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Experimental Application of an Advanced Separation Process for NOM Removal from Surface Drinking Water Supply

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Abstract: Natural organic matter (NOM) in drinking water supplies significantly impacts on water supply quality and treatment, due to observed reactivity with many dissolved and particulate species. Several technologies are used nowadays to remove NOM from the water supply. The evolution of water-related directives, and progressively more restrictive standards for drinking water, however, call for the investigation of advanced, more efficient, and cost-effective water treatment processes. This paper contains a brief overview on the state-of-the-art methods for NOM removal from supply waters, and describes the experimental application of an advanced technology, tested and validated at the pilot scale on the water supply source of a town in Poland. The process allowed significant removal of natural organic matter (about 50% as Dissolved Organic Carbon) and turbidity (from 50% to 90%), however, these results requested significant additions of powdered activated carbon. The key to success of this type of process is a correct setup with the identification of optimal types and dosages of reagents. Based on the results of the tests conducted it is foreseeable that this technology could be used onsite, not only for removal of NOM, but also of other hard-to-tackle pollutants potentially contained in the freshwater supply and not presently considered.

Keywords: natural organic matter (NOM); coagulation; adsorption; flocculation; activated carbon

1. Introduction

Natural organic matter (NOM) is a complex, heterogeneous mixture of organic compounds (aromatic, aliphatic, phenolic, and quinonic structures) with varying molecular sizes and properties, deriving from various sources, commonly present in surface and ground water bodies. NOM can be microbially-derived (autochthonous), result from leaching and extracellular release processes of algae and bacteria, or originate from decomposition and leaching of plant and soil organic matter (allochthonous). Due to its complexity and heterogeneity, the structural and functional characterization of aquatic NOM is extremely difficult. Commonly, it can be characterized into hydrophilic and hydrophobic fractions: the former includes carboxylic acids, carbohydrates, and proteins; the latter, humic substances (HS) [1], a broad class of interrelated compounds, including humic and fulvic acids. The compositions of HS varies from source to source with respect to solubility and reactivity [2,3]. A NOM classification scheme can be represented, as shown in Figure 1 [4]. Online analytical instrumentation has made significant progress recently [5,6]. A range of analytical techniques that can offer detailed information on NOM specific characteristics is reported in Table 1 [7–10].
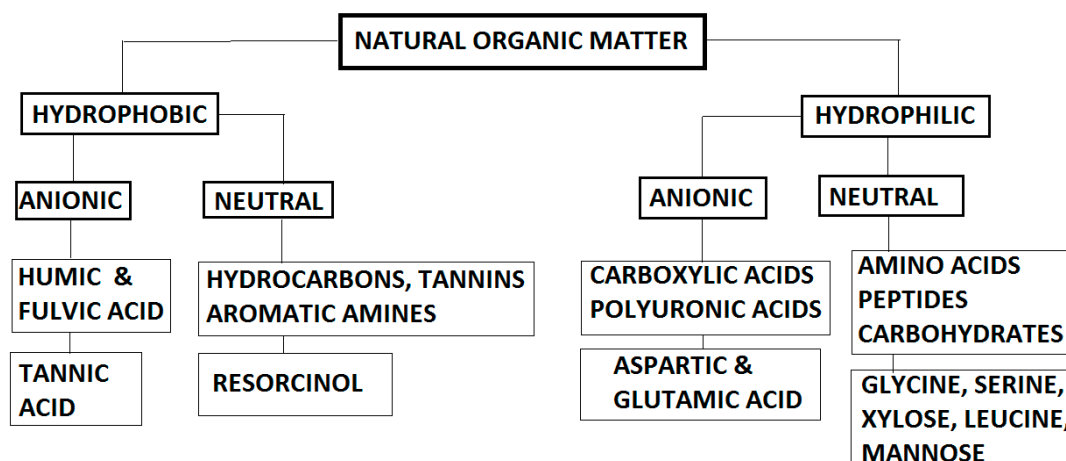
Figure 1. NOM classification tree (redrawn from [1,3,4]).

Table 1. Summary of analytical techniques for NOM investigation.

Parameters	Analytical Tools
Colour	Visible spectrophotometry Visual comparators
Aromaticity (UV [1] absorbance)	UV spectrophotometry
Total organic carbon Dissolved organic carbon (DOC) Biodegradable organic carbon (BDOC)	DOC Analyser, LC-OCD [2] liquid chromatography
Assimilable organic carbon (AOC)	Bioassays (*Pseudomonas fluorescens* P17, *Spirillum* sp. NOX) or (*Stenotrophomonas* sp. ZJ2, *Pseudomonas saponiphila* G3 and *Enterobacter* sp. G6)
Bacterial regrowth	Bacterial regrowth potential (BRP)
Molecular weight distribution	High-performance size exclusion Chromatography (HPSEC)
Hydrophobicity/hydrophilicity	Rapid fractionation (RF)
Trihalomethane formation potential (THMFP)	Gas chromatography (GC)
Functional groups (aliphatic, aromatic, nitrogen-containing)	Gas chromatography-mass spectroscopy (GC-MS) Infrared spectroscopy (FTIR) Nuclear magnetic resonance (NMR)

[1] Ultraviolet (light); [2] Liquid Chromatography—Organic Carbon Detection.

Amount and characteristics of NOM in surface waters depend on climate, geology, and topography, however, recent literature reports a worldwide, continuing increase in colour and NOM of surface waters, in particular in the Northern Hemisphere [11,12]. Temperatures, quality and amount of precipitation, and the decline of acid deposition are being pointed at as reasonable explanations for this phenomenon [13]. Although NOM itself is not known to have any direct effects on human health, reducing its levels before water disinfection and distribution is important to achieve safe, high-quality production of drinking water. Its presence can, in fact, lead to impaired water quality due to reaction with oxidants (e.g., chlorine) during disinfection to form halogenated disinfection by-products (DBPs, namely trihalomethanes—THMs—haloacetic acids, haloacetonitriles, and haloketones) both reducing their disinfection power, and increasing disinfectants demand; stabilization of certain particles, inhibiting their removal during treatment; and behaviour as an electron donor for delayed "regrowth" of heterotrophic bacteria in distribution systems [14].

