Reclaimed water use in industrial cooling circuits: Compatibility with TP11 biocides

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ABSTRACT

Cooling water circuits represent a high-water saving potential that has not been fully exploited yet due to the risk of *Legionella* outbreaks. According to legislation, cooling circuits are subjected to specific biocide treatments which must be considered when water reuse is planned. Biocide effectiveness mainly depends on the type of installation, its operating regime, and the interactions with other chemicals. Therefore, water reuse is critical because its physical, chemical and microbiological characteristics, beside deposit and corrosion problems, may reduce the biocidal power and produce a health risk. However, there is a lack of knowledge on the compatibility of reclaimed water with biocides, and on long-term maintenance problems. This paper validates the long term performance of an industrial cooling tower using reclaimed water, obtained after the treatment of bottle washing water. The compatibility study of the reused water with three non-oxidant commercial products from the TP11 group (quaternary ammonium, tetrakis hydroxymethyl phosphonium sulphate and isothiazolone) shows a reduction lower than 20% of the biocide efficiency between periodic additions. Isothiazolone-based biocide was tested with reclaimed water during 1 year at industrial scale, without detecting any problem. Results show that water quality was always within the values allowed by legislation and slightly better when using reclaimed water (lower ecotoxicity of the purge and higher biocidal residual concentration). With the reuse strategy, water savings of 3750 m^3/y were obtained. Furthermore, to minimize the *Legionella* and corrosion risks, an optimal control of the cooling tower has been developed based on correlations.

1. Introduction

The increasing water concern is promoting the implementation of strategies to reclaim and reuse water in industrial processes. Besides environmental and corporative image advantages, industries must also benefit from improved process efficiency and cost reductions to facilitate the implementation of water reuse concepts. The reuse of industrial reclaimed water is limited by its quality and by the quality requirements of the different uses. Cooling circuits are high water intensive and present a high potential for water savings. However, the used of reclaimed water is limited due to the risk of the proliferation of *Legionella* bacteria [1].

In Spain, legislation regulates both the use of reclaimed water (Royal Decree 1620/2007 [2]) and *Legionella* prevention in cooling systems (Royal Decree 865/2003 [3]) which is based on biocide treatments. In general, biocides need to be effective, accomplish ecotoxicity limits, and be compatible with the water quality and with the presence of other biocides [4]. Therefore, for water reuse in cooling towers, it is important to assess the compatibility and effectiveness of the used biocide with the reclaimed water.

Biocides are classified into 22 types by the European Chemical Agency (ECHA) [5]. TP11 type biocides are “Liquid preservatives used in refrigeration systems and industrial processes”, included in the main group 2, which refers to preservatives [6,7]. The use of TP11 biocides with reclaimed water implies the compliance with European legislation for both biocide (Regulation (EU) No 528/2012) [8]) and water reuse (Regulation (EU) 2020/741 [9]). Quaternary ammonium derivatives are TP11 biocides and include benzalkonium chloride, benzethonium chloride, methylbenzethonium chloride, cetalconium chloride, cetylpyridinium chloride, cetrimonium, cetrimide, tetraethylammonium bromide, didecyldimethylammonium chloride and domiphenium bromide [10]. The preparation of quaternary ammonium halides is based on the exhaustive alkylation of the amines [11]. In general, they are

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Nomenclature

ANOVA	Analysis of variance to compare multiple means
CFU	Colony forming units
DPD	Colorimetric method based on N-Diethyl-phenylenediamine
DBNPA	2,2-dibromo-3-nitrilopropionamide
ECHA	European Chemical Agency
EPA	US Environmental Protection Agency
PET	Polyethylene terephthalat
THPS	Tetrakis hydroxymethyl phosphoric sulphate
TP11 biocides	Group 2 biocides according to ECHA. Used for the preservation of water or other liquids used in cooling systems and industrial processes by controlling harmful organisms such as microbes, algae and mussels. Products used for the disinfection of drinking water or swimming pool water are not included in this product type
T.U.	Toxicity units (Ecot./m^3)
WWTP	Wastewater treatment plant

effective as algaecides and bactericides at neutral or slightly alkaline pH; however, their effectiveness against fungi is very low [12]. Furthermore, its effectiveness is reduced by the presence of organic matter, surfactants and detergents, and at high water hardness [13].

Tetrakis hydroxymethyl phosphoric sulphate (THPS) is also a widely used active ingredient in biocides due to the presence of disulfide bridges [14]. Although it is expensive, it is water soluble and provides very good bactericidal properties. Among its main advantages are the low toxicity of the decomposition products and the possibility of operating at a wide pH range. However, the use of THPS can lead to biofilm formation depending on the water quality [15,16].

More recent is the use of isothiazolones, which are characterized by their high reactivity and biocidal potential due to the presence of 5-chloro-3-isothiazolone, whose preferential decomposition is towards thioacillus chloride [17,18]. Its bactericidal power allows to work in a wide pH range [19].

Biocide are widely used in most industrial sectors and there are many studies assessing their performance. However, most studies do not provide an overall assessment for their performance when water circuits are closed, the effluent is reused or reclaimed water from other sources is used [20–21]. Atei et al. have reported the successful performance of 2,2-dibromo-3-nitrilopropionamide, at a constant concentration, with reclaimed water from the petrochemical industry after a membrane treatment [22]. In the case of cooling towers, Table 1 summarizes the studies related to the use of biocides with different water qualities. The studies cover a wide conductivity range (7.76 to 2200 μS/cm) being the lower values for fresh water or highly treated water. A few cases consider pilot studies of 1–2 months [17,18,22]; however, longer times, covering all seasons, are necessary to assure the correct functionality of the tower operation under different conditions. Most studies are focused on the use of highly oxidizing substances, mainly chlorine derivatives [17,18,22]. However, they require the use of anticorrosive and antifouling chemical products [17,18,27] which, on the other hand, should be minimized to reduce the toxicity of the cooling tower purge and to reduce the cost. In the case of non-oxidizing biocides, isothiazolones were used in combination with an oxidizing biocide [27]. These chemicals act slowly, and they are usually added in large, weekly doses. In this case, their compatibility with the water is critical since the effectiveness must be maintained between dosages. From the safety point of view, special attention must be given to the *Legionella* control, which can be transmitted by aerosols as a consequence of the tower operation itself. This parameter can be used as an indicator to determine the compatibility of the reclaimed water with the used biocide. Unfortunately, only two studies [18,19] (Table 1) evaluate this parameter, which should be analyzed at long term, with controls every 3 months to obtain more conclusive results.

According to the state of the art, the critical consequences of a poor compatibility between biocides and reclaimed water from different sources have not been fully studied yet. Non-oxidizing active substances should be further studied since they produce a lower degradation of the installation. Furthermore, it is necessary to extend the research, considering industrial plants and long term studies, to assess the evolution of the residual biocide concentration as a function of water quality variations; the microbiological quality of the cooling process; the demand of scale and corrosion inhibitors; and to identify deposits and corrosion problems. On the other hand, potential cost savings in cooling towers must be further highlighted as a driver for water saving and for the implementation of circular economy concepts [27].

