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Characterization of clogging deposits in an irrigation pipeline and effect of post-aeration on clogging potential of tertiary-treated wastewater

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ABSTRACT

In Agadir, a water-scarce Moroccan region, municipal and industrial wastewater is tertiary-treated to be reused in golf courses. Wastewater reuse has been constrained by severe clogging of emitters, which caused technical and financial problems. This study aimed to perform an in-depth characterization of the treated wastewater (TWW) in relation to its susceptibility to cause clogging, and to assess the capacity of an aeration post-treatment to reduce the clogging potential. The post-treatment consisted of injecting different airflows (0–33 L/(h L_{reactor})) into the TWW. The structural, morphological and elemental composition of the clogging matter collected in the irrigation pipeline was characterized using scanning electron microscopy, scanning transmission electron microscopy, X-ray diffraction and X-ray energy dispersive spectroscopy. The 15-day aeration post-treatment at 16.5 L/(h L_{reactor}) presented the best cost–benefit ratio. Organic matter was totally degraded. Calcium was reduced by 9%, bicarbonates by 54%. The analysis of the deposits induced by the aeration post-treatment revealed a relevant decrease of the major constituents of the clogging deposits found in the irrigation pipeline. The results show the effectiveness of post-aeration in biodegrading residual organic matter and precipitating several salts, thus reducing the clogging potential.

Key words | biodegradation, clogging, irrigation, post-aeration, precipitation, wastewater reuse

HIGHLIGHTS

- Treated wastewater of Agadir (Morocco), reused for the irrigation of golf courses, presents high clogging potential due to high salinity.
- 15-day post-aeration of the TWW removed organic matter and bicarbonates, determining significant reduction of clogging potential.
- As aeration intensity increased, the average crystal size decreased, further reducing the clogging potential.
- Analysis of the deposits induced by the post-aeration revealed relevant decrease of major constituents of the clogging deposits.

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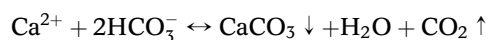
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INTRODUCTION

Wastewater reuse for irrigation has been applied worldwide due to its diverse benefits (Benlouali *et al.* 2017; Frascari *et al.* 2018; Pinelli *et al.* 2020), but it has been limited by technical problems due mainly to clogging of emitters. Emitter clogging affects irrigation uniformity and efficiency, negatively influencing crop growth and yield (Capra & Scicolone 1998). Clogging can fall into three main categories: physical, biological and chemical (Liu & Huang 2009).

As clogging is closely related to water quality, this work focuses on evaluating aeration post-treatment effect on treated wastewater (TWW). Aeration induces precipitation and biological uptake of biodegradable compounds (Mueller *et al.* 2002). Submerged aeration systems are more largely used in wastewater treatment facilities as they are more efficient. Fine bubbles diffusers, made from polymeric or ceramic porous sintered materials or polymeric punched membranes, are more energy-efficient than coarse bubble diffusers (Kaliman *et al.* 2008; Atia *et al.* 2012).

The aeration process increases dissolved oxygen and removes CO₂. This leads to the precipitation of CaCO₃, thus decreasing the clogging potential (Lesch & Suarez 2009):



Aeration improves water quality by accelerating organic matter biodegradation, activating photo-oxidation processes and causing the removal of iron, manganese and H₂S gas.

Treated wastewater (TWW) of both domestic and industrial origin in Agadir (southwestern Morocco) is used for the irrigation of golf courses. The main problem encountered is the clogging of irrigation equipment (filters, drip ramps, emitters) by a brown hard deposit.

The objectives of this work were (a) to characterize both the TWW and the clogging deposits, in order to gain a better understanding of the clogging problem, and (b) to study the effect of an aeration post-treatment on TWW quality and on the reduction of the clogging potential. The main novelties of this work are:

- i. the in-depth characterization of the clogging deposits and the identification of a suitable post-treatment for the agricultural reuse of a highly saline mixture of municipal and industrial wastewater originating mainly from fish industries, whereas the large majority of the studies on this topic focus only on municipal wastewater, or on effluents with less advanced treatments (Liu & Huang 2009)
- ii. the characterization of a P-rich clogging material featuring a unique combination of Ca(PO₄)₃(CO₃)_{0.5}, calcium carbonate (CaCO₃) and tricalcium phosphate (Ca₃(PO₄)₂)
- iii. the reduction of P-based clogging potential by means of an aeration post-treatment of municipal wastewater, whereas the papers on the effect of aeration on clogging deal with swine wastewater (Suzuki *et al.* 2002; Le Corre *et al.* 2009)
- iv. the characterization of the clogging deposits formed in a sprinkler-based irrigation system, whereas the large majority of the studies on this topic deal with drip irrigation systems.

