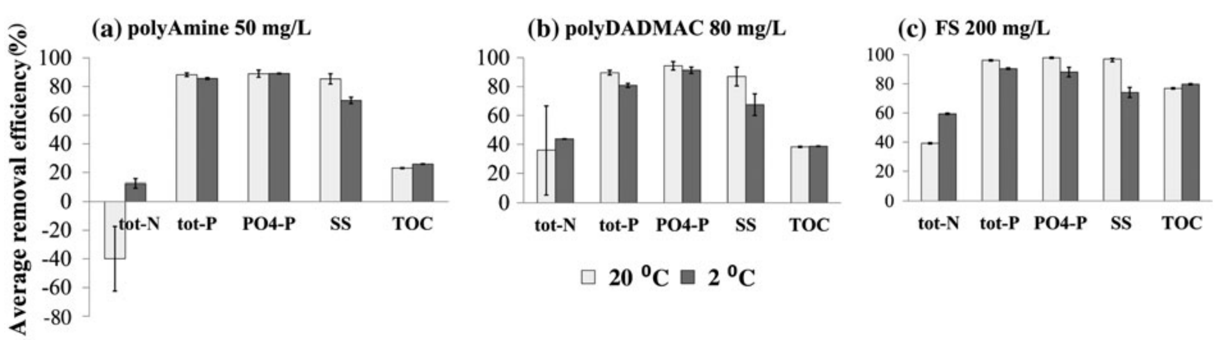

Fig. 4. Influence of temperature on average removal efficiency (including maximum and minimum values of experiment replicates presented as error bars) achieved by the optimum dosage of coagulants at initial pH 6.5.

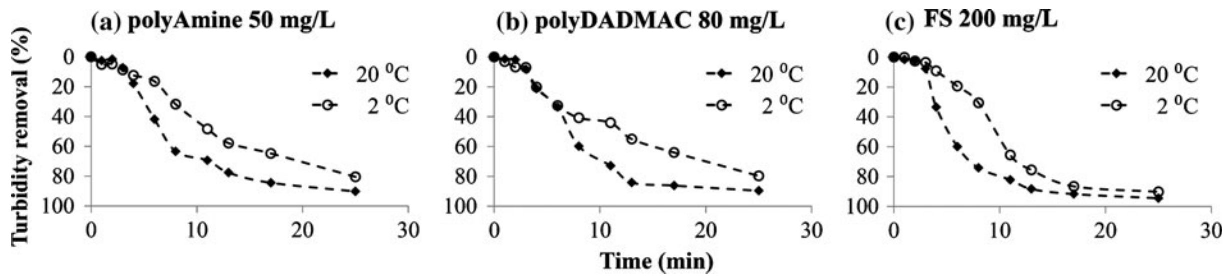

Fig. 5. Comparison of the settling characteristics (turbidity removal with time) of flocs formed by the optimum dosages of coagulants at 20 and 2˚C and initial pH 6.5.

obtained, it appears that temperature has a similar effect on the performance of synthetic organic and metal salt coagulants.

The impact of temperature on the chemical purification process is an important factor in cold climate regions where water temperatures can remain below 10˚C for more than 6 months per year. The addition of a flocculant aid polymer has been found to decrease the required dosage of primary coagulant and to significantly improve the settling characteristics of the flocs formed [13,33]. Thus, the implementation of a dual chemical coagulation method whereby a flocculant aid polymer is introduced after the primary coagulant to enhance the flocculation and sedimentation processes should be explored.

3.5. Influence of pH on dosage requirements and purification efficiency

The decrease in the initial water pH from 6.5 to 5.5 and then sequentially to 4.5 resulted in a substantial decrease in the coagulant dosage required to achieve similar removal of colour and turbidity (Fig. 6). To evaluate the effects of variations in the initial water