Based on the identified research gaps, this paper studies the compatibility of reclaimed water, from bottle disinfection in a food factory, with three types active substances of non-oxidizing biocides: THPS, isothiazolone and quaternary ammonium derivatives. Reclaimed water was obtained by treating the effluent from the industrial washing and disinfection of juice bottles [1]. Additionally, the long term reuse of the reclaimed water as make-up water of a cooling tower using isothiazolone biocide was assessed and compared with a similar tower using drinking water. Finally, to facilitate the control of cooling towers and minimize the risks of *Legionella* and corrosion, correlations between different parameters water quality parameters and the performance of the tower have been studied.

2. Materials and methods

2.1. Materials and analytical methods

The reclaimed water used in this study comes from a process of

Table 1
Studies about the use of biocides in cooling towers.

Ref.	Water source	Average conductivity of the water (μS/cm)	Cooling tower scale/time	Biocide type/active ingredient	*Legionella* Monitoring	Study of the corrosion effect/Use of inhibitors (Calcification and corrosion)
[22]	Fresh water	7.76	Pilot plant/45 days	Oxidant/Ozone		Yes/Orthophosphate
[17]	Tertiary treated domestic effluent	870	Pilot plant/30 days	Oxidant/3 chlorine derivatives		
[18]	Tertiary treated municipal wastewater	739–1030	Pilot plant/60 days	Oxidizer/Chlorine	Yes	Yes/Tolytriazole
[20]	Membrane effluent from petrochemical industrial	2200	45 days of effluent adequacy study to feed towers without studying the response of the towers			
[19]	Desalinated water	40	Industrial plant	Unknown	Yes	
[27]	Reclaimed municipal wastewater			3 chlorine derivatives and 2 isothiazolone	Heterotrophic bacteria and total number	Yes/Iron bacteria in circulating cooling water

washing and disinfection of polyethylene terephthalate (PET) bottles in a Spanish juice plant. The bottles disinfection is carried out with osmotic water with peracetic acid as biocide. After disinfection, residual hydrogen peroxide was removed by a catalytic decomposition process with activated carbon to minimize the oxidation of the cooling circuit [1]. The reclaimed water has the adequate physical-chemical properties (Table 2) to comply with current legislation for water reuse in cooling systems.

Biocides were supplied by Fupinax (Spain) and uses as received without dilution (Table 3). The concentration of biocides was determined by titration using the specific commercial kit for each of them, supplied by the manufacturers (the basis of the titration reaction is not provided since it belongs to the know-how of the suppliers).

The pH, the electrical conductivity and temperature were measured using a HANNA HI98130 device (Spain) (precision ± 0.01 and ±0.01 mS/cm respectively), turbidity was measured with a HANNA HI93703C turbidimeter (Spain) (precision ±5%) following ISO 7027, hydrogen peroxide was measured by a titration method with a HANNA HI3844 equipment (Spain) (precision ±0.25 mg/L), free chlorine was measured using the adaptation of EPA's DPD 330.5 method with HANNA HI83399-02 photometer (Spain) (precision ±0,03 mg/L) and total iron ion content was measured using an adaptation of the EPA 315B phenanthroline method with a Checker HANNA HI721 device (Spain) (precision ± 0,04 mg/L).

Ecotoxicity using luminescent microorganisms (*Vibrio Fischeri)* was evaluated. This parameter has been used to assess the effect of pollutants, such as triclosan [21], pesticides and herbicides [24] and biocides, such as malathion and diazion [25], in wastewater and antifoulants in marine environments [28]. The ecotoxicity was analyzed following the UNE-EN-ISO 11348-2:2009 Standard (Determination of the inhibitory effect of water samples on the luminescence of *Vibrio fischeri,* luminescent bacteria test).

2.2. *Experimental procedure*

The efficiency of the three biocides was assessed using the reclaimed water that was going to be reused as make up water in one of the cooling towers of the juice factory. This recovered water, coming from the washing and disinfection of PET bottles, was treated with activated carbon to remove the residual hydrogen peroxide to avoid any damage in the cooling towers installations due to oxidation [1]. Although the characteristics of the regenerated water accomplish with the Spanish legislation, the performance of already used biocides with this reclaimed water must be evaluated. Fig. 1 shows the procedure to test the biocides performance. The different phases of the research are laboratory, industrial implementation and industrial validation of the research. The biocides were initially dosed at the concentration recommended by the manufacturers (Table 3, 500 mg/L for isothiazolone, 50 mg/L for THPS and 100 mg/L for quaternary ammonium salts). The experiments were performed with 1 L of water, split up into three aliquots, one for each biocide. The water was mixed with the biocide using a slow magnetic agitation (100 rpm) along the experiment. At 30-minute intervals, the residual biocidal product was quantified to determine its persistence and compatibility with the treated effluent. The experiments were performed during 5 h, considering that if the residual concentration was kept at the recommended dose after 5 h, the compatibility of the biocide with the effluent can be assured. Subsequently, the effectiveness of the selected biocide was evaluated during 1 year in an industrial cooling tower, through the determination of pH, turbidity, electrical conductivity and concentrations of hydrogen peroxide, free chlorine, iron ion concentration and residual biocide. In this industrial phase, the synergy between the selected biocide and the sodium hypochlorite was studied because both active substances are usually combined if the chemical analyses of the facility or the microbiological analyses failed. Finally, samples were taken from the cooling tower purge while using the reclaimed water to measure the ecotoxicity. The performance of the cooling tower using reclaimed water was compared with a similar one using drinking water with an average conductivity of 800 μS/cm.

All experiments were replicated three times in the laboratory phase. During the industrial phase official measurements were carried out in the cooling towers according to the legislation [3]. Daily measurement (one replicate) were taken 5 days per week, always at the same time (14:00 h) for 10 weeks. The wide range of data was used to feed the corresponding regression models.

Table 2
Characterization of reclaimed water.

Parameter	Reclaimed water (average from 70 days)
pH	4.36 ± 0.05
Electrical conductivity (μS/cm)	110 ± 5
Turbidity (NTU)	1.26 ± 0.02
Hydrogen peroxide (mg/L)	0.02 ± 0.02

Table 3
Main properties of the studied biocides.

