Zirconium and chitosan coagulants for drinking water treatment – a pilot study

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ABSTRACT

Scientists continuously search for alternative coagulants that would be able to outperform traditionally used aluminium (Al) and iron (Fe). Use of a novel metal coagulant zirconium (Zr) has been associated with enhanced organic matter reduction. On the other hand, eco-friendly non-metal solutions, such as chitosan, can provide non-toxic sludge and water with no metal residue. In fact, Zr and chitosan have been utilized in full-scale operation by several water plants in Norway providing over 50,000 recipients in small and large municipalities with drinking water. However, the use of these two agents is limited in other parts of the world. In the present work, Zr and chitosan coagulants were tested together with Al for drinking water production in both pilot and laboratory trials. All coagulants provided high quality effluents. However, the metals showed higher efficiencies in terms of reduction of humic substances, with better performance of Zr than Al. On the other hand, the amount of suspended solids in sludge produced with chitosan was 25% of the amount produced with metal salts. Chitosan also functioned over a broad pH range without affecting the pH of the treated water.

Key words | chitosan, coagulation, contact filter, drinking water treatment, natural organic matter, zirconium

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INTRODUCTION

Hydrolyzing metal salts, based on aluminium (Al) or iron (Fe), have been used routinely for the removal of particles (turbidity) and natural organic matter (NOM) in the production of potable water since the beginning of the 20th century (Gregory & Duan 2001). Considerable practical and theoretical knowledge about these two agents has been gained, and today they are the most commonly used coagulants in water treatment. However, concern about raised levels of organic matter in surface waters (Garmo et al. 2014) impels research on alternative coagulants that are more effective at reducing NOM. The presence of NOM in water is undesirable due to its contribution to colour, taste, and odour problems. Additionally, NOM forms potentially harmful by-products, following disinfection with chlorine (Matilainen et al. 2010). Reduction in NOM is associated with charge neutralization, which occurs when negatively charged particles in water react with positively charged coagulant. This implies higher neutralising power and lower minimum effective dose of four-valent zirconium (Zr), compared with three-valent Al and Fe. Despite this recognized feature, only a few studies have investigated the use of Zr (Jarvis et al. 2012; Hussain et al. 2014; Zhang et al. 2014), whereas two of these studies have confirmed improved NOM reduction in source water after treatment with Zr salts. Moreover, apart from the study by Jarvis et al. (2012), previous research characterizes Zr only at bench-scale and various aspects that might stimulate its broader application in

water treatment practice are still not fully covered in the literature.

At the same time, there is also a growing interest in natural or so-called 'green' solutions in the water industry, as the use of metal salts is associated with problematic sludge utilization and metal residues in drinking water. Eco-friendly alternatives could be of great interest due to their biodegradability and biocompatibility features. Chitosan is derived from marine crustaceans and may be one of the more promising materials among eco-friendly alternative coagulants (Renault et al. 2009). First attempts to use chitosan for treating aqueous medium were made as far back as 1970 (Johnson & Peniston 1970), and numerous studies on its application in water and wastewater treatment followed, as reviewed in Renault et al. (2009). However, only a few of these studies describe the use of chitosan in pilot or full-scale trials for drinking water production (Saltnes & Eikebrokk 2002) and therefore additional research on chitosan is still required.

The present work evaluates Zr and chitosan coagulants for drinking water treatment in bench- and pilot-scale conditions, and compares them to traditionally used polyaluminium chloride (PACl). The optimal coagulation doses and pH were estimated by a jar-test procedure using river water from a Norwegian drinking water source. Optimization was carried out by comparing residual colour and turbidity in the finished water. During pilot-scale testing, the coagulants were dosed prior to contact filtration, and the effluents were assessed for turbidity, NOM-indicators (such as UV254 and colour), total organic carbon (TOC) and metal residue, along with other operational parameters.