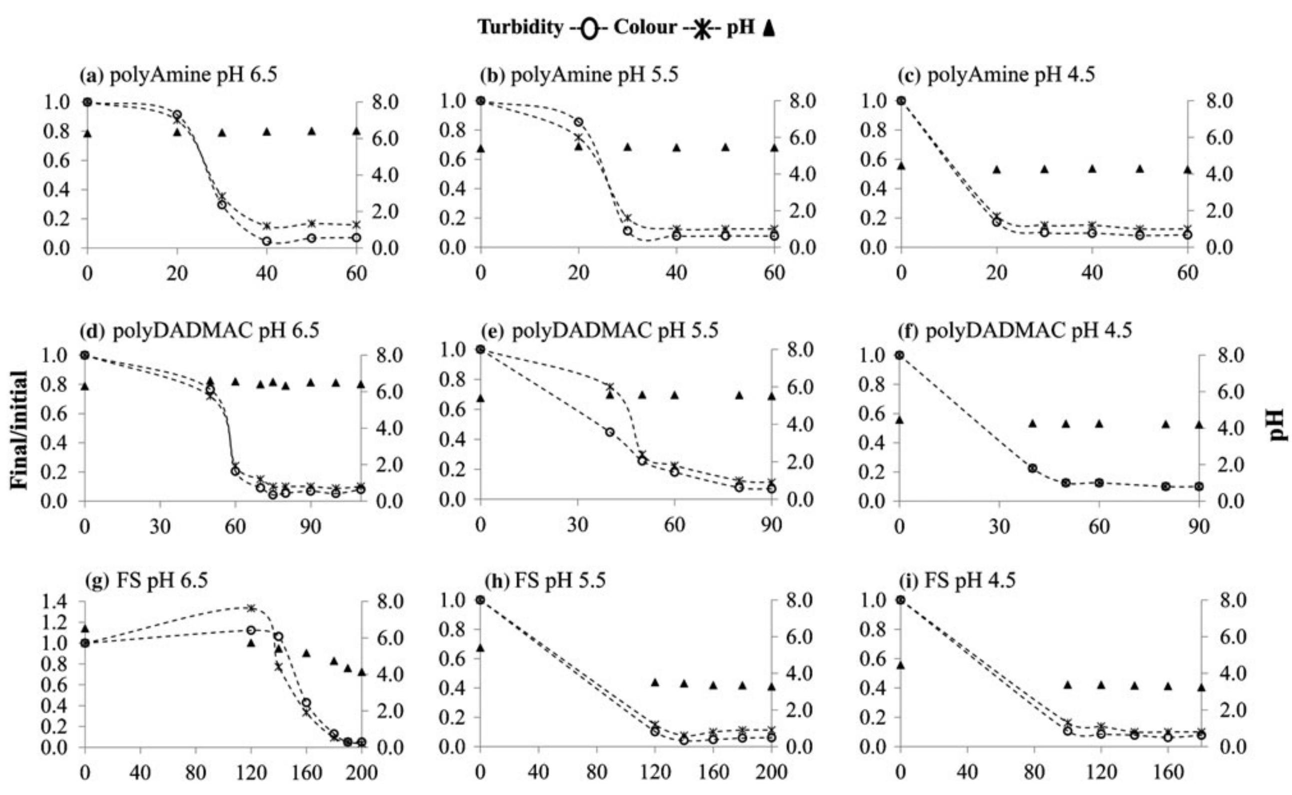

Fig. 6. Removal of turbidity and colour (normalised as final/initial values) with increasing dosages of coagulants for water samples with pH 6.5, 5.5 and 4.5 at 20˚C.

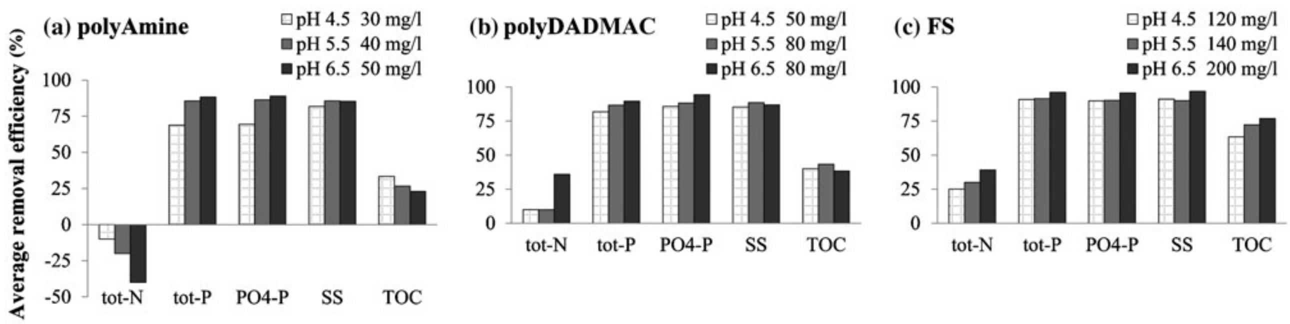

Fig. 7. Average removal efficiency (%) achieved by the coagulants optimum dosage at pH 4.5, 5.5, and 6.5 at 20°C.

