

NOM removal from drinking water by chitosan coagulation and filtration through lightweight expanded clay aggregate filters

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ABSTRACT

Recent innovations in Norway regarding coagulation-contact filtration for the removal of natural organic matter (NOM) include chitosan as a natural and biodegradable coagulant, and filter media based on lightweight expanded clay aggregates (Filtralite). The main advantages associated with chitosan are: reduced solids production compared with conventional coagulants; and treatment and disposal of natural, biodegradable sludge, which does not contain metal hydroxides from metal-based coagulants. Filtralite can be produced with an inverse relationship between grain size and density, thus allowing an approximation to the ideal situation of decreasing grain size in the direction of flow. Traditionally, this important property of a filter bed is utilised in up-flow filters, or in dual or multimedia down-flow filters with combinations of two or more filter media. This paper presents experimental results from pilot-scale treatment of NOM-containing raw waters using chitosan for coagulation and expanded clay aggregates as filter media. A dual media anthracite-sand filter and alum coagulant was used as a reference for comparison with conventional process configurations.

Key words | chitosan, coagulation, direct filtration, expanded clay aggregates, NOM removal

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INTRODUCTION

Natural organic matter (NOM) in drinking water has gained a lot of attention in many countries in recent years. The main reasons for this are concerns regarding colour, taste and odour, known and unknown disinfection by-products (DBP), formation of biofilms in distribution systems, and increased availability of micro-pollutants associated with NOM. In 1998, the applied NOM removal technologies in Norwegian treatment plants included coagulation and filtration (74 plants), macro-porous anion exchange (12), nanofiltration (63), and ozonation-biofiltration (1).

Most coagulation filtration plants apply aluminium-based coagulants and dual media anthracite-sand filters. Recently, some plants have shifted to iron-based coagulants and calcium carbonate (CaCO_3) as a filter medium in up-flow single medium alkaline filters, or in down-flow triple media filters with anthracite, sand and CaCO_3 . The

main goal is to obtain NOM-removal and corrosion control, i.e. increased levels of calcium, alkalinity and pH. A typical scheme of a coagulation-contact filtration plant for NOM removal and corrosion control is shown in Figure 1. Metal-based coagulants are used with conventional dual media anthracite-sand filters, with lime and carbon dioxide for pH and corrosion control purposes. Due to the loose nature of the metal-NOM coagulation products and the high solids production from elevated coagulant doses required for NOM control, the filter run lengths are short compared with those achieved in turbidity removal. In addition, some plants have problems complying with the admissible residual metal concentration levels. Against this background, optimisation of coagulation and filtration design and operation are important issues, including testing and evaluation of alternative coagulants and types of filter media.

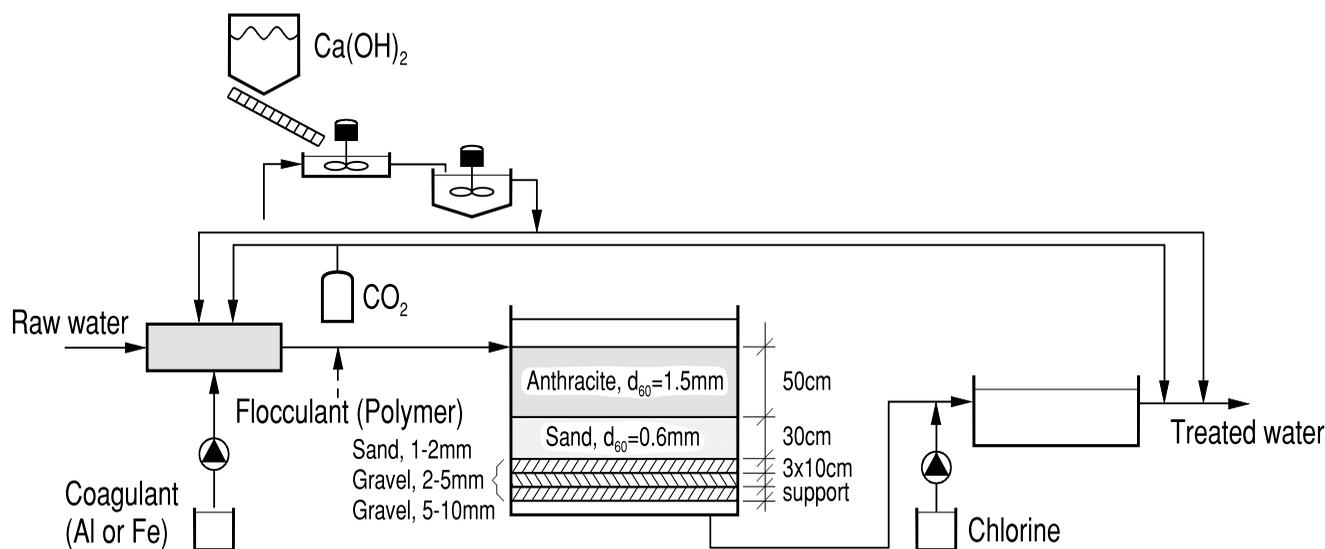


Figure 1 | Schematic of a coagulation-contact filtration process with metal-based coagulants, dual media anthracite-sand filters, and lime and carbon dioxide for pH- and corrosion control (Ødegaard *et al.* 1999).