MATERIAL AND METHODS

Raw water samples

All experiments were performed using water from the Glomma River obtained from a feed pipe at Nedre Romerike Water Treatment Plant in Strømmen, Norway. Raw water for the jar-tests was collected in May, August and November in 2013 and March 2014. The water was stored in plastic containers in a dark and cold room (4 °C) for no longer than one month. The pilot experiments used water collected in May 2015. This water was stored in

a 30 m^3 underground stainless steel tank, equipped with a submersible recirculating pump. During storage for seven months, water temperature ranged between 5–15 °C. Both bench and pilot experiments were preceded by repeated measurements of turbidity, pH and colour to assure that the water quality remained stable upon storage. Raw water parameters exhibited only minor changes during storage, except for the last pilot-scale experiment (Run 4), for which considerable changes in pH, colour, and TOC parameters were registered. Raw water characteristics are given in Tables 1 and 2.

Coagulants

PACl

A commercial PACl product, PAX-18, was obtained from Kemira Chemicals (Norway). The product had basicity of 42% and contained 9% (w/w) of Al.

Zirconium oxychloride

Zirconium (IV) oxychloride octahydrate powder, containing 27% (w/w) of pure Zr, was obtained from Teta Vannrensing Ltd (Norway). A working solution of 15% (w/w) was prepared in distilled water.

Chitosan

The chitosan product KitoFlokk™, Teta Vannrensing Ltd (Norway) was of low molecular weight (100 kDa) and had

Table 1 | Characteristics of the Glomma water samples

Sampling month	pH	Turbidity, NTU	Colour, mg Pt L^{-1}	SCV[a]
May 2013	6.7	98.0	26	−490
August 2013	6.9	1.9	14	−342
November 2013	7.1	7.8	28	−386
March 2014	7.0	3.2	29	NM[b]
Online data (average values for 2013)[c]	7.20	4.4	24	NM

[a]SCV, Streaming current value.
[b]NM, Not measured.
[c]Retrieved from www.nrva.no.

Table 2 | Summary of various physicochemical parameters for the raw, influent (M2, after coagulant dosing) and effluents waters (M3, after filtration), treated with Al, Zr and chitosan coagulants in the pilot study

Parameter	Coagulant			
	Al	Zr	Chitosan	Chitosan + Zr
Raw water (May 2015)				
pH	7.3	7.0	7.2	7.6
Turbidity, NTU	0.8	0.8	0.5	0.7
Colour, mg Pt L^{-1}	26	24	23	19
UV254, cm L^{-1}	0.13	0.13	0.13	0.10
TOC, mg L^{-1}	3.0	3.0	3.0	2.9
M2 – influent				
Dose, mg L^{-1}	1.5	2.5	1.0	1.1 + 0.3
Coagulation pH	5.8	4.2	4.2	6.0
Turbidity, NTU	2.3	2.4	0.8	1.4
Hydraulic head development, mmH_2O $hour^{-1}$	35	35	31	37
TSS, mg L^{-1}	8.2	8.6	2.1	NM[a]
M3 – effluent				
Turbidity, NTU	0.05	0.05	0.05	0.06
Colour, mg Pt L^{-1}	3	2	9	6
UV254, cm L^{-1}	0.039	0.025	0.090	0.060
TOC, mg L^{-1}	2.4	1.4	2.8	2.6
Residual metal, µg L^{-1}	<10	<10	NM[a]	NM[a]
Filter cycle length, h	15	22	17	15[b]

[a]NM, Not measured.
[b]Terminated due to insufficient volume of raw water to complete the run.

an acetylation degree (F_A) close to 0.2. The preparation was made by dissolving chitosan powder in 0.1 M HCl. The concentrations of the working solutions were 2% (w/v) and 0.5% (w/v) for the bench and pilot experiments, respectively.

The working solutions were stored at room temperature, the chitosan solution was stored for no longer than 2 weeks.

Water analysis

Turbidity was measured using a 2100N IS turbidimeter (Hach Company, USA). Colour was measured by a Shimadzu UV Visible Spectrophotometer UVmini-1240 (Shimadzu Corporation, Japan) and by DR3900 Hach spectrophotometer (Hach, USA), following either Standard APHA Method 2120C ($\lambda = 455$ nm) or ISO 7887:2011 ($\lambda = 410$ nm) for the

bench- and pilot-scale tests, respectively. UV254 was measured by a Shimadzu UV Visible Spectrophotometer UVmini-1240 (Shimadzu Corporation, Japan). Prior to colour and UV254 measurements, the samples were filtered through a 0.45 µm syringe polypropylene membrane (VWR, USA), in order to avoid the influence of turbidity. pH was measured with SenTix® 41 pH-sensor (WTW, Germany). Total organic carbon, residual Al and Zr were analysed by commercial laboratories (ALS Laboratory Group Norway AS or Noranalyse AS), following ISO 8245:1999, ISO 17294-1 and ISO 17294-2 procedures, respectively. Total suspended solids (TSS) parameter was determined using ISO 11923:1997 in technical duplicates. Colour and turbidity parameters were analysed in technical triplicates, whereas data for TOC and residual Al and Zr were obtained from single measurements.