METHODS

Layout of the aeration experiments

Experiments were carried out in order to evaluate the effect of aeration on the TWW chemical quality and on the composition and structure of the precipitated material. Two factors were studied: (1) airflow (A0: 0 L_{air}/(h L_{reactor}) (control), A16.5: 16.5 L_{air}/(h L_{reactor}), A33: 33 L_{air}/(h L_{reactor}) and (2) aeration duration (T15: 15 days and T30: 30 days). The tests consisted of injecting different airflows in aeration tanks containing 20 liters of TWW placed at room temperature (20 °C). Each tank was provided with 0, 1 or 2 ceramic fine pore diffusers connected to aquarium aerators. Diffusers had a rectangular shape (1.9 cm × 20 cm), provided 5.5 L/min each, and were placed at the bottom of the tanks. TWW samples were taken from each tank before the beginning of aeration and on the 15th and 30th day. Variations of the TWW chemical parameters were analyzed using the statistical analysis software Minitab 1.

Sampling and analytical methods

Three samples of clogging material (Figure 1), as well as TWW samples, were collected at intervals of 20 days from the main pipeline that delivers TWW from the treatment plant to the golf course. A fourth sample of clogging material obtained from the combination of equal portions of the first three samples was used to perform surface morphological characterizations.



Figure 1 | Morphology of the clogging matter.

Clogging matter collected from the irrigation pipeline

The clogging material collected from the pipeline was characterized in terms of elemental analyses, organic matter content (calcination at 450 °C), loss to fire (calcination at 1,000 °C) and Ca content (inductively coupled plasma-atomic emission spectrometry). Surface morphology of the material was characterized by scanning electron microscopy (SEM) and X-ray mapping. SEM investigations were performed using an MEB Quanta 600 FEG environmental scanning electron microscope. Transmission electron microscopy (TEM) investigations were carried out using a JEM-ARM 200F Cold FEG TEM/STEM (scanning transmission electron microscopy) operating at 200 kV and equipped with a spherical aberration (Cs) probe and image correctors (point resolution in TEM and STEM modes were respectively 0.12 and 0.078 nm). Further investigations were made by STEM, X-ray diffraction (XRD) and X-ray energy dispersive spectroscopy (EDS).

Treated wastewater collected from the golf course

The pH and EC were measured respectively by a 3310 Jenway pH meter and an EC 4310 Jenway conductivity meter. Dry residues were determined by evaporation at 108 °C during 4 hours. Ammonia, nitrogen and nitrate were determined by distillation using the Kjeldahl method. Chloride was analyzed by AgNO₃ titration, using potassium dichromate (K₂CrO₄) as indicator. Organic matter was determined by calcination at 450 °C. Sodium, potassium, calcium and magnesium were determined using an atomic absorption spectrophotometer.

Precipitated matter collected from the aeration tanks

At the end of the aeration tests, treated water was filtered in order to retrieve the precipitated matter, which was weighted and characterized by SEM and EDS.

RESULTS AND DISCUSSION

Characterization of the clogging matter collected from the irrigation pipeline

Table 1 shows the values of various parameters related to the composition of the clogging matter. The alkalinity of the sample (pH 8.6) is probably related to the presence of carbonates and bicarbonates. The loss to fire at 1,000 °C, equal to 25%, suggests the presence of carbonate and silicate minerals (Qlihaa et al. 2016).

SEM investigations were performed according to two approaches. Firstly, they were conducted on the three samples taken from the pipeline every 20 days to detect possible differences. These analyses showed the same crystal morphology for the three samples. The SEM micrographs, at an enlargement of 100 (Figure 2(a)), revealed that the clogging matter collected from the pipeline has an irregular and rough surface as well as marked reliefs. It is made of a cluster of well-cemented crystals characterized by different shapes and sizes. The general shape is determined by big crystals to which smaller ones stick. A difference in size between crystals at the surface of the matter and those located deeper can be noticed (Figure 2(b)). This illustrates different stages of crystal growth formed during the nucleation of the deposit. The X-ray mapping of the samples at an enlargement of 300 shows a relatively homogenous repartition of the elements with a predominance of calcium and phosphorus (Figure 2(c)). The presence of calcite crystals is confirmed by the X-ray maps that show the predominance of calcium and the absence of phosphate in those specific crystals (Figure 2(b)).

Table 1 | Characterization of the clogging matter sampled in the irrigation pipeline

| Parameter | Value |
|-------------------------|-------|
| pH | 8.60 |
| Ca | 30.5% |
| Loss to fire (1,000 °C) | 25.0% |
| Organic matter (450 °C) | 18.7% |