NOM-RELATED WATER QUALITY REGULATIONS

In order to maintain low concentrations of DBP, water quality standards normally regulate the maximum admissible concentration levels of NOM before chlorination. In general, the Norwegian water quality standard has set the maximum colour and organic carbon levels to 20 mg Pt l^{-1} and 5 mg TOC l^{-1} , respectively. The maximum levels of aluminium and iron are 0.2 mg l^{-1} . However, when used as coagulants in water treatment the maximum admissible level is 0.1 mg l^{-1} . In contrast to the maximum colour and TOC levels established in Norway, the US regulations on disinfectants and DBPs (USEPA 1998) require 0–50% removal of TOC depending on raw water TOC and alkalinity levels. In addition, many countries also regulate the maximum admissible level of DBP, i.e. trihalomethanes (THM) and haloacetic acids (HAA).

NOM COAGULATION AND FILTRATION

In the US the term ‘enhanced coagulation’ has evolved to describe a coagulation process optimised for NOM-removal, which was initially designed for turbidity

removal. Enhanced coagulation normally implies the use of elevated coagulant doses and stricter pH control to obtain the required 0–50% reduction in TOC. In high alkalinity waters an inorganic acid or coagulant overdosing is used to reduce the pH to optimum levels, normally in the range of 5–6. In low alkalinity raw waters, however, a base is normally required to prevent the pH from dropping below the optimum level due to the acid reaction of the metal coagulants. The elevated coagulant dose requirements and sludge production rates normally associated with increased NOM removal result in relatively short filter runs due to early breakthroughs, more rapid headloss development, increased backwash water consumption, and the need for increased sludge processing and disposal capacity. The importance of these factors is even more pronounced in direct or contact filtration systems. In this context it is important to evaluate alternative types of coagulants with respect to the potentials for obtaining reduced coagulant doses and sludge production rates, as well as a more easily disposable sludge. In addition, new types of filter media need to be considered that may be more adapted to or tailor-made for coagulation-contact filtration processes primarily designed for NOM removal. In Norway there is considerable interest in chitosan as a natural and non-toxic

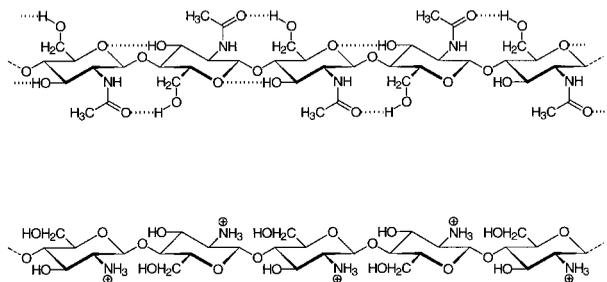


Figure 2 | Characterisation of chitin (top) and chitosan (Smidsrød & Moe 1995).

alternative to metal-based coagulants, and in lightweight expanded clay aggregates (Filtralite) as an alternative filter media.

Chitosan as a coagulant

Chitosan (Figure 2) is a natural cationic biopolymer obtained from full or partial deacetylation of chitin, the structural polymer of the outer skeleton of insects and crustaceans (shrimp and crab shells). The production process involves processing of the shells, deacetylation, drying and milling. The degree of acetylation of the product used here (Primex ChitoClear 90) is more than 90%. The cationic charge stems from protonation of the amino groups. In the experiments reported here the coagulant was dissolved in hydrochloric acid, with a concentration of the dosing solution of 10 g l^{-1} . The coagulation abilities have been known for a long time and, as it is virtually non-toxic, this coagulant has undoubtedly a potential also for the coagulation of NOM (Eikebrokk 1999). The disadvantage is that the current price level of chitosan makes competition with metal-based coagulants and synthetic polymers difficult. However, few results have been presented regarding important aspects of NOM-coagulation and filtration performance with chitosan.

Expanded clay aggregates as filter media

Lightweight expanded clay aggregates (Filtralite) are produced by burning clay at high temperatures (1100°C). Filtralite can be produced with different porosity, i.e. dry density. In the experiments presented here, the qualities of

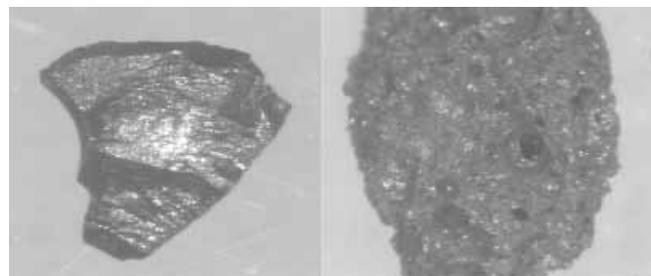


Figure 3 | Grains of anthracite (left) and Filtralite NC (right).