To assess the charge neutralization dose, a streaming current parameter (SCV) was used. Measurements of SCV were performed under gradual addition of coagulant until zero SCV was achieved. SCV was registered using an ECA2100 Charge Analyzer (Chemtrac, Inc., USA).

Jar-tests

Two experimental setups were used to estimate the optimal coagulant dose (Setup A) and pH (Setup B). Further details for each setup are given under the relevant sections below. For both setups, the container with water was shaken for 30 s to resuspend settled solids, and 500 mL was poured into glass beakers and held at room temperature for at least 1 h. Cylindrical 1 L glass beakers and a Flocculator 2000 apparatus (Kemira AS, Finland), equipped with six flat paddles, were used to conduct jar-tests. After adding coagulants, the water was stirred for 30 s at 400 rpm (413 s^{-1}) followed by 10 min at 50 rpm (18 s^{-1}). For pH adjustment, predetermined amounts of 1 M NaOH or 1 M HCl were added to the water prior to the coagulant. Floc settling was for a minimum of 2 h to ensure complete settling, as determined by initial tests. After sedimentation, 100 mL supernatant was collected 2–3 cm below the surface and analysed for turbidity, colour and pH.

Optimization of coagulant dose (Setup A)

Coagulant doses varied between 2 and 11 mg L^{-1} (as metal or chitosan concentration). One individual test was

conducted per dose and repeated three times on the May, March and November waters. In order to detect the primary dose requirements and their impact on pH, initial tests with Zr and chitosan were conducted without pH adjustment.

Coagulant dose and coagulation pH (Setup B)

Two-factor experiments were performed with the March water. pH values between 3 and 8 were tested. The coagulant doses for PaCl were within the dose range applied at the drinking water treatment plant, which provided water for the experiments, whereas doses for Zr and chitosan were selected based on the results in Setup A: (a) 1, 3 and 5 mg Al L^{-1}; (b) 5, 9 and 12 mg Zr L^{-1} and (c) 1, 2 and 4 mg L^{-1} of chitosan. Two individual tests were conducted for each dose-pH combination.

Pilot tests

The pilot-scale system combined coagulation with filtration in a dual-media contact filter column, which is schematically presented in Figure 1. The column, 10 cm in diameter and 2.5 m high, was packed with support gravel (0.1 m), followed by 0.5 m-layer of Rådasand® sand (Rådasand AB, Sweden, $d_{10} = 0.4$ mm) and 0.8 m of Filtralite®NC 0.8–1.6 mm (Weber Leca Raelingen, Norway, $d_{10} = 0.95$ mm, 500 kg m^{-3} dry bulk density). Filtralite is a coarse filter media, consisting of expanded clay aggregates (Eikebrokk & Saltnes 2001). The column design was similar to the filtration system at Nedre Romerike Water Treatment Plant.

Several days prior to the experiment, approximately 1,500 L of raw water was pumped to an indoor feed tank, equipped with a paddle mixer, in order to equilibrate water to room temperature, usually within 11–18 °C. Thereafter, the water was continuously fed to the filtration column, using a peristaltic pump P1 (620 U, Watson-Marlow, UK) at a constant filtration rate of 5.9 m h^{-1}. After each run, the filter was backwashed for 15–30 min by upflow of tap water at about 55 m h^{-1}.

Hydrochloric acid (1 M) and coagulants were continuously fed to the inlet pipe at constant flow rates by two peristaltic dosing pumps (120 U/DV, Watson-Marlow, UK). The dose of HCl depended on the coagulant used and desired process pH. Three static mixers along the inlet pipe were used to provide uniform suspension. Contact time between the coagulants and water was close to 7 min. Three ports were available for manual sampling: (a) inlet pipe (M1, prior to coagulant dosing point); (b) above the Filtralite® layer (M2, after coagulant dosing point); and (c) outlet pipe (M3).