	Quaternary ammonium	Tetrakis hydroxymethyl phosphonium sulphate (THPS)	Isothiazolone
pH	7.0–8.0	4.0–5.0	7.0–8.5
Recommended dose (mg/L)	100	50	500
Specific weight (20 °C) (N/m^3)	0.98	0.99	0.95

2.3. *Experimental design*

Correlations between the parameters were studied by performing the analysis of the multivariate correlation as well as the analysis of variance (ANOVA), using the Multiple Correlation Package (Excel, Microsoft). The parameters considered to find the correlations were the residual concentration of biocide, the iron ion concentration, the residual concentration of free chlorine, pH and electrical conductivity. In the industrial phase, the dosing pumps operated under a set point that provided a fixed initial concentration of free chlorine and isothiazolones of 2.20 mg/L and 500 mg/L, respectively. From the dosed time these concentrations started to decrease (as a function of water chemistry, operation regime of the cooling tower, purging, etc.). The residual concentrations of biocide and free chlorine were considered as the main parameters for the correlations. The residual concentration of biocide provides critical information about the performance of the biocide in the cooling tower. On the other hand, the iron ion concentration is an indicative of the possible corrosion and depreciation phenomena in the installations.

First-degree empirical polynomial equation (Eq. (1), where Y is the dependent variable, x_i represents the independent variables and b_0 and b_i are the corresponding regression coefficients) were selected for the correlation because it provided the best fit after trying multiple adjustments to different functions.

$$Y = b_0 + \Sigma b_i x_i \tag{1}$$

The correlations studied were:

- Effect of both pH (7.0–8.6), and electrical conductivity (1500–3000 μs/cm), on the residual biocide concentration, as dependent variable.
- Effect of both pH (7.0 and 8.6), and residual free chlorine concentration (0.06–2.20 mg/L), on the residual biocide concentration, as dependent variable.
- Effect of both residual biocide concentration (100–500 mg/L), and residual free chlorine concentration (0.06–2.20 mg/L), on the iron ion concentration, as dependent variable.

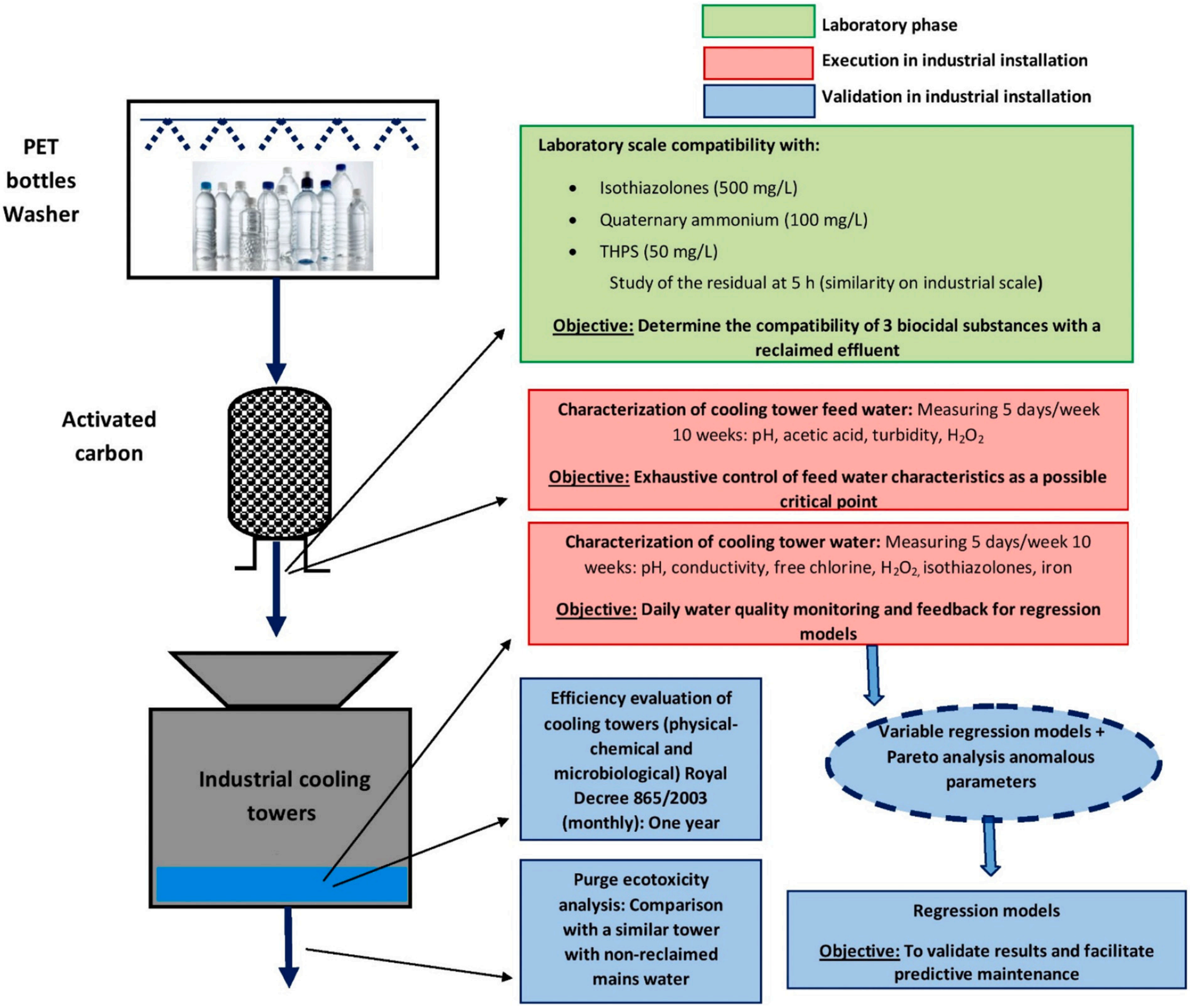


Fig. 1. The experimental procedure and different phases of the research.

These correlations were calculated based on the data from 70 days and 50 daily measurements in the installation.

The Pareto's Diagram was obtained with Excel (Microsoft) to determine the influence of the studied parameters on the process.

3. Results and discussion

3.1. *Preliminary laboratory trials of biocides compatibility with regenerated water*

Although the regenerated water accomplishes the legislation limit to be reused, before its use at industrial scale its compatibility with different biocides used at the plant need to be asses in order to assure a good performance in the cooling towers and to select the most adequate, without corrosion issues.

Fig. 2 shows the evolution of the concentration of each studied biocide during 5 h (initial doses are those recommended by the manufacturer based on Table 3). Isothiazolone biocide had the higher decrease in concentration, 20%, being only 10% for the other two biocides. All biocides maintained an adequate residual concentration after a contact time with the reclaimed water of 5 h, applying the manufacturer's recommended dose. It is concluded that the regenerated water and the active ingredients of the tested biocides are compatible. None of them has a reduction percentage higher than 50% of the initial concentration, being the 20% reduction in the isothiazolones the highest one. Even the quaternary ammonium salts, whose optimum working pH is neutral or slightly alkaline [23], has shown an adequate stable residual concentration.