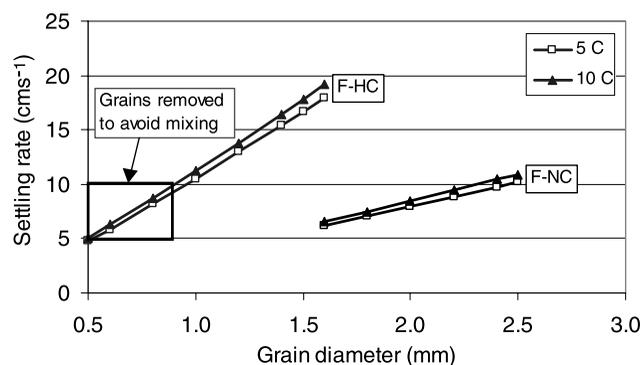


Figure 4 | Calculated settling rates of Filtralite HC and NC grains at transient hydraulic conditions (5 and 10°C). Assumed wet densities: $1,850$ and $1,240 \text{ kg m}^{-3}$, respectively.

Filtralite used were high density crushed (F-HC) and normal density crushed (F-NC), with approximate wet densities of about $1,800$ and $1,200 \text{ kg m}^{-3}$, respectively. Pictures of Filtralite and anthracite grains are presented in Figure 3, illustrating well the difference in porosity for the anthracite and Filtralite NC grains. The settling velocity of the filter grains following bed expansion during backwash determines the stratification and the layer structure of a filter bed. Thus, a correct combination of grain size and filter material (i.e. density) in the different layers is essential to obtain the required decrease in grain size and increase in grain settling rates with depth in a down-flow filter bed (Ives 1979). As presented in Figure 4, initial calculations on the settling rates at transient hydraulic conditions (Newton) of the initially produced 0.5 – 1.6 mm Filtralite HC and 1.6 – 2.5 mm NC grains showed a risk of intermixing of the F-HC grains below 0.8 mm with the largest F-NC grains (above 2.3 mm). Therefore, F-NC grains below 0.8 mm in size were removed before the start

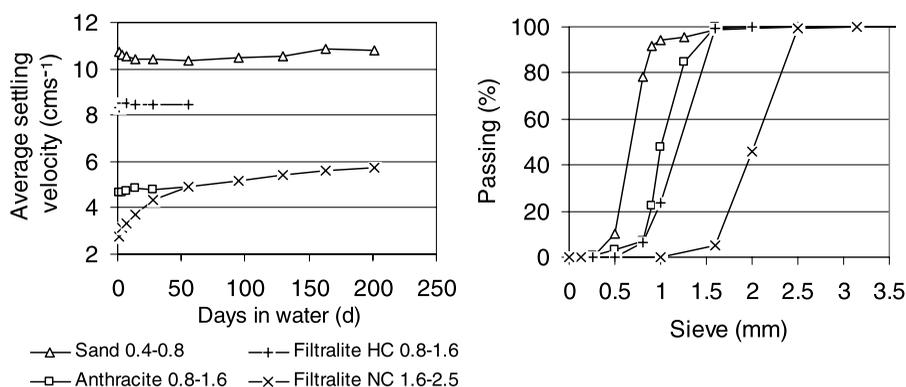


Figure 5 | Average settling rates (30 grains) and sieve size analysis for grains of Filtralite NC and HC, anthracite and sand.

of the experiments. In these calculations, the anticipated wet densities were set to 1240 and 1850 kg m⁻³ for F-NC and F-HC.

In order to characterise the grains by settling velocity, 30 grains covering the given size range of the two Filtralite fractions were measured and compared with anthracite and sand grains (Figure 5). The settling velocities of the grains were measured in a column of water as a function of grain storage time in water. When soaked in water, grain density and settling rates may increase because water is penetrating the pores. Figure 5 shows that this is true for the high porosity grains of F-NC where settling rates appear to increase for a period of several weeks. However, the settling rates of grains of F-HC, anthracite and sand are constant during storage in water. The measured settling rates are lower than those calculated in Figure 4, for F-HC grains in particular, indicating that the actual wet densities are lower than those used for the calculations. However, no significant overlap in settling rates between the grains of the different fractions was detected, and the given Filtralite fractions were applied in pilot-scale coagulation-contact filtration experiments.

COAGULATION-CONTACT FILTRATION EXPERIMENTS

The range of raw waters tested was considered to cover most Norwegian humic waters commonly treated by

coagulation and filtration. The raw waters had typical colour levels from 15 (RW15) to 50 mgPt l⁻¹ (RW50). The corresponding typical organic carbon levels were 2.3 and 5 mgNPOC l⁻¹, respectively, and the range of specific UV-absorption (SUVA) was 3.8–5 l m⁻¹ mgC⁻¹. Turbidity levels were in the range of 0.1–0.2 NTU. The coagulants tested with this raw water included:

- alum (ALG)
- poly aluminium chloride (PAX14), and PAX with high calcium content (Ca- PAX)
- ferric chloride sulphate (JKL)
- chitosan (Chi), a natural cationic biopolymer.