On-line monitoring of pH (SensoLyt 700 IQ, WTW, Germany) and turbidity (VisoTurb 700 IQ, WTW, Germany) was performed on the inlet and outlet water. Prior to each run, online instruments were calibrated. The column was equipped with eight pressure transmitters, which were used to monitor a course of pressure within the filter bed. All online measurements were logged by LabView software (National Instruments, USA). On-line readings were also controlled by manual measurements. Several litres of water were collected above the filter bed (port M2) by the end of each run for TSS measurement.

As the present study was limited to testing of a single coagulant dose-pH combination, application of minimal effective doses was implemented. The effective doses were identified by a new series of jar-tests, using turbidity and colour as indicators. However, application of these doses was accompanied by cake filtration in the initial pilot tests, and additional dose optimization was performed prior to the final pilot experiments. Treatment conditions for three coagulants, including Al (Run 1), Zr (Run 2), chitosan (Run 3) and a mixture of chitosan with Zr (Run 4) were optimized to assure turbidity <0.2 NTU, colour <5 mg Pt L^{-1} and residual Al and Zr <0.15 mg L^{-1} in the outlet water, as required by the Norwegian and European drinking water regulations (European Directive 98/83) (European Commission 1998). For non-metal agents, like chitosan, colour up to 10 mg Pt L^{-1} is allowed, as there is no problem with metal residue. The same principle was used for all coagulants. However, pH below 5.7–5.8 (PACl) and 4.0–4.2 (Zr and chitosan) were not studied, since they were respectively outside the generally accepted optimal pH-range (Gregory & Duan 2001) or could potentially contribute to corrosion.

The following treatment conditions were chosen: (Run 1) 1.5 mg Al L^{-1} at pH 5.8; (Run 2) 2.4 mg Zr L^{-1} at pH 4.2; (Run 3) 1 mg L^{-1} of chitosan at pH 4.2; (Run 4) 1 mg L^{-1} of chitosan mixed with 0.3 mg Zr L^{-1} at pH 6.0. Originally, lower coagulation pH was chosen for the last run, however, a slight change in water quality during storage affected the system, and the pH was unintentionally raised to 6.0. For
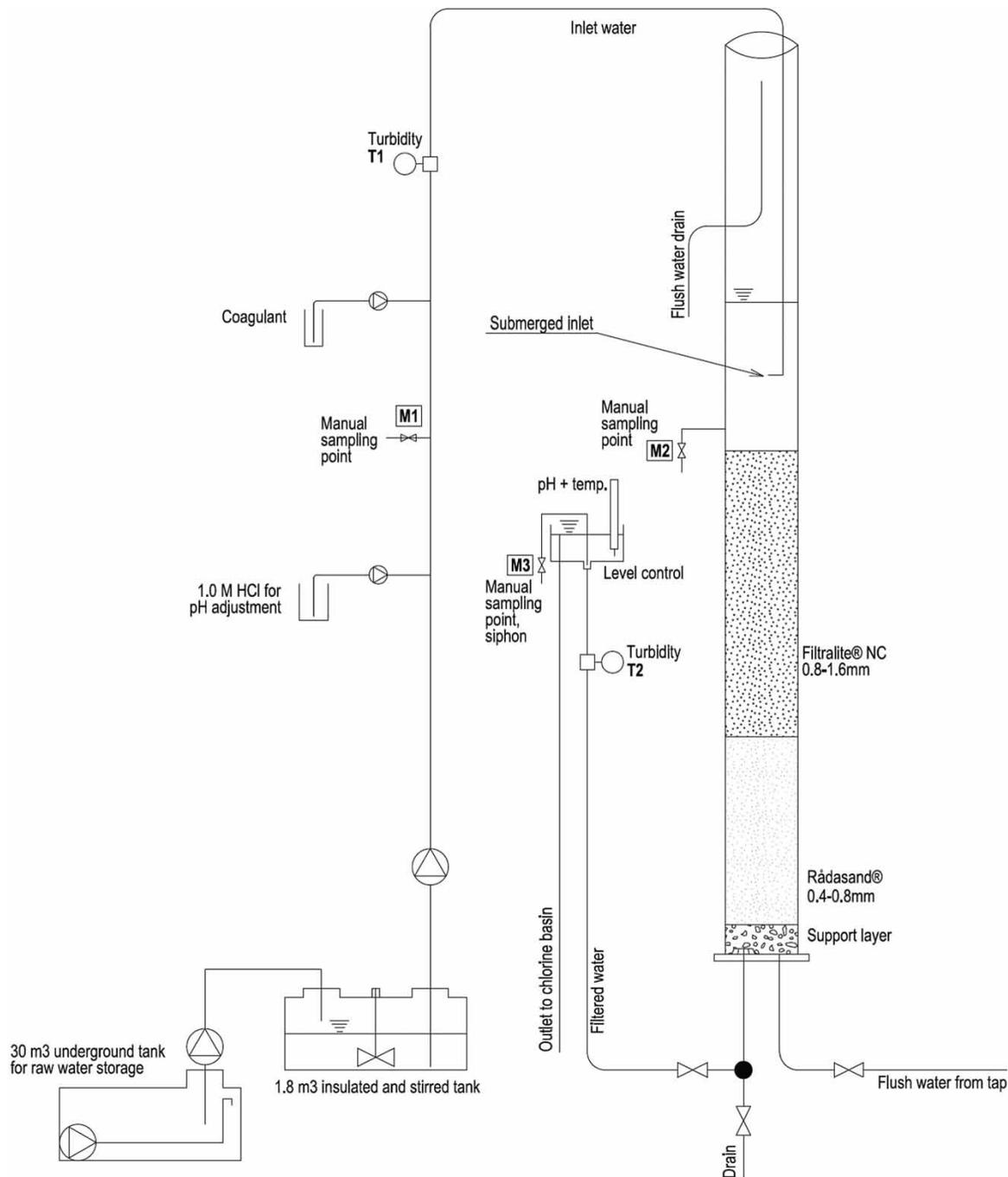
Figure 1 | A schematic of the pilot plant: M, ports for manual sampling; T, turbidimeters.