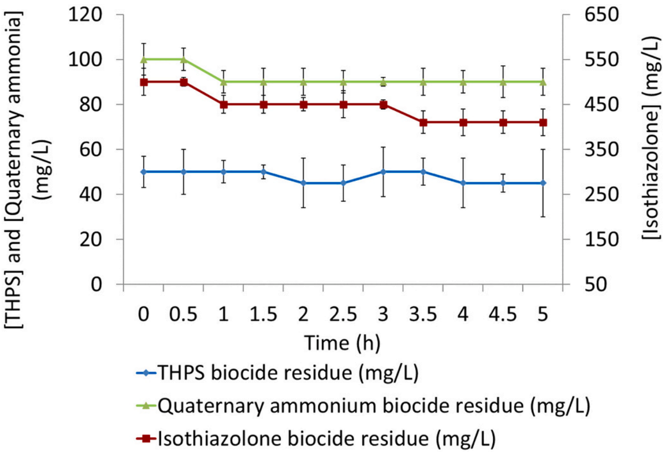


Fig. 2. Concentration of residual biocides as a function of time with the regenerated water.

The higher reduction of isothiazolones in the regenerated water could be related to their structure, cyclic ketones, which can be oxidized into an ester by peroxyacids or hydrogen peroxide, according to the

Baeyer-Villiger reaction [26]. The regenerated water was treated to remove the hydrogen peroxide with acid washed activated carbon, however, it can still have traces of peracetic acid and hydrogen peroxide, beside the acetic acid in the water, that can promote the Baeyer-Villiger reaction and, therefore, oxidized isothiazolone. Sayantan (2020) [29] also observed this oxidation reaction, working with porous materials in presence of hydrogen peroxide at trace level.

The possibility of oxidation of acetic acid to isothiazolone has also been considered. However, Silva et al. (2020) [30] determined that isothiazolones in their biodegradable degradation processes one of their products is acetic acid, so this oxidation and therefore degradation is not contemplated. In turn, the acidity of the medium produced by acetic acid favours the biocidal action of isothiazolones, so acetic acid can be considered a promoter of their biocidal action [30]. For the rest of the biocides, the percentages of variation are practically minimal, so it can be concluded that they are fully compatible with the regenerated effluent.

Given the successful results achived by the three products, for the industrial scale study, isothiazolones biocide was selected despite its higher concentration reduction, because it was the one being used in the cooling towers of the plant. The use of this active substance is conditioned by the plant's own criteria because it has excellent functionality for *Legionella* prevention, and its cost is intermediate in the TP11 biocides market. This aspect will make it possible to evaluate in the ecotoxicity analysis the response of the same with the regenerated effluent.

3.2. Industrial scale results

The industrial reclaimed water was reused in one of the cooling circuit of the factory, using the isothiazolones as biocide. Water parameters were monitored daily to determine the stability of the quality of the reclaimed water and of the cooling process water, on one hand and to asses the potential chemical interactions, on the other. The study has been carried out during 70 calendar days of process operation. Table 4 shows the average value of the parameters per week, including the maximum and minimum values of the weekly averages, as well as the maximum and minimum values of the specific daily measurements.

According to the supplier isothiazolone residual biocide concentration should be maintained between 100 and 500 mg/L in the cooling process water. The values measured during the 10 weeks trial have always met that criterion as shown in Table 4. Moreover, minimum residual concentration of 50 daily measurements was 100 mg/L and the maximum value was 500 mg/L, strictly meeting the criteria. Minimum and maximum weekly average values also show a good biocide performance during the cooling tower operation.

Table 4
Water quality of the reclaimed water and cooling circuit. Weekly monitoring (5-day averages).

RECLAIMED WATER					COOLING TOWER CIRCUIT					
Week	pH	Acetic acid (mg/L)	Turbidity (NTU)	Hydrogen Peroxide (mg/L)	pH	Electrical conductivity (µS/cm)	Hydrogen Peroxide (mg/L)	Residual biocide isothiazolone (mg/L)	Residual free chlorine (mg/L)	Iron (mg/L)
1	4.15 ± 0.05	448.3 ± 0.7	0.6 ± 0.1	0.00 ± 0.00	7.99 ± 0.03	2562 ± 10	0.00 ± 0.00	170.0 ± 5.0	0.97 ± 0.05	1.41 ± 0.05
2	4.10 ± 0.03	322.7 ± 0.3	0.3 ± 0.1	0.00 ± 0.01	7.96 ± 0.05	2578 ± 15	0.00 ± 0.00	162.5 ± 7.3	0.97 ± 0.05	1.27 ± 0.06
3	5.67 ± 0.05	291.8 ± 0.7	0.0 ± 0.0	0.00 ± 0.00	7.74 ± 0.05	2465 ± 15	0.00 ± 0.00	137.5 ± 5.0	1.29 ± 0.09	1.04 ± 0.03
4	4.89 ± 0.05	399.5 ± 0.5	0.0 ± 0.0	0.00 ± 0.00	7.63 ± 0.07	2300 ± 10	0.00 ± 0.00	175.0 ± 5.5	1.59 ± 0.08	1.11 ± 0.02
5	4.14 ± 0.01	374.2 ± 0.7	0.3 ± 0.1	0.00 ± 0.00	7.57 ± 0.05	2160 ± 25	0.00 ± 0.00	212.5 ± 8.7	1.76 ± 0.09	0.92 ± 0.04
6	4.65 ± 0.03	390.8 ± 0.5	1.0 ± 0.1	0.00 ± 0.00	7.46 ± 0.03	2098 ± 40	0.00 ± 0.00	287.5 ± 10.3	1.66 ± 0.12	1.24 ± 0.04
7	4.06 ± 0.05	432.7 ± 0.3	1.6 ± 0.2	0.00 ± 0.00	7.45 ± 0.05	2078 ± 35	0.00 ± 0.00	280.0 ± 10.1	1.52 ± 0.04	1.28 ± 0.03
8	4.33 ± 0.01	421.7 ± 0.7	2.0 ± 0.1	0.00 ± 0.00	7.48 ± 0.03	2048 ± 10	0.00 ± 0.00	325.0 ± 9.5	1.35 ± 0.12	1.35 ± 0.03
9	3.89 ± 0.01	220.3 ± 0.7	2.5 ± 0.1	0.01 ± 0.02	7.59 ± 0.07	2088 ± 25	0.01 ± 0.00	325.0 ± 10.1	1.08 ± 0.11	1.26 ± 0.04
10	5.58 ± 0.03	178.9 ± 0.8	2.3 ± 0.3	0.01 ± 0.03	7.52 ± 0.05	2038 ± 15	0.01 ± 0.00	300.0 ± 3.3	0.84 ± 0.06	1.18 ± 0.01
Maximum average weekly value	5.67 ± 0.01	448.3 ± 0.7	2.5 ± 0.2	0.01 ± 0.01	7.99 ± 0.04	2578 ± 15	0.00 ± 0.00	325 ± 4,5	1.76 ± 0.04	1.41 ± 0.06
Minimum average weekly value	3.89 ± 0.02	178.9 ± 0.4	0.0 ± 0.0	0.00 ± 0.00	7.45 ± 0.06	2038 ± 20	0.00 ± 0.00	138 ± 3.9	0.84 ± 0.06	0.92 ± 0.03
Maximum value of 50 daily measurements	7.36 ± 0.04	530.4 ± 0.7	6.0 ± 0.4	0.50 ± 0.09	8.60 ± 0.08	3000 ± 15	0.00 ± 0.00	500 ± 5.8	2.20 ± 0.02	2.00 ± 0.04
Minimum value of 50 daily measurements	2.14 ± 0.02	0.2 ± 0.5	0.0 ± 0.0	0.00 ± 0.00	7.00 ± 0.07	1500 ± 35	0.00 ± 0.00	100 ± 3.8	0.06 ± 0.02	0.02 ± 0.01