As an example of the performance of metal-based coagulants, Figure 6 shows the minimum specific ALG-doses required to comply with a residual aluminium standard of 0.1 mg Al l⁻¹ (<0.1 res. Al). Also shown in Figure 6 are the doses required to obtain 70–90% colour removal and 50–60% removal of organic carbon. Dose requirements are related to the specific UV-absorption (SUVA) of the tested raw waters.

It can be concluded from Figure 6 that residual aluminium controls the minimum dose requirement for raw waters with SUVAs of 4.3 or higher unless the required colour or organic carbon removal exceeds 90% or 60%, respectively. As raw water SUVA decreases below 4.3, indicating a shift towards lower molecular weight NOM, colour and organic carbon in particular become more important relative to residual aluminium with respect to

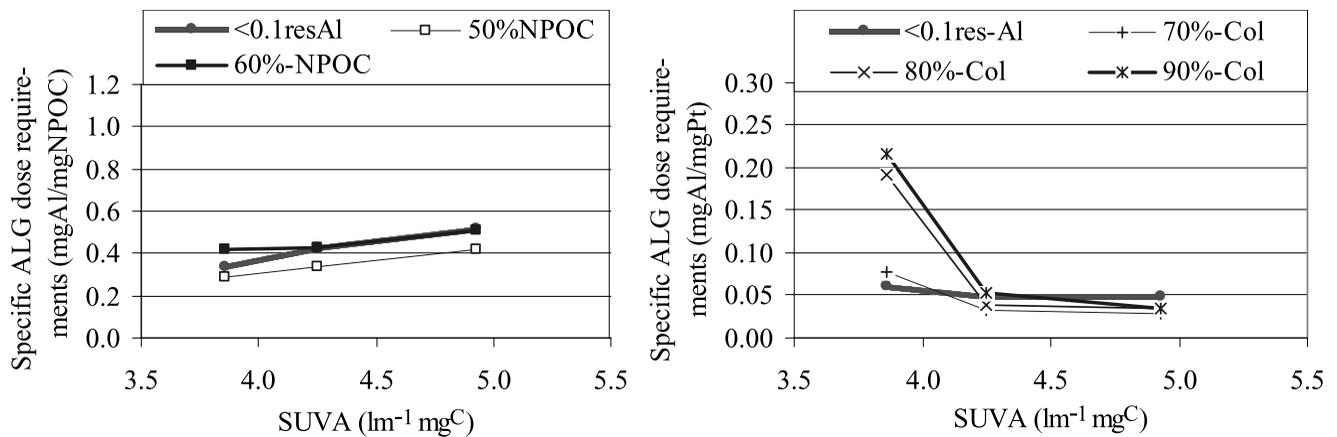


Figure 6 | Specific dose requirements as function of raw water SUVA when using ALG for coagulation of the tested raw waters (Eikebrokk and Saltnes 2000).

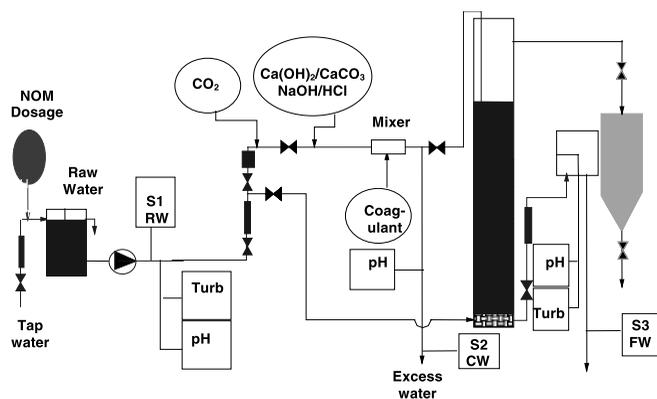


Figure 7 | Scheme of the pilot plant used in the coagulation-filtration experiments.

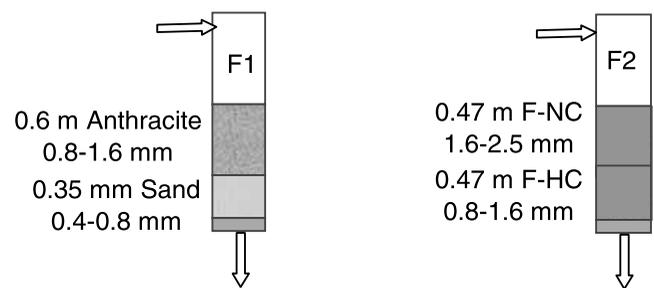


Figure 8 | Scheme of the parallel anthracite-sand reference (F1) and Filtralite (F2) filters.

controlling the coagulant dose requirements. Even in that case, removal requirements of more than about 65% and 50% with respect to colour and NPOC are needed before NOM removal (i.e. colour or NPOC) controls the minimum coagulant dose requirement.