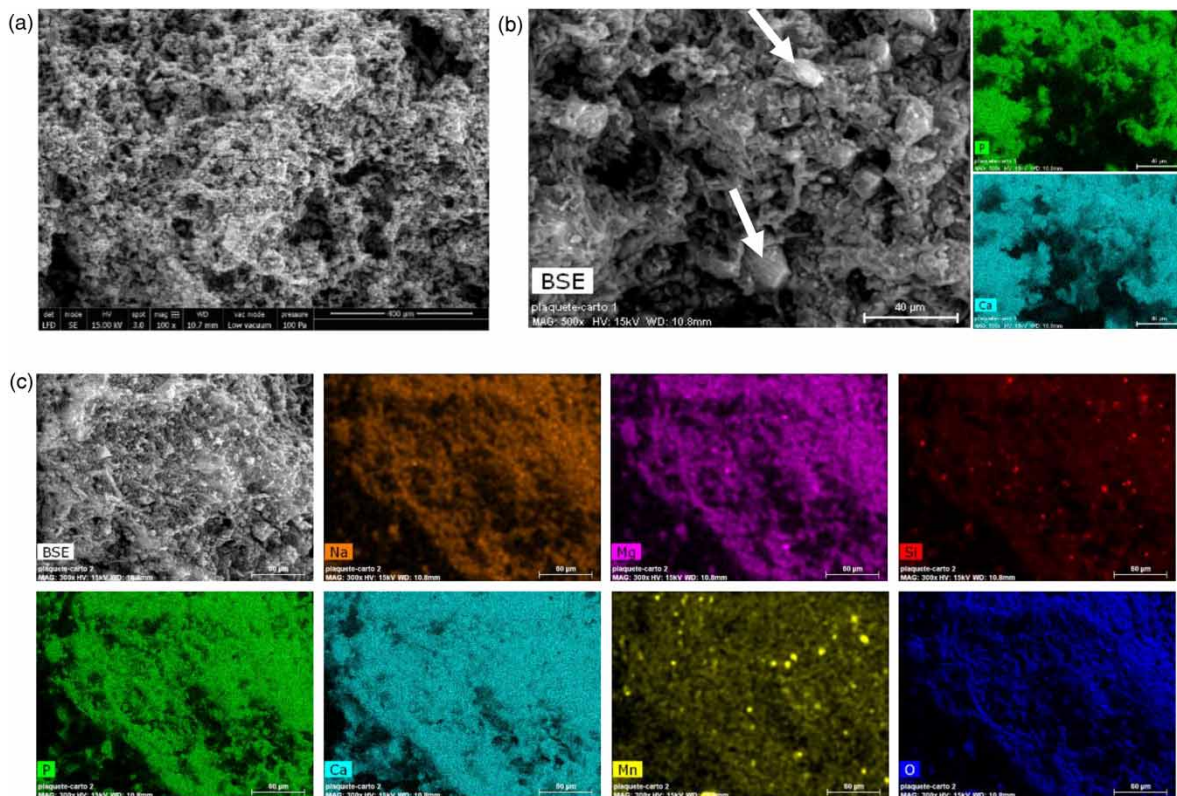


Figure 2 | (a) SEM micrograph of the clogging matter surface (x100); (b) SEM and elemental X-ray mapping micrographs showing the presence of calcite crystals (x500); (c) elemental X-ray mapping of the clogging matter surface (x300).

The EDS analyses of the three samples taken at different times are reported in Table 2. Oxygen represented the main element ($68\% \pm 1\%$), followed by calcium and phosphorus. Other elements were present with EDS peaks of low

intensity, as shown in Figure S1 in the Supplementary Material (Wunderlich *et al.* 1993). Statistical t-tests (significance level 0.05) were applied for each element, to assess the differences in composition between sample 1 (reference

Table 2 | EDS analyses of the clogging matter collected from the irrigation pipeline at three different times (sample 1: reference time t_0 ; sample 2: $t_0 + 20$ days; sample 3: $t_0 + 40$ days), and application of a t-test (significance level 0.05) to assess the statistical differences between the three compositions

| Element | Sample 1 % content | Sample 2 % content | $p_{t\text{-test}}^a$ | Sample 3 % content | $p_{t\text{-test}}^a$ | Mean % content |
|---------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------|
| O | 67 ± 3 | 68 ± 3 | $7.4 \cdot 10^{-1}$ | 69 ± 3 | $5.1 \cdot 10^{-1}$ | 68 ± 2 |
| Ca | 22 ± 1 | 20 ± 1 | $8.0 \cdot 10^{-2}$ | 21 ± 1 | $3.2 \cdot 10^{-1}$ | 21 ± 21 |
| P | 9.0 ± 0.5 | 9.2 ± 0.5 | $6.2 \cdot 10^{-1}$ | 9.2 ± 0.5 | $6.2 \cdot 10^{-1}$ | 9.1 ± 0.3 |
| Mn | 0.19 ± 0.02 | 0.87 ± 0.09 | $1.9 \cdot 10^{-4*}$ | 0.64 ± 0.06 | $3.1 \cdot 10^{-4*}$ | 0.57 ± 0.04 |
| Mg | 0.43 ± 0.04 | 0.52 ± 0.05 | $8.2 \cdot 10^{-2}$ | 0.32 ± 0.03 | $2.4 \cdot 10^{-2*}$ | 0.42 ± 0.02 |
| Si | 0.51 ± 0.05 | 0.57 ± 0.06 | $2.5 \cdot 10^{-1}$ | 0.14 ± 0.01 | $2.7 \cdot 10^{-4*}$ | 0.41 ± 0.01 |
| Na | 0.34 ± 0.03 | 0.19 ± 0.02 | $2.6 \cdot 10^{-3*}$ | 0.14 ± 0.01 | $7.1 \cdot 10^{-4*}$ | 0.22 ± 0.03 |
| Al | 0.20 ± 0.02 | 0.24 ± 0.02 | $9.1 \cdot 10^{-2}$ | 0.010 ± 0.001 | $8.0 \cdot 10^{-5*}$ | 0.15 ± 0.01 |
| S | 0.12 ± 0.01 | 0.13 ± 0.01 | $3.8 \cdot 10^{-1}$ | 0.12 ± 0.01 | $1.0 \cdot 10^0$ | 0.123 ± 0.007 |
| Cl | 0.20 ± 0.02 | 0.040 ± 0.004 | $1.7 \cdot 10^{-4*}$ | 0.010 ± 0.001 | $8.0 \cdot 10^{-5*}$ | 0.083 ± 0.007 |