The pH of the cooling water circuit is close to neutral due to the gradual water evaporation, typical of this type of circuits. This is a good indication of the recovered water performance and its chemical stability. It should be considered that under normal cooling conditions, the evaporation process in cooling circuits leads to a water pH as consequence of the evaporation of pure water that leaves the salts in the cooling water, producing the alkalization of the medium. It is usual, depending on the supply water, to use pH reducers, however, in this case it is not necessary, due the quality of the reclaimed water. pH values above 8.5 greatly increase the risk of calcification with the subsequent associated issues, mainly reduction of heat transmission coefficients, greater risk of *Legionella* proliferation and a lower biocide efficiency. However, win this case, pH was maintained neutral between 7 and 8, avoiding calcification and/or corrosion phenomena thanks to a well balance process water.

As it has already been mentioned the reclaimed water contains acetic acid, as the result of the peracetic acid decomposition, which acts as a neutralization buffer, avoiding an excessive increase of the pH in the cooling towers due to water evaporation. Therefore, the presence of acetic acid has several advantages, as the reduction of the calcification phenomena, the improvement of energy yields, the lower risk of a reservoir for *Legionella* proliferation and the reduction of corrosion phenomena under calcification deposits.

The addition of sodium hypochlorite to improve the control of aerobic microorganisms, that remained in non-oxidizing values that were not aggressive for the installation.

The iron ion concentration values shown in Table 4 are also within the established limit to avoid corrosion phenomena in the metallic components of the refrigeration circuits.

The official results, corresponding to the preventive maintenance of the cooling towers installation corroborate the effectiveness of the use of reclaimed water with isothiazolones as biocide, accomplishing with current legislation (Royal Decree 865/2003 [3]). All the microbiological parameters shown in Table 5 (*Legionella* spp. and aerobes at two temperatures) are completely satisfactory. *Legionella* spp. was not detected in the measurements performed every three months, and the aerobic counts were always well below 10,000 CFU that is the maximum level allowed.

To complete the investigation, samples were taken from the cooling tower purge to evaluate the ecotoxicity of this effluent. Comparison was made with another tower of similar characteristics using fresh water (average conductivity of 800 µS/cm) and the same isothiazolones biocide (Table 6). The ecotoxicity results provide an overview of the entire reuse concept.

Table 5
Annual evolution of the microbiological quality in industrial process according to Royal Decree 865/2003 [3]. (*) Detection limit 1 CFU/mL.

Month	*Aerobic count (CFU/mL) 22 °C	*Aerobic count (CFU/mL) 36 °C	*Legionella spp.* (CFU/L)
February 19	1800	970	
March 19	3700	2800	
April 19	810	590	Not detected
May 19	550	60	
June 19	200	340	
July 19	8700	9500	Not detected
August 19	7500	8100	
September 19	230	260	
October 19	350	410	Not detected
November 19	120	310	
December 19	340	380	
January 20	300	670	Not detected
February 20	60	100	
March 20	100	356	

It can be observed that the ecotoxicity values are higher in the tower using fresh water. Although both towers operate under similar residual biocide concentration and conductivity, it is possible that the reclaimed water produces a reduction in the biocide concentration due to its interaction with other species present in the water. Therefore, the reuse of reclaimed water provides an additional environmental advantage due to the lower toxicity of the purge.

3.3. *Correlations between cooling towers variables*

The results obtained at the industrial scale were used to generate new knowledge on the main water variables that affect the biocide efficiency. The proposed correlations are specific to the operating regime and the climatic conditions of the target cooling tower. However, they can serve as a reference in future studies.

Although during the full trial all parameters were within the legislation limits, several anomalous values were observed in the daily measurements Therefore, Pareto's diagram was applied to all anomalous values to determine which of them were statistically significant parameters are those that sums up 80% of accumulated frequency (Fig. 3). Considering the total amount of values, those anomalous are very few; therefore, none of them are significant. The out-of-range values for the concentration of iron ion were those above 1.5 mg/L because the limit is 2.0 mg/L. Likewise, the out-of-range values for free chlorine were those above 2.0 mg/L because it would exceed the legal limit. In the case of residual isothiazolone biocide, values under 250 mg/L were considered out of range because it's very low residual concentration. The out-of-range values of electrical conductivity and pH were those above 2.5 mS/cm and 8.5, respectively, because the tendency of the water to fouling increases, negatively affecting the level of maintenance and the energy efficiency. The parameter that showed the most out-of-range values in the studied period was the residual isothiazolone concentration, followed by the electrical conductivity and the iron ion concentration. The least frequent were the pH and the concentration of residual free chlorine. 80% of the accumulative frequency was only reached with the residual isothiazolone concentration and the electrical conductivity. This aspect is highly relevant when possible, deviations are studied since the less influential factors are those more regulated by the legislation, being the most influential factors those that should be controlled when deviations are produced to assure the operability of the cooling process.

Several correlations were proposed and studied. It is important to consider that all the correlations were obtained for an initial concentration of isothiazolones of 500 mg/L, and an initial free chlorine concentration of 2.2 mg/L, supplied through the corresponding calibrated dosing pumps. Therefore, the variables considered in the models were the residual concentrations of both free chlorine and isothiazolones. Initially, the effect of pH and conductivity was studied on the residual biocide concentration. However, in this case, no linear correlation was found (Table 7) because the statistical analysis that considers the multivariate regression resulted in inadequate values of both R^2 and F value. This last parameter is higher than the level α corresponding to the selected confidence.

Subsequently, the effect of pH and residual free chlorine was studied on the residual biocide concentration (Table 8) finding a good correlation. The statistical analysis of the multivariate regression provides adequate values of both R^2 and F value, being the F value lower than the level α, corresponding to the selected confidence interval. According to the negative sign of the coefficients of the independent variables, the concentration of the residual biocide increases when pH and/or residual free chlorine decrease. It is expected that the correlation of residual biocide concentration with acetic acid would be determined by the pH, having a higher residual concentration of biocide when the concentration of acetic acid is higher, and the pH is lower. Therefore, as the reclaimed water used in the cooling tower has an acid pH that increases up to nearly neutral values, it makes sense that there is a higher residual concentration of biocide while the pH is lower, to decrease thereafter.

