Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1044476

57 (2016) 7679–7689
April

Taylor & Francis
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A selection framework for NOM removal process for drinking water treatment

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Received 27 December 2014; Accepted 12 April 2015

ABSTRACT

NOM (natural organic matter) is increasing in water resources worldwide and is becoming more difficult to treat. Drinking water guidelines are becoming more stringent so NOM removal is becoming more critical and requires consideration as a major treatment process, rather than just a polishing step on top of turbidity removal. In this study, a review of available methodologies to determine the required degree of NOM removal was undertaken. It is demonstrated that chlorine decay and THM (trihalomethane) formation modelling of laboratory-treated water samples provides a sound guide to determine the level of NOM removal needed for a given situation. The level of NOM removal needed is linked to a specific distribution system at given water temperature and water age profile. A sample of raw water treated by a given NOM removal process is tested for chlorine decay rates and THM formation kinetics, and these results are used to evaluate the performance of a distribution system with a given configuration. Frequently used and proven processes for NOM removal are: enhanced coagulation, granulated activated carbon, ozone with biological activated carbon and ion exchange resins. The impact of any of these processes can be predicted by the proposed methodology. General guidelines for process selection are presented.

Keywords: DOC removal; Enhanced coagulation; Drinking water quality; Chlorine decay model; THM formation

1. Introduction

NOM (natural organic matter) is present in practically all sources of drinking water, in widely variable concentration. It is a mixture of organic compounds of various molecular structures and masses including a significant amount of humic substances. The humic substances are formed by decomposition of vegetation with assistance of soil bacteria. These compounds are relatively biologically stable, but interfere with production and distribution of drinking water.

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Presented at the 7th International Conference on Challenges in Environmental Science and Engineering (CESE 2014) 12–16 October 2014, Johor Bahru, Malaysia

An emerging group of chemicals are the anthropogenic endocrine disruptors, which present a concern to human health at very low concentrations (0.01 μg/L). As these are mainly a subject of research and not commonly targeted in commercial WTPs, here we concentrate on NOM and problems of maintaining the disinfectant residual and complying with THM (trihalomethane) guidelines.

NOM, often characterised as dissolved organic carbon (DOC), is not an essential component of drinking water, but it is often directly or indirectly responsible for lower quality of drinking water and its rapid degradation in a distribution system. Specific problems caused by NOM are:

- Colour [1].
- Taste (for example, Geosmin and MIB in tens of ng/L, produced by algae). [2].
- Increased chlorine decay requiring higher doses or multiple dosing [3].
- Disinfectant by-product formation (THMs, haloacetic acids (HAAs) and other halogenated organics) as a result of reaction of NOM with disinfectants.
- Bacterial regrowth in the distribution system as a result of biologically available organic carbon present, either in the water and not removed by the treatment [4] or produced by reaction with disinfectants [5].
- Metal complexes [6], making them harder to treat.

Concerns about NOM in water sources are aggravated by the fact that DOC has been increasing since the beginning of its monitoring in 1988 [7]. In the UK, DOC of lakes and streams has approximately doubled in the last 20 years and there are indications that the situation is similar in other parts of the world. Not only is the concentration of DOC increasing but DOC is also becoming more difficult to treat [8,9]. The suspected causes for the increasing and changing nature of DOC are changing land use, urbanisation, global warming and reduction of sulphur dioxide emissions [10]. The increasing general shortage of drinking water sources increases pressure to utilise sources of lower water quality which are frequently associated with higher DOC.

Historically, a drinking water treatment process was primarily concerned with removal of turbidity, which was achieved by coagulation, sedimentation and sand filtration. Only with the regulation of disinfection by-products (DBPs) such as THMs and HAAs has NOM removal become necessary [11,12].

NOM is also removed by the coagulation process as colloidal NOM particles are aggregated and as coagulant hydroxides (aluminium and ferric hydroxides) adsorb high molecular mass, hydrophobic NOM [13]. However, the degree of NOM removal is dependent on type of NOM, coagulant dose and pH. Enhanced coagulation, where the coagulant dose is increased with or without pH adjustment [13] is frequently used by water industry to improve NOM removal. However, it may not sufficiently reduce NOM, especially with high NOM concentration in the raw water or with high water age and temperature in the distribution system. In such situations, additional technologies such as granulated activated carbon (GAC), ozone/biological activated carbon (BAC) and anion exchange resin treatment need to be considered. However, it is very challenging to identify and design a technological set-up which provides acceptable water quality at the minimum cost. Membrane filtration technologies such as NF or RO are also capable of reducing DOC, but due to their cost their implementation cannot usually be justified without additional benefits such as pathogen removal or salinity reduction. They are therefore not considered here [14].

