Reclamation of urban pollution impacted groundwater by advanced treatment processes: Effect of prechlorination on the removal of metals, ammonium and NOM at pilot scale

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ABSTRACT

The need for new water resources in water scarcity regions has driven the exploration of water reclamation through a variety of treatment technologies. The present study aims at reclaiming impacted urban groundwater through two different treatment routes: one based on adsorption and ion-exchange processes on consecutive pyrolusite, granular activated carbon, zeolite and Fe(*oxy*)hydroxide filters (route L1) and a second one relying on sorption (on pyrolusite) and RO-membrane filtration (route L2). Both routes were operated without and with prechlorination to ascertain whether NaClO, beyond inactivating undesired pathogens, affected the removal of target parameters (Mn, As, NH_4^+, DOC) and the formation of trihalomethanes (THMs). Results showed that route L1 was successful at removing Mn, As, pathogens and THMs at levels below those stipulated by the legislation on reuse and drinking water. Only NH_4^+ failed to decrease below its threshold limits for drinking water, but only in the absence of prechlorination. However, concentration of Cl^- and Na^+ increased during treatment due to the chemicals used, compromising reuse of the produced water in specific industrial sectors requiring low contents of these ions. Route L2 showed a consistent high removal of all targeted parameters (also NH_4^+) without and with prechlorination conditions, producing a finished water with high potential for reuse and production of drinking water. DOC and its fluorescent fulvic and humic-like fractions were moderately removed by route L1 but highly removed by route L2. The outperformance of route L2 in terms of produced water quality must be balanced by the associated treatment cost, as it was 8–10 % higher for route L2 than for route L1. This made evident that a trade-off between quality and cost must be faced. This study demonstrates that reclamation of urban groundwater through the proposed treatment routes has a huge potential for reuse for a wide diversity of final purposes (urban, agricultural, industrial, environmental and recreational uses) and, although it may need further exploration, likely for drinking water purposes.

1. Introduction

Reclamation of low-quality water (wastewater, impacted urban groundwater, stormwater…) for further reuse has been acknowledged as an effective way to alleviate the shortage of fresh water and increase water self-sufficiency, especially for regions where freshwater is limited [1,2]. However, low-quality waters commonly contain chemicals and pathogens that often compromise their reuse without proper treatment.

When the quality of water to be treated is poor (e.g. with high turbidity and elevated load of organic matter and pathogens, typical of municipal wastewater) and end uses do not require very high-quality water (e.g. non-food crop irrigation, street or vehicle washing…) conventional treatment including coagulation, sedimentation, rapid sand filtration, biological degradation and disinfection usually suffice [3,4]. However, and although there exist abundant literature for water reclamation for these reclamation scenarios when end-uses do not require a

high-quality treated water, much less is available when high-quality is required (e.g. irrigation of food crops eaten raw, usage in electronics industry, conditioning of boiler feed water…). In these cases, more advanced treatments may be needed, commonly including adsorption, ion-exchange and membrane filtration processes [5,6]. Selecting the appropriate advanced technologies to guarantee safety of reclaimed water is currently a matter of intensive research.

Urban groundwater (UGW) in the aquifer of Sant Adrià del Besòs (Barcelona, NE Spain) represents an example of a waterbody with an enormous potential for reclamation. Moreover, the high water table of the aquifer results in flooding of municipal subterranean structures, causing serious deterioration of these structures, making necessary a continuous pumping of large volumes of UGW (approximately 5 Hm^3 per year) to avoid seepage problems [7]. This huge amount of UGW is currently discharged into the sewage system and directed to a nearby wastewater treatment plant (WWTP). This practice implies a loss of hydric resources, a deterioration of the sewer systems and the subsequent increase of their maintenance costs, a continuous pumping to the WWTP and a decrease of the efficiency of the WWTP due to dilution of water to be treated [7,8]. Treating and rendering this UGW suitable for reuse would undoubtedly improve the management of the hydric resources in the area of Sant Adrià de Besòs [9].

This UGW nowadays presents a relatively good chemical quality with ammonium (NH$_4^+$) (1–15 mg/L), manganese (Mn) (2–825 μg/L), ferrous iron (Fe) (12–3600 μg/L) and arsenic (As) (2–32 μg/L) as the identified chemical parameters of concern of this UGW [7]. These contaminants, which often coexist in groundwater, are associated not only to organoleptic nuisance but also to adverse health impacts and operational problems [10–13]. Obviously, other parameters apart from NH$_4^+$, Mn, Fe and As must be monitored to guarantee that treated water fulfils the regulations on the specific reuse of reclaimed water (Spanish RD 1620/2007) and, eventually, on drinking water (EU Directive 2020/2184). Examples of these parameters are pathogens, hazardous transition metals and THMs.

Several approaches have been applied for the removal of Mn, Fe, As and NH$_4^+$, including coagulation, precipitation, biological processes and filtration through reverse osmosis (RO) membranes. However, these approaches present significant hindrances, such as chemicals consumption, need of high levels of targeted solutes, treatment inefficiency at low temperature and under shock loading of contaminants, difficulties to operate and high energy consumption, among others [12,14–16]. More cost-efficient alternatives must be considered before selecting a definitive treatment method. Sorption has also largely been explored for the removal of Mn, Fe, As and NH$_4^+$, besides other hazardous pollutants [17,18]. Among the outperforming sorbents are manganic dioxide (MnO$_2$) for Mn and Fe [10,13,19], Fe-oxyhydroxides for As [11,20], and zeolite and carbon-based materials for NH$_4^+$ ([21] and references therein). Although a notable hindrance of sorption is that the process may suffer from competition between ions, treatments relying on sorption (i.e. adsorption, ion-exchange, surface complexation…) emerge as alternatives to more expensive RO-based treatments for the production of treated water at lower costs.

Regardless of the type of technology applied for the removal of dissolved species, current regulations imply the application of a disinfection process (commonly chlorination) to ensure that reclaimed water is safe from a microbiological point of view. However, the effect of chlorination in a water treatment goes beyond the inactivation of microorganisms. Chlorination can oxidise dissolved Fe^{2+}, Mn^{2+} and As(III) favouring their removal through precipitation and/or sorption processes [13,19,22]. In addition, chlorine-based reagents (Cl$_2$, NaClO or ClO$_2$) can react with natural organic matter (NOM) and form undesired disinfection by-products (DBPs) [23], which have been linked to public health concerns. One measure to reduce DBPs is removing NOM prior chlorination, usually through adsorption onto GAC [24]. Chlorination can also result in the breaking down of NOM into smaller fragments, which can exhibit different reactivity (e.g. in forming DBPs, in adsorbing

Table 1

Composition of UGW from the parking lot in Sand Adrià de Besòs used as feedwater in this study.

Parameter	Units	UGW composition	EU Directive 2020/2184
pH		7.3 ± 0.3	6.5–9.5
Conductivity	μS/cm	1562 ± 187	2500
Na	mg/L	142.4 ± 14.5	200
Ca		101.1 ± 16.6	–
Mg		22.4 ± 2.4	–
K		13.5 ± 2.1	–
NH$_4^+$		**1.1 ± 0.3**	0.5
HCO$_3^-$		348.4 ± 11.1	–
Cl$^-$		221.1 ± 5.5	250
SO$_4^{2-}$		130.8 ± 3.2	250
NO$_3^-$		8.1 ± 2.7	50
F		<0.5	1.5
Br$^-$		<0.5	–
HPO$_3^{2-}$		<0.5	–
Si		2.5 ± 18.1	–
B		147.0 ± 33.7	1500
Mn		**96.2 ± 31.8**	50
Al		36.5 ± 14.4	200
Ni		13.2 ± 19.4	20
Cu	μg/L	5.8 ± 2.8	2000
As		**4.4 ± 0.4**	10
Pb		<1.0	5
Cd		<1.0	5
Cr		<1.0	25
Fe		<1.0	200
DOC	mg/L	**2.3 ± 0.5**	Without abnormal changes

Values in bold indicte values above thresholds set by the EU Directive 2020/2184

onto GAC…) [25–27]. Finally, chlorination can alter the adsorption capacity of filtering media by modifying the physicochemical properties of the adsorbent and/or adsorbate [28]. Together through these reactions, the fate of chlorine is also largely determined by the concentration of some species such as Br$^-$ and NH$_4^+$/NH$_3$, compromising the performance of a disinfection process [29,30].

All these effects are not always fully addressed or explicitly discussed in treatments involving chlorination. Most studies on this topic have been often performed at bench-scale, sometimes using synthetic solutions, and therefore their results cannot always be extrapolated to polluted waters. Furthermore, the effects of chlorination are usually focused on one single process, but rarely along treatment trains comprising different units [22,24,25]. Studies at full-scale plants are scarcer and sparser. Moreover, these studies commonly comprise conventional treatment with limited presence of advanced treatment and/or the effect of chlorination on the removal of specific species is not always discussed [31–33].

The main objective of this study was 1) to evaluate and compare two different treatment trains at a pilot scale for reclaiming UGW from Sant Adrià de Besòs. One of the treatment lines comprised a sequence of different filters to undergo sorption and ion-exchange processes (L1), while the second relied on sorption and RO filtration (L2). Chemical and microbiological parameters of concern (Mn, NH$_4^+$, As, DOC, pathogens) were exhaustively monitored through each line to discern whether treated water met the current legislation for reclaimed water before reuse. Both lines were operated under two scenarios: without and with prechlorination for getting insight in what was a second objective: 2) to elucidate the effect, if any, of NaClO on the behaviour of the targeted contaminants along each treatment line. The study finally aimed to 3) identify potential end-uses of the produced water by L1 and L2 by comparing their quality against current legislation for reuse purposes.
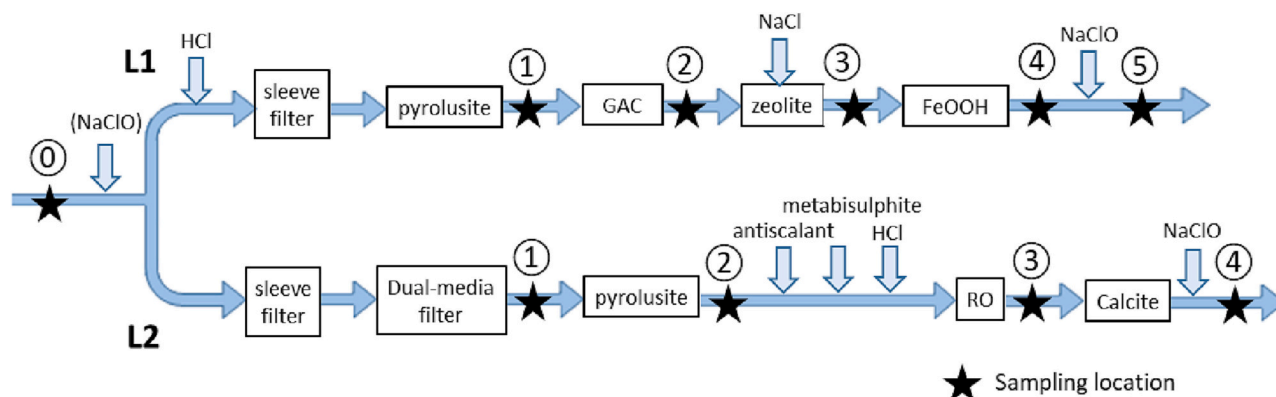
Fig. 1. Flow diagram of the pilot-scale plant, showing the whole treatment for both lines L1 and L2 and the location of manual collection of water samples for further laboratory analysis.