Table 6
Ecotoxicity of cooling tower purging (T.U.)

Samples	Tower using reclaimed water			Tower using fresh water		
	Ecotoxicity T.U. (Ecot./m^3)	Isothiazolone (mg/L)	Electrical conductivity (µS/cm)	Ecotoxicity T.U. (Ecot./m^3)	Isothiazolone (mg/L)	Electrical conductivity (µS/cm)
1	6.0	510	1980	10.9	380	2010
2	6.9	505	2090	12.0	390	1980
3	7.3	450	1870	13.5	510	1990

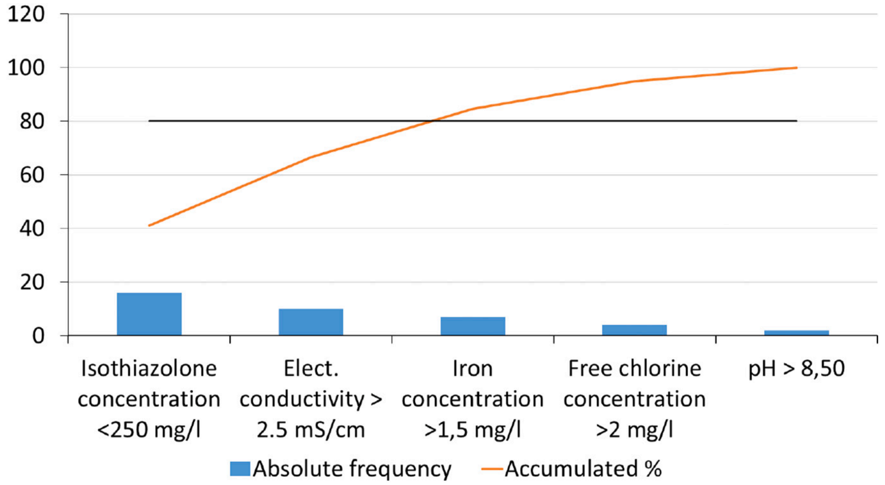
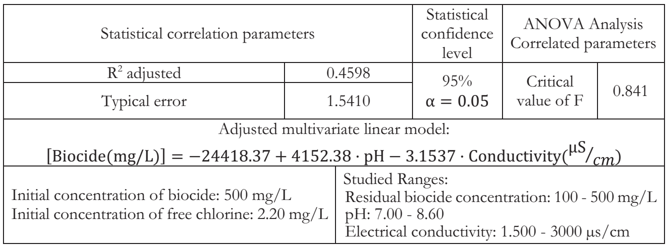


Fig. 3. Pareto's Diagram for anomalous values of parameters in process functionality.

Table 7
Correlated parameters: residual biocide concentration (mg/L) as response variable and pH and electrical conductivity (µS/cm) as independent variables.



Statistical correlation parameters		Statistical confidence level	ANOVA Analysis Correlated parameters	
R^2 adjusted	0.4598	95% $\alpha = 0.05$	Critical value of F	0.841
Typical error	1.5410			
Adjusted multivariate linear model: $[\text{Biocide(mg/L)}] = -24418.37 + 4152.38 \cdot \text{pH} - 3.1537 \cdot \text{Conductivity}(^{\mu S}/_{cm})$				
Initial concentration of biocide: 500 mg/L Initial concentration of free chlorine: 2.20 mg/L		Studied Ranges: Residual biocide concentration: 100 - 500 mg/L pH: 7.00 - 8.60 Electrical conductivity: 1.500 - 3000 µs/cm		

Table 8
Correlated parameters: residual biocide concentration (mg/L) as response variable and pH and residual free chlorine (mg/L) as independent variables.

Statistical correlation parameters		Statistical confidence level	ANOVA Analysis Correlated parameters	
R^2 adjusted	0.9143	95% $\alpha = 0.05$	Critical value of F	0.032
Typical error	0.0075			

Adjusted multivariate linear model:
$[\text{Residual biocide(mg/L)}] = 3550.65 - 419.62 \cdot \text{pH} - 82.48 \cdot [\text{Residual free chlorine (mg/L)}]$

Initial concentration of biocide: 500 mg/L Initial concentration of free chlorine: 2.20 mg/L	Studied Ranges: Residual biocide concentration: 100–500 mg/L pH: 7.00–8.60 Residual free chlorine concentration: 0.06–2.20 mg/L

That explains the higher concentration of residual biocide obtained at laboratory scale (Fig. 2), where there is no evaporation process and therefore neither the pH increase observed at industrial scale (Table 4)

In the case of residual free chlorine concentration, which is a biocide with greater oxidizing power, it makes sense that as free chlorine is consumed in the system, more isothiazolone remains without being degraded.

Finally, the effect of residual biocide concentration and residual free chlorine concentration on iron ion concentration was studied. As in the previous case, these variables showed proper correlation (Table 9). The statistical analysis that considers the multivariate regression gives adequate values of both R^2 and F, being the F value lower than α corresponding to the selected confidence interval, so it is concluded that there is correlation between the three variables. The positive sign of the coefficients implies an increase in the concentration of iron ion when residual biocide and/or residual free chlorine concentrations increase, leading to higher corrosion levels. The chlorine coefficient is about 10 times higher, corroborating the higher oxidizing power.

In order to provide greater detail for process optimization, regression models were analyzed to ensure that the manufacturer's recommended dose of biocide is accomplished, and the iron ion concentration is below

Table 9
Correlated parameters: iron ion concentration (mg/L) as response variable and residual biocide concentration (mg/L) and residual free chlorine (mg/L) as independent variables.

Statistical correlation parameters		Statistical confidence level	ANOVA Analysis Correlated parameters	
R^2 adjusted	0.8895	95% $\alpha = 0.05$	Critical value of F	0.028
Typical error	0.0093			

Adjusted multivariate linear model:
$[\text{Fe (mg/L)}] = 0.4441 + 0.000829 \cdot [\text{Residual biocide(mg/L)}] + 0.009312 \cdot [\text{Residual free chlorine (mg/L)}]$

Initial concentration of biocide: 500 mg/L Initial concentration of free chlorine: 2.20 mg/L	Iron ion concentration: 0.02–2.00 mg/L Residual biocide concentration: 100–500 mg/L Residual free chlorine concentration: 0.06–2.20 mg/L

the value specified by current legislation. The intervals studied for the considered parameters in the simulation with the model that correlates the residual biocide concentration (mg/L) with the pH and the residual free chlorine (Table 8) were:

- Biocide: It is possible to operate at high concentrations to ensure maximum asepsis of the water. However, it is recommended to work between 100 and 500 mg/L of residual concentration. This would be more environmentally friendly and cheaper.
- pH was studied in the interval allowed by the Royal Decree 865/2003 [3], between 6.5 and 9.0.
- Residual free chlorine was studied in the interval allowed by the Royal Decree 865/2003 [3], between 0.0 and 2.00 mg/L.

