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Research article

Production of demineralized water for use in thermal power stations by advanced treatment of secondary wastewater effluent

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A B S T R A C T

The operation and efficiency of a modern, high-tech industrial full-scale water treatment plant was investigated in the present study. The treated water was used for the supply of the boilers, producing steam to feed the steam turbine of the power station. The inlet water was the effluent of municipal wastewater treatment plant of the city of Bari (Italy). The treatment stages comprised (1) coagulation, using ferric chloride, (2) lime softening, (3) powdered activated carbon, all dosed in a sedimentation tank. The treated water was thereafter subjected to dual-media filtration, followed by ultra-filtration (UF). The outlet of UF was subsequently treated by reverse osmosis (RO) and finally by ion exchange (IX). The inlet water had total organic carbon (TOC) concentration 10–12 mg/L, turbidity 10–15 NTU and conductivity 3500–4500 μS/cm. The final demineralized water had TOC less than 0.2 mg/L, turbidity less than 0.1 NTU and conductivity 0.055–0.070 μS/cm. Organic matter fractionation showed that most of the final DOC concentration consisted of low molecular weight neutral compounds, while other compounds such as humic acids or building blocks were completely removed. It is notable that this plant was operating under "Zero Liquid Discharge" conditions, implementing treatment of any generated liquid waste.

1. Introduction

Wastewater reclamation and further reuse for different applications has been considered nowadays as a viable and economically attractive approach to deal with the major issue of water scarcity in local and global scale. The reclaimed water after appropriate treatment can be reused in several fields, such as in agricultural activities (irrigation), industrial uses (e.g. in power production plants as process or cooling water), for groundwater recharge and more recently, even as drinking water, e.g. according to Singapore's Public Utility Board (Tang et al., 2014).

To achieve the requested high degree of purification of wastewater, there is no single treatment process that can remove effectively all the residual constituents, such as NOM, heavy metals, organic or inorganic micro-pollutants, turbidity, hardness etc. To obtain, water of quality able to be reused as drinking, or ultra-pure demineralized water (i.e. with conductivity of less than 1 μS/cm) for industrial reuse (Särkkä et al., 2015), water should be subjected to post-treatment mainly by integrating membrane systems (Chon et al., 2012b).

Among the various constituents that have to be efficiently removed in these cases, the dissolved organic matter is probably the most critical, because its presence can influence both the water treatment processes (i.e, by causing membrane fouling), as well as the quality of finished water (Cornelissen et al., 2008). The presence of NOM compounds can cause several operational etc. problems, e.g. some components of NOM can cause colouration of water, or encourage microbiological growth. NOM compounds can also cause scaling of heat exchanger surfaces in industrial applications, as well as the formation of dangerous disinfection by-products during the final treatment for the production of drinking water (Mikola et al., 2013). The presence of low molecular weight organic acids can decrease the pH value in the boiler water, where very high temperatures and pressures over 10^4 kPa are commonly applied, creating gradually corrosion problems.

Other important water constituents, which have to be efficiently removed before the production of ultra-pure steam water, is the turbidity, caused by the presence of dispersed (mainly colloidal, of

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List of abbreviations

A	anion exchanger
BB	building blocks
BP	Biopolymers
C	cation exchanger
CDOC	chromatographic dissolved organic carbon
DOC	dissolved organic carbon
HOC	hydrophobic organic carbon
HS	humic substances
LC-OCD	liquid chromatography-organic carbon detection
LMW	low molecular weight
MB	mixed-bed (ion exchange) resins
MMF	multi-media filtration
NOM	natural organic matter
NTU	nephelometric turbidity units
OND	organic nitrogen detection
PAC	powdered activated carbon
RO	reverse osmosis
SEC	size exclusion chromatography
TOC	total organic carbon
UF	ultra-filtration
UVD	ultra-violet detection
ZLD	zero liquid discharge

organic or inorganic nature) matter, as well as the suspended matter and the hardness, which is mainly caused by the presence of soluble polyvalent metallic ions such as Ca and Mg. The latter, when added to water, is known to significantly affect separation processes, such as froth flotation, as suggested by the work of Ozkan and Acar (2004) who investigated their effect on borate ore flotation and showed that flotation results were negatively influenced by their presence.