2. Materials and methods

2.1. Urban groundwater composition

The UGW treated in this study was pumped from below the parking lot located under the Plaça de la Vila in Sant Adrià de Besòs. The drainage and water level control system consisted of four extraction wells installed in the aquifer. The purpose of this system was to keep groundwater levels low enough to not affect or avoid seep into nearby underground infrastructure such as building foundations and basements or other underground parking lots. A summary of the chemical composition of the pumped UGW is presented in Table 1. For comparative purposes, Table 1 also lists the required quality of water for human consumption set by EU Directive 2020/2184.

As can be seen, water was generally of good quality except for NH_4^+ and Mn, which clearly exceeded the thresholds of the EU Directive 2020/2184. This composition generally agreed with previous campaigns carried out by Jurado et al. [7], who found however exceedances also for Fe and As. With regards to Fe, the apparent discrepancy was likely due to the fact that UGW in this study was taken from the parking lot, where oxidation of Fe^{2+} and subsequent precipitation of $Fe(OH)_3$ took place, while Jurado et al. [7] analysed UGW from monitoring wells between the Besòs river and the parking lot, where more anoxic conditions prevailed. With regard to As, the small difference was probably due to the unavoidable variations in water level and/or occasional anthropogenic recharges. Despite the concentrations of As and DOC were moderate, but because of their potential hazardous effect, they were also considered together with Mn and NH_4^+ as targeted species of concern in this study (in bold in Table 1). It is worth noting that suspended solids were found at low levels (<1 mg/L) because, as found in a previous study [7], the riverbed is highly effective in removing particulate materials from groundwater. This allowed to deem coagulation not necessary when designing the pilot-scale plant for the treatment of the

UGW from Sant Adrià de Besòs.

2.2. Pilot description

The pilot-scale plant, housed inside a 40 ft shipping container, comprised two parallel treatment lines, namely line 1 (L1) and line 2 (L2), each containing different treatment units as displayed in Fig. 1 and explained below.

Before being diverted to each line, feed groundwater coming from the parking lot was optionally subjected to prechlorination. When applied, prechlorination was performed by injecting NaClO at a dose of 5 mg/L. After pre-chlorination, feed water was split into two streams: one undergoing L1 and the other L2.

2.2.1. Treatment line 1 (L1)

Treatment line L1 included an initial acidification (optional), sequential filtration through sleeve, pyrolusite, granular activated carbon (GAC), zeolite (clinoptinolite) and Fe-(oxy)hydroxide (FeOOH) filters, and final disinfection with NaClO. The purpose of the initial acidification was to lower pH around 7.0–7.5 and shift the equilibrium between $HClO/ClO^-$ towards HClO, which is more effective for disinfection than ClO^-. The function of the sleeve filter (Cintropur, with a cut off of 25 μm) was to remove any particulate material and therefore avoid clogging of the downstream filters, of the pyrolusite (β-$MnO_2(s)$) filter to remove Mn through sorption and/or oxidation followed by precipitation, of the GAC filter to adsorb DOC, of the zeolite filter to exchange NH_4^+ and of the FeOOH filter to adsorb As. Finally, water was subjected to final disinfection (5 mg/L NaClO) to protect produced water from recontamination from harmful microorganisms. All filter media (pyrolusite, GAC, zeolite and FeOOH) were packed in cylindrical columns, where filtration took place in a down-flow mode. Because the cycle of the zeolite filter before saturation was short at the scale of operation of the study, the zeolite stage consisted of two filters working in parallel, in

Table 2
Media, dimensions and operation conditions for each filter of L1 and L2.

	Line L1				Line L2	
Filter material	Pyrolusite[a]	GAC	Zeolite	FeOOH	Dual media	Calcite
Commercial product	Mn48	CG900	Zeolite	Bayoxide E33	Silica Anthracite	Juraperle
Column diameter (mm)	555	366	411	411	369	555
Column height (mm)	1968	1921	1893	1893	1921	1968
Filtering medium mass (kg)	325 (+200 of silica)	50	105	60	43 (anthracite) 45 (silica)	325
Filtering depth (mm)	1000	1500	1500	1400	1600	900
Gravel mass in bottom (kg)	35	10	10	15	10	35
Filtration velocity (m/h)	15	14	12	12	14	6

[a] Also applicable to pyrolusite-filter for L2.

such a way that when one of them was switched on for regeneration, the other remained in operation, ensuring continuous operation of the pilot. All filters were periodically backwashed (on average every 8.0 days and for 10 min) with filtered water in counter-current mode to remove particles trapped in the filter media. The arrangement and design of the filters were so to allow each of them be backwashed independently. Regeneration of the zeolite filters was practiced after backwashing and was accomplished with NaCl solution to restore the zeolite in its initial Na-form. Regeneration lasted ca. 100 min, after which filtration resumed again. Details on media, columns dimensions and operating conditions for each filter are shown in Table 2.

2.2.2. Treatment line 2 (L2)

Treatment line L2 comprised the following units: a sleeve filter, a dual-media filter, a pyrolusite filter, a RO-membrane unit, a calcite filter and final disinfection with NaClO. As in L1, the sleeve filter served for the removal of particulate material, the dual-media filter for the removal of remaining residual solids to better protect the downstream RO unit and prolong its life, and the pyrolusite filter for the removal of Mn. The RO membrane unit acted as a major and ultimate barrier against solutes and microorganisms, while calcite filter had the purpose of increasing pH and remineralizing the RO-permeate. Post-disinfection (5 mg/L NaClO) was applied also as in L1. Details on filters in L2 are shown in Table 2.

The RO unit was arranged as a three-stage configuration with 5 pressure vessels in a 2–2–1 arrangement. Each pressure vessel contained one spiral-wound element Lewabrane RO B085 ULP 4040 (4 in. in diameter and 40 in. in length, with a membrane area of 7.9 m^2), which is an aromatic polyamide-based membrane designed for low salinity water to operate at ultralow pressure (ULP). The pressure of the inlet water to the RO unit was raised to 12 bar using a booster pump (Alfa 540). For scaling control, acid (HCl), antiscalant (commercial name Hidroglobal Vitec 3000) and a dechlorination agent to remove chlorine (sodium metabisulphite) were dosed prior to the entrance into the RO unit. Operating the RO membranes with a recovery of 60 %, in combination with the above mentioned reagents for scaling control, appeared to result in stable operation over the whole experimental period, during which cleaning of the membrane elements was not necessary.

2.3. Pilot operation

The operation of the plant was fully automated including chemical dosing of reagents (NaClO, HCl, antiscalant and sodium metabisulphite), backwashing of the media filters and regeneration of the zeolite filters, which could all be controlled with a control panel. The backwashing and regeneration streams were discharged to a municipal sewer, in coordination with the Consorci del Besòs, which also assisted with on-site logistics and provided water, electricity and site security.

The pilot plant was run for 8 months between September 2021 and April 2022 and was operated under two different scenarios: without prechlorination and, from January 2022 onwards, with prechlorination with the purpose of evaluating the effect of NaClO on the behaviour of each targeted species. Chlorine was applied as NaClO at a dose of 5 mg/ L. To ensure that the comparison between L1 and L2 was fair and unbiased, they were run in parallel under the same conditions. The work time was limited to 5 h per day for constraints from the Consorci del Besòs, except for occasional brief periods when the pilot was shut down for repairs. Water flow rates at the entrance of the pilot were 55.8 and 70.8 L/min for L1 and L2, respectively (for L2, conversion of 60 % for RO resulted in a produced water flow rate of approx. 42.5 L/min).

2.4. Pilot monitoring and analysis

2.4.1. Automatic in-situ monitoring and analysis

The pilot was equipped with in-line systems for pH, temperature, conductivity, ORP pressure and flow rate determinations at different locations of the pilot. It also included a datalogger which recorded the totalized water treated by the pilot plant.

2.4.2. Off-site water quality analysis

Water samples were taken at least twice per week from all sampling locations (see Fig. 1) and transferred directly to the laboratory where they were stored refrigerated until analysis. pH was measured using a pH-meter connected to a pH electrode (Crison GLP-22). Metals and As were analysed in filtered (0.22 μm) and acidified (with HCl) samples by Inductively Coupled Plasma Mass Spectrometer (7800 ICP-MS, from Agilent Technologies). Major anions were determined by ionic chromatography (IC) (Dionex, ICS-1000) coupled to cationic and anionic detectors (ICS-1000 y ICS-1100, respectively) and controlled by software Chromeleon®chromatographic. NH_4^+ was analysed by the indophenol blue spectrophotometric method (using a Shimadzu UV-1603) and occasionally also by the o-phthalaldehyde (OPA) fluorometric method (using a FP 2020 Plus, from Jasco). Bicarboante was analysed by titration with HCl using an automatic titrator (Mettler Toledo, Titrator Excellence T5) equipped with an autosampler (Mettler Toledo, Rondolino). The determination of dissolved organic carbon (DOC) in 0.45 μm-filtered samples was performed using a TOC-L Shimadzu organic carbon analyzer by high temperature catalytic oxidation (HTCO). The non-purgeable organic carbon method was selected (ISO number method 8245). Analytical precision and accuracy were tested against Reference Material provided by the DOC-CRM program (University of Miami-D.A. Hansell). In order to get insight into the DOC nature, DOC was characterized by FEEM, recorded by a fluorescence spectrophotometer (Cary Eclipse). The excitation wavelengths were determined from 200 to 500 nm and the emission spectra were scanned in the range of 250 to 600 nm, both with an increment of 5 nm. The spectrofluorometer was autozeroed before each analysis. Free chlorine residual (FCR) concentration was determined using N,N-diethyl-p-phenylenediamine (DPD) method-based test kits (Hanna HI3875). The concentration of the four regulated THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) was done using a gas chromatography–mass spectrometry (GC–MS) system equipped with headspace injection (Trace GC and DSQII model MS equipped with a Triplus autosampler from Thermo Fisher Scientific Limited).