Chlorine is the most popular water disinfectant [15] used worldwide for both primary and secondary disinfection. This paper focuses on selection of a treatment process for a chlorinated distribution system to achieve complying water quality in every location. The worst affected customers are those who receive the oldest water with the lowest chlorine residual, and hence face the greatest microbiological risk. The last customer also is at risk of exposure to the highest level of DBPs.

Treatment can only be optimised if several aspects are considered simultaneously; namely, treated water NOM, disinfectant and DBP concentrations. Reduction of regulated DBPs can be achieved by lowering the disinfectant dose, but this may reduce the disinfectant concentration below the minimum at the last customer's tap that is required to prevent compromising microbiological water quality.

In this paper, we attempt to solve the problem of selection of the optimal NOM removal process by firstly identifying how to monitor for NOM removal and what level of removal is required. Then individual processes are tested to determine whether they can achieve this limit and at what cost. Our objective is to deliver water of complying quality to the customer tap, using the most cost effective water treatment technology.

2. Selection of a method to monitor NOM removal for optimisation

NOM in water is derived mainly from decaying vegetation and consists of a complex mixture of organic compounds which can be subdivided into groups according to their chemical nature and separation methods. DOC refers to all dissolved organic carbon which is determined by oxidation to carbon dioxide, after subtracting carbonates present in water. Unfortunately, this relatively reliable and cost efficient analytical method does not provide information about the carbon compounds present, their reactivity and how can they be removed. Characterisation methods have been reviewed and their limitations evaluated [12,16]. It is accepted ([16]) that NOM composition is far too complex to identify individual compounds and, as in other technical fields such as petroleum refining, a group characterisation is practical; e.g. [17]. Useful information may be obtained from various forms of size exclusion chromatography, but even it provides only distribution of molecular mass.

Such analytical techniques can be useful to gain an insight into various DOC removal processes. However, a translation is still needed from the individual fractions to their effects, in practical terms of water disinfection and disinfectant stability, bacterial regrowth and DBP formation. Additionally, there is a risk that such findings may be specific for a given water and may be difficult to generalise. The generic problem is that all these indicators need to be translated into pragmatic properties of reactivity with chlorine and THM formation and that translation process is, at best, only qualitative. There are surprisingly few direct testing techniques which attempt to determine parameters directly relevant to a water treatment process. One such approach [18,19] is based on adsorption of DOC on aluminium and ferric hydroxide floc, which characterised three DOC groups:

1. Inert (non-adsorbing).
2. Non-polar compounds, (non-dissociated) adsorbing independently of pH.
3. Polar compounds, of which the associated forms adsorb (with pH dependence).

This approach is by definition the most accurate for determination of DOC removability by enhanced coagulation and it can be argued that its complexity and cost are comparable with, or better than, other fractionation methods.

For the purposes of this paper, the use of NOM characterisation techniques can be reduced to DOC analysis (as it is generally available, fast and not too costly), and chlorine decay and THM formation tests, which provide accurate determination of reaction rate with all organic compounds in water.

3. Determination of maximum acceptable DOC in treated water

Often it is a non-trivial matter to determine acceptable limits for DOC and water utilities usually accept guidelines from a regulatory authority. For example, USEPA [20] is quite prescriptive in stipulating the percentage of DOC that should be removed, given raw water DOC and alkalinity, as shown in Table 1.

From Table 1, it is apparent that this approach to DOC removal is rather pragmatic, suggesting treatment within the limitations of enhanced coagulation technology, rather than targeting the final DOC regardless of its concentration in raw water. The USEPA considers enhanced coagulation to be the best available technology (BAT). The main mechanism of DOC removal by enhanced coagulation is adsorption [19]. Therefore, it is easier to remove higher concentration as it imposes a higher driving force for adsorption. However, it is more difficult to treat water with higher alkalinity as it requires a large dose of coagulant (or combination of coagulant and acid) to suppress pH to the optimum for DOC removal (approximately 5.5 in the case of ferric salts). This approach seems to encourage a reasonable effort in treatment rather than to put a limit on the minimum drinking water quality delivered to the consumer regardless of quality of the source water. We can only speculate that this is a practical approach which considers realistic cost to communities. Shortcomings of this approach are that it does not enable prediction of the water quality that will be delivered and whether this approach is adequate. Considering only the treated water quality neglects the impact of a distribution system and water temperature, which is crucial for