In addition to these effects, NOM may affect organoleptic properties of water, such as colour, taste, and odour, rendering its consumption unpleasant. It may also affect process design, operation and maintenance of water treatment plants; modify coagulation conditions and process performance,

and increase coagulants demand; affect corrosion processes and form complexes with, or increase the mobility of, chemical substances found in nature; foul membranes; reduce adsorption capacity of granular or powdered activated carbon (GAC/PAC) by pore blocking; and compete with taste and odour compounds for adsorption sites in GAC/PAC processes [15].

NOM-related issues can raise to significant proportions in view of the current water use paradigms, promoting local recycling and reuse of wastewater [16–18]. More frequently wastewater could (will) be treated to discharge standards, temporarily stored in surface or ground water reservoirs [19], and abstracted later for water supply purposes, pending additional treatment [20].

This paper will first present a brief state-of-the-art summary of NOM removal technologies, and will then illustrate results obtained by the authors in a case study concerning NOM removal with an advanced separation process involving coagulation/flocculation and ballasted sedimentation processes on an artificial surface water body near a Western Polish town that is being targeted as a possible source of supply water for a bottled beverage industrial facility. The reservoir had shown periodically high NOM (and turbidity) content, and local water was, hence, treated in a pilot plant with the objective to verify whether good quality drinking water could be obtained, and under which process conditions.

2. Drinking Water NOM Removal: A Current State-Of-The-Art Summary

NOM can be removed by means of several processes, including GAC adsorption, coagulation, membrane filtration, and biological degradation. Coagulation is often used as a pretreatment, and in cases where microfiltration, alone, is inadequate. NOM can also be partly transformed by advanced oxidation processes, which have gained some importance in water treatment. Filtration by ultrafiltration (UF) and nanofiltration (NF) membranes can also effectively remove NOM with relatively low operating pressure [21]. Some state-of-the-art processes are briefly analysed in the following sections.

2.1. Coagulation

Coagulation is a process commonly used to neutralize suspended particle charges in a solution, forming a gelatinous mass that traps them, thus forming a mass large enough to settle, or be trapped in a downstream filter. It is probably the most commonly used method for NOM removal. Conventional coagulation processes may be complemented by other physicochemical processes, including rapid and slow mixing (flocculation), to increase floc dimensions, sedimentation, filtration, and disinfection. Coagulation reactions take place almost instantaneously in a rapid mix stage, and continue until water is filtered or settled. Its effectiveness affects the efficiency of the subsequent sedimentation/filtration processes. Effective coagulation is achieved by the addition of charged species into the water. The two most commonly used, in practice, are hydrolysing metal ions Al^{3+} or Fe^{3+}, typically as aluminum sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$), respectively. The former, commonly referred to as alum, is the most widely used coagulant in water treatment processes.

NOM removal by coagulation is due to several mechanisms, which include double layer compression, charge neutralization, sweep coagulation, and interparticle bridging [22]. Several factors influence efficiency and effectiveness of coagulation by metal salts, including, but not limited to, coagulant dose, pH, alkalinity, temperature, and ions present in the solution. Although maximum adsorption of humic and fulvic acids occurs under acidic conditions, studies have shown that this is the key mechanism for their removal over the entire pH range [23]. Hydrophobic humic molecules, those most easily removed by coagulation, are strongly influenced by physical adsorption [24]. There is general evidence that higher molecular weight NOM-compounds are more easily removed than their low molecular weight counterparts.

Synthetic and natural polymers have been used for some time as primary coagulants or flocculant aids. Cationic polyelectrolytes are most commonly used, since NOM in solution is likely to be negatively charged. It is well established that polymer flocculants increase floc size and strength, improving floc sedimentation, however, their effect on NOM removal is not well understood, yet.

Polymers are commonly used in combination with conventional coagulants to lower process costs by lowering coagulant demand and creating larger aggregates in the liquid from already-formed microflocs. Polyelectrolytes may achieve better floc characteristics in terms of size, strength, settleability, and filterability, resulting in smaller residual sludge volumes, and have shown to be more resistant to pH changes than conventional coagulants. NOM-removal capacity of different polyelectrolytes will vary amply on a case-by-case basis.

Recently, new technology has been introduced to coagulation processes, in the form of composite inorganic–organic coagulants, obtained combining organic polymers to inorganic polymer flocculants (IPFs), with the aim of combining advantages of both components [25]. Electrocoagulation-electroflotation (ECF) technology is a new treatment process consisting of applying an electrical current to coagulate and flocculate contaminants without the need of the addition of coagulation aids. Electrocoagulation occurs with the current being applied, setting particles into motion, and causing their agglomeration [26]. Electrocoagulation-flotation is an alternative method to classic chemical coagulation. Interest on ECF is mainly due to its capacity of reducing the need for chemicals, as electrodes provide the substitute coagulation capacity (coagulants and electrodes perform similar functions, neutralizing the charge of the particles, allowing them to agglomerate and settle). Therefore, ECF reduces waste production from water/wastewater treatment, and reduces the process time necessary for treatment.

Coagulation has also been used in combination with other treatment processes; for example, magnetic ion exchange resin (MIEX), pre-oxidation, AC (activated carbon) and membrane filtration. Some combination processes will be discussed in the following sections.