2.4.3. Microbiological analysis

According to the Spanish RD 1620/2007 for wastewater reclamation, *E. coli*, *Legionella* spp. and intestinal nematodes were analysed in order to assess water quality prior to any reuse. Water samples from the entrance and exit (of both L1 and L2) of the pilot (and occasionally from each unit along L1) were taken for microbiological analysis. A total of 12 L of sample were collected in 10-L and 2-L sterile bottles (containing sodium thiosulphate to quench residual NaClO), immediately transported to the laboratory and analysed within 4 h according to the mentioned legislation. Briefly, *E. coli* enumeration was carried out on 100 mL filtered (though 0.45 μm filters) or 200 mL centrifuged (at 15000 g for 10 min) samples. For both cases, volumes of 2 mL were platted onto Chromogenic Coliform agar (from Oxoid) and *E. coli* strains β-glucuronidase positive were enumerated. *E. coli* were detected as blue-green colonies and total coliforms as pink colonies. For *Legionella* spp. analysis, each sample was divided into three aliquots, according to ISO 11731: 2017: one was heat treated, another was acid treated, and the third one was untreated. Then, each aliquot was cultured on cycloheximide (GVPC) Legionella agar media (Oxoid) (and on buffered charcoal yeast extract (BCYE) agar media with and without L-cysteine for confirmation). Intestinal nematodes eggs were analysed using the Bailenger process modified and updated according to the RD 1620/2007. Briefly 10-L sample were concentrated to 1 mL, which was moved to a McMaster counting slide. The quantity of eggs was then recognized and counted. Though not mandatory for the RD 1620/2007, Total Heterotrophs were also determined as a disinfectant indicator and for assessing the cleanliness of distribution systems. Briefly, direct samples, concentrated samples (from 200 mL to 2 mL by centrifugation at 15000 g for 10 min)
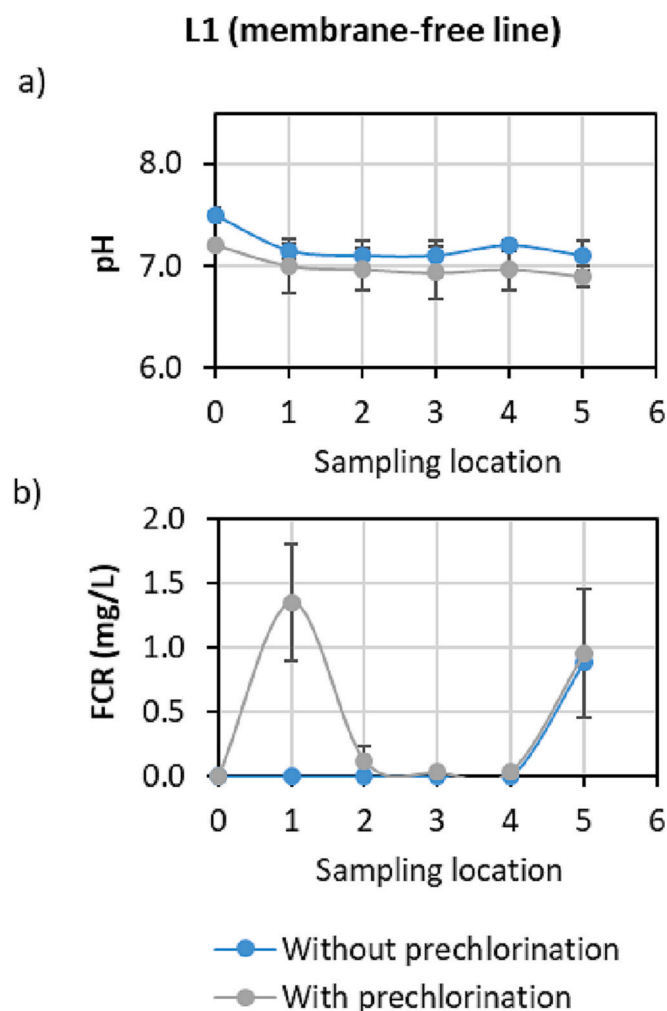
L1 (membrane-free line)

Fig. 2. Changes in pH (a) and FCR (b) along the membrane-free treatment line L1. Each plotted trend includes the average (with the standard deviation).

and tenfold diluted samples were cultured in Water Plate Count Agar (Oxoid) and incubated at 20 °C for 72 h before counting the resultant colonies on the plates.

3. Results

3.1. Performance of the membrane-free line L1

The figures that follow plot the average pH value and concentration of free chlorine residual (FCR), target species (Mn, As and NH_4^+), other ions of interest and DOC and organic fractions as analysed by FEEM along treatment line L1 under non-prechlorination and prechlorination conditions.

3.1.1. Profile of FCR and pH in L1

When added in water for disinfection, the stabilized form of chlorine ($Cl_2(g)$) in neutral to basic pH ($HClO/ClO^-$) reacts first with water constituents that exert chlorine demand, including metals such as Fe(II) and Mn(II), NOM, hydrogen sulphide and ammonium (e.g. dominant form at the typical pH values of groundwater). The chlorine that is left over, referred to as free chlorine residual (FCR) consists primarily of HClO and ClO^-, their relative prevalence depending on pH (pK_a of HClO at 298 K at 6.8). Fig. 2 shows the profile of pH and FCR along L1.

The initial acidification decreased pH of entering UGW to values around 7.0 for both operation conditions (Fig. 2a), making possible the prevalence of HClO (87 %) over ClO^- (17 %). It must be pointed that

HClO has a disinfection power almost 100 times higher that ClO^- thanks to its enhanced penetration through the microbial cell membrane.

Under non-prechlorination conditions, FCR obviously remained under detection limit until the exit of the pilot, where post-chlorination increased FCR to values around 0.8 mg/L (as Cl_2), which is within the recommended range for treated waters. Under prechlorination conditions in which NaClO was applied at a dose of 5 mg/L, FCR was found at 1.4 mg/L at the exit of the pyrolusite filter due to the chlorine demand of UGW, and then dropped down to <0.1 mg/L after the passage through the GAC filter. The capacity of GAC to remove chlorine has long been recognized [34]. Rather than through an adsorption process of chlorine on GAC as long perceived, dechlorination involves a chemical reaction between the GAC surface carbon and chlorine, which is reduced to chloride [35]. The FCR maintained undetectable through the subsequent zeolite and FeOOH filters and only increased again to around 0.9 mg/L after post-chlorination.

3.1.2. Removal of inorganic ions in L1

Prechlorination showed distinct effects on the removal of targeted components. Mn, As and NH_4^+ were all removed by L1 both without and with prechlorination, although at different stages of the line (Fig. 3).

Under non-prechlorination conditions, Mn was mainly removed in the pyrolusite filter by 88 %, from average 87 µg/L to average 10 µg/L at the exit of this filter (Fig. 3a), which was already well-below the threshold set by the EU Directive 2020/2184 (Table 1). Under these conditions, Mn was retained by sorption (through a combination of ion exchange, chemisorption and adsorption processes) [19] and/or, in the presence of dissolved oxygen, by MnO_2-mediated catalytic oxidation followed by precipitation as MnOOH or other oxides of intermediate oxidation states of Mn [10,36]. From this filter onwards, the concentration of Mn slightly decreased downwards to an average of 2.3 µg/L at the exit of L1. Under prechlorination conditions, Mn was removed in a similar high percentage, indicating that prechlorination had little effect on the overall Mn removal percentage. The retention mechanism was likely the same as in under non-prechlorination conditions. In fact, although it is known that NaClO may oxidise adsorbed Mn^{2+} and enhance its removal in the form of insoluble oxide forms (MnOx(s)), it is also known that for chlorine to effectively oxidise Mn^{2+} water pH needs to be raised to 8–8.5 [13]. As water pH at the entrance of L1 was around 7.0–7.5, oxidation of Mn^{2+} was not expected to be significant. From the pyrolusite filter onwards, Mn remained below 50 µg/L and was not deemed of concern.

Arsenic (As) was removed basically in the pyrolusite filter (28–37 %) and, especially, in the FeOOH filter (64–92 %), regardless the application of prechlorination (Fig. 3b). In both cases, the final average concentration of As was <2.0 µg/L, well below the threshold of 10 µg/L set by the EU Directive 2020/2184. Pyrolusite has been reported to remove both As(III) (through oxidation followed by precipitation as $Mn_3(AsO_4)_2(s)$) and As(V) (through electrostatic processes) [37]. The removal of As(III) and As(V) by FeOOH has been described to occur by binding of As(III) and As(V) oxyanions on iron oxides via surface complexation and/or ligand exchange process [11]. The application of NaClO results in a rapid oxidation of As(III) to As(V) [22] and, therefore, the effect of NaClO on As removal would depend on the relative adsorption of As(III) and As(V) on FeOOH. According to the manufacturer, the FeOOH used in this study (commercialized under the name of Bayoxide E33) exhibits a high similar sorption capacity for both As species. Comparable sorption extents of As(III) and As(V) on different forms of iron oxides (magnetite, goethite) have also been reported [38]. This explained why As removal was similar under both non-prechlorination and prechlorination scenarios.

Unlike Mn and As, NH_4^+ removal appeared to be affected by the addition of NaClO. Under the non-prechlorination scenario, NH_4^+ concentration was seen to remain unaltered through the pyrolusite and GAC filters (Fig. 3c). The removal of NH_4^+ in L1 took place in the zeolite filter, where NH_4^+ concentration was lowered from 1.1 mg/L to 0.6 mg/L
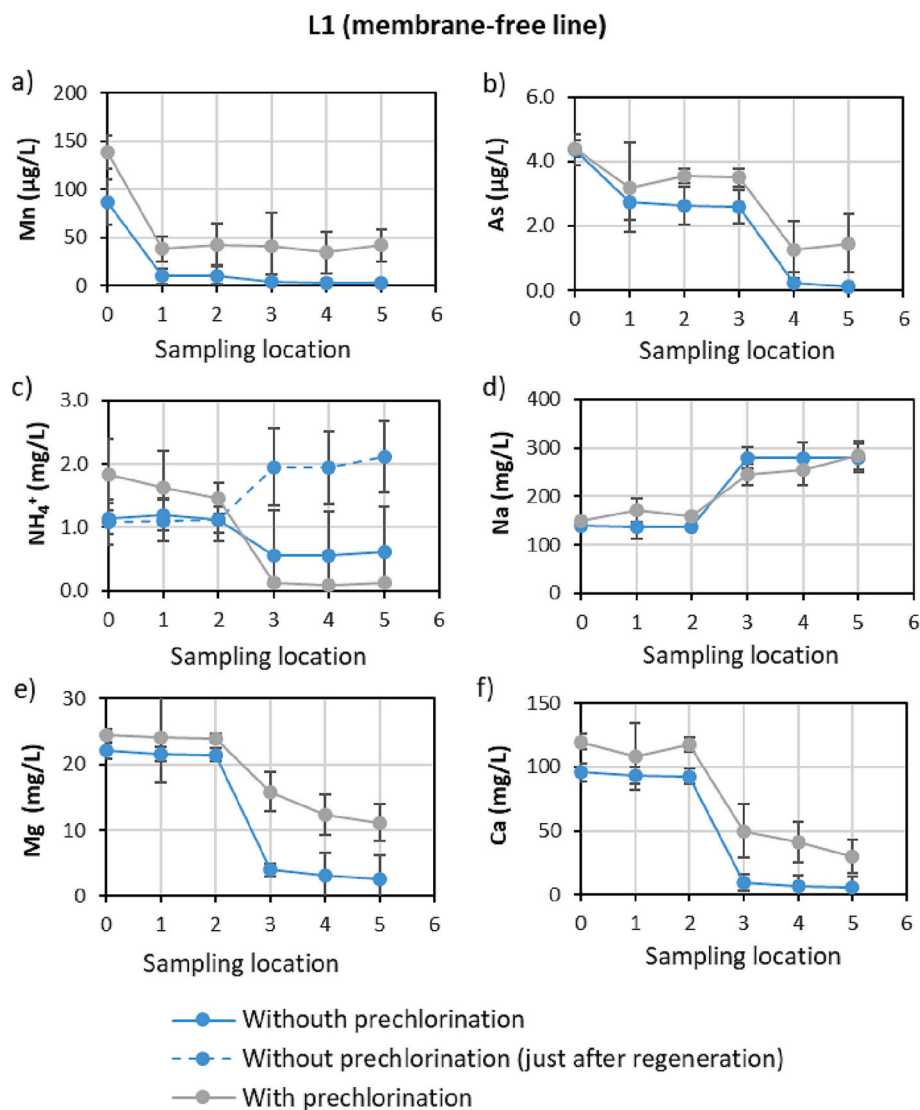
L1 (membrane-free line)

Fig. 3. Changes in concentrations of Mn (a), As (b), NH_4^+ (c), Na (d), Mg (e) and Ca (f) along the membrane-free treatment line L1. Each plotted trend includes the average (with the standard deviation).

(removal of almost 50 %). The removal was due to ion-exchange with the Na of the Na-form zeolite and, as expected, was accompanied by an increase in Na concentration (Fig. 3d). The unbalance between retained NH_4^+ ions and released Na^+ ions clearly pointed out that other cations were exchanged by the zeolite. In fact, profiles of Ca^{2+} and Mg^{2+} (Fig. 3d and e, respectively) made evident that they were also exchanged (and at higher extents than NH_4^+). A balance between charges of retained ions (NH_4^+, Ca^{2+} and Mg^{2+}) and of released ions (Na^+) showed a difference < 5 %, highlighting that these were the major ions involved in the exchange. Published studies report adsorption of NH_4^+ onto zeolite, but at higher NH_4^+ concentrations (up to 300 mg/L, much higher than 1 mg/L of this study) and with no or lower concentrations of competing ions (e. g. <90 mg/L Na) [39,40] or after chemical or physical modifications of zeolite to enhance NH_4^+ sorption [41]. Even being far away from these favourable conditions, in this study NH_4^+ sorption onto zeolite was quite remarkable.