^aProbability that there are no statistically significant differences between the % content of each monitored element in sample 2 or 3 and the corresponding % content in sample 1. The probabilities lower than the significance level (0.05), corresponding to statistically different % contents, are indicated with an asterisk.

time t_0), sample 2 (20 days after t_0) and sample 3 (40 days after t_0). As reported in Table 2, no statistically significant differences were found in terms of the main constituents of the deposit (O, Ca, P), indicating a substantial stability of the deposit composition over time. On the other hand, some significant differences were detected between sample 1 and sample 3 in terms of minor constituents (Mn, Mg, Si, Na, Al, Cl).

For further investigations, a sample was constituted by the combination of an equal ground portion of the three above-described samples. The SEM analyses of this ground sample revealed that the crystals had different sizes, from 0.5 μm to 450 μm (Figure 3). Their morphologies were characterized by various geometrical forms with sharp edges and relatively plane surfaces containing very fine

particles. The major regular structure characterized by defined cubic crystals corresponds to calcite (Ketrane *et al.* 2009).

Following a second approach, complementary TEM and dark field STEM (STEM-DF) analyses were carried out, confirming thus the difference in the sample particles sizes (Figure 4). The majority of the particles were characterized by irregular shapes. The elemental X-ray mapping showed the presence of calcium as a main compound, followed by phosphate, manganese oxide, silica, aluminum, magnesium and iron (Figure 5).

In order to gain more information on the spatial distribution of the elemental composition of the clogging matter, in-depth EDS analyses were performed on 13 regions of one sample of clogging matter, represented in

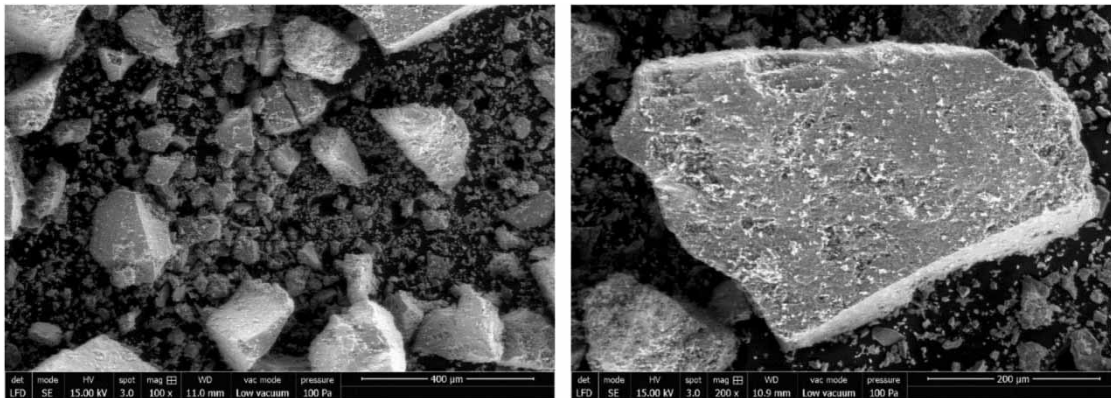


Figure 3 | SEM micrographs of the ground clogging matter (left: x100; right: x200).

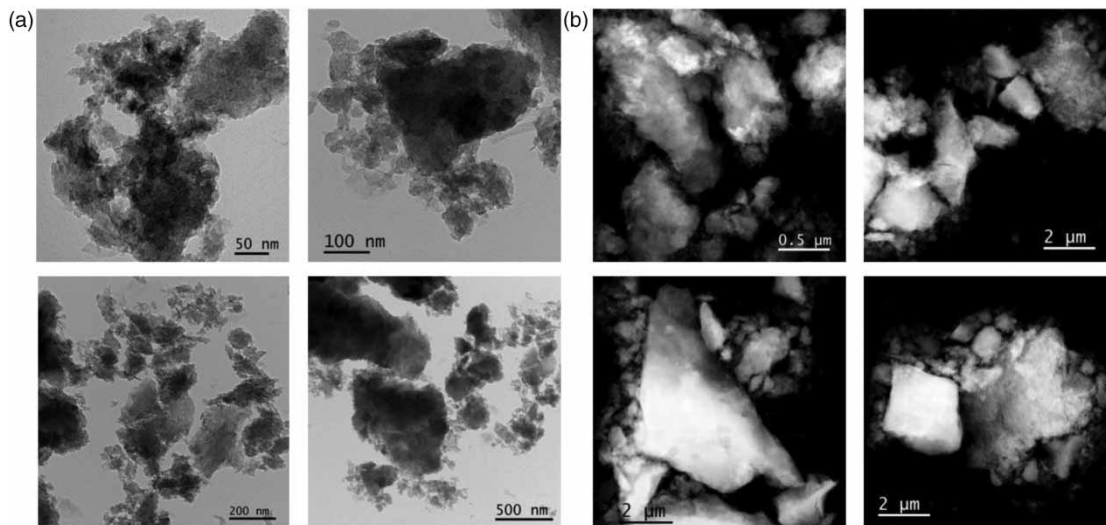


Figure 4 | (a) TEM bright field micrographs of the clogging matter; (b) STEM dark field micrographs of the clogging matter.