Table 1
Required per cent removal of TOC by enhanced coagulation [20]

	Source water alkalinity, mg $CaCO_3$/L		
Source water TOC, mg/L	0–60	>60–120	>120
>2.0 to 4.0	35	25	15
>4.0 to 8.0	45	35	25
>8.0	50	40	30

long distribution systems in a warm climate. The reader can easily imagine that a different level of DOC will be needed in a distribution system with residence time 3 d and maximum water temperature of 15°C, compared with a distribution system with water age 7 d and maximum temperature 26°C [21].

In our approach to determine an optimal DOC level for a given distribution system, we would like to predict directly water quality at consumers' taps, in terms of chlorine concentration and THMs and to base an acceptable DOC concentration on the required levels of those variables in the "worst case" locations. To target water quality at a consumer's tap, DOC level has to be translated to chlorine stability and by-product levels. Thanks to the recent development of chlorine decay and THM formation models [22], it is now possible to predict an acceptable level of treatment for a specific water, distribution system and water temperature [21]. This method predicts chlorine and THM formation due to reactions in bulk water, neglecting the effect of wall reaction. Such an approach is justified in the case of lined, larger diameter pipes (ID > 0.3 m). In smaller or unlined pipes, additional chlorine decay is to be expected, and therefore DOC will need to be reduced even further. In that respect, the proposed method represents the best possible chlorine and THM outcome in a clean and inert distribution system. This approach is schematically shown in Fig. 1.

Fig. 1 shows that a water sample prepared by a given DOC removal technology can be tested for DOC and ultimately linked with water quality in a distribution system and customers' taps. It should be noted that this relationship of Cl and THMs with DOC may be valid only for the tested water and DOC removal technology and that a different removal technology may provide marginally different DOC results. This is due to the fact that each DOC removal technology removes different fractions of DOC, and therefore each may result in a different reactivity of remaining DOC. Despite this limitation, we still use DOC to characterise each treatment, as it is a relatively fast and cheap method which provides good insight into optimisation of each DOC removal technology.

Chlorine is the most frequently used disinfectant and chloramine is an alternative for secondary disinfection. As chlorine is a stronger and cheaper disinfectant, it is the natural first choice. Chloramine should be considered only if chlorine cannot provide acceptable water quality, usually due to rapid loss of residual and high THM formation. For that reason, the feasibility of treating water to such a degree that chlorination can be used to deliver acceptable quality within the distribution system needs to be determined first.

Chlorine concentration within the distribution system is limited to an operational window, usually close to 0.2–0.6 mg/L. The chlorine level must be sufficient to provide microbial safety (≥0.2 mg/L) and it must not cause excessive taste and odour (≤0.6 mg/L) [23].

In practical terms, it is desirable that, a chlorine dose of approximately 1 mg/L can sustain the residual >0.2 mg/L until the maximum water age is reached. Chlorine stability is a key to control the THM formation. Commonly it can be expected that 1 mg Cl/L is capable of generating 3–6% of THMs or 0.03–0.06 mg TTHMs/L; therefore, a dose of 1 mg/L would generate THMs well within the USEPA limit of 0.08 mg/L. Here, it is assumed that the initial dose of 1 mg/L will rapidly decay to 0.6 mg/L or lower before reaching the first customer [23]. As the initial chlorine dose is limited by the acceptable concentration at this point, rechlorination is the only option which can maintain chlorine concentration further into the system. The bottleneck for use of rechlorination would be the concentration of THMs and cost of the rechlorination stations. Assuming an average THM yield of 4% of reacted chlorine, a total dose of 2 mg Cl/L would comply with the USEPA limit of 0.8 mg/L of THMs. If the total dose of 2 mg of Cl/L cannot maintain an acceptable residual at the end of the system, then the only option is to further reduce DOC. Benefits of single and multiple dosing of chlorine have been examined [24], from which it was concluded that rechlorination can better distribute chlorine

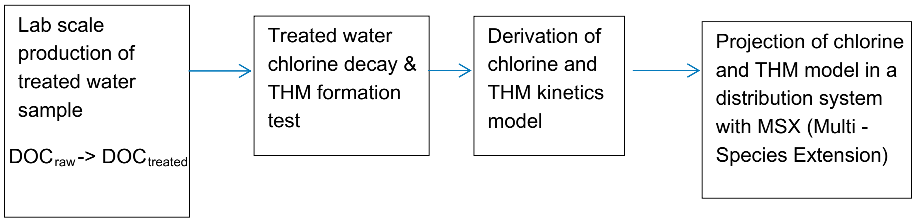

Fig. 1. Schematic of determination of water quality at the consumer tap for a tested DOC removal technology.

concentration and results in lower final THMs for the same total dose of chlorine.