Under chlorination conditions, a moderate decrease in NH_4^+ concentration (21 %, from 1.8 mg/L to 1.5 mg/L) was observed over the first (pyrolusite) and second (GAC) filters. This decrease was due to the reaction between NH_4^+ and ClO^- to form chloramines (NH_2Cl, $NHCl_3$ and NCl_3). Minor adsorption of NH_4^+ onto GAC has also been reported [42]. Nevertheless, the major removal of NH_4^+ under prechlorination

conditions was again in the zeolite filter, with a NH_4^+ removal of 91 % (from 1.5 mg/L to 0.1 mg/L).

It is worth noting that for occasional sampling events, NH_4^+ concentrations were observed to surprisingly increase after the zeolite unit. A careful examination of the monitoring plan detected that these occasional increases coincided with samplings conducted just after regeneration the zeolite filters, suggesting that NH_4^+ was present in pore water in the filters when filtration resumed after a regeneration event. These samplings were pooled apart in Fig. 2 to better visualize these increases in NH_4^+ concentration. The undesired washing out of NH_4^+ was corrected by discarding the pore water collected just after each regeneration step.

Values of anions (SO_4^{2-}, HCO_3^-) concentrations and conductivity remained fairly constant along L1 (not shown), with the exception of Cl^- (which will be discussed later).

3.1.3. Removal of organic matter and its fluorescent components in L1

Fig. 4 shows the profile of DOC (a) and of the fluorescent DOC protein-like compounds (b) and fulvic-like compounds (c) along L1. The content of each fluorescent component was tracked using its maximum fluorescence intensity (F_{max}), which gives an estimation of the relative concentration of the component.

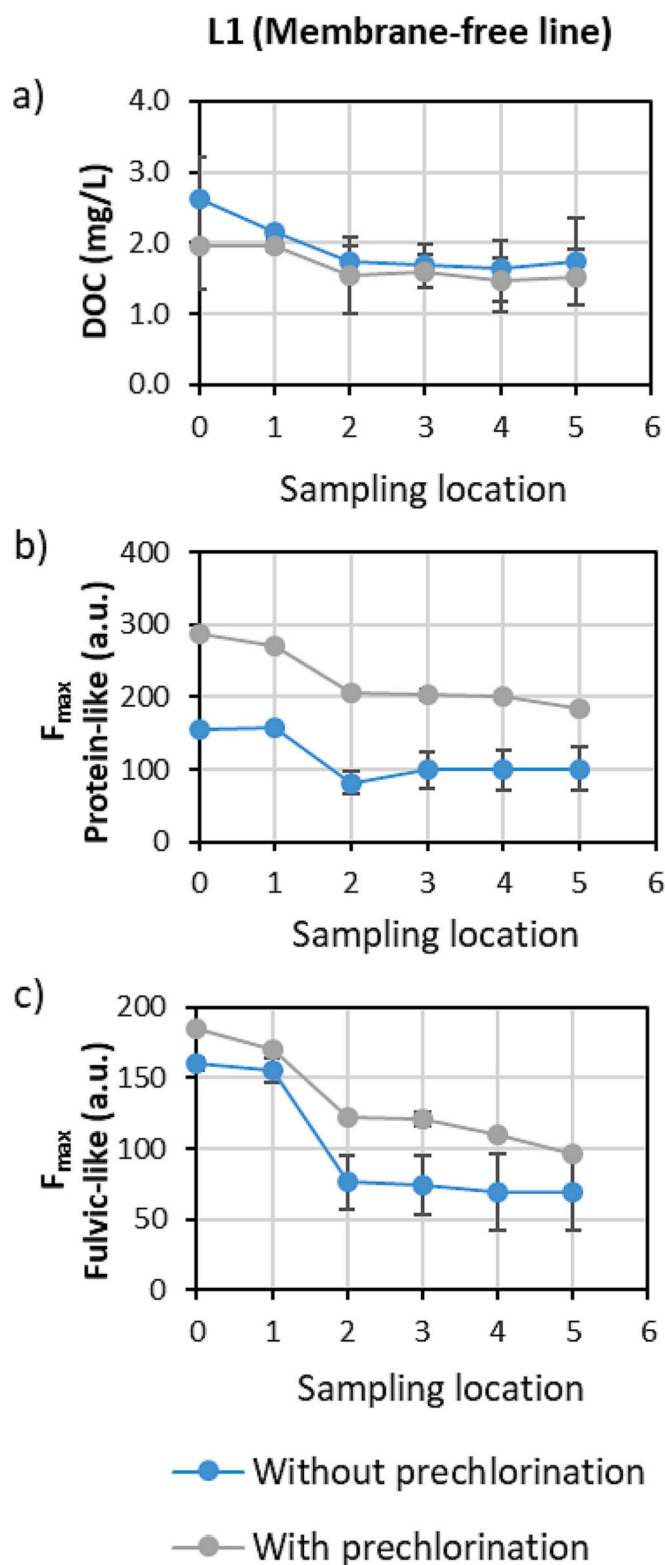DOC was moderately removed (by 33 % and 29 % without and with

L1 (Membrane-free line)

Fig. 4. Changes in DOC (a), F_{max} of protein-like organic matter (b) and F_{max} of fulvic-like organic matter (c) along the membrane-free treatment line L1. Each plotted trend includes the average (with the standard deviation).

prechlorination), basically in the GAC filter, undoubtedly through adsorption [26,43]. The extent of DOC removal by GAC strongly depends on GAC properties and DOM nature [24,25], making comparison between studies difficult. The DOC removal observed in this study with GAC Chemivall CG900 compared well to that of reported by Ponce-

Robles et al. [44] also using the same GAC (25 %). Prechlorination did not seem to enhance DOC removal. It is known that chlorination, as any other oxidation process, can break large molecular weight DOM into smaller and less aromatic organic fragments, which may exhibit different sorptive behaviour [26,27]. However, this difference was not observed in this study.

Concerning the fDOC fractions, average F_{max} for both protein- and fulvic-like substances also decreased basically in the GAC filter (Fig. 3b and c). Under non-prechlorination conditions, the decrease of F_{max} was around 35 % for protein-like compounds, and 57 % for fulvic-like compounds, while under prechlorination conditions F_{max} maintained around 35 % for protein-like compounds and decreased to 48 % for fulvic-like compounds. Removal percentages seemed to indicate a slight preference of GAC towards fulvic-like compounds over protein-like compounds. Similar findings are reported by Maqbool et al. [32], who concluded that pre-oxidation of natural water (with NaClO but also $KMnO_4$ and O_3) preferentially decreased humic-like fluorescence over that of protein-like, and justified it on the basis that humic-like aromatic structures were more prone to chemical oxidation than the large molecular-weight biopolymers including protein-like components. Similar patterns are reported by Lavonen et al. [31].

3.1.4. Removal of microorganisms in L1

Microbiological analysis showed that microbiological quality of raw and L1-treated water was not to be of concern, as contents of Coliforms, *E. coli*, *Legionella* and nematodes were very low (or undetectable) in raw water and mostly undetectable in the L1-treated water (with occasional detections of very low counts), even without prechlorination (Table 3). In all cases quality of treated water met, with regard to microbiological parameters, the quality stated by the legislation for reuse water (Spanish RD 1620/2007) and drinking water (EU Directive 2020/2184). As expected, only heterotrophs were detected in all sampling events, as heterotrophs are usually more abundant, but they were also detected at low to very low contents and were not of concern either.

Under non-prechlorination conditions, it was observed that counts of heterotrophs in the treated water were occasionally higher than that in raw water (Table 3). This was attributed to malfunction of the backwashing system in the FeOOH filter during the first weeks of operation, which likely resulted in regrowth in the filter and occasional high counts in the effluent. Once the problem was fixed, the backwash could be applied as planned. Despite this, two additional campaigns (during non-prechlorination and prechlorination periods) were carried out to get insight into changes in heterotrophs counts along the treatment lines. The profiles obtained in these sampling events (Fig. 5) showed that regrowth apparently took indeed place in the GAC filter (under non-prechlorination conditions) and in the GAC and zeolite filters (under prechlorination conditions), but also that the regrowth was localised to these filters and that heterotrophs counts decreased towards the exit of L1. Colonization of GAC filters with controlled releases of microorganisms by backwashing has been reported in drinking water treatment [45].

3.2. Performance of the RO membrane-based line L2

3.2.1. Profile of FCR and pH in L2

Fig. 6 shows the changes in pH and FCR along L2. Unlike in L1, no preacidification was applied in L2 as RO was expected to act as a complete barrier for any remaining microorganism. pH maintained around 7.2–8.0 across the first two filters (dual media and pyrolusite), and decreased to 6.5 after the acidification applied ahead the RO unit to prevent scaling. pH of the osmotized water rose to around 7.0–7.5 by the passage through the calcite filter where water was remineralized with calcite.

Under non-prechlorination conditions, FCR remained as expected under detection limit until the exit of the pilot, when FCR increased to 0.6 mg/L by post-chlorination. Under prechlorination conditions CFR

Table 3

Concentration of indicator microorganisms in raw water, L1-treated water and L2-treated water.

		Entrance		Exit L1		Exit L2	
		average count	s.d.[a]	average count	s.d.[a]	average count	s.d.[a]
Without prechlorination							
E. coli	CFU/100 mL	1	2	0	1	0	0
Coliforms	CFU/100 mL	4	3	1	4	1	2
Legionella spp.	CFU/1 L	0	0	0	0	0	0
Nematodes	eggs/10 L	0	0	0	0	0	0
Heterotrophs	CFU/100 mL	63	52	5045*	12556*	105	188
With prechlorination							
E. coli	CFU/100 mL	0	0	0	0	0	0
Coliforms	CFU/100 mL	7	10	0	0	0	0
Legionella spp.	CFU/1 L	0	0	0	0	0	0
Nematodes	eggs/10 L	0	0	0	0	0	0
Heterotrophs	CFU/100 mL	4394**	9228**	0	0	0.2	0.4

[a] Standard deviation.

* The high count and high s.d. value was probably due to malfunction of the backwashing system in the FeOOH filter during the first weeks of operation, which likely resulted in regrowth in the filter and occasional high counts in the effluent (in the order of 10^3/100 mL) (see discussion).

** The high count and high s.d. value due heavy rain episodes occurred in January 2022.
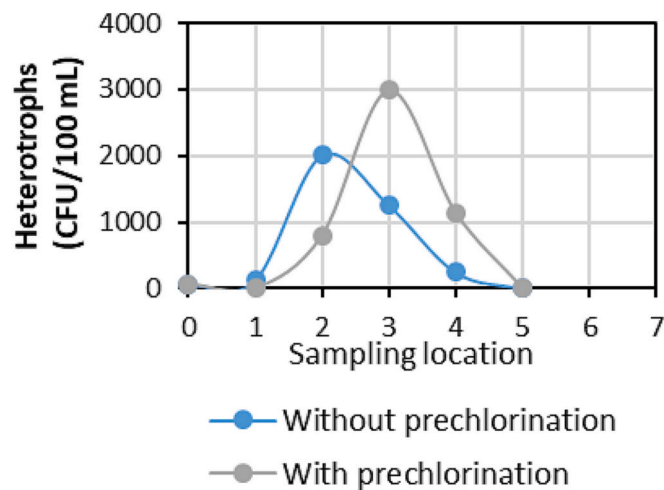

Fig. 5. Count of heterotrophic bacteria along treatment L1.

averaged 1.4 mg/L at the exit of dual media filter and 0.7 mg/L at the exit of the pyrolusite filter. As in L1, the consumption of FCR in these two filters was due to the chlorine demand by metals, organic matter, ammonia... The level of FCR dropped to virtually 0 by the application of metabisulphite ahead the RO unit to protect the membranes. Depletion of chlorine is essential because polymeric membranes may be severely damaged by chlorine, even in low concentrations [46]. ORP measured just ahead of RO was always in the range of 150–250 mV, which is below the maximum value of ca. 300 mV recommended by RO membrane manufacturers to ensure integrity of polyamide membranes [47]. Again, the FCR finally increased to around 0.6 mg/L at the exit of L2 due to postchlorination.