all filter runs turbidity breakthrough was reached prior to terminal head loss. An exception was Run 4, which was terminated due to insufficient volume of raw water to complete the run. Development of the head loss during an initial run with chitosan indicated solids accumulation only on the top

of the filter, which is typical of cake filtration. The problem was not eliminated even after numerous efforts to adjust the treatment conditions, and was usually worse at higher chitosan dosing. Overall, conditions within 1.0–2.7 mg L^{-1} and pH 4.2–6.1 ranges were tested. Choice of chitosan dosage

was therefore a compromise between the acceptable effluent quality and prolonged filter run. For Run 4 chitosan was combined with a small amount of Zr (0.3 mg L^{-1}). The mix was screened for different coagulation/pH ratios, but not for various chitosan/Zr ratios, due to source water shortage.

RESULTS AND DISCUSSION

Raw water characteristics

Parameters of the raw water collected for the jar-tests are summarized in Table 1. Overall, the water from the Glomma river had low turbidity and medium colour. The exception was the May sample that was collected during a flood event, and which exhibited an elevated turbidity level. An increase in NOM is unusual during flooding, and therefore it was assumed that the particles that entered the water source during the flood were probably inorganic.

Jar-tests

The effectiveness and required doses of the coagulants were initially evaluated by the jar-test procedure.

The reduction in turbidity and colour as a function of coagulant dosage is shown in Figure 2. The inverted u-shaped curves depicted the system entering a state of destabilization at a minimum effective dose, followed by the restabilization phase when the coagulant was in excess or pH became suboptimal (Bratby 2006).

The high particle concentration observed in the May sample could enhance contact opportunities for aggregation and precipitation of the destabilized particles, and therefore improve reduction efficiencies. Lower coagulant doses were therefore required to induce destabilization (Shin *et al.* 2008). A related phenomenon explains the limited destabilization efficiency registered for the August sample, which had the lowest concentrations of both inorganic particles and humic substances.