The core objective of this study was to evaluate the removal of main undesirable constituents during each separate treatment stage of a combined tertiary industrial water treatment plant and to shed light on the removal of the several fractions of natural organic matter, after each of treatment processes, namely coagulation with iron salts, lime softening, activated carbon filtration, dual-media filtration, ultra-filtration, reverse osmosis and ion exchange. In addition, this plant was operating under Zero Liquid Discharge (ZLD) conditions, which represent a cutting-edge approach for the total elimination of liquid wastewater effluents.

In most of the relevant studies, the used raw water for the production of demineralized water is surface or groundwater and treatment is based simply on ultrafiltration followed by reverse osmosis or ion exchange. To the author's best knowledge, this the first work to describe an application of such a complex industrial treatment plant for the post-treatment of secondary (biologically) treated urban wastewater, for the production of demineralized water for use in steam production in a power plant, covering also all other industrial water needs, such as water storage for fire fighting or for watering of plants.

2. Materials and methods

2.1. Description of water treatment plant

The industrial water treatment plant received the secondary (biologically) treated municipal wastewater from the city of Bari (South Italy). The major chemical characteristics of the raw water are presented in Table 1. This water had conductivity values around 4000 μS/cm and total organic carbon (TOC) concentrations approximately 10 mg/L, which fall in the range of other relevant wastewaters after biological treatment (Haaken et al., 2014; Lahnsteiner et al., 2007).

The following treatment plant was applied, to enable production of ultra-pure water. Initially, common oxidant chemical agents were added to inlet water, i.e. hydrogen peroxide and chlorine (NaClO) concentrate solutions, before entering the storage basin, which was then called as "raw water". At this stage, oxidation-reduction potential was monitored at the raw water inlet point, where these oxidants were added, to achieve a potential of about +600 mV. Raw water was then treated by coagulation with iron salt ($FeCl_3$) (at around 10 ppm concentration), lime softening (by concentrated $Ca(OH)_2$ addition 50 mg/L), and powdered activated carbon addition (PAC) (20 mg/L) all of them dosed prior to the sedimentation tank, aimed to remove most of the formed precipitates.

Hydrogen peroxide and chlorine were initially used to reduce odour problems and to achieve preliminary disinfection, as well as some degree of oxidation for the entering TOC compounds, enhancing the performance of following treatment processes. Coagulation with iron salt was used to destabilize particles (especially those of colloidal size) and with the combined use of anionic polyelectrolytes (1 ppm) to provide the necessary augmentation of particle size in order to achieve more efficient separation and reduction of turbidity by the following (gravity) sedimentation process. The particle size was not measured, but since it was retained by more than 99% at the UF stage, we assume to be smaller than 0.1. μm. The objective of lime softening process was the removal of hardness (Ca^{2+} and Mg^{2+} cations) in order to avoid the formation of scaling in the subsequent UF and RO processes. The use of PAC aimed to preliminary adsorption and removal of the organic matter content.

The treated water was subsequently filtered through a dual-media filter bed (comprised of quartz sand and pyrolusite), operating in up-flow mode, followed by the application of ultra-filtration (using commercial poly-vinylidene fluoride (PVDF) membranes, supplied by the private company DOW), before being subjected to reverse osmosis membrane filtration (using polyamide (PA) membranes and RO modules FILMTEC BW30-400-FR, supplied also by DOW) for the further reduction of TOC concentration, heavy

Table 1
Main chemical characteristics of inlet (raw) water, of service water (obtained after the RO treatment) and of the finally obtained demineralized (ultra-pure) water.

Chemical parameter	Incoming wastewater	Service water (RO outlet)	Demineralized water
pH	7–8	7–8	5–6
Conductivity (μS/cm)	3500–4500	5–10	0.055
TOC (mg/L)	10–12	0.1–0.2	<0.2
Hardness (total) (mg/L)	600–800	0	0
Turbidity (NTU)	10–15	<0.1	<0.1