While the rate of chlorine decay cannot be calculated based on the water composition (for example, DOC concentration or any other NOM characteristic), it can be readily measured by exposing a sample to various concentrations of chlorine and monitoring the resulting concentration over time. Such data can be used as a direct simulation or converted into a chlorine decay and THM formation model. Suitable models for simulation of chlorine decay and THM formation were evaluated [25]. It was concluded that two organic components reacting with chlorine is the simplest and sufficiently accurate description, over the usual operating ranges of initial and booster doses, and water temperature; viz.:

$$\mathrm{Cl} + \mathrm{F} = \mathrm{Cl}^- + \mathrm{THMs} \tag{1}$$

$$\mathrm{Cl} + \mathrm{S} = \mathrm{Cl}^- + \mathrm{THMs} \tag{2}$$

where F is the fast reacting component, S is the slow reacting component and THMs are trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$).

The reactions in Eqs. (1) and (2) are of first-order with respect to both chlorine and organic compounds, so the reaction rates can be described by Eqs. (3)–(6).

$$\frac{\mathrm{d}c_{\mathrm{Cl}}}{\mathrm{d}t} = -k_{\mathrm{F}} * c_{\mathrm{Cl}} * c_{\mathrm{F}} - k_{\mathrm{S}} * c_{\mathrm{Cl}} * c_{\mathrm{S}} \tag{3}$$

$$\frac{\mathrm{d}c_{\mathrm{F}}}{\mathrm{d}t} = -k_{\mathrm{F}} * c_{\mathrm{Cl}} * c_{\mathrm{F}} \tag{4}$$

$$\frac{\mathrm{d}c_{\mathrm{S}}}{\mathrm{d}t} = -k_{\mathrm{S}} * c_{\mathrm{Cl}} * c_{\mathrm{S}} \tag{5}$$

$$\frac{\mathrm{d}c_{\mathrm{THM}}}{\mathrm{d}t} = -y_{\mathrm{THM}} * \frac{\mathrm{d}c_{\mathrm{Cl}}}{\mathrm{d}t} \tag{6}$$

where k is the reaction rate constant for a given component [$(\mathrm{mg/L})^{-1}\ \mathrm{h}^{-1}$],

c is the concentration of a given component [mg/L],

y_{THM} is yield for THM [mg THM/mg Cl reacted] and

t is time [h]

From Eq. (6), formation of THMs is directly proportional to concentration of reacted chlorine. For this reason, it is not recommended to use chlorine in pre-chlorination of raw water. This practice used to be common as pre-chlorination provides benefits in reduction of turbidity, but it invariably results in production of THMs, which are often not removed by subsequent treatment processes and so contribute to the final concentration of THMs in the distribution system. The modelling approach described above quantifies formation of THMs for any given dose of chlorine and position in the distribution system. Such an approach is superior to a THM formation potential, which only determines maximum concentration of THMs, which can also be derived by the model (on the basis of the initial concentration of fast and slow reacting compounds and the THM yield).

As can be expected, each DOC removal technology may have a different impact on fast- and slow-reacting components. Therefore, the desirable level of DOC removal would be specific for a given technology. It would be expected that more DOC needs to be removed by enhanced coagulation to obtain comparable chlorine stability than by the O_3/BAC process, where the major effect is in changing the chemical structure of DOC, rather than its plain removal. To demonstrate the effect of DOC removal by enhanced coagulation, the effect of DOC removal on reduction of fast- and slow-reacting components of chlorine decay was tested [26]. It was found that increasing coagulation dose sharply reduced the slow-reacting component. This is understandable as enhanced coagulation more easily removes the slow-reacting, high molecular mass compounds than the low molecular mass, fast-reacting component.