For Zr, reductions above 80% were observed within $8.5–10.0 \text{ mg L}^{-1}$ dose range for all waters. Efficiencies for chitosan were close to 60–78% for colour, and 50–95% for turbidity, when dosages between 4.0 and 6.0 mg L^{-1} were applied. The raw water pH was changed under Zr dosing, whereas chitosan had no influence on the pH of the samples. An increase in Zr dose from 8.0 to 10.0 mg L^{-1} resulted in the pH drop by 1 unit (from approximately 6.0 to 5.0). However, both coagulants could be applied without
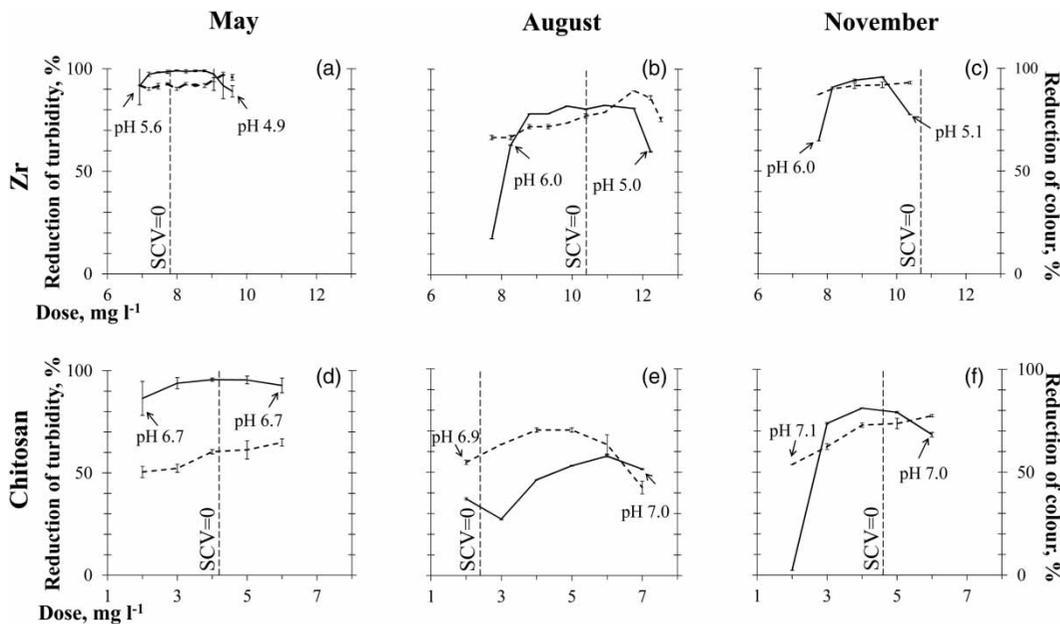
Figure 2 | Setup A: reduction (%) in turbidity (left Y-axis) and colour (right Y-axis) vs the coagulant dose for Zr (a)–(c) and chitosan (d)–(f) for water from the Glomma river, collected in May, March and November 2013. The results are expressed as the mean values and SD. Scales on X-axes vary between the coagulants.

pH-adjustment, and, as a result, consumption of the chemicals could be lowered.

Measurement of SCV enabled detection of the doses required for colloidal neutralization. Zero charge was reached between 8–11 mg Zr L^{-1} and 2–5 mg chitosan L^{-1}. These doses were consistent with high reduction efficiencies, but did not coincide exactly with the minimum effective doses. Apparently, the destabilization for these two coagulants occurs earlier than complete neutralization of colloids in the solution. A similar phenomenon was also demonstrated previously (Vogelsang *et al.* 2004; Jarvis *et al.* 2012).

The impact of pH on the destabilization efficiency is shown in Figure 3. Reductions in colour by 80–90% occurred for the metal-based coagulants at pH between 5.0–7.0 for Al and 3.5–6.3 for Zr. Efficiency between 60–80% was registered for the selected chitosan doses, applied at pH within 4.0–7.0. For all coagulants an effective minimum dose was decreasing upon protonation, implying involvement of H$^+$ ions in charge neutralisation mechanism (Vogelsang *et al.* 2004; Shin *et al.* 2008). Optimization of the coagulation process for the correct dose and pH was shown to be important, not only for colour reductions, but also to minimize metal residues in the treated samples (Figure 3).