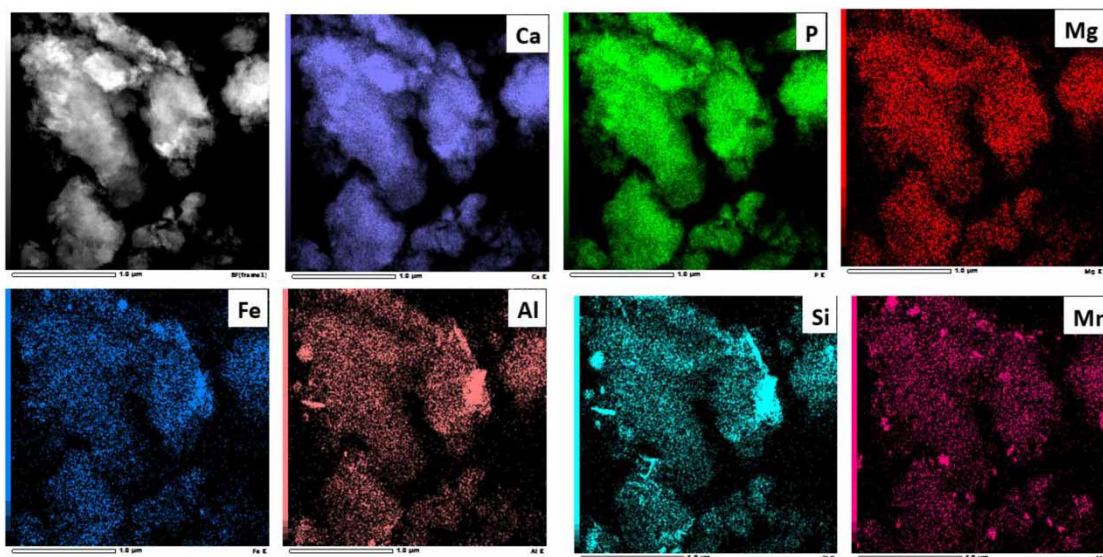


Figure 5 | Elemental X-ray mapping of the distribution of the different chemical elements.

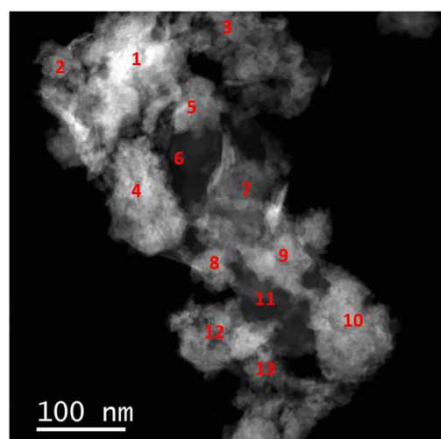


Figure 6 | STEM-DF micrograph representing the 13 regions of a clogging deposit sampled from the irrigation pipeline.

the STEM-DF micrograph of Figure 6. The micrograph showed the presence of different phases characterized by different intensities (Figure 6). The grains labeled 7 and 12 in Figure 6 represent different phases, as the second major element in their composition is respectively manganese and silicon. The EDS results are shown in Table 3. A statistical F-test (significance level 0.05) was applied in order to assess the significance of the observed variations in composition, in relation to the experimental errors. As shown in Table S1 in the Supplementary Material, the composition detected in the 13 regions was statistically different for all the compounds except oxygen, indicating a not negligible variability between the 13 sampling positions.

XRD characterization of the three samples taken from the irrigation pipeline was performed for further

Table 3 | EDS analyses relative to the STEM-DF micrograph representing the 13 regions of a clogging deposit sampled from the irrigation pipeline

| Composition in each of the 13 regions | | | | | | | | | | | | | | |
|---------------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|---------------------|
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | Average composition |
| O | 65 | 71 | 67 | 57 | 63 | 71 | 52 | 54 | 63 | 67 | 67 | 63 | 56 | 63 ± 6 |
| Ca | 21 | 19 | 23 | 28 | 23 | 3.8 | 24 | 26 | 18 | 23 | 0.86 | 28 | 28 | 20 ± 9 |
| P | 8.1 | 8.8 | 7.8 | 13 | 6.9 | 0.12 | 8.6 | 10 | 5.0 | 8.7 | 0.84 | 7.6 | 14 | 8 ± 4 |
| Mn | 0.09 | 0.13 | 0.38 | 0.26 | 2.4 | 22 | 12 | 7.5 | 0.02 | 0.01 | 0.03 | 0.16 | 0.07 | 4 ± 7 |
| Si | 4.8 | 0.17 | 0.94 | 0.36 | 2.6 | 0.73 | 0.56 | 0.34 | 10 | 0.34 | 23 | 0.33 | 0.54 | 3 ± 6 |
| Al | 0.18 | 0.13 | 0.11 | 0.08 | 0.70 | 0.02 | 0.24 | 0.30 | 2.9 | 0.20 | 7.2 | 0.12 | 0.19 | 1 ± 2 |
| Mg | 0.74 | 0.61 | 0.55 | 0.83 | 0.94 | 1.7 | 1.3 | 1.5 | 0.43 | 0.57 | 0.09 | 0.88 | 0.75 | 0.8 ± 0.4 |
| Fe | 0.13 | 0.14 | 0.15 | 0.24 | 0.32 | 0.67 | 0.50 | 0.29 | 0.50 | 0.12 | 0.89 | 0.16 | 0.38 | 0.3 ± 0.2 |