2.2. Activated Carbon Adsorption

AC is an extremely effective adsorbent used widely in environmental applications and in drinking water treatment, which has proven to remove micropollutants, pesticides, organic chemicals, tastes, odours, and algal toxins. NOM is removed by granular or powdered AC (GAC/PAC), although often in competition for adsorption sites, decreasing adsorptive removal of other pollutants. Although the adsorption behaviour of NOM is difficult to understand due to its heterogeneous nature [27], studies have shown that this process is controlled predominantly by the relationship between NOM's molecular size distribution and pore size distribution of AC [28]. For this reason, direct NOM adsorption on GAC is generally not recommended, since adsorption media capacity is quickly saturated by large humic molecules causing early pore blocking. Pre-coagulation applied before GAC filtration has frequently proven to remove particles that might otherwise clog filters. Pre-coagulation, itself, may remove a fraction of NOM, reducing the load on filters, and extending their useful life [29].

AC post-filtration has also shown efficiency in protecting treated water quality in terms of DBP formation. AC filters can, in fact, be colonized by heterotrophic biomass, creating biological AC processes (BAC), which reduce concentrations of easily-assimilated, biodegradable compounds. PAC addition may also enhance coagulation, reducing required coagulant doses and increasing process efficiency [30].

The lifetime of GAC filters can be extended by thermal reactivation, but this can lead to burn-off enlargement of medium macropores, increasing removal of high molecular weight (M_W) NOM and decrease that of low M_W [31]. Guirguis et al. showed that GAC filters performance can be improved by pre-ozonation, by rendering certain organic species more sorbable and biodegradable: at ozone dosages between 3 and 14 mg/L, addition enhanced effluent quality, extended operation life and working capacity of the activated carbon, and resulted in high cumulative removals [32].

GAC adsorption can be preceded by ClO_2 oxidation or ozonation: it has been shown that, in small doses, it can increase molar mass of some NOM molecules, increasing their adsorption in the high MW range [33]. At high dosages, however, ClO_2 may actually break-up larger NOM molecules [34]. Additionally, interaction among these compounds may lead to the undesired formation of toxic organic by-products. Lately, new sustainable materials from waste recovery have been indicated as potential

GAC substitutes. In particular, biochar from organic waste pyrolysis has been positively tested for this purpose [35,36].

2.3. Membrane Filtration

Membrane filtration processes have recently become a common application in many compartments of water and wastewater treatment processes. These include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) processes, all requiring an induced pressure gradient for operation. These are characterized by differently-sized retention ranges: microfiltration: 0.1 to 10 μm (macromolecules of molecular weights generally less than 100,000 g/mol); ultrafiltration: 0.1 to 0.01 μm (able to retain proteins, endotoxins, viruses and silica); nanofiltration: 0.001 to 0.01 μm (filters multivalent ions, synthetic dyes, and sugars); and reverse osmosis operates with the finest separation membranes from 0.0001 to 0.001 μm (retaining almost all molecules except for water).

Nanofiltration (NF) technology has proved to be a successful alternative process for drinking water treatment, including NOM removal, due to its superior removal of disinfection by-product precursors, minimal use of chemicals, reduction in sludge production, and potential for use in compact systems [37,38]. Membrane fouling and the decline of flux capacity are the major problems associated to membrane techniques at the moment [39]. Additionally, process cost is presently higher than both coagulation and GAC adsorption; on the other hand, its rate of decrease over the past years has been greater than that of others, so it might become competitive in the near future. Typical pore size of these membranes is 1–5 nm, operated at a pressure of 4–8 bar [40]. Studies in Norway [41] showed that the success criteria for operating NOM-removal NF-processes consist of the use of low flux (<20 L/m^2·h), combined with low recovery (<70%), and adoption of proper cleaning procedures.

Special attention should be paid to membrane treatment waste disposal (reject water), containing all the components that are rejected by the membrane. Different treatments, including coagulation (iron and alum), oxidation (chlorine, permanganate, and ozone), and powdered activated carbon (PAC) adsorption, can be used to recover the residual micropollutants and organic matter from UF and NF retentates. Ozone usually exhibits better micropollutants, organics, and UV254 removal efficiencies than chlorine and permanganate, while coagulation preferentially removes high molecular weight compounds [42].

2.4. Oxidation and Advanced Oxidation Processes

An alternative group of technologies to remove NOM and minimize DBP formation are the advanced oxidation processes (AOPs). These are near-ambient-temperature processes that involve generation of highly reactive radical intermediates, especially hydroxyl radicals. These are extremely reactive, and capable of oxidizing NOM fractions present in raw waters. The most common process to generate OH is through the use of combined catalytic oxidants, such as ozone-ultraviolet (O_3-UV) and hydrogen peroxide ultraviolet (H_2O_2-UV). Although both the above processes can produce OH, the O_3-UV process provides the maximum yield of ·OH per oxidant [43]. Photo-Fenton processes, where iron species may function as enhanced catalysts, as well as the coagulant, have been investigated for NOM removal with good results [44], but it must be said that none of all these mentioned technologies, including AC and ultrafiltration, can completely remove NOM. An overview of recent studies dealing with AOP methods for removal of NOM and related compounds from drinking water was presented recently by Matilainen and Sillanpää [45]. Recently, a more efficient radiolysis-based process has been indicated as a possibly efficient means to remove most organic compounds from water, however, it has not been specifically tested for NOM removal purposes, yet [46,47].