3.2.2. Removal of inorganic ions in L2

Profiles of concentrations along L2 resembled for almost all species: values hardly changed across the first filters but totally dropped after the RO unit. This was expected as RO membranes act as a total barrier for most solutes [14].

Mn was the solute that most differed from this general behaviour: it was mostly removed in the dual media filter (up to 35 %) and in the pyrolusite filter (up to 96 %), showing that these filters preceding the RO unit were already able to remove Mn to levels (around 10 μg/L) below the maximum admissible concentration. The application of NaClO seemed to hinder the removal in the dual media filter, but pyrolusite was
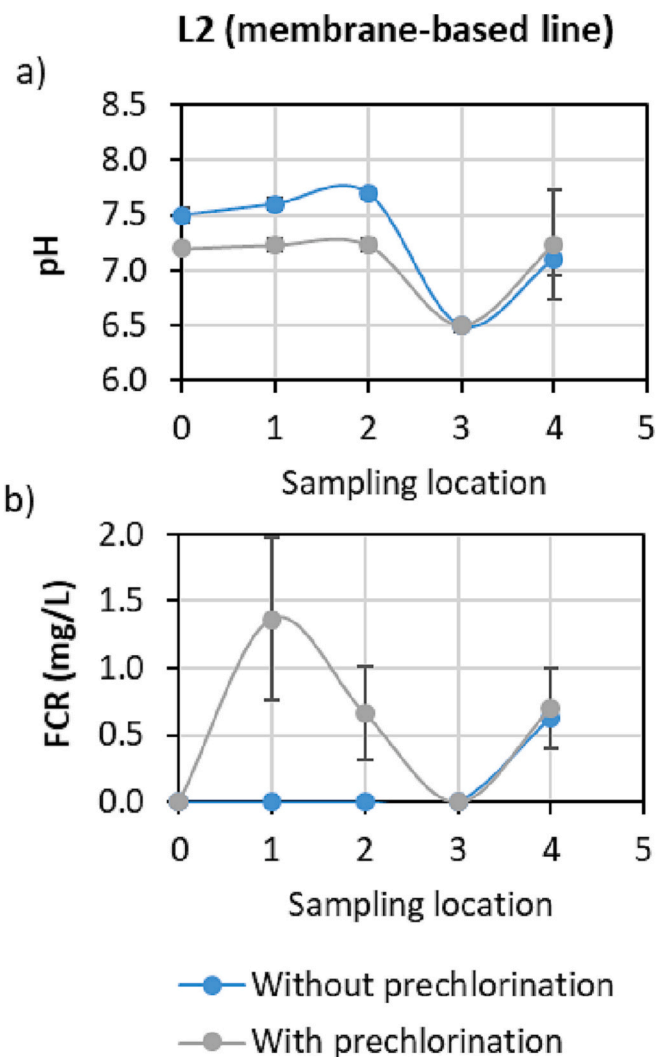

Fig. 6. Changes in pH (a) and FCR (b) along the membrane-based treatment line L2. Each plotted trend includes the average (with the standard deviation).

able to lower the Mn concentrations at the same level as it did without prechlorination. The removal mechanism was the same as discussed for L1. Remaining Mn^{2+} after the passage of the pyrolusite filter was totally
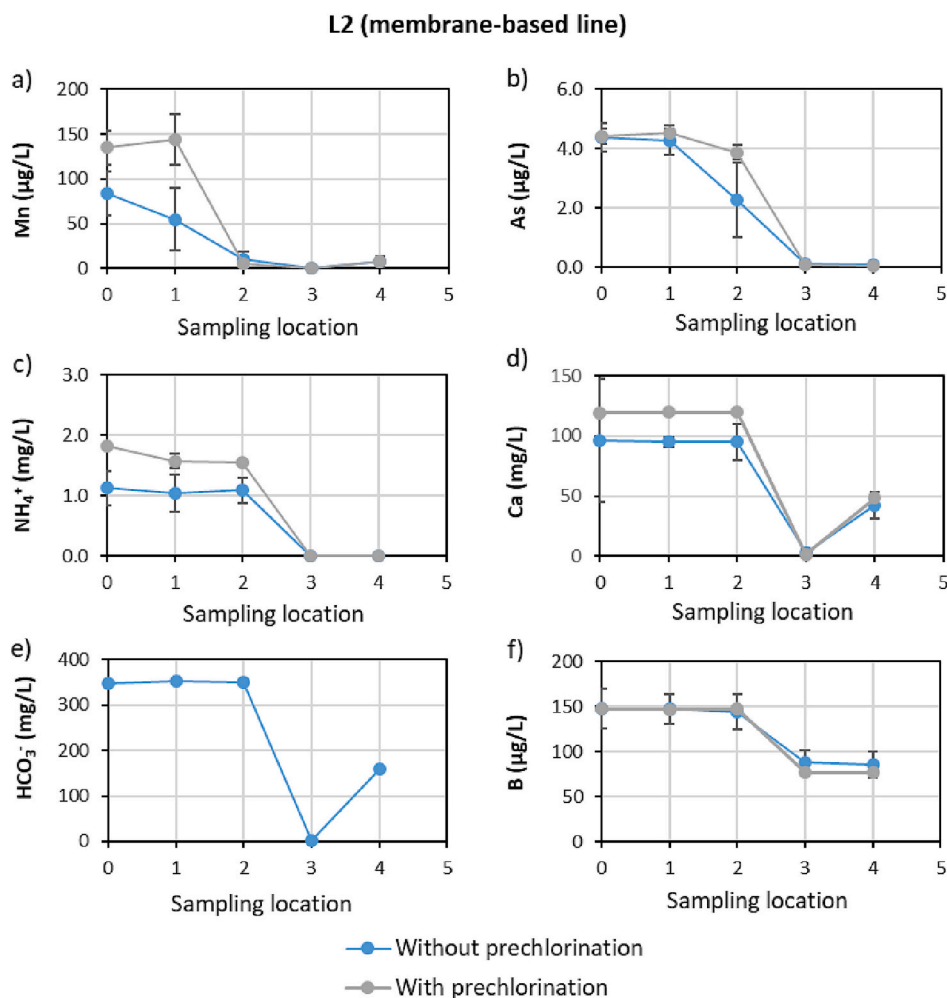
Fig. 7. Changes in concentrations of Mn (a), As (b), NH_4^+ (c), Ca (d), HCO_3^- (e) and B (f) along the membrane-based treatment line L2. Each plotted trend includes the average (with the standard deviation).

removed (>99 %) by the RO membrane. The low concentration of Mn maintained until the exit of L1.

Arsenic (As) was not removed at all by the dual-filter but partially removed by the pyrolusite filter (15–45 %) to concentrations <4 µg/L. The removal mechanism was the same as discussed for L1. The remaining As was then completely removed by RO, providing a concentration at the exit of <0.1 µg/L, far below the limit established by the EU Directive 2020/2184. The total removal of As by the polyamide active layer of the RO membrane was an indication that As(III) was totally oxidized to As(V) (in the form of $H_2AsO_4^-$), as it is only when As is present as As(III) (mainly in the form of the non-charged species H_3AsO_3) that it is only partially rejected by RO membranes [48].

Concentration of NH_4^+ hardly changed across dual-media and pyrolusite filters (a slight decrease was observed when NaClO was injected due to the formation of chloramines), but completely (>99 %) by the RO unit. Concentration at the exit was <0.1 mg/L, again well below the threshold set by the EU Directive 2020/2184.

Ions other than the target ones (Na^+, Mg^{2+}, K^+, Si, Ni^{2+}, Cu^{2+}, Cl^-, SO_4^{2-}…) behaved as expected: they crossed unaltered the first two filters but were highly removed (95–99 %) by the RO unit (not shown). Worth mentioning are the profiles of ions Ca^{2+} and HCO_3^-, which increased their concentration after the passage through the last filter due to calcite dissolution (Fig. 7d and e), and B, which was only partially removed (≈48 %) by RO (Fig. 7f). Difficulties in removing B by RO membranes have been largely reported. The reason of this difficulty is that, at neutral pH, B is found mainly as H_3BO_3, which is a small, non-polar

molecule and, as such, not well retained by polyamide-based RO membranes [49].

3.2.3. Removal of organic matter in L2

DOC and its fluorescent components showed similar profiles along L1 without and with prechlorination: they were hardly removed by the dual-media and pyrolusite filters (<5 %) and highly or totally removed by the RO unit (75–90 % for DOC and > 99 % for both the protein-like and humic-like components) (Fig. 8). As solute size is an important factor governing its removal by RO, it can be inferred that fDOC contained a higher content of larger organic molecules than DOC. This would be in agreement with the statement that oxidation and consequent splitting of large molecular weight NOM results into less fluorescent smaller fragments [50]. Published studies have also reported high removals of DOC (>92 %, with low molecular weight acid compounds partially permeating through the RO membrane) [51] and protein-like and humic-like compounds [33] by RO membranes.

3.2.4. Removal of microorganisms in L2

Microbiological analysis of L2-treated water showed that contents of Coliforms, *E. coli*, *Legionella* and nematodes were undetectable under both non-prechlorination and prechlorination conditions (only Coliforms were occasionally detected at very low counts (Table 3). In all cases, quality of treated water met the quality stated by the European legislation for drinking water (Directive 2020/2184).
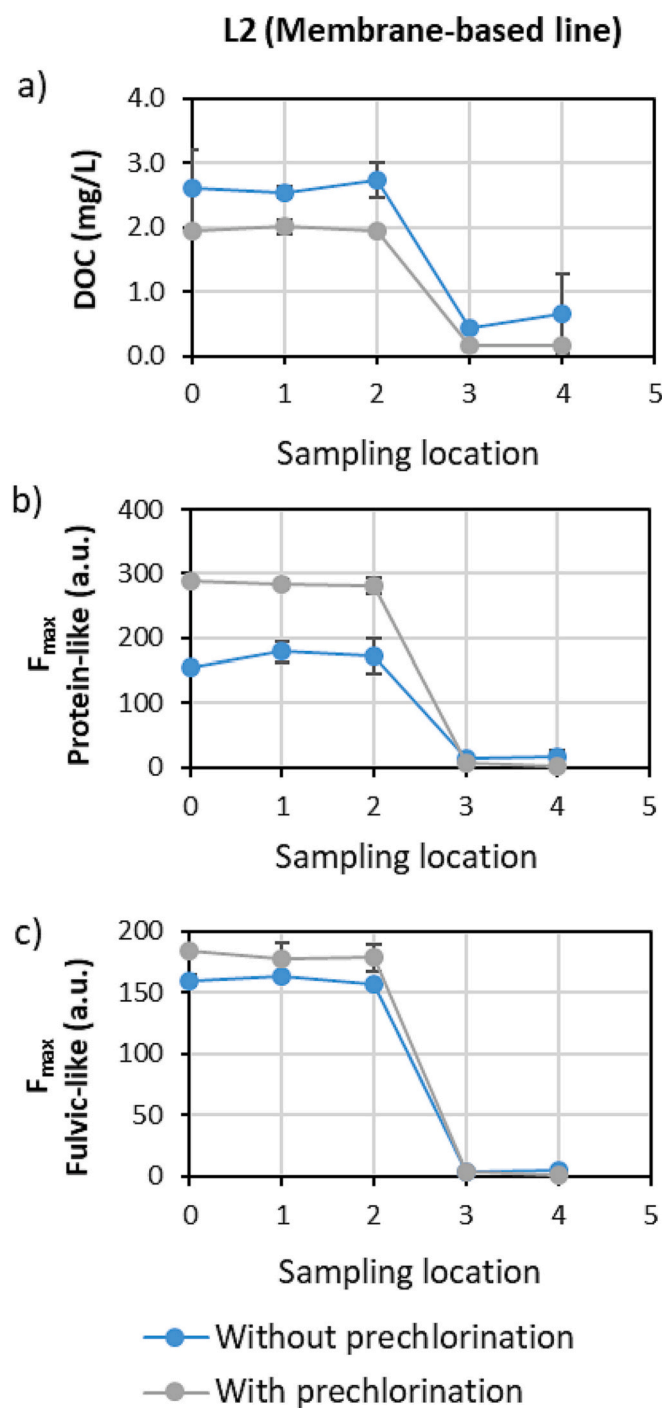
L2 (Membrane-based line)