The experiments were run in a pilot-scale coagulation filtration plant shown in Figure 7, described in more detail elsewhere (Østerhus & Eikebrokk 1994; Eikebrokk 1996). The identical and parallel filter columns used in this study, i.e. the anthracite-sand reference filter (F1) and the Filtralite filter (F2) are shown in Figure 8. The Filtralite NC and HC used in F2 had an effective size (d_{10}) of 1.65 and 0.84 mm, and uniformity coefficient (d_{60}/d_{10}) of 1.29 and 1.54, respectively. Dried and sieved samples taken from the middle sections of the anthracite and sand layers in the dual media filter (F1), showed effective sizes (d_{10}) of

0.82 and 0.50 mm, and uniformity coefficients (d_{60}/d_{10}) of 1.44 and 1.32, respectively.

By splitting the flow after coagulation and pH control, possible differences in inlet water quality to the filters is minimised. A direct comparison of the performance of the two filters is then possible. The data from the flow meter, on-line pH and turbidimeters (Hach Low Range 1720) were continuously presented graphically on a PC-screen and stored electronically.

The water sampling points (as shown in Figure 7) were: (1) raw water (RW), (2) coagulated water (CW), and (3) filter effluent water (FW). The raw water and filter effluent water were characterised by:

- pH
- turbidity
- true colour

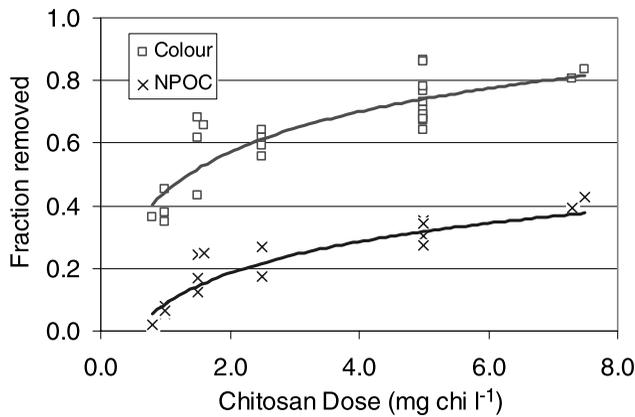


Figure 9 | Obtained colour and organic carbon removal efficiencies when using chitosan for coagulation of the raw waters RW15 and RW50. Water temperature: 6–11°C (Eikebrokk and Saltnes 2000).

- total organic carbon as non-purgeable carbon, NPOC (Dohrman DC-190)
- metal coagulant residues (according to the applied coagulant).

Coagulated water samples were analysed with respect to:

- suspended solids (SS)
- zeta potential (Coulter Delsa 440 SX).

Water samples were stored at 4°C before analysis according to the Norwegian Standard for Water and Wastewater analysis. In addition, samples of raw water and filter effluent water were analysed by Aquateam a.s with respect to molecular weight fractionation (HPLC Sigmachrome GFC-100) and biodegradable dissolved organic carbon (BDOC) according to procedures described by Charnock & Kjønne (2000).

Evaluation criteria

Coagulation and filtration performance was evaluated on the basis of filter effluent quality and headloss data. From the linear relationship between headloss and time, the slope of the line is kC_0v (McEwen 1998):

$$H_t = H_0 + k C_0 v t \quad (1)$$

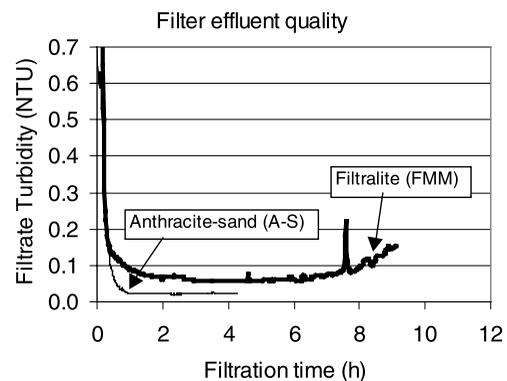
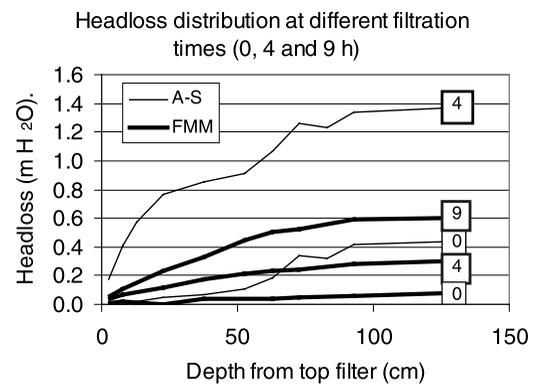
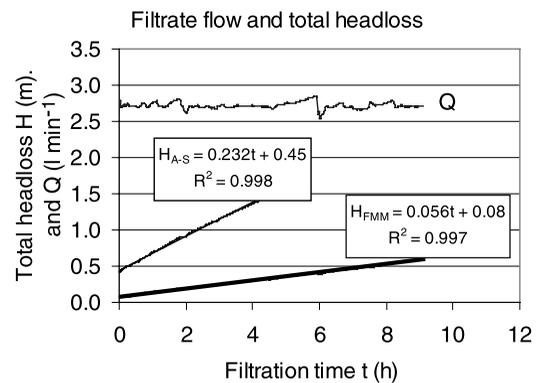