Analysis of the jar-test data defined the optimal treatment conditions as 1–5 mg L^{-1} at pH 5.0–7.0 for Al, 5–12 mg L^{-1} at pH 4.5–6.3 for Zr, and 2–6 mg L^{-1} at pH 4.0–7.0 for chitosan. These data were in good agreement with previous reports. PACl dosed at 1.0–2.5 mg Al L^{-1} and pH 5.7–6.7 are recommended for contact filtration of Norwegian raw waters at colour levels of 15–50 mg Pt L^{-1} (Ødegaard *et al.* 2010). The same report prescribes 1.7–3.5 mg chitosan L^{-1} with the pH between 5 and

6. Published studies on Zr (Jarvis *et al.* 2012; Hussain *et al.* 2014; Zhang *et al.* 2014) report optimum dose and pH within ranges 5–16 mg L^{-1} and 4.5–6.0, respectively.

Pilot tests

Data from the pilot testing are summarised in Table 2. The raw and treated waters were additionally characterized for TOC and UV254 parameters. Water from a surface water source with no or low algae growth was used in the present study and it was therefore assumed that a major fraction of TOC consisted of humic matter.

The selected coagulants provided high quality effluents, although individual parameters varied for each run.

PACl is generally considered to be a robust and effective agent for water treatment (Saltnes & Eikebrokk 2002; Yan *et al.* 2007; Zhang *et al.* 2014). Indeed, the present research presented improvements of water quality by 88% for colour and 70% for UV254 for that coagulant. However, the effect of PACl on TOC was somewhat modest and did not exceed 20%. TOC provides an estimate of the amount of NOM in the water source, whereas the humic fraction of NOM is usually assessed indirectly as light absorbency in the visible (true colour) and UV wavelength range. True colour and UV254 are routinely applied surrogates for the TOC parameter in water treatment practice in Norway (Vik *et al.* 1985; Ratnaweera *et al.* 1999). However, as shown in Table 2, the correlation between colour and UV254 parameters and TOC appeared to be limited in the present study. Consequently, treatment conditions, defined via the colour surrogate, should not necessarily be interpreted as being effective for TOC removals. In such cases, coagulant assessment with respect to residual TOC could provide more reliable data. Alternatively, as the TOC data
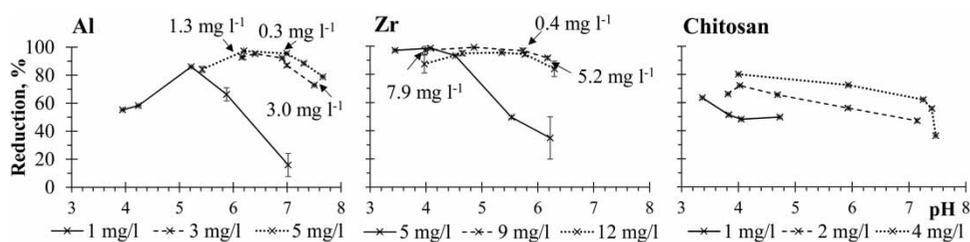
Figure 3 | Setup B: reductions (%) in colour vs coagulation pH for three different doses of Al, Zr and chitosan. The results are expressed as the mean values and SEM calculated for two independent replicates on the March water. Arrows indicate values for the residual metals measured in supernatants after sedimentation.

presented in the experiments were obtained from single measurements, poor removals that were observed for PACl and other coagulants could also be a result of measurement errors.

The effluent produced with Zr contained less organic matter than in the run with Al by 33%, as assessed by TOC measurements. In turn, results for residual colour (92% reduction) and UV254 (81% reduction) suggested a similar or slightly higher ability of Zr to reduce humic substances in water than that of Al. At these conditions, it can be speculated that Zr may be more effective against non-humic, hydrophilic NOM fractions, which, along with humic substances, contribute to water's organic carbon content. Hydrophilic NOM is undesirable in finished water and difficult to remove. Notably, the minimum effective dose of Zr was significantly lower in the pilot tests than that recorded from the jar-test results.