understanding of the material composition (Figure 7). The three samples presented the same phases, confirming the findings of SEM and EDS analyses. According to XRD analyses, the clogging matter can be characterized by the presence of three main phases: $\text{Ca}(\text{PO}_4)_3(\text{CO}_3)_{0.5}$, CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$. To the authors' knowledge, no previous research found a combination of these three phases in a clogging precipitate, and no research reported clogging problems due to $\text{Ca}_3(\text{PO}_4)_2$. CaCO_3 has been discussed in studies on TWW or groundwater (Liu & Huang 2009). Phosphate-based precipitates such as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and hydroxyapatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$) were found mainly in primary treatments of wastewater, especially in the swine industry (Le Corre *et al.* 2009).

The comparison of the above-described analyses indicates that calcium, phosphorus, carbonates/bicarbonates and organic matter should be primarily removed from the TWW, in order to reduce its susceptibility to generate clogging. Previous studies reported several approaches to address scaling problems, such as acid injections, threshold inhibitors and post-aeration (Moulick *et al.* 2012; Chaussemier *et al.* 2015). Among these approaches, the second part of this paper focuses on post-aeration.

Characterization of the TWW

The characteristics of the TWW are reported in Table 4, together with the Food and Agriculture Organization (FAO) (Ayers & Westcot 1985) and ISO 16075 (ISO 2015)

recommendations for TWW reuse in agriculture. The TWW is fully compliant with the ISO 16075 guidelines for the irrigation of non-food crops. According to the FAO recommendations, it presents severe restrictions for agricultural reuse in relation to its high electrical conductivity (EC) and to the high content of bicarbonates, chloride, sodium, nitrate and total dissolved solids. The pH value is in agreement with the range suggested by FAO.

The particularly high salinity of the Agadir TWW is due to the relevant presence of fish industries in the Agadir region. The high salinity of the fish industry WW is partly due to the large use of chloride-rich brine in the fish transformation process. Another source of salinity is the composition of fish scales, largely found in factory effluents (Mouhanni *et al.* 2013). Bones, teeth and scales contain 99% of the calcium and 80% of the phosphorus present in the fish body (Huss 1988). Table 5 presents minimum, maximum and average values of selected parameters in the effluents of fish factories in Agadir (Ziani *et al.* 2007). The chloride level is very high. The load of phosphorus exceeds the Moroccan standard that sets the amount of total phosphorus for direct and indirect discharges to 10 mg/L (El-Ogri *et al.* 2016).

Effect of post-aeration on TWW quality

The values of the main TWW parameters at the beginning of the test and after 15 days of post-aeration at three different aeration intensities are reported in Table 6, together with

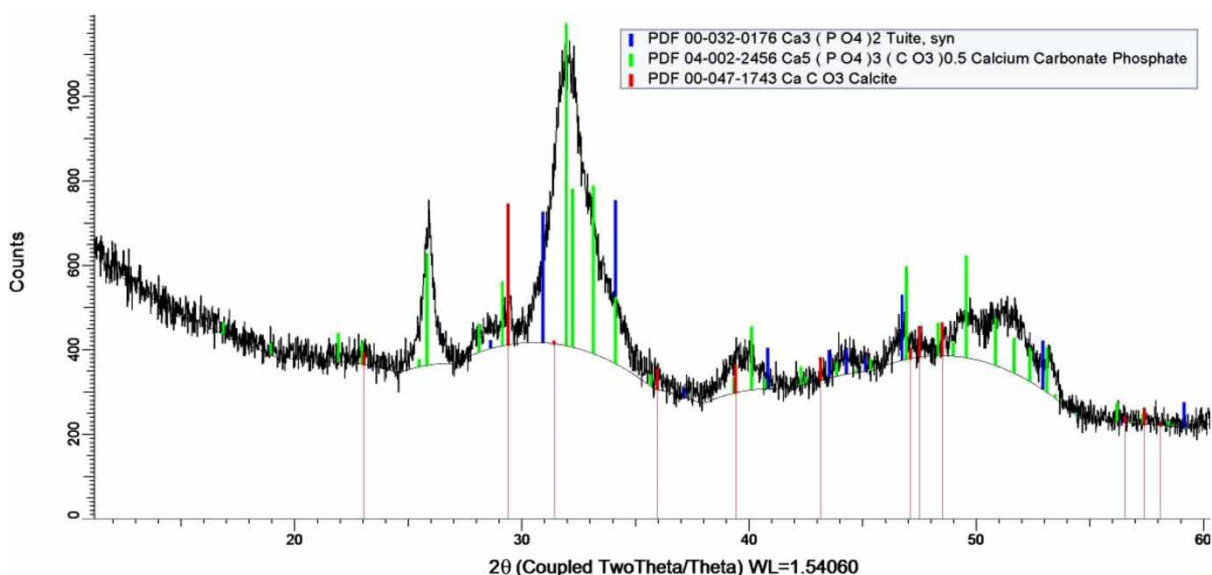


Figure 7 | Phases of the clogging material investigated by X-ray diffraction analyses.