Fig. 8. Changes in DOC (a), F_{max} of protein-like organic matter (b) and F_{max} of fulvic-like organic matter (c) along the membrane-based treatment line L2. Each plotted trend includes the average (with the standard deviation).

3.3. Formation of disinfection by-products (DBPs) in L1 and L2

It is well acknowledged that water chlorination poses the additional risk of promoting the formation of DBPs. The EU Directive 2020/2184 sets a threshold for the sum of trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) of 100 µg/L for a water to be drinkable. In our study, L1-treated and L2-treated water, both without and with prechlorination, showed THMs contents always <5.0 µg/L and therefore the formation of DBPs was not considered of concern.

These low values even under pre-chlorination conditions were likely favoured by 1) the fairly low content of DOC in UGW and therefore the

low potential formation of DBPs, 2) the low content of Br^- in UGW (<0.5 mg/L, see Table 1) and therefore the low formation of brominated -THMs, which are reported to be less rejected by RO than chlorinated-THMs [52], 3) the removal of formed DBPs along L1 (particularly in the GAC filter by adsorption) [24] and L2 (in the RO unit) [53], and/or 4) the lower propensity of chloramines to form DBPs in comparison to chlorine [30].

3.4. Quality of produced water and potential for reuse

Table 4 compares the quality of treated water by lines L1 and L2 (without and with prechlorination) with the quality of water for reuse and drinking water purposes specified by the Spanish RD 1620/2007 and the EU Directive 2020/2184, respectively. For water reuse maximum allowed contents are given as ranges because the RD 1620/2007 differentiates up to 14 uses under five main areas (urban, agricultural irrigation, industrial, recreational and environmental), each with its own threshold(s).

As can be seen in Table 4, treated water by both L1 and L2 accomplished the quality required regarding microbiological and chemical parameters for all reuse purposes tabulated in the RD 1620/2007, even for the most stringent one (i.e. irrigation of crops using a system whereby reclaimed water comes into direct contact with edible parts of crops to be eaten raw). Therefore, treated water can be considered suitable for urban, agricultural, industrial, recreational and environmental purposes. Treated water also fulfils the Spanish RD 817/2015 on the status of surface waters and environmental quality standards. Actually, 1 % of the UGW pumped from the parking lot is already used for urban and environmental uses (street washing and gardening, and streamflow augmentation in the Besòs river).

It should be taken in mind that specific industrial sectors may require more stringent thresholds that those stipulated in the RD 1620/2007 and therefore quality of reclaimed water should be determined on a case-by-case basis. For instance, an important parameter in textile industry is the content of Fe, which must be kept at low levels comparable to those for drinking water [54]. Other industrial sectors that may require high quality waters with low concentration of dissolved species (e.g. dissolved solids, DOC...) are the micro-electronics, pharmaceuticals and food and beverage. Also boiler feed water for steam turbines usually requires quality comparable to that of drinking water [55].

Cl^- has recently received attention as a species of concern in reclaimed water after removal of mandatory components (pathogens, micropollutants, dissolved solids) [56]. Cl^- has multiple harmful effects on water reuse, including crop yield loss (at concentrations above 180 mg/L in irrigation water), soil salinization (at contents above 200 mg/kg in soil), equipment corrosion and incrustations problems, and limitations of the final product quality (making necessary concentrations below 250 mg/L in recirculating cooling water for boilers, wash water and process water, or even below 2 mg/L in water for electrolysis and electronics industries) ([56] and references therein). If that was not enough, Cl^- is difficult to remove, and it can even increase along a treatment train through processes that involve chlorine (acidification with HCl, oxidation with NaClO...). In our pilot, an increase of Cl^- occurred in L1, caused by the preacidification with HCl and prechlorination with NaClO (Fig. 9a), but not in L2 where RO removed Cl^- almost totally (Fig. 9b). This resulted in concentrations in L1-treated water around 310 mg/L for Cl^- (and 280 mg/L for Na) with and without prechlorination (in bold in Table 4) that might make it unsuitable for very high-quality water requiring purposes.

Although drinking water production was not targeted at this stage of the project, it can be added that treated water by L2 (with and without prechlorination) and L1 (only with prechlorination) accomplished the EU Directive 2020/2184 on drinking water with regards to targeted species of this study (Mn, As, NH_4^+, DOC and pathogens), with values far below the thresholds of 50 µg/L for Mn, 10 µg/L for As, 0.5 mg/L for NH_4^+..., with the exception of NH_4^+ in line L1 when operated without

Table 4
Quality of treated water by L1 and L2 (both under non-prechlorination and prechlorination conditions) and comparison against legislation water quality limits.

Parameters	Units	L1 (Membrane-free) Without prechlorination	L1 (Membrane-free) With prechlorination	L2 (Membrane-based) Without prechlorination	L2 (Membrane-based) With prechlorination	RD 1620/2007[a]	Directive 2020/2184[b]
pH		7.1 ± 0.1	6.9 ± 0.1	7.1 ± 0.1	7.2 ± 0.5	–	6.5–9.5
Conductivity	μS/cm	1485 ± 38	1470 ± 128	302 ± 71	344 ± 74	3000000[d]	2500
SS	mg/L	<1	<1	<1	<1	5-35[c]	1
Turbidity	NTU	n.a.	n.a.	n.a.	n.a.	1-15[c]	–
Na		**279.0 ± 71.7**	**283.8.0 ± 64.2**	12.5 ± 13.9	34.6 ± 20.2	–	200
K		8.0 ± 12.8	18.6 ± 16.0	0.3 ± 0.1	0.3 ± 0.1	–	–
NH_4^+		**1.0 ± 1.0**	<0.1	<0.1	<0.1	–	0.5
Mg		2.7 ± 7.5	11.1 ± 13.6	<0.1	<0.1	–	–
Ca		6.2 ± 18.5	30.0 ± 32.3	42.3 ± 9.9	48.5 ± 3.5	–	–
Cl^-		**312.6 ± 6.1**	**313.2 ± 3.6**	37.3 ± 0.3	37.3 ± 0.5	–	250
NO_3^-	mg/L	<3.0	<3.0	<0.5	<0.5	25[d]	50
SO_4^{2-}		131.4 ± 0.9	121.4 ± 1.4	1.6 ± 0.4	1.0 ± 0.2	–	250
HCO_3^-		276.7 ± 37.7	n.a.	159.2 ± 12.7	n.a.	–	–
F^-		<0.5	<0.5	<0.5	<0.5	–	1.5
Br^-		<0.5	<0.5	<0.5	<0.5	–	–
HPO_3^{2-}		<0.5	<0.5	<0.5	<0.5	2[d] (total P)	–
Si		38.7 ± 2.5	7.0 ± 0.7	6.0 ± 1.7	<0.1	–	–
B		136.4 ± 13.8	132.8 ± 44.1	85.6 ± 26.3	76.9 ± 9.6	500[d]	1500
Al		<0.2	<0.2	<0.2	<0.2	–	200
Mn		2.3 ± 3.2	41.7 ± 17.0	8.3 ± 3.3	7.9 ± 6.4	200[d]	50
Ni		2.3 ± 0.6	2.7 ± 0.6	0.5 ± 0.5	0.5 ± 0.5	200[d]	20
Cu		0.9 ± 0.4	1.4 ± 0.6	0.2 ± 0.2	0.3 ± 0.4	200[d]	2000
As		0.1 ± 0.1	1.5 ± 1.8	0.1 ± 0.1	0.1 ± 0.1	100[d]	10
Pb	μg/L	<1.0	<1.0	<1.0	<1.0	–	5
Cd		<1.0	<1.0	<1.0	<1.0	10[d]	5
Cr		<1.0	<1.0	<1.0	<1.0	100[d]	25
Fe		<1.0	<1.0	<1.0	<1.0	–	200
Sb		n.a.	n.a.	n.a.	n.a.	–	5
Hg		n.a.	n.a.	n.a.	n.a.	–	1
Se		n.a.	n.a.	n.a.	n.a.	20[d]	10
DOC	mg/L	1.8 ± 0.6	1.5 ± 0.2	0.7 ± 0.6	0.2 ± 0.1	–	–
E.coli	CFU/100 mL	0	0	0	0	0-10000[c]	0
Enterococo	CFU/100 mL	n.a.	n.a.	n.a.	n.a.	n.a.	0
Clostridium perf.	CFU/100 mL	n.a.	n.a.	n.a.	n.a.	n.a.	0
Coliforms	CFU/100 mL	1 ± 4	0	1 ± 2	0	–	0
Legionella spp.	CFU/1 L	0	0	0	0	100-1000[c]	
Nematodes	eggs/10 L	0	0	0	0	0-1[c]	
Heterotrophs	CFU/100 mL	5045 ± 12556*	0	105 ± 188	0.2 ± 0.4	–	10,000
THMs	μg/L	<5	<5	<5	<5	–	100
CFR	mg/L	0.9 ± 0.4	0.9 ± 0.5	0.6 ± 0.3	0.7 ± 0.3	–	1

* The high count and high s.d. value was probably due to malfunction of the backwashing system in the FeOOH filter during the first weeks of operation, which likely resulted in regrowth in the filter and occasional high counts in the effluent (in the order of 103/100 mL) (see discussion).
n.a.: not analysed.
[a] Spanish Water Reuse legislation.
[b] European Drinking Water legislation.
[c] Depending on the use of reclaimed water (urban, agricultural, industrial, recreational, environmental).
[d] Applicable only for water intended for irrigation requiring the highest quality (irrigation of crops eaten raw).

prechlorination (for which the concentration in the produced water was 1.0 mg/L). Therefore, and with the exception of the latter scenario, the possibility of producing drinking water could be considered if needed.

3.5. Cost estimation of produced water through lines L1 and L2

Costs of treated water production were calculated considering the following items: capital cost (site preparation, design, construction, mobilization and installation of the pilot, piping and electricity distribution system, etc.), treatment materials (filtering media and RO membranes), reagents dosage, energy consumption and maintenance (3 % of total cost). Personnel salary and legal fees were not included. All capital cost components were amortized over the design life of the pilot plant, which was assumed to be 12 years. The lifetime of filtering media and RO membranes was considered to be 2 and 5 years, respectively.