Table 10 shows the predicted concentration of residual biocide as a function of the residual free chlorine concentration and the pH. The process works under optimum residual biocide concentration (100–500 mg/L) by keeping the pH between 7.30 and 7.70 for any residual free chlorine value under study (0–2.00 mg/L). That is the 34% of the analyzed points (green region). However, it is not possible to work at pH values higher than 8.1 and residual free chlorine concentration above 0.6 mg/L because at these conditions, the residual biocide concentration does not reach the minimum recommended value. That is the 8.5% of the analyzed points (yellow region). In the pH interval between 6.5 and 6.7, for any studied value of residual free chlorine concentration, high values of biocide are obtained, which is technically effective, but economically expensive. That is the 23.8% of the analyzed points (blue region). The remaining points, usually for pH above 8.5 and any studied residual free chlorine value, make the algorithm invalid. That is the 33.3% of the analyzed points (red region).

White values provide 95% confidence because they are in the limits of the model, which are the maximum and minimum daily measurement intervals.

Table 11 shows the iron ion concentration (corrosion level) as a function of chlorine and biocide concentrations. The permitted values for chlorine are 0–2 mg/L and the biocide dosages are 100–500 mg/L.

Irrespective of the ratio of variables at different concentrations, a corrosion level higher than that specified by current legislation (2.00 mg/L) is never reached. This aspect indicates the compatibility of the reclaimed water with the approved biocides, reaching 73% of the points depending on the resolution of the measuring equipment (green zone). There is an important tendency, the higher the concentration of chlorine and biocide, the higher the degree of corrosion in the installation (red zone). From industrial experience it is considered that an iron ion concentration above 0.95 mg/L indicates an increase in corrosion phenomena (red zone). For the resolution of the measuring equipment, a minimum percentage of situations under this effect (when the biocide is higher than 650 mg/L outside the manufacturer's recommendation and when iron and when iron is above 0,95 mg/L) is observed (27% of the points, red zone).

White values provide 95% confidence because they are interpolated in the maximum and minimum daily measurement intervals.

3.4. Industrial validation of the models

The validation of the correlation models has been carried out with the data obtained from the official maintenance program of cooling towers in subsequent months. Table 12 shows the obtained ranges of values. The measured values and the predicted residual isothiazolone concentration and the iron ion concentration values, obtained with the regression models shown in Table 8 and Table 9, are presented in Figs. 4 and 5 respectively. The good agreement between real and predicted values allows the validation of the models.

In economic terms, the replacement of drinking water by the reclaimed effluent in one cooling tower represents a 100% water savings (3740 m^3/year) with an economic saving of 9874 €/year (the cost of fresh water is 2.64 €/m^3).

Table 10

Predicted residual biocide concentration (mg/L) as function of pH and residual free chlorine concentration (mg/L).

Free chlorine (mg/L)	pH 6.50	6.70	6.90	7.10	7.30	7.50	7.70	7.90	8.10	8.30	8.50	8.70	8.90	9.10
0.00	823	739	655	571	487	404	320	236	152	68	🟥	🟥	🟥	🟥
0.10	815	731	647	563	479	395	311	227	143	60	🟥	🟥	🟥	🟥
0.20	807	723	639	555	471	387	303	219	135	51	🟥	🟥	🟥	🟥
0.30	798	714	631	547	463	379	295	211	127	43	🟥	🟥	🟥	🟥
0.40	790	706	622	538	454	371	287	203	119	35	🟥	🟥	🟥	🟥
0.50	782	698	614	530	446	362	278	194	110	27	🟥	🟥	🟥	🟥
0.60	774	690	606	522	438	354	270	186	102	18	🟥	🟥	🟥	🟥
0.70	765	681	598	514	430	346	262	178	94	10	🟥	🟥	🟥	🟥
0.80	757	673	589	505	421	338	254	170	86	2	🟥	🟥	🟥	🟥
0.90	749	665	581	497	413	329	245	161	77	🟥	🟥	🟥	🟥	🟥
1.00	741	657	573	489	405	321	237	153	69	🟥	🟥	🟥	🟥	🟥
1.10	732	648	565	481	397	313	229	145	61	🟥	🟥	🟥	🟥	🟥
1.20	724	640	556	472	388	305	221	137	53	🟥	🟥	🟥	🟥	🟥
1.30	716	632	548	464	380	296	212	128	45	🟥	🟥	🟥	🟥	🟥
1.40	708	624	540	456	372	288	204	120	36	🟥	🟥	🟥	🟥	🟥
1.50	699	615	532	448	364	280	196	112	28	🟥	🟥	🟥	🟥	🟥
1.60	691	607	523	439	355	272	188	104	20	🟥	🟥	🟥	🟥	🟥
1.70	683	599	515	431	347	263	179	95	12	🟥	🟥	🟥	🟥	🟥
1.80	675	591	507	423	339	255	171	87	3	🟥	🟥	🟥	🟥	🟥
1.90	666	582	499	415	331	247	163	79	🟥	🟥	🟥	🟥	🟥	🟥
2.00	658	574	490	406	322	239	155	71	🟥	🟥	🟥	🟥	🟥	🟥

Dosing pumps calibrated in:

- Set point [biocide]: 500 mg/L
- Set point [free chlorine]: 2.20 mg/L

Table 11
Predicted iron ion concentration (mg/L) as function of residual biocide concentration (mg/L) and free chlorine concentration (mg/L).