Chitosan is known to be less effective in NOM reduction than the metal salts due to the weaker charge derived from the amino- and hydroxyl-groups on its backbone. This is also a reason for its improved performance at acidic conditions, explained by the higher protonation of the amine groups (Guibal *et al.* 2006). Vogelsang *et al.* (2004) reported a reduction of colour by 80%, UV254 by 60% and TOC by 40% for the Glomma water after treatment with 3–4 mg L^{-1} of chitosan at pH 5.0 in jar-tests. Adequate performance of chitosan even on highly coloured water (50 mg Pt L^{-1}) was observed by Eikebrokk & Saltnes (2002). In the present work chitosan gave reliable colour reduction (by 61%), but its impact on UV254 and TOC was poor, at 31 and 7%, respectively. A somewhat moderate performance could be a result of a low chitosan dose applied under the pilot tests. Low chitosan dosage was selected to minimize an impact of cake filtration, discussed later in the text. As an explanation for low efficiency of chitosan against TOC, Eikebrokk & Saltnes (2001) suggested that high organic carbon content in the effluent, treated with chitosan, may be due to chitosan itself. Nevertheless, the quality of the effluent produced with chitosan complied with the Norwegian and European requirements for drinking water (European Directive 98/83). As demonstrated previously (Vogelsang *et al.* 2004), chitosan performance can also be strengthened by metal addition. However, in the present work a combination of chitosan and Zr was effective for

colour and TOC reductions to some degree. This is probably a result of the application of a relatively high pH: acidic pH would probably be more favourable for both coagulants. Additional tests would be necessary to define the optimal pH range, effective mixing ratios between these two components and their effect on NOM.

Chitosan was noted to destabilize over a broad pH range without affecting the pH of the treated water. These properties of chitosan make its application especially convenient for small treatment facilities that might have difficulty in attaining optimal and stable coagulation steps, and sometimes lack the necessary expertise for solving specific operational problems.

Filter function

Filter cycle length describes the time the effluent turbidity is below 0.2 NTU. The filter cycle time for Zr was 5–7 hours longer than for Al or chitosan (Table 2). Both Jarvis *et al.* (2012) and Hussain *et al.* (2014) reported that flocs formed by Zr had greater strength characteristics than Al. Stronger flocs are more resistant to shear forces and may be sustained in the filter bed over a longer period of time. However, it is also possible that the different filter cycle lengths could be attributed to a pH-factor, which might affect electrostatic interactions between filter media and flocs. Longer filter runs are considered to be favourable for plant operation, as fewer filter 'starts and stops' are required and, therefore, both energy and backwash water can be saved.

Four-fold less suspended solids in the influent when using chitosan was assessed by TSS analysis. Lower sludge load in the experiment with chitosan was also reflected by the influent turbidity level and hydraulic head parameter. As hydroxides are not formed with chitosan, it is believed to produce smaller flocs and lower sludge and hydraulic loads than metal salts. As a result, chitosan is often associated with prolonged filter runs. Indeed, full-scale water plants in Norway, using chitosan in everyday practice, report doubling of the filter cycle times. However, as noted here and previously (Saltnes & Eikebrokk 2002), application of chitosan can be challenging for fine filter beds due to filter cake formation. Monitoring of head loss during the chitosan run revealed no solids accumulation at depths below 20 cm. That eventually resulted in early

turbidity breakthrough, observed already after 17 hours of operation with chitosan. In treatment practice, filter clogging is usually associated with coagulant or polymer overdose, but the chitosan dose used in the present study was too low for this. The problem was not eliminated even after numerous efforts to adjust the treatment conditions, nor after mixing with Zr. The explanation is unknown, but the phenomenon could be specific for pilot plants only.

CONCLUSIONS

In the present work the four-valent Zr and natural polymer chitosan were compared with the traditional PACl coagulant for use in drinking water treatment. The results showed that both filter operation and reduction of humic substances were improved with Zr coagulant. Therefore, it was suggested that the use of Zr could be especially convenient for the treatment of highly coloured and/or NOM-rich waters. Although chitosan gave acceptable colour reduction, it was poor for reduction of TOC in the pilot trials. Further research could potentially investigate that chitosan performance might be strengthened by use of higher doses or metal addition. Notably, operation with chitosan was accompanied by cake filtration that was difficult to explain. Another drawback with the use of chitosan is its cost, which is higher than for PACl or Zr. Nevertheless, chitosan possesses some valuable features that the metal coagulants lack: chitosan's ability to destabilize over a broad pH range without affecting the pH of the treated water, production of water with no metal residues and reduced amount of sludge under the filter operation. This makes chitosan a suitable alternative for small water treatment plants that might have difficulty in attaining optimal and stable coagulation steps or would like to reduce costs associated with sludge treatment and utilization.

ACKNOWLEDGEMENTS

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