Figure 10 | A typical example of process performance with chitosan coagulation and filtration in the parallel anthracite-sand (A-S) and Filtralite (FMM) filters (RW50, 7.5 mg Chi l⁻¹, 10°C, 10 m h⁻¹, pH 5.7–5.9).

where:

H_t = headloss after filtration time t

H_0 = initial head loss at time 0 ('clean' bed)

k = constant

C_0 = concentration of particles in filter influent water

Table 1 | Process performance and filtration characteristics when using chitosan or ALG in anthracite-sand (F1) or Filtralite (F2) filter beds. (Raw water 50 (RW50) indicates a raw water colour level of 50 mg Pt l⁻¹)

Run no	Raw water	Coag type	Dose (mg l ⁻¹)	Filtration rate (m h ⁻¹)	C ₀ (gSS m ⁻³)	Anthracite-sand (F1)			Filtralite (F2)		
						H ₀ (mH ₂ O)	K (mH ₂ O h ⁻¹)	k=K/vC ₀ (cmH ₂ O/(gSS m ⁻²))	H ₀ (mH ₂ O)	K (mH ₂ O h ⁻¹)	k=K/vC ₀ (cmH ₂ O/(gSS m ⁻²))
201	50	Chi	7.5	10	9	0.45	0.232	0.26	0.08	0.056	0.06
205	50	Chi	5	10	6	0.34	0.144	0.23	0.09	0.031	0.05
206	50	Chi	5	7.5	7	0.30	0.114	0.22	0.06	0.028	0.05
Avg		Chi	5.8	9.2	7	0.36	0.163	0.24	0.08	0.038	0.05
204	50	ALG	3.1	7.5	15	0.38	0.070	0.06	0.06	0.019	0.02
208	50	ALG	3.1	12.5	16	0.59	0.160	0.08	0.13	0.041	0.02
211	50	ALG	3.1	7.5	16	0.30	0.061	0.05	0.07	0.019	0.02
Avg		ALG	3.1	10.0	16	0.42	0.097	0.06	0.09	0.026	0.02

Table 2 | Average effluent water quality data from filters F1 and F2 with ALG and Chi as coagulants (RW 50, three runs with every coagulant as shown in Table 1)

Coag-Filter	Filtr. rate (m h ⁻¹)	pH	Turb. (NTU)	Colour (mgPt l ⁻¹)	Org. carbon (mgNPOC l ⁻¹)	Removed fractions			K (mH ₂ O h ⁻¹)	k (cmH ₂ O/gSS m ⁻²)
						Colour	Org. carbon	H ₀ (mH ₂ O h ⁻¹)		
ALG-F1	10	6.5	0.42	3	1.7	0.94	0.65	0.42	0.097	0.06
ALG-F2	10	6.5	0.93	3	1.9	0.95	0.62	0.09	0.026	0.02
Chi-F1	9.2	6.5	0.09	9	3.1	0.80	0.36	0.36	0.163	0.24
Chi-F2	9.2	6.6	0.10	9	3.2	0.79	0.34	0.08	0.038	0.05

v = rate of filtration (m h⁻¹)

t = time of filtration (h)

In a particular case of filtration with constant conditions regarding inlet water quality, type and dose of coagulant, rate of filtration, etc., the equation can be simplified:

$$H_t = H_0 + K t \quad (2)$$

where K is a 'constant' depending on the type of particles to be removed and properties of the filter bed. In the experiments presented here comparing two filter beds that are tested in parallel and receiving the same water, different K-values illustrate differences in filter bed properties and different distribution patterns of deposited particles within the beds.