2.5. Ballasted Flocculation and Separation

Ballasted flocculation (BSF) is a physical-chemical separation process that employs a high-density additive to promote the formation of a heavier-than-usual floc, which then settles more rapidly than in

the traditional flocculation process. Even these particular processes have, in time, been modified by the addition of AC/PAC, or other additives, in order to improve their performance. As an example, a patented version of BSF, called Actiflo-Turbo®, developed by Veolia Water Solutions (St. Maurice, France), could be mentioned. A field test of this system in France, was described by Aliverti et al. [20]. Microsand (40–150 μm) used as ballast agent increases settling velocity and overflow rate, reducing the system areal footprint compared to conventional coagulation/flocculation/clarification processes and making ballasted flocculation significantly different from the conventional flocculation treatment. Different types and doses of coagulants (usually alum and ferric chloride), flocculants (cationic/anionic polymer) and microsand are needed, depending on influent hydraulic loadings and water quality constituents' characteristics. In most cases, removal rates of turbidity and solids have been above 90%, and above 60% for organic matter. A notable property of these systems is that they can be quickly stepped up to treat larger flows on demand, without sensible loss of performance [48]. A typical application scheme of ballasted flocculation to drinking water treatment is depicted in Figure 2. The BSF process for surface water treatment has been shown particularly effective in eliminating turbidity, colour, suspended solids, SS-attached bacteria, and NOM.
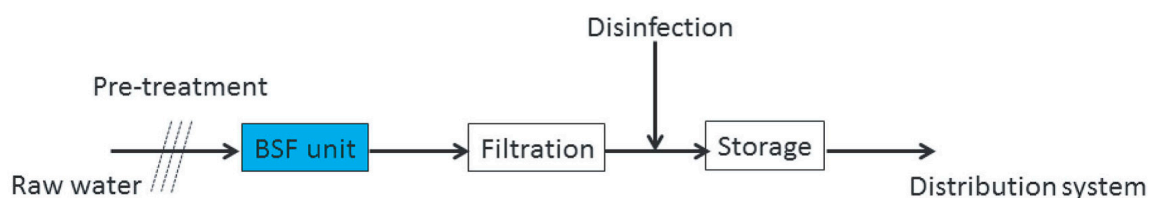

Figure 2. Ballasted flocculation scheme for drinking water treatment.

Generally, dosages of additives vary widely: alum from 5 to 150 mg/L; ferric chloride from 40 to 190 mg/L, polymer from 0.3 to 1 mg/L, sand from 3 to 12 g/L (as an initial dose, which is then recycled within the system) for different types of application. Not necessarily large dosages of additives would increase removal efficiency of the process: this has to be optimized in accordance with influent hydraulic loads and water quality constituents and, therefore, dosages of chemicals are highly case specific and need to be determined locally by jar tests. Limitations of the BSF system are: higher chemical dosage requirements than the traditional process, possible pump problems due to ballast material, and relatively new technology without long-term performance history.

Additional versions of this technology have been developed using magnetic powder (MP) as a ballast agent instead of microsand. Reportedly, use of MP generates more compact, though larger, flocs: MP ballasted flocs were shown to be nearly three times larger than ballasted MS, and six times larger than in conventional coagulation; thus, small suspended particles are better enclosed and removed by flocs [49].

After examining various options, it was decided to adopt ballasted flocculation as a test technology for this case study. The choice was due to several factors, including previous experiences, search for simple, low maintenance processes, avoid risk of DBP formation, and, finally, the availability of a pilot, left from previous studies that could be easily adapted to investigate the present technology.

3. Materials and Methods

A simple pilot plant for ballasted flocculation, with a nominal 50 L/h capacity was built and installed near an artificial reservoir in a western province of Poland to test the possibility of drawing additional good quality supply water, potentially needed in view of possible operation expansion of a local industrial soft drink factory that expressed the wish to remain anonymous. The reservoir had shown periodically high NOM contents in the past, therefore, this study was conducted to verify the feasibility of its water's use. This was treated with the objective of achieving drinking water standards.

3.1. Experimental Design

The pilot scheme is shown in Figure 3: it is composed by a contact basin where coagulant dosage and PAC addition (optional) are carried out, a second coagulation basin with sand and polymer injection, both stirred at 100–200 rpm, and a clarification tank with lamella settler and very slow mixing, for solid/liquid separation. Fine gradation sand is dosed in the second tank with polymer and is recycled from the lamella settling tank to the same place, with periodical addition of new sand. If PAC is added in the first basin, it is recycled together with the sand in the second, with new PAC addition, as needed, in the first.
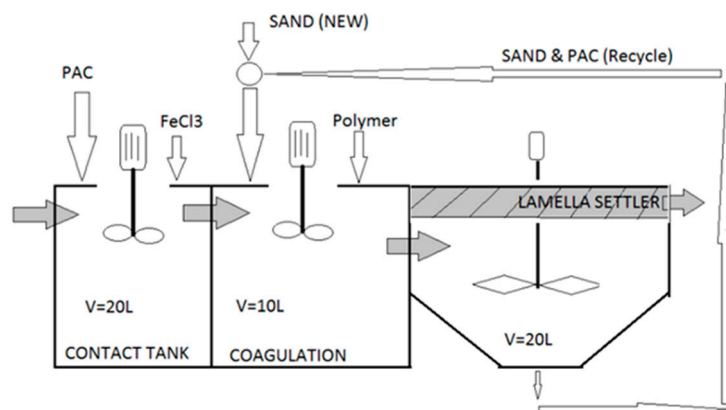

Figure 3. Pilot plant scheme.

At nominal flow capacity, residence times are 24 min in the contact tank, 12 min in the coagulation tank, and 24 min in the settler. Contact times can vary depending on the actual flow rate adopted. In order to optimize the performance of the pilot plant, jar tests were preliminarily conducted to determine the ideal type, the best dosage of reagents to add during operation, and the dosage sequence. Other investigated variables included operational pH, sand granulometry, and contact times in the basins. In the case of PAC addition, one additional parameter was the ratio between new and recirculated PAC. A large number of possible combinations among these factors were investigated. The best combinations were employed for validation of operations in the pilot plant.

Untreated source water characteristics are summarized in Table 2. Turbidity shows the highest seasonal variability (+92/−84% from average value), dissolved organic carbon (DOC) values are more consistent (varying in a ±20% range), while the other parameters do not vary more than 30–40% from the average.

Table 2. Source water characteristics during the experimental period.