Unfortunately these conclusions are only qualitative and chlorine reactivity has to be determined experimentally for each water and DOC removal technology. In practice, this means that every DOC removal technology to be evaluated has to be tested by preparing samples treated to various degrees and to test them for chlorine stability. It is relatively straightforward to prepare samples treated by enhanced coagulation in a jar test, providing confidence that such an approach will approximate a full-scale plant. For other DOC removal technologies such as GAC and O_3/BAC, it is much more difficult to generate samples representing a full-scale plant. The reason is that, while ozone dose and reaction can be readily simulated in laboratory-scale equipment, the simulation of BAC is more difficult to scale and its performance is determined by long-term maturation of microbial populations in the BAC column. Similarly, production of a representative sample from a GAC column is difficult as it produces a variable sample for the duration of a run.

If chlorine stability is not satisfactory, or THM formation is too great, chloramination can be considered before investing in further DOC removal. However, there is no equivalent methodology currently available to assess water quality in a distribution system from a sample of chloraminated water. Chemical decay of chloramine is described by a complex set of reactions in the US EPANET MSX and Innovyze H_2OMap MSX software [27]. Chemical stability of chloramine is not a limiting factor because chloramine (as formed for water disinfection) decays by less than 5% per day [28]. Therefore, after 10 d, there would still be more than 50% of chloramine available. As mentioned above, the major concern is microbially assisted chloramine decomposition. This process is understandably complex and no adequate description is yet available.

In summary, for a chlorinated system, it is possible to predict the system performance in terms of chlorine and THM concentration profiles, on the basis of chlorine decay tests on a sample of treated water, assuming that a representative water sample can be produced by the DOC removal process of interest.

4. Evaluation procedure for DOC removal processes

From a large number of potential DOC removal processes reported in the literature [29] and [12], only a small number are implemented as DOC removal technologies. While we could not identify any statistical data on implementation of DOC removal technologies, based on our experience and recommendations of US EPA, the following processes are the most frequently used:

- Enhanced coagulation.
- Activated carbon (either as powdered activated carbon (PAC) or GAC).
- Oxidative processes (Ozone/BAC).
- Ion exchange (IEX).

As well as being cost-effective, a DOC removal process is also expected to have easily verifiable performance for a given water and can be designed with a predictable outcome. For each DOC removal technology, the following aspects need to be considered:

- Can a sample be prepared at acceptable cost to evaluate treated water quality (Test to produce water sample).
- How well can DOC removal be predicted for various process parameters (DOC removal model for the process).
- How well can impact of process parameters on Cl and THM reactions be predicted (Cl and THM model as a function of DOC).
- How well can the full-scale process be designed and the cost of water treatment be estimated.

A qualitative evaluation of aspects for each DOC removal process is shown in Table 2.

Table 2 shows that enhanced coagulation can be relatively easily simulated and, based on the jar tests, a DOC removal model can be formulated. It is also feasible to derive the model for chlorine reaction and THM formation. The main advantage is that the jar test, although a batch process, represents the continuous full-scale operation reasonably well. This may be to some extent true for an ion exchange process, where a jar test is also used in batch mode to estimate performance of a full-scale plant, but modelling of this DOC removal process to use in plant design is not as practical and accurate [30,31] as in the case of enhanced coagulation [19].

The GAC process is not steady state by its nature, as each column is continually changing its performance while carbon is becoming saturated with DOC. This process is more difficult and time-consuming to measure in the laboratory and due to involvement of biological processes not always directly scalable. One possible method of designing a GAC absorber is to use rapid small-scale column experiments [32] or to use a mathematical model based on batch experiments [33]. Similar problems exist in the case of ozone/BAC where GAC first needs to be saturated and the biological processes stabilised to produce a realistic water sample.

Based on the above described difference in assessing performance of various DOC-removal/ chlorine-

Table 2
Qualitative comparison of predictability of DOC process performance by laboratory tests and modelling

Process	Test to produce water sample	DOC removal model	Cl/THM model	Process cost /predictability
EC	Jar test	+++	++	+/+++
GAC	Column test	++	+	++/++
IEX	Jar test	+	+	+++/++
O_3/BAC	Ozonation/BAC	?	?	+++/+

Notes: +++ high, ++ medium, + low, ? uncertain.

stabilising technologies, it is not practical/cost-effective to produce data for all of them that are sufficient for rigorous comparison. Based on generic features of the considered processes, it appears practical to evaluate capability of enhanced coagulation and determine how close to acceptable water quality it is possible to get. If it becomes apparent that enhanced coagulation on its own is not sufficient, then an additional process needs to be investigated. On the basis of water and system specifics, one of the processes described may appear to be preferable and can justifiably be investigated further.