pH on purification efficiency, the following coagulant dosages were selected at each pH level: (1) pH 6.5: polyAmine 50 mg/L, polyDADMAC 80 mg/L, FS 200 mg/L; (2) pH 5.5: polyAmine 40 mg/L, polyDADMAC 80 mg/L, FS 140 mg/L; (3) pH 4.5: polyAmine 30 mg/L, polyDADMAC 50 mg/L, FS 120 mg/L.

Similar removal rates of TOC, SS, tot-P, PO_4-P and tot-N were achieved at all pH levels, although significantly lower dosages were required in the purification of samples with lower initial pH (Fig. 7). The pH at which coagulation takes place is known to have a significant effect on purification results by affecting the way that the added coagulant reacts with the water and the physical and chemical characteristics of pollutant substances [34–36]. Decreasing the water pH decreases the ionisation of carboxylic and phenolic functional groups of humic acids, resulting in a net decrease in negative charge and consequently decreasing the coagulant dosage required [34,35]. Furthermore, at lower pH, the hydrolysis species of metal salt coagulants are believed to be that of a polymeric and more positive nature [37], while the non-polar characteristics of the organic polymers also improve their interaction with the more hydrophobic molecules of organic compounds [20].

Effective coagulation with iron salts is reported to occur at pH values between 5 and 8.5 with lower values suggested (3.7–4.2) for optimum removal of DOC [9,37]. Cationic polymers generally possess functional groups such as quaternary ammonium which provide cationic charges at a wide pH range decreasing the influence of pH on the products performance [10,38]. Typical variations in the pH of peat extraction runoff water ranges between 4.5 and 6.5 [39]. Therefore, the selected pH variations tested reflected real operational conditions. Satisfactory purification efficiency was achieved at lower pH levels and at substantially lower coagulant dosages. Consequently, pH adjustments should be conducted at the outflow of chemical purification. If synthetic organic polymers were to replace metal salt coagulants, pH adjustment would only be necessary in occasions when the pH of runoff water decreased to values below 5. However, pH adjustments are continuously required when FS is the coagulant of choice.

4. Conclusions

The two synthetic organic polymers tested have the potential to replace metal salts as primary coagulants in the treatment of humic and sediment-rich water. Generally, the performance of the organic polymers was satisfactory, and the purification rates achieved were inside the required range for chemical purification of peat extraction runoff (SS 30–90%; tot-N 30–60%; tot-P 75–95%). Furthermore, the use of the organic products did not alter the pH of the water, eliminating the need for pH adjustments and avoiding the environmental impacts related to the discharge of acidic, metal-rich and sulphate-rich water. The tested polyDADMAC product achieved slightly better purification rates and required lower effective dosage (16 mg/L) than the polyAmine product (25 mg/L). Nevertheless, further investigations are required to determine the influence of factors such as mixing on the polymers performance and to determine the true cost of treatment when these products are applied.

Overall, FS achieved higher purification levels than polyDADMAC and polyAmine. However, it required up to fourfold higher dosages (mg product/L) than the organic polymers. The most significant difference in the coagulant performance was in the removal of TOC, which was substantially higher when FS was applied. Evaluation of synthetic organic products with varying MW and CD is suggested with the objective of achieving higher removal of organic matter. Low temperature had a negative impact on the performance of all three coagulants, especially regarding the removal of SS (20% reduction in removal efficiency). The impact of temperature on the chemical purification process is an important factor in cold climate regions. The implementation of a dual chemical coagulation method whereby a flocculant aid polymer is introduced after the primary coagulant to enhance the flocculation and sedimentation processes should be explored. Decreasing the initial water pH from 6.5 to 5.5 and sequentially to 4.5 resulted in a substantial decrease in the coagulant dosage required to achieve satisfactory purification efficiency.

Acknowledgements

This research was funded by Vapo Oy and also supported by Maa-ja Vesitekniikan tuki r.y and Thule Institute. The authors would like to recognise the support received from the personnel of the Water Resources and Environmental Engineering Research Group, University of Oulu.

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