Observed Values	Turbidity (NTU)	DOC (mg/L)	pH	Conductivity (mS/cm)	UV 254 nm Absorption (Abs/m)
Average	2.5	3.1	7.8	202	23
Max value	4.8	3.8	8.4	270	37.9
Min value	0.4	2.5	7.2	185	18.3

3.2. Jar Tests

Multiple jar tests were preliminarily carried in a six-jar experimental setup, to determine the best ranges of additive dosage to be used as initial values in the actual pilot testing. Conditions of the jar tests are summarized in Table 3 below. Initially, dosages were ranked against turbidity and UV 254 absorbance of the treated solution, since these parameters had shown good correlation with DOC content. Some tests were also ranked against filtration time (a vacuum filtration test of the jar-treated solution on paper filter), since it was assumed that filtration time would be somehow

indicative of the flocculating matter ability to achieve good separation efficiency in the actual pilot plant. Except for an initial "blank" test, where only ferric chloride and an anionic polymer (AN 905) were dosed, two quartz sands, with D_{50} = 91 μm (range 65–150 μm) and D_{50} = 125 μm (range 90–190 μm), and anionic polymers AN 905 and AN 934 were tried in all other tests. Sand with D_{50} = 91 μm and polymer An 905 yielded the best results and were selected in the end. Final coagulant ($FeCl_3$) doses were 160 mg/L without PAC or flocculant addition, and 0.5 mg/L when biodegradable flocculant AMIDONC* 35704 was also added (1.2 mg/L) to the mix. Organic coagulant Polydadmac (a synthetic product of of the monomer Dadmac) was also tested in substitution of $FeCl_3$; in this case the most convincing results were obtained with a dosage of 0.1 mg Polydadmac/L. Fresh PAC optimal dosage resulted in the order of 20 mg/L, and UV adsorption removal values increased by increasing its contact time. By increasing or decreasing the amount of treated flow, abatement performances could be modified without additional test facility modifications.

Table 3. Summary of the conducted jar tests.

Test No.	Additive(s) Studied	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
0 Non-ballasted	$FeCl_3$ (mg/L)	80	100	120	140	160	180
	Other test conditions (all jars): polymer AN 905: 0.2 mg/L, no sand HRTs: coagulation 2 min @ 200 rpm, flocculation 4 min @ 100 rpm, clarification 4 min						
1 Coagulant dosage	$FeCl_3$ (mg/L)	80	100	120	140	160	180
	Other test conditions (all jars): polymer AN 905: 0.2 mg/L, sand D_{50} 91 μm: 5 g/L HRTs: coagulation 2 min @ 200 rpm, flocculation 4 min @ 100 rpm, clarification 4 min						
2 Flocculant dosage, sand type	AN 934 (mg/L)	0.1	0.2	0.3	0.1	0.2	0.3
	Sand D_{50} (μm)	91	91	91	125	125	125
	Other test conditions (all Jars): $FeCl_3$: 160 mg/L, sand D_{50}: 5 g/L (regardless of size) HRTs: coagulation 2 min @ 200 rpm, flocculation 1 min @ 200 rpm, clarification 4 min						
3 Coagulant w/biod. Polymer	$FeCl_3$ (mg/L)	0.2	0.4	0.5	0.6	0.8	1.0
	Other test conditions (all jars): sand D_{50} 91 μm: 5 g/L, AMIDONC* 35704: 1.2 g/L HRTs: coagulation 1 min @ 200 rpm, flocculation 1 min @ 100 rpm, clarification 4 min						
4 Biodegrad. polymer	AMIDONC* 35704 (g/L)	0.5	1.0	1.5	2.0	2.5	3.0
	Other test conditions (all jars): sand D_{50} 91 μm: 5 g/L, $FeCl_3$: 0.5 mg/L HRTs: coagulation 1 min @ 200 rpm, flocculation 1 min @ 100 rpm, clarification 4 min						
5 Organic coagulant	Polydadmac (g/L)	0.05	0.1	0.15	0.2	0.25	0.3
	Other test conditions (all jars): sand D_{50} 91 μm: 5 g/L, AN 905: 0.6 mg/L HRTs: coagulation 2 min @ 200 rpm, flocculation 5 min @ 100 rpm, clarification 4 min						
6 PAC contact time	Contact time (min)	1	3	5	10	15	20
	Other test conditions (all jars): sand D50 91 μm: 5 g/L, AN 905: 0.8 mg/L, $FeCl_3$: 0.3 mg/L, PAC = 3 mg/L HRTs: coagulation 2 min @ 200 rpm, flocculation 5 min @ 100 rpm, clarification 4 min						
7 Recycle PAC dosage	PAC (mg/L)	0	1	2	3	5	10
	Other test conditions (all jars): Sand D50 91 μm: 5 g/L, AN 905: 0.8 mg/L, FeCl3: 0.3 mg/L HRTs: coagulation 10 min @ 200 rpm, flocculation 2 min @ 100 rpm, clarification 4 min						
8 New PAC dosage	PAC (mg/L)	0	5	10	15	20	25
	Other test conditions (all jars): Sand D50 91 μm: 5 g/L, AN 905: 0.8 mg/L, FeCl3: 0.3 mg/L HRTs: coagulation 10 min @ 200 rpm, flocculation 2 min @ 100 rpm, clarification 4 min						