5. Description of DOC removal technologies

In this part we will focus on a description of most commonly used DOC removal processes and how to determine which one is suitable in a given situation.

5.1. Enhanced coagulation

In its Disinfection By-Product Rule, USEPA recognises enhanced coagulation as BAT for removal of THMs and HAAs precursors [34]. Coagulation is traditionally used for removal of turbidity caused by colloidal particles in sources of drinking water. These particles (size 0.001–1 μm) are too small to be directly filtered, so it is much more efficient to aggregate them in larger particles by a process referred to as coagulation. Larger coagulated particles settle at a much faster rate than colloidal particles and are also filterable by media (sand) filters.

Traditionally, aluminium and ferric salts are used to flocculate colloidal particles. This process also reduces the concentration of DOC and this removal can be increased by increasing the dose of metal salts above the demand for flocculation. Since ferric salts provide higher removal of DOC, it is considered further. Ferric chloride in water hydrolyses to ferric hydroxide and hydrochloric acid:

$$\mathrm{FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl} \qquad (7)$$

Ferric hydroxide has a role in coagulation and adsorption of DOC while anions Cl^- or SO_4^{2-} cause acidification so that addition of ferric salts, usually ferric chloride, to raw water affects its alkalinity, pH and ultimately salinity according to the equation:

$$\mathrm{3NaHCO_3 + FeCl_3 + 3H_2O = 3NaCl + Fe(OH)_3 + 3H_2CO_3} \qquad (8)$$

Carbonic acid has the capacity to reduce pH to 4.5. If natural alkalinity of raw water or the resulting pH is too low, an alkali such as sodium hydroxide, sodium carbonate or calcium hydroxide needs to be added:

$$\mathrm{3NaOH + FeCl_3 = 3NaCl + Fe(OH)_3} \qquad (9)$$

$$\mathrm{3Na_2CO_3 + 2FeCl_3 + 6H_2O = 6NaCl + 2Fe(OH)_3 + 3H_2CO_3} \qquad (10)$$

$$\mathrm{3Ca(OH)_2 + 2FeCl_3 = 3CaCl_2 + 2Fe(OH)_3} \qquad (11)$$

According to above equations Eqs. (9) and (10), 1 mg Fe in the form of $FeCl_3$ generates $3 \times (23 + 35)/56 = 3.11$ mg NaCl/mg Fe.

Increase in salinity, together with the disposal cost of ferric hydroxide sludge, limit the maximum dose of ferric chloride. While MIEX resin is dosed at 2–15 mL/L, ferric chloride dose is generally limited to approximately 100 mg/L. The situation is even more critical in the treatment of recycled water where increased coagulant dose causes accumulation of salinity in water and limits the fraction of water which can be recycled. As evident from the above, there is a significant limitation on utilising the full potential of enhanced coagulation or rather maximising utilisation of adsorption of DOC on ferric hydroxide.

Another weakness of the enhanced coagulation process is the concurrent flow of DOC in water and the adsorbent ($Fe(OH)_3$). The situation is shown in Fig. 2.

Fig. 2 shows that ferric hydroxide, formed after addition of ferric chloride, flows with water. At the end of the process, assuming the equilibrium, ferric hydroxide is loaded with DOC by the lowest DOC concentration in the finished water. This makes the process inefficient and large amount of ferric hydroxide would be needed to further reduce DOC in water. In conjunction with the limit on the dose of coagulant, this is the limiting factor for DOC reduction by enhanced coagulation. This situation is shown in Fig. 3, which compares DOC removal by iron oxide-coated sand for two process flows.

Fig. 3 shows that for lower doses of ferric oxide (<100 mg/L Fe) the difference between concurrent and counter-current flow is minimal. At higher doses, the difference in DOC removal becomes more

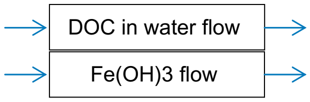

Fig. 2. Schematics of flow of water with DOC and ferric hydroxide adsorbent.