Table 4 | Physical and chemical properties of the TWW before the aeration post-treatment, compared to the FAO recommendations on the degree of restriction for TWW reuse for irrigation and to the ISO 16075 standard

| Parameter | Value in the TWW | FAO degree of restriction for TWW use for irrigation ^a | | | ISO 16075 guideline for TWW reuse for irrigation ^b |
|--|------------------|---|--------------------|--------|---|
| | | None | Slight to moderate | Severe | |
| pH | 7.44 ± 0.02 | Normal range: 6.5–8 | | | |
| EC (dS/m) | 3.55 ± 0.09 | <0.7 | 0.7–3.0 | >3.0 | |
| CO ₃ ²⁻ (mg/l) | 0 | | | | |
| HCO ₃ ⁻ (mg/l) | 576 ± 23 | <92 | 92–519 | >519 | |
| Ca ²⁺ (mg/l) | 139 ± 4 | | | | |
| Mg ²⁺ (mg/l) | 51 ± 2 | | | | |
| Cl ⁻ (mg/l) | 666 ± 26 | <142 ^c | >142 ^c | | |
| Na ⁺ (mg/l) | 203 ± 6 | <69 ^c | >69 ^c | | |
| K ⁺ (mg/l) | 45 ± 2 | | | | |
| NH ₄ ⁺ (mg/L) | 1.8 ± 0.1 | | | | |
| P (mg/L) | 0.90 ± 0.04 | | | | |
| NO ₃ -N (mg/L) | 55 ± 3 | <5 | 5–30 | >30 | |
| Organic matter (mg/L) | 150 ± 8 | | | | |
| 5-day biochemical oxygen demand (mg/L) | 12 ± 1 | | | | <35 |
| Total suspended solids (mg/L) | 12 ± 1 | | | | <50 |
| Thermo-tolerant coliforms (n./100 mL) | 60 ± 6 | | | | <10,000 |
| Total dissolved solids (mg/L) | 2 595 ± 180 | <450 | 450–2,000 | >2,000 | |

^aAyers & Westcot (1985).^bValues corresponding to category C (irrigation of non-food crops) of the ISO 16075 standard (ISO 2015).^cRefers to the case of sprinkler irrigation.**Table 5** | Minimum, maximum and average values of selected parameters in the wastewater produced by fish industries in Agadir, according to Ziani et al. (2007)

| Parameter | Minimum | Maximum | Average |
|-------------------------|---------|---------|---------|
| pH | 6.5 | 9.5 | 7.7 |
| EC (dS/m) | 3.4 | 96 | 24 |
| Chloride (mg/L) | 2,270 | 42,370 | 9,904 |
| Total phosphorus (mg/L) | 22 | 342 | 113 |

the FAO standards for reusing TWW for irrigation, as established by Ayers & Westcot (1985). The graphs representing the values of the same parameters at both 15 and 30 days are shown in Figures S2 to S7 in the Supplementary Material. Statistical t-tests (significance level 0.05) were applied for each monitored parameter, to assess the differences in composition between the initial TWW and the post-treated WW at three aeration intensities.

Independently of air flow rate, aeration led to a statistically significant increase in pH by about 1 unit (Table 6 and Figure S2 in Supplementary Material). The pH increase

can be tentatively explained as a response to respiratory CO₂ production by bacteria and other organisms (Pescod 1992), which results in bicarbonate production (Jirou 2015). The rise in pH leads to the precipitation of dissolved elements. This permits the disposal of clogging materials in the aeration tank, before the TWW is sent to the irrigation pipeline.

Aeration had a minor effect on calcium, with a modest but statistically significant decrease in calcium concentration at 16.5 L/(h L_{reactor}) (−9%) and a negligible variation at 33 L/(h L_{reactor}) (Table 6 and Figure S3 in Supplementary Material). As for bicarbonates, at both aeration intensities the aeration process resulted in a roughly 50% decrease, reducing them to about 260 mg/L (Figure S4, Supplementary Material). This allowed the degree of restriction of TWW reuse for irrigation to be reduced from severe to slight/moderate, according to the FAO standards (Ayers & Westcot 1985). The decrease in bicarbonate is presumably due to its precipitation as calcium carbonate, as illustrated in Equation (1). However, the significantly higher extent of the bicarbonate decline in comparison