The most cost-sensitive additive turned out to be PAC as, at required doses, this additive would contribute to ca. 70% of the operating costs of the overall treatment. A summary of some of the tests carried out is graphically summarized in Figure 4, as an indication of the preliminary results obtained. It can be seen that the initially high tentative $FeCl_3$ dosage proved excessive when also adding anionic polymer and/or flocculant, and sand. The final values of additives determined by jar tests were used as the initial tentative values for the pilot testing application.
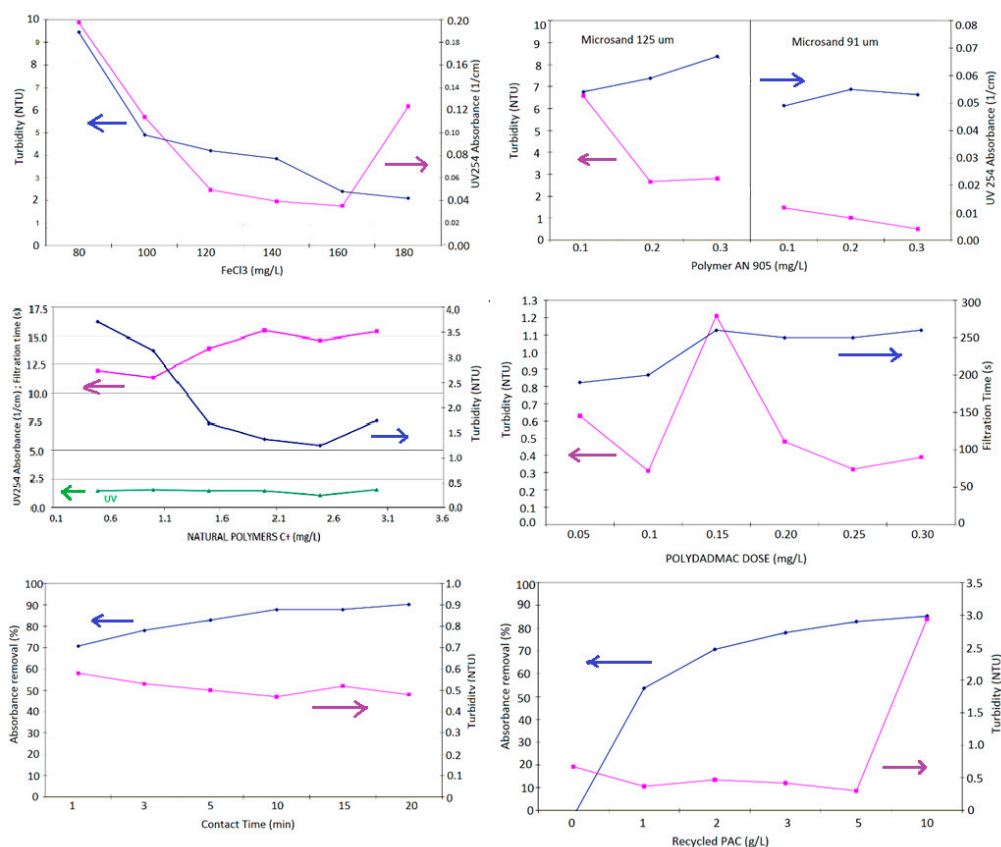
Figure 4. Examples of some of the jar tests carried out.

3.3. Pilot Testing

After the preliminary jar test phase, a pilot test phase was started, with a duration close to 4.5 months. Additive types and dosages were initially chosen among those determined by jar tests, and varied along the course of the experiment, with ranges shown in Table 4. Initially, treated flow was equal to the pilot's nominal capacity (50 L/h), and was varied in the ±30% range during the test in order to maintain desired effluent parameters values (DOC ≤ 2 mg/L, turbidity ≤ 0.5 NTU). NOM removal was compared to DOC and turbidity removal efficiencies using an online UV turbidimeter monitor probe, which was preventively cross-calibrated and proven to carry very high correlation with traditional measurement methods (Figure 5 shows correlation between DOC measurements and UV probe absorbance).

Table 4. Summary of experimental conditions (ranges) during the pilot study.

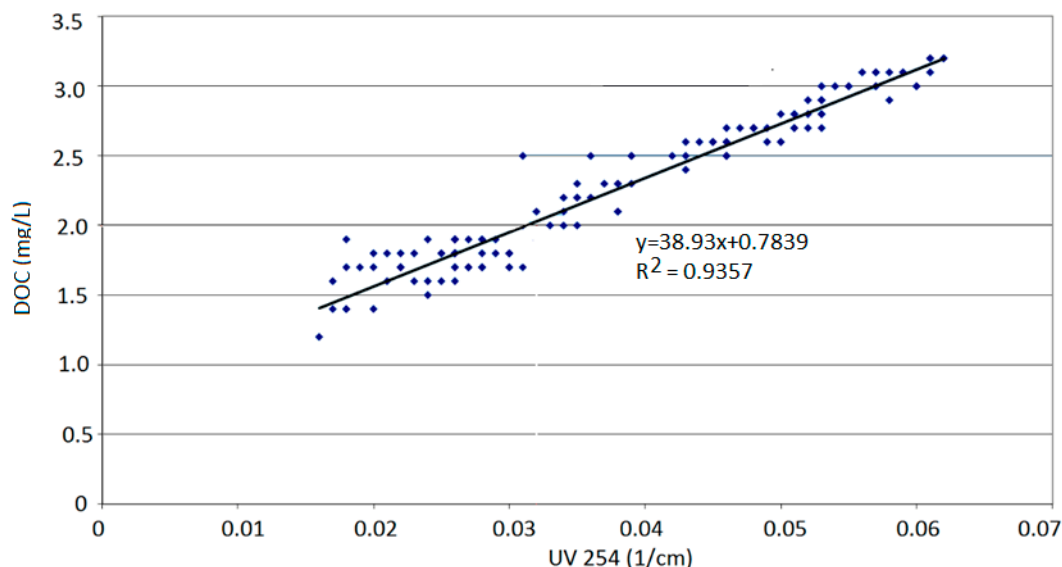| Parameter/Additive	Range Tested and Units	Value for Which Best Results Were Observed
Flow	50 ± 30% (L/h)	Not applicable
FeCl$_3$	Initially 80–180 mg/L, then 0.2–1 mg/L	0.5 mg/L
Polydadmac	0–5 mg/L	0.1 mg/L
Amidon C 35704	0–5 mg/L	1.2 mg/L
Anionic Polymer AN 905	0–1 mg/L	0.
Anionic Polymer AN 934	0–1 mg/L	Not applicable
Sand 91 μm	0–20 mg/L	5 mg/L
Sand 125 μm	0–10 mg/L	Not applicable
PAC	0–40 mg/L	20 mg/L

Figure 5. Experimental correlation between DOC and UV 254 absorbance.