Costs were calculated differentiating the two operation conditions tested, i.e. without and with prechlorination. The reagents applied were HCl, NaCl and NaClO for postchlorination and optionally for prechlorination (for L1) and antiscalant, metabisulphite, HCl and NaClO for postchlorination and optionally for prechlorination (for L2). With regard to energy cost, the power consumption of each electric device (pumps to move water through the lines, dosing pumps, backwashing pumps, sensors…) and its operation time were used. An electricity tariff of 0.2876 €/kWh (average between September 2021 and April 2022) was considered. A cost breakdown (expressing costs per cubic metre of water produced) is presented in Table 5.

As shown in Table 5, the total cost of produced water without prechlorination was 0.896 €/m³ for L1 and 0.968 €/m³ for L2. These costs increased to 0.928 €/m³ for L1 and 1.027 €/m³ for L2 under prechlorination conditions due to the continuous addition of NaClO.
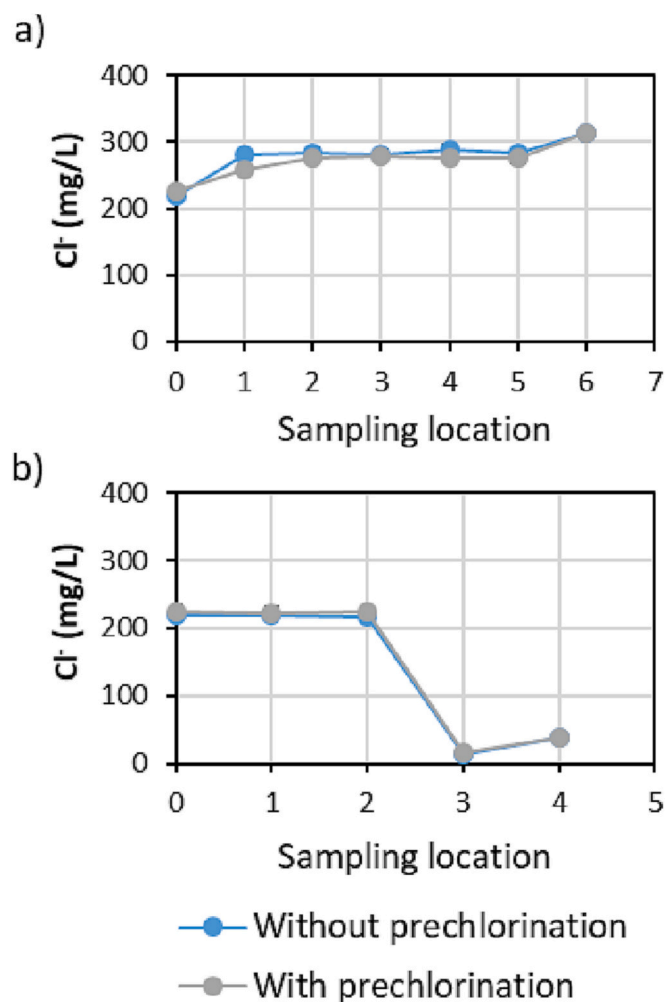
Fig. 9. Evolution of Cl⁻ concentration along L1 (a) and L2 (b) under non-prechlorination and prechlorination conditions.

Differences in cost of produced water between L1 and L2 were thus of 8–10 %.

The cost values for produced water through L1 and L2 compared well with those reported by other studies applying advanced treatments (microfiltration/ultrafiltration, GAC, reverse osmosis) at pilot-scale (1,16 €/m³ by [57]; 0.85 €/m³ by [58]). These values, however, should be viewed as an estimation when extrapolating the results observed in this study to long-term operation periods. First, because the quality of raw UGW may change, and so the lifetime of filtering media and RO membrane. Second, the electricity tariff can largely change between countries and also along the year. Furthermore, it can be added that applying the same treatment trains at higher scale can modify costs, since plant capacity affects capital costs through economies of scale. And related to this, larger plants offer the possibility of introducing energy recovery units, allowing to decrease energy consumption by up to 50 %.

However, the analysis allowed to identify the items that most contributed to the final cost of treated water in this study. The major contributors to the total cost for L1 were the filtering media replacement (33 %) and the reagents dosed (28 %), while for L2 it was the energy consumption (41 %), mostly coming from the booster pump for the RO filtration. Another aspect that helps explain the higher cost for L2 is that amount of produced water is lower than in L1, as RO in L2 converts only a fraction (in this study 60 %) of the incoming water into produced water.

4. Conclusions

This study has demonstrated that reclamation of UGW from Sant Adrià del Besòs has a huge potential for reuse for a wide diversity of final purposes (urban, agricultural, industrial, environmental and recreational uses) and, although it may need further exploration, likely for drinking water purposes. The UGW was treated through two treatment lines both based on advanced treatments: line L1 included different sorption and ion-exchange filters, while line L2 relied on a sorption filter and a RO filtration step. Both lines were operated without and with prechlorination to ascertain whether NaClO favoured or hindered (and to what extent) the removal of target parameters (Mn, As, NH_4^+, DOC, pathogens, THMs).

L1 was successful at removing Mn, As, pathogens and THMs at levels below those stipulated by the RD 1620/2007 for reuse and even those by the EU Directive 2020/2184 for drinking water, without and with pre-chlorination. Only NH_4^+ failed to decrease below its threshold limits, but only in the absence of prechlorination. When NaClO was applied, also NH_4^+ met the limit for reuse and drinking water. It must be bear in mind that, for specific industrial uses requiring high-quality reclaimed water, additional specific ones beyond the mandatory parameters set by the legislation on reuse and drinking water may need to be removed. In that regard, Cl⁻ and Na may appear as problematic species. L2 showed a consistent high removal of all targeted parameters (also NH_4^+) without and with prechlorination conditions, producing a finished water with excellent quality with high potential for reuse and also for production of drinking water.

The outperformance of L2 in terms of produced water quality must be balanced by the cost: 0.896 €/m³ (without prechlorination) and 0.928 €/m³ (with prechlorination) for L1 and 0.968 €/m³ (without prechlorination) and 1.027 €/m³ (with prechlorination) for L2, meaning that a trade-off between quality and cost must be faced. If solutes concentrations in the produced water do not need to be reduced to an excessively low level, then less costly L1 may suffice. Intermediate solution could be achieved by blending L1- and L2-treated waters if the resulting quality already matches the one required according to its final intended purpose.

Declaration of competing interest

Hereby, the authors declare that the content of this article is subject to no conflict of interest.

Table 5
Cost breakdown for lines L1 and L2 operated without and with prechlorination (costs expressed in €/m³ of produced water).

€/m³	L1 (membrane-free line)		L2 (membrane-based line)	
	Without prechlorination	With prechlorination	Without prechlorination	With prechlorination
Capital cost	0.225	0.225	0.296	0.296
Filter media and RO membranes	0.304	0.304	0.116	0.116
Energy consumption	0.100	0.100	0.403	0.421
Reagents dosage	0.241	0.271	0.125	0.165
Maintenance	0.027	0.028	0.029	0.031
TOTAL	0.896	0.928	0.968	1.027

Data availability

Data will be made available on request.

References

[1] M. Rygaard, P.J. Binning, H.J. Albrechtsen, Increasing urban water self-sufficiency: new era, new challenges, J. Environ. Manag. 92 (2011) 185–194, https://doi.org/10.1016/j.jenvman.2010.09.009.

[2] N. Voulvoulis, Water reuse from a circular economy perspective and potential risks from an unregulated approach, Curr. Opin. Environ. Sci. Health 2 (2018) 32–45, https://doi.org/10.1016/j.coesh.2018.01.005.

[3] J. Fito, S.W.H. Van Hulle, Wastewater reclamation and reuse potentials in agriculture: towards environmental sustainability, Environ. Dev. Sustain. 23 (2021) 2949–2972, https://doi.org/10.1007/s10668-020-00732-y.

[4] R. Roccaro, Treatment processes for municipal wastewater reclamation: the challenges of emerging contaminants and direct potable reuse, Curr. Opin. Environ. Sci. Health 2 (2018) 46–54, https://doi.org/10.1016/j.coesh.2018.02.003.

[5] C.Y. Chen, S.W. Wang, H. Kim, S.Y. Pan, C. Fan, Y.J. Lin, Non-conventional water reuse in agriculture: a circular water economy, Water Res. 199 (2021), 117193, https://doi.org/10.1016/j.watres.2021.117193.

[6] P. Kehrein, M. Jafaria, M. Slagt, E. Cornelissen, P. Osseweijer, J. Posada, M. van Loosdrecht, A techno-economic analysis of membrane-based advanced treatment processes for the reuse of municipal wastewater, Water Reuse 11 (2021) 705–725, https://doi.org/10.2166/wrd.2021.016.

[7] A. Jurado, E. Vázquez-Suñé, E. Pujades, Potential uses of pumped urban groundwater: a case study in Sant Adrià del Besòs (Spain), Hydrogeol. J. 25 (2017) 1745–1758, https://doi.org/10.1007/s10040-017-1575-3.

[8] A. Jurado, A. Margareto, E. Pujades, E. Vázquez-Suñé, M.S. Diaz-Cruz, Fate and risk assessment of sulfonamides and metabolites in urban groundwater, Environ. Pollut. 267 (2020), 115480, https://doi.org/10.1016/j.envpol.2020.115480.

[9] N.A. Ramírez-Agudelo, J. de Pablo, E. Roca, Exploring alternative practices in urban water management through the lens of circular economy–a case study in the Barcelona metropolitan area, J. Clean. Prod. 329 (2021), 129565, https://doi.org/10.1016/j.jclepro.2021.129565.

[10] L. Pietrelli, N.M. Ippolito, S. Ferro, V.G. Dovì, M. Vocciante, Removal of Mn and As from drinking water by red mud and pyrolusite, J. Environ. Manag. 237 (2019) 526–533, https://doi.org/10.1016/j.jenvman.2019.02.093.

[11] S.I. Siddiqui, S.A. Chaudhry, Iron oxide and its modified forms as an adsorbent for arsenic removal: a comprehensive recent advancement, Process. Saf. Environ. Prot. 111 (2017) 592–626, https://doi.org/10.1016/j.psep.2017.08.009.

[12] A.G. Tekerlekopoulou, S. Pavlou, D.V. Vayenas, Removal of ammonium, iron and manganese from potable water in biofiltration units: a review, J. Chem. Technol. Biotechnol. 88 (2013) 751–773, https://doi.org/10.1002/jctb.4031.

[13] J.E. Tobiason, A. Bazilio, J. Goodwill, X. Mai, C. Nguyen, Manganese removal from drinking water sources, Curr. Pollut. Rep. 2 (2016) 168–177, https://doi.org/10.1007/s40726-016-0036-2.

[14] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, Desalination 267 (2011) 1–8, https://doi.org/10.1016/j.desal.2010.09.001.

[15] D.S. Patil, S.M. Chavan, J.U.K. Oubagaranadin, A review of technologies for manganese removal from wastewaters, J. Environ. Chem. Eng. 4 (2016) 468–487, https://doi.org/10.1016/j.jece.2015.11.028.

[16] B.K. Pramanik, S.K. Pramanik, F. Suja, Removal of arsenic and iron removal from drinking water using coagulation and biological treatment, J. Water Health 14 (2016) 90–96, https://doi.org/10.2166/wh.2015.159.

[17] A. Choudhry, A. Sharma, T.A. Khan, S.A. Chaudhry, Flax seeds based magnetic hybrid nanocomposite: an advance and sustainable material for water cleansing, J. Water Process Eng. 42 (2021) 102150, https://doi.org/10.1016/j.jwpe.2021.102150.