Free chlorine (mg/L)	Isothiazolone residual concentration (mg/L)													
	100	150	200	250	300	350	400	450	500	550	600	650	700	800
0.00	0.53	0.57	0.61	0.65	0.69	0.73	0.78	0.82	0.86	0.90	0.94	0.98	1.02	1.12
0.10	0.53	0.57	0.61	0.65	0.69	0.74	0.78	0.82	0.86	0.90	0.94	0.98	1.03	1.11
0.20	0.53	0.57	0.61	0.65	0.69	0.74	0.78	0.82	0.86	0.90	0.94	0.98	1.03	1.11
0.30	0.53	0.57	0.61	0.65	0.70	0.74	0.78	0.82	0.86	0.90	0.94	0.99	1.03	1.11
0.40	0.53	0.57	0.61	0.66	0.70	0.74	0.78	0.82	0.86	0.90	0.95	0.99	1.03	1.11
0.50	0.53	0.57	0.61	0.66	0.70	0.74	0.78	0.82	0.86	0.90	0.95	0.99	1.03	1.11
0.60	0.53	0.57	0.62	0.66	0.70	0.74	0.78	0.82	0.86	0.91	0.95	0.99	1.03	1.11
0.70	0.53	0.57	0.62	0.66	0.70	0.74	0.78	0.82	0.87	0.91	0.95	0.99	1.03	1.11
0.80	0.53	0.58	0.62	0.66	0.70	0.74	0.78	0.82	0.87	0.91	0.95	0.99	1.03	1.11
0.90	0.54	0.58	0.62	0.66	0.70	0.74	0.78	0.83	0.87	0.91	0.95	0.99	1.03	1.12
1.00	0.54	0.58	0.62	0.66	0.70	0.74	0.79	0.83	0.87	0.91	0.95	0.99	1.03	1.12
1.10	0.54	0.58	0.62	0.66	0.70	0.74	0.79	0.83	0.87	0.91	0.95	0.99	1.03	1.12
1.20	0.54	0.58	0.62	0.66	0.70	0.75	0.79	0.83	0.87	0.91	0.95	0.99	1.04	1.12
1.30	0.54	0.58	0.62	0.66	0.70	0.75	0.79	0.83	0.87	0.91	0.95	1.00	1.04	1.12
1.40	0.54	0.58	0.62	0.66	0.71	0.75	0.79	0.83	0.87	0.91	0.95	1.00	1.04	1.12
1.50	0.54	0.58	0.62	0.67	0.71	0.75	0.79	0.83	0.87	0.91	0.96	1.00	1.04	1.12
1.60	0.54	0.58	0.62	0.67	0.71	0.75	0.79	0.83	0.87	0.91	0.96	1.00	1.04	1.12
1.70	0.54	0.58	0.63	0.67	0.71	0.75	0.79	0.83	0.87	0.92	0.96	1.00	1.04	1.12
1.80	0.54	0.59	0.63	0.67	0.71	0.75	0.79	0.83	0.88	0.92	0.96	1.00	1.04	1.12
1.90	0.54	0.59	0.63	0.67	0.71	0.75	0.79	0.83	0.88	0.92	0.96	1.00	1.04	1.12
2.00	0.55	0.59	0.63	0.67	0.71	0.75	0.79	0.84	0.88	0.92	0.96	1.00	1.04	1.13

Dosing pumps calibrated in:

- Set point [biocide]: 500 mg/L
- Set point [free chlorine]: 2.20 mg/L

Table 12
Monthly physical-chemical results in the cooling tower for the verification of regression models.

Date	Iron (mg/L)	Isothiazolone (mg/L)	pH	Free Chlorine (mg/L)	Conductivity (µS/cm)	95% confidence region
March 20	0.65	300	7.40	1.80	1800	Yes
April 20	0.95	700	6.70	0.75	2100	No
May 20	0.55	120	8.10	0.45	2200	Yes
June 20	0.85	550	6.90	1.20	1450	Yes
July 20	0.95	500	6.95	1.75	2500	No
August 20	0.95	700	6.70	0.40	2850	No
September 20	0.65	250	7.65	1.10	2680	Yes
October 20	0.55	170	7.95	0.45	1150	Yes
November 20	0.85	450	7.35	0.26	1120	Yes
December 20	0.50	150	7.89	1.10	1750	Yes

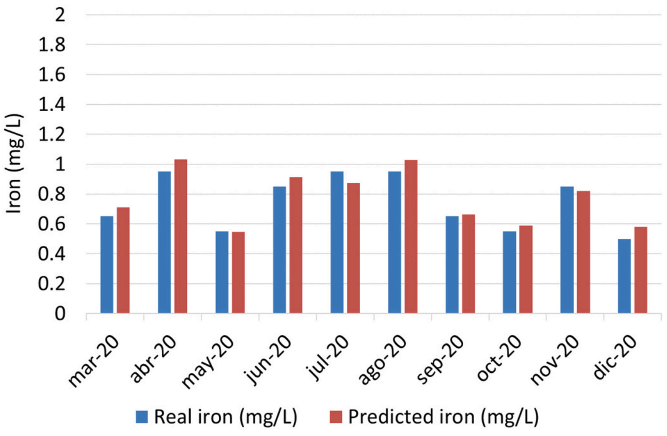


Fig. 4. Comparison of the parameter iron ion concentration (real vs. predicted) monthly.

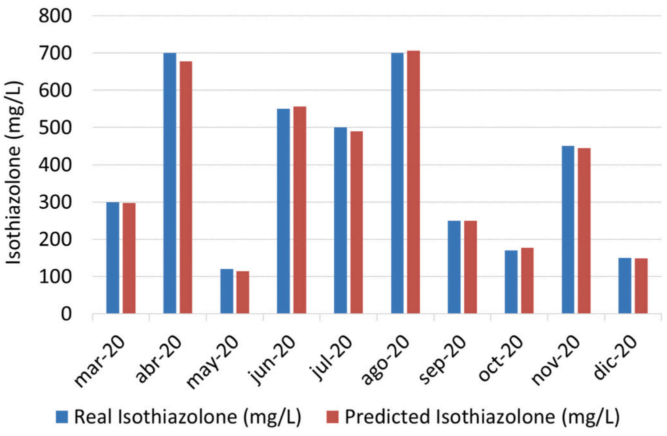


Fig. 5. Comparison of the parameter isothiazolone concentration (real vs. predicted) monthly.

4. Conclusions

Reclaimed water, coming from activated carbon treatment of wastewater from bottle is compatible with various commercial biocides (quaternary ammonium salts, tetrakis (hydroxymethyl) phosphonium sulphate (THPS) and isothiazolones) and can be successfully used as make-up water in cooling towers. At the recommended biocide doses, the tested products maintain the residual concentrations above the recommended ones with losses between 10 and 20% in 5 h.

The long term industrial reuse of the reclaimed water in a cooling tower, using isothiazolones as main biocide, was successfully carried out. All microbiological analyses complied with the specifications and no negative effects were observed after one year. The application of the reuse water concept obtained additional benefits when compared with a cooling tower using drinking water as make up water as, for example, a higher residual biocidal concentration and a lower ecotoxicity of the purge. Evaporation of the water during the cooling process leads to an increase in the pH, however, the chemical composition of the water remains stable without the need of pH control and with minimum calcification risks.

A successful correlation was obtained at industrial scale between the residual biocide concentration and the residual free chlorine concentration and the pH ($R^2 = 0{,}9143$). Higher residual biocide concentrations are achieved at lower values of both pH and free residual chlorine. To predict corrosion problems a successful correlation was obtained between the iron ion concentration and the residual free chlorine and the residual biocide concentrations. In all cases, iron ion concentration values were below the limit of current legislation, even under high concentration of both residual biocide and residual free chlorine. These models open new possibilities for a better control of cooling towers.

From the economic point of view, the replacement of drinking water by reclaimed water in one cooling tower represents 3740 m^3 of water saving per year with an economic saving of 9874 €/year. Therefore the plant will use reclaimed water in all the cooling towers.

In relation to future research, this study can be extended to obtain an industrial response with the other two active substances not evaluated in the industrial phase (THPS, quaternary ammonium salts and others). For application in other sector the biocide compatibility with other reclaimed water sources should be further explored. It is also proposed to carry out more frequent ecotoxicity analysis to assess the possibility of finding a correlation with other variables.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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