4. Results

The results obtained with the continuously-running pilot show that DOC removal is somehow proportional to PAC dosages (Figure 6). Optimal PAC dosages lie generally below 25 mg/L, as higher dosages do not achieve a correspondingly higher removals, and were also determined to be too expensive for prolonged treatment. From Figure 6 it can be seen that maximum DOC removal was about 80%, with the average around 45%.
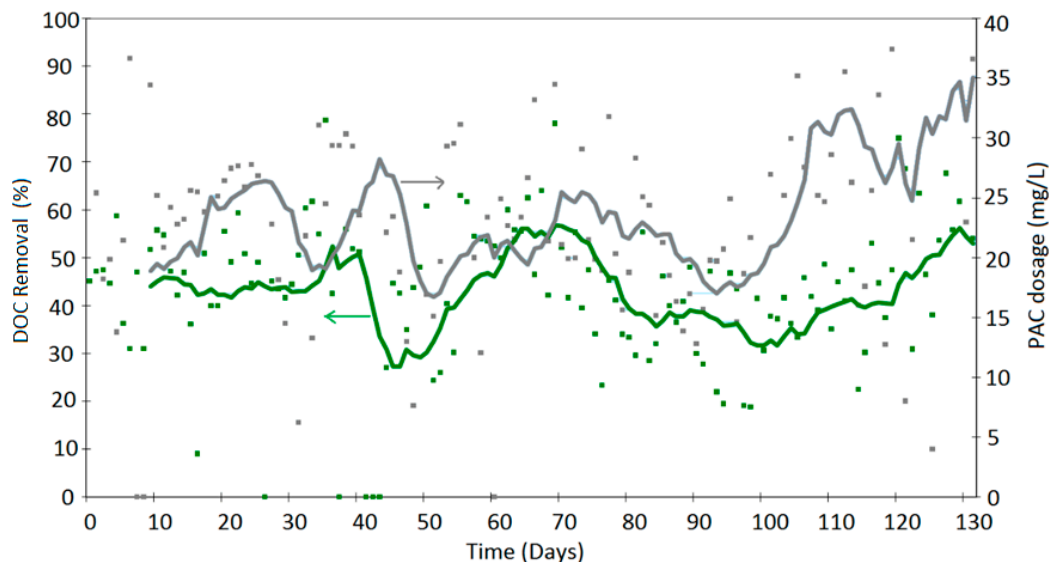

Figure 6. Relationship between PAC dosage (right scale) and DOC removal (left scale).

Figure 7 shows effluent DOC concentration values, PAC dosages, and type. During the test period, effluent DOC was practically always below the desired 2 mg/L value, except for a short period, in which a different PAC types (finer granulometry of 8–15 μm versus the previous 15–35 μm) was briefly tested, showing inferior performance, and slightly worse results. Data from this figure express fairly explicitly the inverse proportionality effect between PAC dosage and DOC effluent concentration.
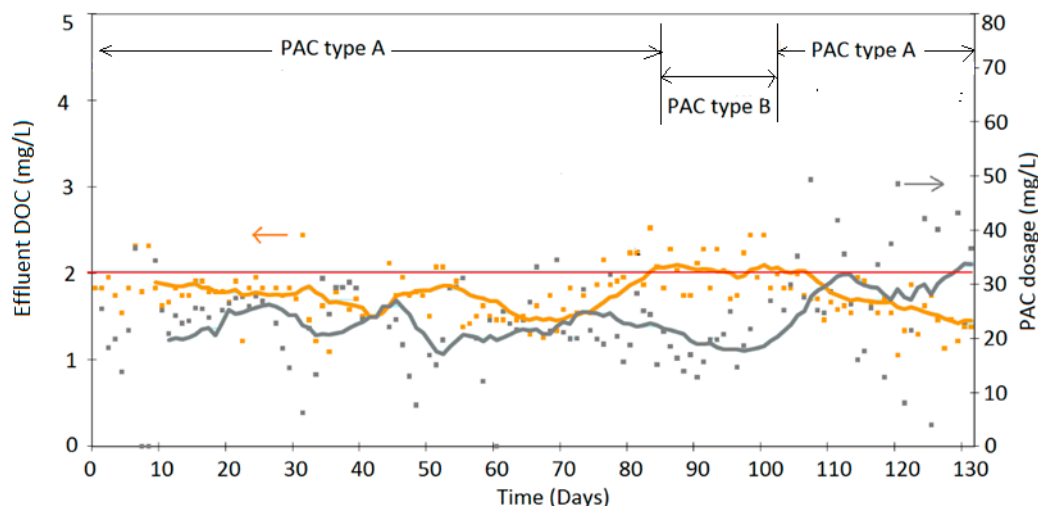
Figure 7. Effluent DOC concentration values (left scale), PAC dosages (right scale) and PAC type (overhead line) during the experimental period. Dots indicate actual data, lines represent eight-day running averages for ease of interpretation.