[18] A. Sharma, D. Mangla, S.A. Chaudhry Shehna, Recent advances in magnetic composites as adsorbents for wastewater remediation, J. Environ. Manag. 306 (2022), 114483, https://doi.org/10.1016/j.jenvman.2022.114483.

[19] S.R. Taffarel, J. Rubio, Removal of Mn^{2+} from aqueous solution by manganese oxide coated zeolite, Miner. Eng. 23 (2010) 1131–1138, https://doi.org/10.1016/j.mineng.2010.07.007.

[20] L. Weerasundara, Y.-S. Ok, J. Bundschuh, Selective removal of arsenic in water. A critical review, Environ. Pollut. 268 (2021), 115668, https://doi.org/10.1016/j.envpol.2020.115668.

[21] J. Huang, N.R. Kankanamge, C. Chow, D.T. Welsh, T. Li, P.R. Teasdale, Removing ammonium from water and wastewater using cost-effective adsorbents: a review, J. Environ. Sci. 63 (2018) 174–197.

[22] S. Sorlini, F. Gialdini, Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine, Water Res. 44 (2010) 5653–5659, https://doi.org/10.1016/j.watres.2010.06.032.

[23] N. Chaukura, S.S. Marais, W. Moyo, N. Mbali, L.C. Thakalekoala, T. Ingwani, B.B. Mamba, P. Jarvis, T.T.I. Nkambule, Contemporary issues on the occurrence and removal of disinfection byproducts in drinking water - a review, J. Environ. Chem. Eng. 8 (2020), 103659, https://doi.org/10.1016/j.jece.2020.103659.

[24] D.M. Golea, P. Jarvis, B. Jefferson, G. Moore, S. Sutherland, S.A. Parsons, S.J. Judd, Influence of granular activated carbon media properties on natural organic matter and disinfection by-product precursor removal from drinking water, Water Res. 174 (2020), 115613, https://doi.org/10.1016/j.watres.2020.115613.

[25] C.U. Erdem, M. Ateia, C. Liu, T. Karanfil, Activated carbon and organic matter characteristics impact the adsorption of DBP precursors when chlorine is added prior to GAC contactors, Water Res. 184 (2020), 116146, https://doi.org/10.1016/j.watres.2020.116146.

[26] O. Gibert, B. Lefèvre, M. Fernández, X. Bernat, M. Paraira, M. Pons, Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production, Water Res. 47 (2013) 2821–2829, https://doi.org/10.1016/j.watres.2013.02.028.

[27] J. Świetlik, E. Sikorska, Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone, Water Res. 38 (2004) 3791–3799, https://doi.org/10.1016/j.watres.2004.06.010.

[28] N.A. Klymenko, L.A. Savchyna, L.K. Patiuk, S.V. Grechanik, Application of chlorine dioxide for restoring the adsorption capacity of activated carbon wasted under industrial conditions, J. Water Chem. Technol. 42 (2020) 171–177, https://doi.org/10.3103/S1063455X20030078.

[29] S. Beeharry, S. Sihota, C. Kelly, Profiling chlorine residuals using DPD and amperometric field test kits in a chlorinated small drinking water system with ammonia present in source water, Environ. Health Rev. 61 (2018) 39–49, https://doi.org/10.5864/d2018-011.

[30] H.A. Duong, M. Berg, M.H. Hoang, H.V. Pham, H. Gallard, W. Giger, U. von Gunten, Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam, Water Res. 37 (2003) 3242–3252, https://doi.org/10.1016/S0043-1354(03)00138-6.

[31] E.E. Lavonen, D.N. Kothawala, L.J. Tranvik, M. Gonsior, P. Schmitt-Kopplin, S.J. Köhler, Tracking changes in the optical properties and molecular composition of dissolved organic matter during drinking water production, Water Res. 85 (2015) 286–294, https://doi.org/10.1016/j.watres.2015.08.024.

[32] T. Maqbool, Y. Qin, Q.V. Ly, J. Zhang, C. Li, M.B. Asif, Z. Zhang, Exploring the relative changes in dissolved organic matter for assessing the water quality of full-scale drinking water treatment plants using a fluorescence ratio approach, Water Res. 183 (2020), 116125, https://doi.org/10.1016/J.WATRES.2020.116125.

[33] M. Vera, S. Cruz, M.R. Boleda, J. Mesa, J. Martín-Alonso, S. Casas, O. Gibert, J.L. Cortina, Fluorescence spectroscopy and parallel factor analysis as a dissolved organic monitoring tool to assess treatment performance in drinking water trains, Sci. Total Environ. 584–585 (2017) 1212–1220, https://doi.org/10.1016/j.scitotenv.2017.01.184.

[34] M.J.B. Evans, E. Halliop, S. Liang, J.A.F. MacDonald, The effect of chlorination on surface properties of activated carbon, Carbon 36 (1998) 1677–1682.

[35] B. Li, H. Zhang, W. Zhang, L. Huang, J. Duan, J. Hu, W. Ying, Cost effective activated carbon treatment process for removing free chlorine from water, Asia Pac. J. Chem. Eng. 5 (2010) 714–720, https://doi.org/10.1002/apj.396.

[36] J. Jèz-Walkowiak, Z. Dymaczewski, A. Szuster-Janiaczyk, A.B. Nowicka, M. Szybowicz, Efficiency of Mn removal of different filtration materials for groundwater treatment linking chemical and physical properties, Water 9 (2017) 498, https://doi.org/10.3390/w9070498.

[37] V. Lenoble, C. Chabroullet, R. al Shukry, B. Serpaud, V. Deluchat, J.C. Bollinger, Dynamic arsenic removal on a MnO_2-loaded resin, J. Colloid Interf. Sci. 280 (2004) 62–67, https://doi.org/10.1016/j.jcis.2004.07.034.

[38] J. Giménez, M. Martínez, J. de Pablo, M. Rovira, L. Duro, Arsenic sorption onto natural hematite, magnetite, and goethite, J. Hazard. Mat. 141 (2007) 575–580, https://doi.org/10.1016/j.jhazmat.2006.07.020.

[39] H. Huang, L. Yang, Q. Xue, J. Liu, L. Hou, L. Ding, Removal of ammonium from swine wastewater by zeolite combined with chlorination for regeneration, J. Environ. Manag. 160 (2015) 333–341, https://doi.org/10.1016/j.jenvman.2015.06.039.

[40] N. Widiastuti, H. Wu, H.M. Ang, D. Zhang, Removal of ammonium from greywater using natural zeolite, Desalination 277 (2011) 15–23, https://doi.org/10.1016/j.desal.2011.03.030.

[41] B. Han, C. Butterly, W. Zhang, J.Z. He, D. Chen, Adsorbent materials for ammonium and ammonia removal: a review, J. Clean. Prod. 283 (2021), 124611, https://doi.org/10.1016/j.jclepro.2020.124611.

[42] E. Okoniewska, J. Lach, M. Kacprzak, E. Neczaj, The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon, Desalination 206 (2007) 251–258, https://doi.org/10.1016/j.desal.2006.04.055.

[43] O. Gibert, B. Lefèvre, A. Teuler, X. Bernat, J. Tobella, Distribution of dissolved organic matter fractions along several stages of a drinking water treatment plant, J. Water Process Eng. 6 (2015) 64–71, https://doi.org/10.1016/j.jwpe.2015.03.006.

[44] L. Ponce-Robles, B. Masdemont-Hernández, T. Munuera-Pérez, A. Pagán-Muñoz, A.J. Lara-Guillén, A.J. García-García, F. Pedrero-Salcedo, P.A. Nortes-Tortosa, J.J. Alarcón-Cabañero, WWTP effluent quality improvement for agricultural reuse

using an autonomous prototype, Water 12 (2020) 2240, https://doi.org/10.3390/w12082240.

[45] O. Gibert, B. Lefèvre, M. Fernández, X. Bernat, M. Paraira, M. Calderer, X. Martínez-Lladó, Characterising biofilm development on granular activated carbon used for drinking water production, Water Res. 47 (2013) 1101–1110, https://doi.org/10.1016/j.watres.2012.11.026.

[46] J.M. Gohil, A.K. Suresh, Chlorine attack on reverse osmosis membranes: mechanisms and mitigation strategies, J. Membr. Sci. 541 (2017) 108–126, https://doi.org/10.1016/j.memsci.2017.06.092.

[47] R. Verbeke, V. Gómez, I.F.J. Vankelecom, Chlorine-resistance of reverse osmosis (RO) polyamide membranes, Prog. Polym. Sci. 72 (2017) 1–15, https://doi.org/10.1016/j.progpolymsci.2017.05.003.

[48] T. Geucke, S.A. Deowan, J. Hoinkis, C. Pätzold, Performance of a small-scale RO desalinator for arsenic removal, Desalination 238 (2009) 198–206, https://doi.org/10.1016/j.desal.2008.03.018.

[49] Y. Cengeloglu, G. Arslan, A. Tor, I. Kocak, N. Dursun, Removal of boron from water by using reverse osmosis, Sep. Purif. Technol. 64 (2008) 141–146, https://doi.org/10.1016/j.seppur.2008.09.006.

[50] S.A. Baghoth, S.K. Sharma, G.L. Amy, Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC, Water Res. 45 (2011) 797–809, https://doi.org/10.1016/j.watres.2010.09.005.

[51] F.X. Simon, Y. Penru, A.R. Guastalli, S. Esplugas, J. Llorens, S. Baig, NOM characterization by LC-OCD in a SWRO desalination line, Desalin. Water Treat. 51 (2013) 1776–1780, https://doi.org/10.1080/19443994.2012.704693.

[52] E. Agus, D.L. Sedlak, Formation and fate of chlorination by-products in reverse osmosis desalination systems, Water Res. 44 (2010) 1616–1626, https://doi.org/10.1016/j.watres.2009.11.015.

[53] K. Doederer, M.J. Farré, M. Pidou, H.S. Weinberg, W. Gernjak, Rejection of disinfection by-products by RO and NF membranes: influence of solute properties and operational parameters, J. Membr. Sci. 467 (2014) 195–205, https://doi.org/10.1016/j.memsci.2014.05.029.

[54] H. Yin, P. Qiu, Y. Qian, Z. Kong, X. Zheng, Z. Tang, H. Guo, Textile wastewater treatment for water reuse: a case study, Processes 7 (2019) 34, https://doi.org/10.3390/pr7010034.

[55] É. Hansen, M.A.S. Rodrigues, P.M. de Aquim, Characterization of aqueous streams in a petrochemical industry: a study for the reuse of industrial effluents, J. Water. Process Eng. 27 (2019) 99–109, https://doi.org/10.1016/j.jwpe.2018.11.018.

[56] K.-F. Cao, Z. Chen, Y.-H. Wu, Y. Mao, Q. Shi, X.-W. Chen, Y. Bai, K. Li, H.-Y. Hu, The noteworthy chloride ions in reclaimed water: harmful effects, concentration levels and control strategies, Water Res. 215 (2022), 118271, https://doi.org/10.1016/j.watres.2022.118271.

[57] R. Lo, S.-L. Lo, A pilot plant study using ceramic membrane microfiltration, carbon adsorption and reverse osmosis to treat CMP (chemical mechanical polishing) wastewater, Water Sci. Technol. Water Supply 4 (2004) 111–118, https://doi.org/10.2166/ws.2004.0013.

[58] M.E. Ersahin, H. Ozgun, R. Kaya, B.K. Mutlu, C. Kinaci, I. Koyuncu, Treatment of produced water originated from oil and gas production wells: a pilot study and cost analysis, Environ. Sci. Pollut. Res. 25 (2018) 6398–6406, https://doi.org/10.1007/s11356-017-0961-7.