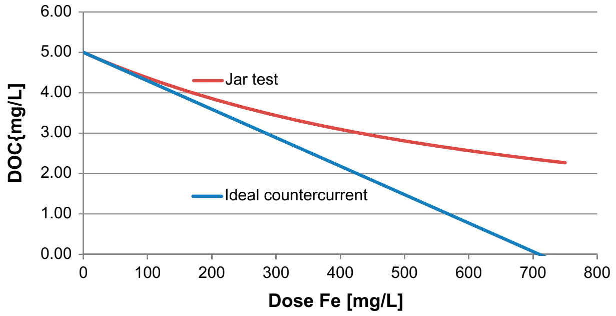

Fig. 3. Comparison of DOC removal by iron oxide media in concurrent (Jar test) and counter current process flow of water and ferric hydroxide, based on [35] data.

pronounced, so that at 400 mg Fe/L the counter-current process would reduce DOC from the original 5 mg/L to approximately 2 mg/L and concurrent only to 3 mg/L. This comparison is based on data with iron-coated sand [35], which had significantly lower capacity than ferric hydroxide formed during enhanced coagulation.

5.2. Activated carbon

Activated carbon is thermally treated organic material which is pyrolysed to practically remove most of the hydrogen and oxygen, leaving only carbon and some inorganic constituents (ash). This material is further treated to increase its porosity and internal surface, which facilitates adsorption of molecules. In water treatment, two forms of carbon are used—powdered and GAC. Activated carbon, given sufficient contact time and dose, can remove a significant proportion of DOC. The problem is usually its cost and the disposal of spent activated carbon. Activated carbon can also be thermally regenerated, but the logistics of the process often makes it uneconomical.

PAC can be used in combination with coagulant to increase removal of DOC [36] and other compounds such as algal toxins and taste- and odour-causing compounds. The PAC process can be tested in a jar test and PAC is dosed only when required by the inlet water quality. The disadvantage is that it is also a concurrent process, so PAC loading is driven by the lowest concentration of DOC leaving the process. GAC operated in columns approaches a counter-current process, where GAC at the entry point of water is maximally loaded, but the process is in its nature unsteady. New GAC generates water practically without DOC and older GAC only partially reduces DOC. Direct control of DOC removal on the GAC column is difficult without modifying contact time. Usually a number of columns are employed with a range of service time, which enables partial control of the final DOC. GAC is also recommended by the USEPA as BAT and it additionally has benefits of removing many other contaminants including heavy metals (such as As, Cu, Pb, Hg and Cd). Usually water utilities are comfortable with operating GAC contactors after coagulation and filtration as a polishing step. Cost of GAC has been reduced recently to approximately \$1,000/m^3.

5.3. Magnetic ion exchange resin (MIEX)

In the MIEX process, the resin particles are small (0.1 mm) with a magnetic core which makes them cluster into larger lumps which have higher sedimentation velocity so they can be readily separated. MIEX has capacity to exchange Cl^- for weak organic acids R-COOH. The mechanism of DOC removal is different from adsorption technologies such as activated carbon and enhanced coagulation. Its advantage is that it can remove small polar (negatively charged) molecules of organic acids and partially bromide [37], which are not amendable to removal by enhanced coagulation.

MIEX is typically used as a pre-treatment before coagulation/enhanced coagulation. It has the capacity to reduce DOC and also the subsequent dose of coagulant. As indicated, direct comparison of the cost of various combinations of technologies is difficult and usually based on over-simplification. The cost of the MIEX process was compared with GAC and Ozone/BAC processes and it was concluded that MIEX has the lowest nett present value [38]. The difference was mainly in the operation cost, which was higher for GAC and for O_3/BAC. This was probably strongly influenced by the relatively short assumed GAC life of two months for the plain GAC adsorption process and two and four months for O_3/BAC. MIEX can prove useful in high DOC waters that are difficult to treat. Probably its main drawbacks are attrition loss of resin which can reach 0.05% of the dosed resin and disposal of salty regenerator solution with removed DOC.

5.4. Ozone/BAC

Ozone/BAC is a technology usually used as a final polishing step of water treatment. Coagulated, settled and filtered water is exposed to a dose of ozone, which reacts with part of the DOC, converting it to BDOC (biodegradable dissolved organic carbon). Ozonated water is biostabilised by BAC, which removes the BDOC fraction. Generally, this process does not reduce DOC as much as other removal processes such as enhanced coagulation and GAC, but its impact on chlorine reactivity and THM formation is higher than would be proportional to the level of DOC removal. This is due to ozone reacting in a way similar to chlorine, therefore oxidising chlorine reactive compounds which are subsequently removed by BAC. In that respect, the combination of ozone/BAC is more selective in removing chlorine reactive compounds than other processes. The combination is advantageous as full mineralisation of DOC by ozone would be exceedingly expensive, but just converting refractory DOC to BDOC which can be removed by a much cheaper BAC process presents a significant advantage in comparison with employing processes separately. This principle was utilised by repeating the ozonation and BAC treatment [39]. DOC removal of 95% was achieved by repeating the process ten times (O_3 + BAC). The utilisation of ozone was better that in a single large dose when ozone would also react with BDOC, and therefore consume expensive ozone on a process which can be done much cheaper by a biological process. In a focus on DOC removal, the true objective of achieving chlorine stability and reduction of THMs was unfortunately lost and no chlorine decay and THM formation tests were presented.