Figure 8 represents the behaviour of influent and effluent turbidity from the pilot plant. Turbidity is the main immediate process control parameter (as its removal in this process is somewhat correlated with NOM removal) and was used to continuously check online plant operation. Particles with a diameter between 1 and 10 μm (especially colloidal ones) are the primary cause of turbidity. High turbidity can interfere with subsequent water disinfection, and its measurement is rather important, as it tells how efficiently a process is removing particles and pollutants, including pathogens, such as *Giardia* and *Cryptosporidium*. Online turbidity measurement can be achieved by dedicated online instrumentation based on UV-VIS spectrometry: many such instruments are commercially available today. In this application, the i::scan monitoring probe measuring turbidity according to EPA 180.1 and ISO 7027 spectrometry, was used.
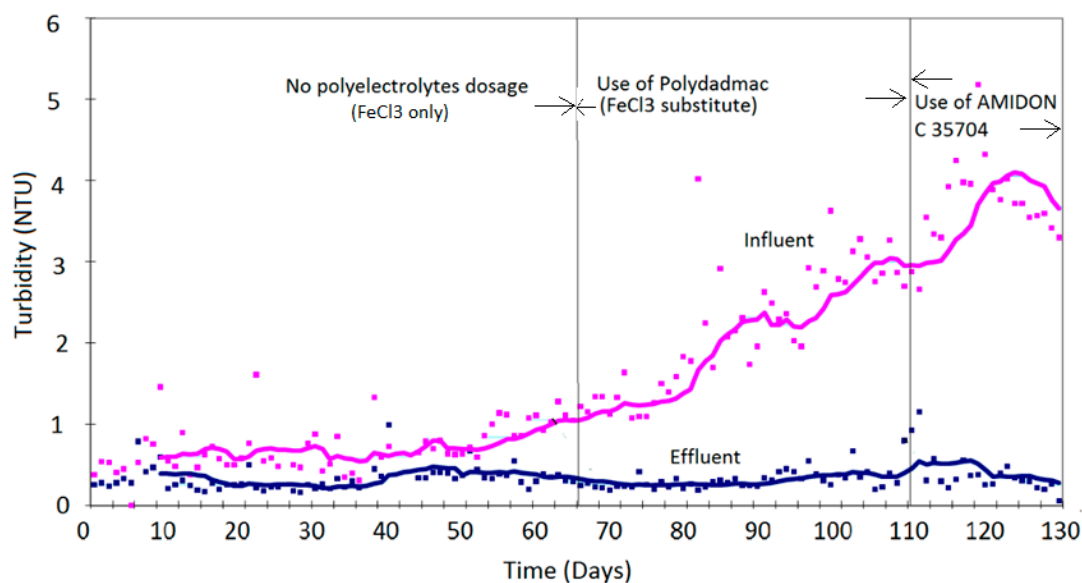

Figure 8. Influent and effluent turbidity from the pilot plant.

From Figure 8 it can be seen that, even with influent turbidity values at 4 NTU or above, effluent turbidity values were consistently around 0.5 NTU, or less. On Day 65, coagulant $FeCl_3$

was substituted by organic coagulant polydadmac, offering better performance in terms of turbidity and DOC abatement, consistently with other studies where this was used as the primary coagulant for NOM removal [50]. From Day 110, natural, biodegradable coagulant AMIDON C 35704 was tested, with similar results. This coagulant showed excellent capacity of controlling influent turbidity.

Discussion

Ballasted flocculation appears to be an efficient process to reduce the presence of NOM in natural waters for drinking (soft-drink bottling industry). Patented versions of BSF have been developed by, among the others, Veolia Eau (France), using specific additives, including a patented, calibrated microsand (available in different gradations, between 40–150 μm) and a sand-recovery cyclone. In this case, commercially-available quartz sand with a nominal average size of 91 and 125 μm, respectively, was used. The fact that commercial sand has a wider particle size distribution and lower homogeneity makes it much cheaper than the one used in proprietary systems, and, at least during our tests, made a recovery system anti-economical. During the operational period of the pilot plant, which exceeded four months, the ballasted flocculation process proved to achieve satisfactory results in terms of NOM, DOC, and turbidity removal from the source water. Among other additives tested, ferric chloride, anionic polymers, biodegradable flocculants, organic coagulants, and PAC were used. From a preliminary survey of commercial costs (that was conducted using the well-known commercial website Alibaba for large-quantity orders, therefore actual prices may vary depending on shipping locations, market price oscillations, and needed quantities) the relative cost of all additives lies approximately in the range of 1 to 4, that is, roughly: ($FeCl_3$):(anionic Polymers and biodegradable flocculants): PAC: AMIDON $\approx$ 1:2:3:4.

This considered, and considering the quantities needed for a full-scale application, PAC would be the second-most expensive process supply. Notwithstanding the positive performance of the pilot, it was observed that the relatively high PAC requirements for DOC removal (ca. 25 mg/L), would make this solution somewhat expensive to run continuously, even without considering the additional inevitable costs for spent PAC disposal or regeneration. It was, hence, decided in this specific instance to start investigating other possible alternative solutions for long-term efficiency and cost comparison.

In general, BSF processes have demonstrated to be relatively easy to operate, requiring a smaller areal footprint than traditional flocculation technology to operate. This, among other issues, would facilitate the installation of a BSF in the existing industrial setting for which it was foreseen, where availability of additional free space could be an issue.

5. Conclusions

A small-scale pilot plant was used to test the feasibility of a surface reservoir water treatment for NOM removal. The plant uses coagulation ($FeCl_3$), flocculation (anionic flocculant AN 905), commercial sand as a floc-ballasting agent, and powdered activated carbon to achieve the desired objectives. Additives were pre-tested with laboratory jar tests applied and their dosages further refined during almost 4.5 months of continuous pilot operation.

Use of PAC to enhance drinking water treatment processes can be considered almost standard procedure nowadays. This study presents an application where PAC is added to a ballasted clari-flocculator, whose special performance enhancement is based on the addition of sand to ballast-forming flocs, allowing their rapid settling. Ballast sand and PAC are then returned to the coagulation basin after their sedimentation, with periodic replenishment of the exhausted PAC fraction.

The process allowed satisfactory removal of natural organic matter, as both DOC (about 50%) and turbidity (from 50% to 90%), which would constitute an acceptable result in terms of water use in the destination facility. The key to success in this type of process is a correct setup with the identification of optimal types and dosages of reagents. Based on the results of the tests conducted it is foreseeable that this technology could be used onsite, not only for the removal of NOM, but also for the removal

of other hard-to-tackle pollutants potentially contained in the freshwater supply and not presently considered. It was also pointed out, however, that PAC replacement costs could be a limiting factor of technology choice, therefore, other treatment options are currently considered for testing in order to obtain additional technical and economic data.

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