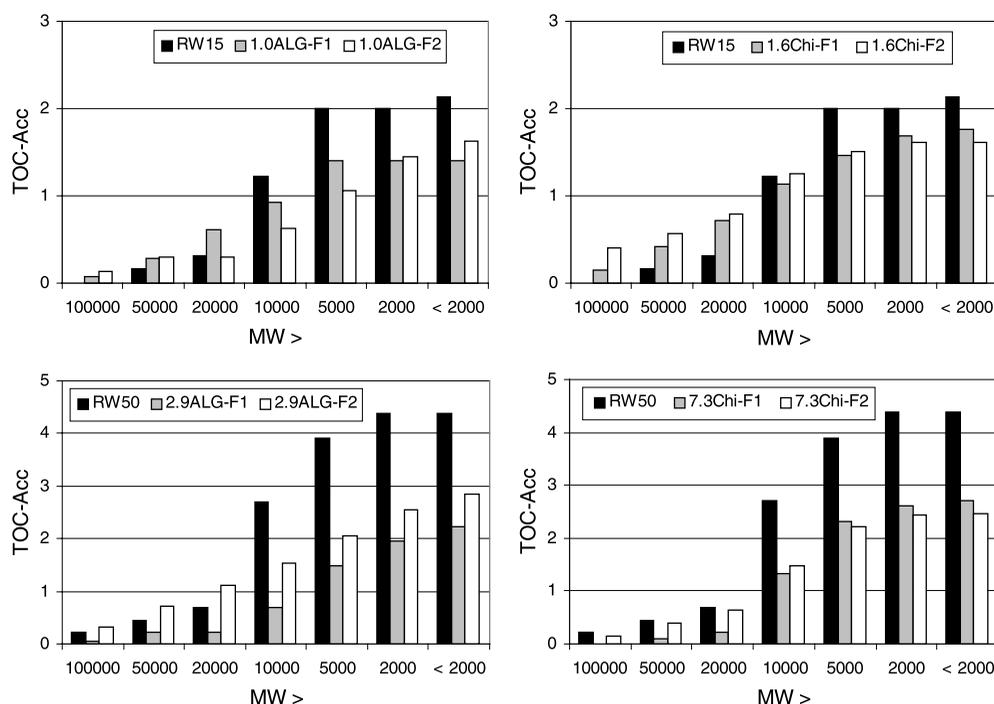


Figure 11 | MW distribution in untreated raw waters RW15 and RW50, and in filter effluent water from anthracite-sand (F1) and Filtralite (F2). Coagulation of RW15 (upper) and RW50 (lower) with 1.0 and 2.9 mg Al l⁻¹ as ALG (left), and 1.6 and 7.3 mg l⁻¹ as Chi (right).

RESULTS OF EXPERIMENTS WITH CHITOSAN AND FILTRALITE FILTERS

The relationship between chitosan dose and removal efficiencies with respect to colour and TOC is shown in Figure 9 (Eikebrokk 2000). It was demonstrated before that Filtralite may serve as an efficient substitute for anthracite in dual media filters when ALG, JKL and chitosan are used for coagulation (Eikebrokk & Saltnes 2000; Eikebrokk 2000).

A typical example of the performance of chitosan coagulation and filtration in anthracite-sand and Filtralite filters is presented in Figure 10. Data on process performance and filter effluent quality obtained in the experimental runs with chitosan and Filtralite are summarised in Table 1. Table 2 presents the average values obtained with ALG and chitosan in filters F1 and F2. Removal efficiencies with respect to colour and TOC are in the range of 79–80% and 34–36%, respectively. Corresponding efficiencies with ALG are 94–95%, and 62–65%. The solids

production with Chi is in the range of 6–9 mg SS l⁻¹ with 15–16 mg l⁻¹ with ALG at the given dose levels of 5–7.5 mg Chi l⁻¹ and 3.1 mg Al l⁻¹. The benefits of the Filtralite filter (F2) are obvious in terms of lower initial headloss and rate of headloss increase compared with anthracite-sand (F1). This is true regardless of the coagulant used. The typical range of optimum pH values is 5.8–6.6 with ALG and 5.0–6.5 with Chi, with typical optimum zeta potentials of –10 to +20 mV. The increase in zeta potential with increasing coagulant dosage seems more consistent with chitosan. The filter run lengths obtained until the occurrence of breakthrough or headloss termination are considerably longer with chitosan than with ALG.

Although chitosan is able to meet the TOC and colour removal requirements in most cases, ALG turns out to be more efficient in this respect, especially with regard to TOC removal. When ALG is used for coagulation, the results show that effluent turbidity is higher from filter F2 than F1. This is probably due to the increased minimum