Cost of membranes (MF,UF,NF and RO), ozone, hydrogen peroxide, UV and BAC for treatment of recycled water were compared [40], with the conclusion that membranes were the most expensive and ozone the cheapest. Here, the focus was on the removal of trace organics such as endocrine disrupting compounds, which were present in lower concentrations than typical DOC in drinking water. Ozone has a distinct advantage of being one of the strongest disinfectants inactivating even the most resilient pathogens. This effect needs to be taken into account when considering ozone for DOC removal. On the other hand, ozone tends to oxidise bromide in water to bromate. With the WHO guideline for bromate of 0.01 mg/L [41], formation of bromate needs to be considered when evaluating suitability of an ozone process.

A case where a distribution system was switched to chloramine disinfection to remove high THM formation was reported [42], but the chloramine residual was difficult to sustain, due to extensive nitrification. Subsequently, the WTP was upgraded with ozone/BAC. With time, a more serious nitrification problem developed, compromising disinfection. Use of jar testing and chlorine stability modelling indicated that after the upgrade (to ozone/BAC) the system would perform well with chlorine in terms of both residual maintenance and THM formation. This was confirmed after switching back to chlorine.

6. Selection of BAT for DOC removal

There is currently no analysis/procedure which can determine either DOC removal or chlorine stability and THM formation for a given treatment method, without laboratory experiments. Therefore, laboratory tests need to be performed for:

(1) DOC removal.
(2) Chlorine decay.
(3) THM formation.

While there are other analytical techniques providing more detailed insight into composition of DOC in water, it can be argued that their usefulness is restricted as ultimately it is chlorine stability and by-product formation which are the centre of interest. Unfortunately, only direct testing with chlorine provides quantitative answers. From this point of view, even DOC measurement can be bypassed and only chlorine decay jar tests performed. For practical purposes, DOC measurement appears very useful as it is a relatively fast technique with low operation cost.

It would be rational to test the most commonly used DOC removal processes first. These are:

(1) Enhanced coagulation (as the coagulation process is expected to be included in most treatments).
(2) Ozone/BAC.
(3) GAC of coagulated and filtered water.
(4) MIEX and its synergy with coagulation.

These tests of individual DOC removal methodologies would determine DOC removal by a single process. In practice the processes are usually combined; for example, the MIEX process is commonly used as “pre-treatment” for coagulation. To be able to optimise individual processes and their combination, it seems that the only plausible way to do so is to build at least an approximate mathematical model. There is no absolute rule about which would be the most suitable additional process if enhanced coagulation is not sufficient. Generally speaking, for modest polishing of chlorine reactivity and THMs formation, O_3/BAC process can be considered. For moderate additional removal of DOC (around 1–2 mg/L) GAC may be suitable and for high DOC waters (DOC > 10 mg/L) MIEX may be a reasonable choice.

7. Conclusion

There is a lack of process selection methodologies for DOC removal. The removal of DOC in drinking water treatment can be achieved by a number of processes. The main ones adopted, as they are usually most cost-effective, are enhanced coagulation, ozone/BAC, GAC and MIEX.

Chlorine decay and THM formation testing of a sample of treated water (usually from a bench scale test rig), and modelling of chlorine decay in a distribution system, has proven a robust method to verify suitability of the tested process for a given situation.

Since coagulation, sedimentation and filtration constitute a traditional water treatment train, which needs to be adopted to remove turbidity, it appears logical to extend this process to enhanced coagulation and determine whether it provides acceptable water quality for the conditions in the distribution system.

The enhanced coagulation process should therefore be optimised first, to determine whether it can provide the desired end-of-system quality. If it cannot, only then should ozone/BAC, GAC or ion exchange processes be considered. In the majority of cases, all these technologies can reach the desirable DOC removal, but are usually less cost-effective.

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