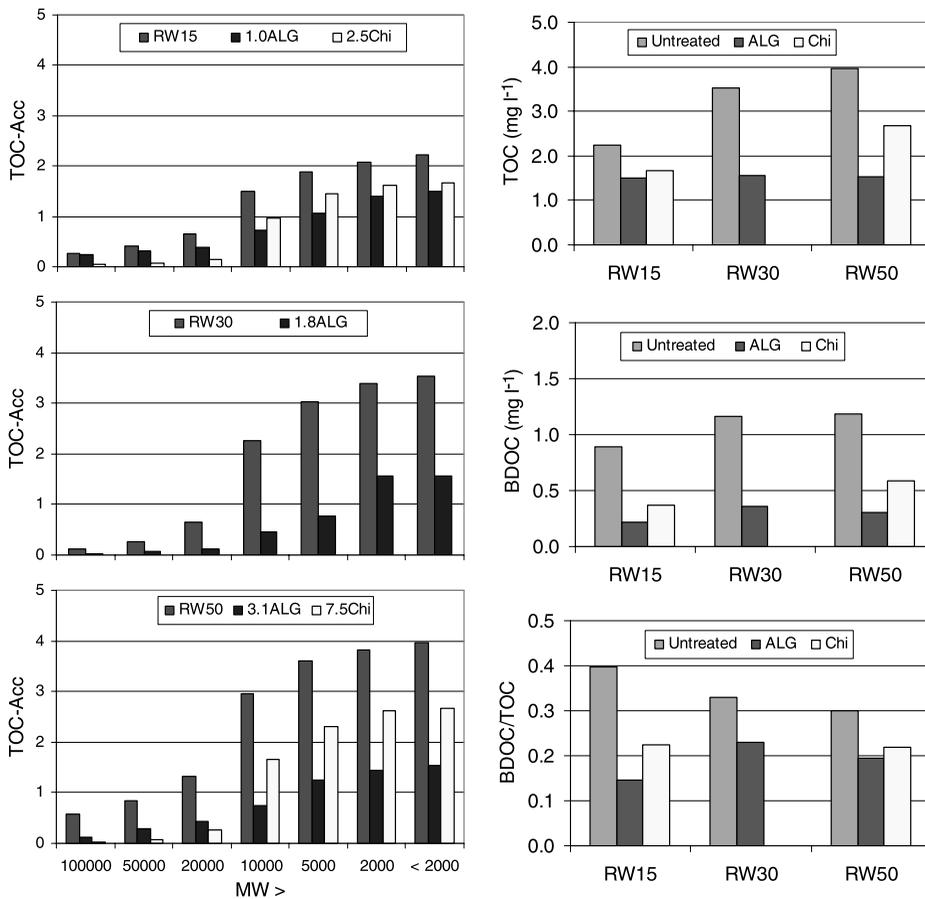


Figure 12 | Distribution of TOC in different molecular weight fractions in untreated and ALG or Chi coagulated waters (left). Total TOC, BDOC and TOC/BDOC ratios for untreated and coagulated waters (right). Anthracite-sand filter (F1) only.

grain size used in F2 (0.8 mm versus 0.4 mm in F1). Thus, the relatively loose metal-NOM floc particles have a tendency to penetrate the filter F2. However, when using chitosan, effluent turbidities are low in both filters.

Figure 11 shows the distribution of TOC present in the different molecular weight fractions in raw waters and treated water samples, demonstrating how the different fractions of NOM are removed in the process. It can be seen that a large part of the total TOC is in the 5,000–20,000 molecular weight fraction. There is a considerable difference between the results from the two filters, especially when coagulating the most concentrated raw water (RW50) with ALG. There is a tendency for ALG to be able to remove more of the lower MW fractions than Chi, probably due to adsorption to aluminium hydroxide products.

From the data presented in Figure 12 it is evident that although chitosan does not reduce TOC by more than about 35%, the reduction in BDOC is close to 50%. This is also indicated by the decrease in the BDOC to TOC ratio as a result of water treatment. Hence, both ALG and Chi are capable of removing the BDOC to a larger extent than the DOC. It should be noted here that chitosan adds TOC, and probably also BDOC, to the water.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Chitosan is able to remove colour and organic carbon from NOM-containing raw waters. At doses

- up to 7.5 mg l^{-1} , about 80% of the colour is removed. However, the removal of organic carbon is only 35–40%.
2. Sludge solids production with chitosan is less than 50% compared with alum.
 3. Lightweight expanded clay aggregates (Filtralite) can be used successfully as a substitute for anthracite in dual media filters. Filtralite in two size and density fractions (F-NC and F-HC) can also be used alone as the only filter material. The size fractions of 1.6–2.5 mm F-NC and 0.8–1.6 F-HC used in this study performed well although the grains of F-NC increased in density and settling rate due to water uptake during the first 2–3 months.
 4. Because the minimum grain size used in the single medium two-layer Filtralite filter was 0.8 mm in order to avoid mixing of the layers, the effluent turbidity was higher for this filter than from the reference anthracite-sand filter when alum was used for coagulation. However, with respect to colour and TOC removal, no major differences were observed between the Filtralite and the anthracite-sand reference filters when ALG or chitosan were used as coagulants.
 5. When chitosan was used for coagulation, a similar effluent quality was obtained from the Filtralite and the anthracite-sand reference filter. However, Filtralite was advantageous in terms of initial headloss and rate of headloss increase.
 6. Both chitosan and alum were able to remove biodegradable organic carbon more efficiently than dissolved organic carbon. The dominating molecular weight fractions in the raw waters used were in the range of 5,000–20,000.

7. Although the best TOC removal with ALG and chitosan was achieved in the molecular weight range of 5,000–20,000, TOC was removed to some extent over a wide range of MW.

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