Table 6 | Effect of the 15-day aeration post-treatment at different air flow rates on selected parameters of the TWW, and application of a t-test (significance level 0.05) to assess the statistical differences between the initial and final TWW composition in each treatment

| Parameter | Control (no aeration) | | | 16.5 L/(h L _{reactor}) aeration | | | 33 L/(h L _{reactor}) aeration | | | FAO degree of restriction for TWW use for irrigation ^a | | |
|-------------------------|-----------------------|-------------|--------------------------|---|--------------------------|------------------------|---|--------------------------|------------------------|---|-----------------|--------|
| | Initial value | Value | % variation ^b | Value | % variation ^b | pF _{test} | Value | % variation ^b | pF _{test} | Low | Slight/moderate | Severe |
| pH | 7.44 ± 0.02 | 8.52 ± 0.02 | +15% | 8.53 ± 0.02 | +15% | 3.0·10 ⁻⁷ * | 8.54 ± 0.02 | +15% | 2.9·10 ⁻⁷ * | Normal range : 6.5–8 | | |
| Ca (mg/L) | 139 ± 4 | 135 ± 4 | -3% | 127 ± 4 | -9% | 3.0·10 ⁻¹ | 147 ± 4 | +6% | 8.5·10 ⁻² | - | | |
| HCO ₃ (mg/L) | 576 ± 23 | 488 ± 20 | -15% | 268 ± 11 | -53% | 7.2·10 ⁻³ * | 265 ± 11 | -54% | 2.9·10 ⁻⁵ * | 92 | 92–519 | >519 |
| Organic matter (mg/L) | 150 ± 8 | 0 | -100% | 0 | -100% | 4.1·10 ⁻⁶ * | 0 | -100% | 4.1·10 ⁻⁶ * | - | | |
| EC (dS/m) | 3.55 ± 0.09 | 3.75 ± 0.09 | +6% | 3.65 ± 0.09 | +3% | 8.9·10 ⁻² | 3.63 ± 0.09 | +2% | 4.1·10 ⁻¹ | <0.7 | 0.7–3.0 | >3.0 |

^aAyers & Westcot (1985).

^b% variation in relation to the corresponding initial value.

*Probability that there are no statistically significant differences in the concentration of each compound or parameter between the initial TWW composition (2nd column) and the TWW composition after 15 days of post-treatment at different aeration intensities. The probabilities lower than the significance level (0.05), corresponding to statistically different values, are indicated with an asterisk.

with calcium suggests that other forms of bicarbonate precipitated.

Independently of treatment time (15 or 30 days) and aeration rate, the post-treatment resulted in a complete elimination of organic matter (Figure S5, Supplementary Material). This result suggests that organic matter was removed mainly by sedimentation.

Despite the marked reduction in bicarbonates, the aeration/sedimentation post-treatment did not determine any statistically significant decrease in electrical conductivity (Figure S6, Supplementary Material).

Overall, 15-day aeration with a 16.5 L/(h L_{reactor}) flow rate had a substantial effect on the reduction of bicarbonates (-53%) and organic matter (-100%), and a secondary but not negligible effect on calcium (-9%) (Table 6). This operational condition therefore results in being the recommended one.

In order to assess the actual feasibility and costs of the proposed aeration post-treatment, a preliminary assessment of the tank volume and energy consumption associated with the 15-day treatment at 16.5 L/(h L_{reactor}) for the irrigation of 1 ha of olive trees was conducted, under the following assumptions: aerator efficiency 2.2 kgO₂/(h kW), crop water requirement 5,500 m³/y (Doorenbos et al. 1992). The results indicate that the proposed process requires a reasonable tank volume (226 m³, for example 8 × 8 × 3.5 m) but a particularly high electric energy consumption (742 kWh/m³). Considering that southern Morocco has a very intense solar radiation (global horizontal irradiation = 6 kWh/(m² d); Solargis 2020), assuming a photovoltaic efficiency of 0.22, the production of the needed electric energy would require to cover with photovoltaic panels a surface equal to 85% of the irrigated crop surface, an excessively high value. On the other hand, considering that the TWW treatment performances obtained after 15 days were not statistically different from those obtained after 30 days, and that the typical retention times for WW treatment are in the 0.5–2 day range, it is reasonable that the post-aeration retention time can be considerably reduced without major variations in treatment performance. The repetition of the same preliminary assessment under the reasonable hypothesis of a 1-day post-aeration led to the following results: 15 m³ tank volume, 7.4 kWh/m³ electric consumption, 560 m² (5.6% of irrigated crop surface) to be covered with photovoltaic panels in order to make the processes self-sustainable. This analysis suggests that the proposed post-aeration process can be performed with acceptable investment and operational costs, if the retention time can be reduced to about 1 day. Further research is thus needed in order to

assess the effectiveness of post-aeration at shorter retention times.

Characteristics of precipitates formed in the post-aeration reactors

The precipitated matter collected in the post-aeration tanks was characterized by SEM analysis (Figure 8). SEM micrographs revealed that aeration intensity had an impact on

both the size and shape of the crystals. Indeed, in the absence of aeration crystals exceeded $500\ \mu\text{m}$, whereas their size decreased to 150 and $85\ \mu\text{m}$ for aeration intensities of 16.5 and $33\ \text{L}/(\text{h L}_{\text{reactor}})$, respectively.

This result indicates that, as aeration intensity increased, the average crystal size decreased, thus reducing the clogging potential of the TWW. As for the shape of crystals, in the absence of injected air the particles were subdivided into flower-like crystals and sticks made of a cluster of

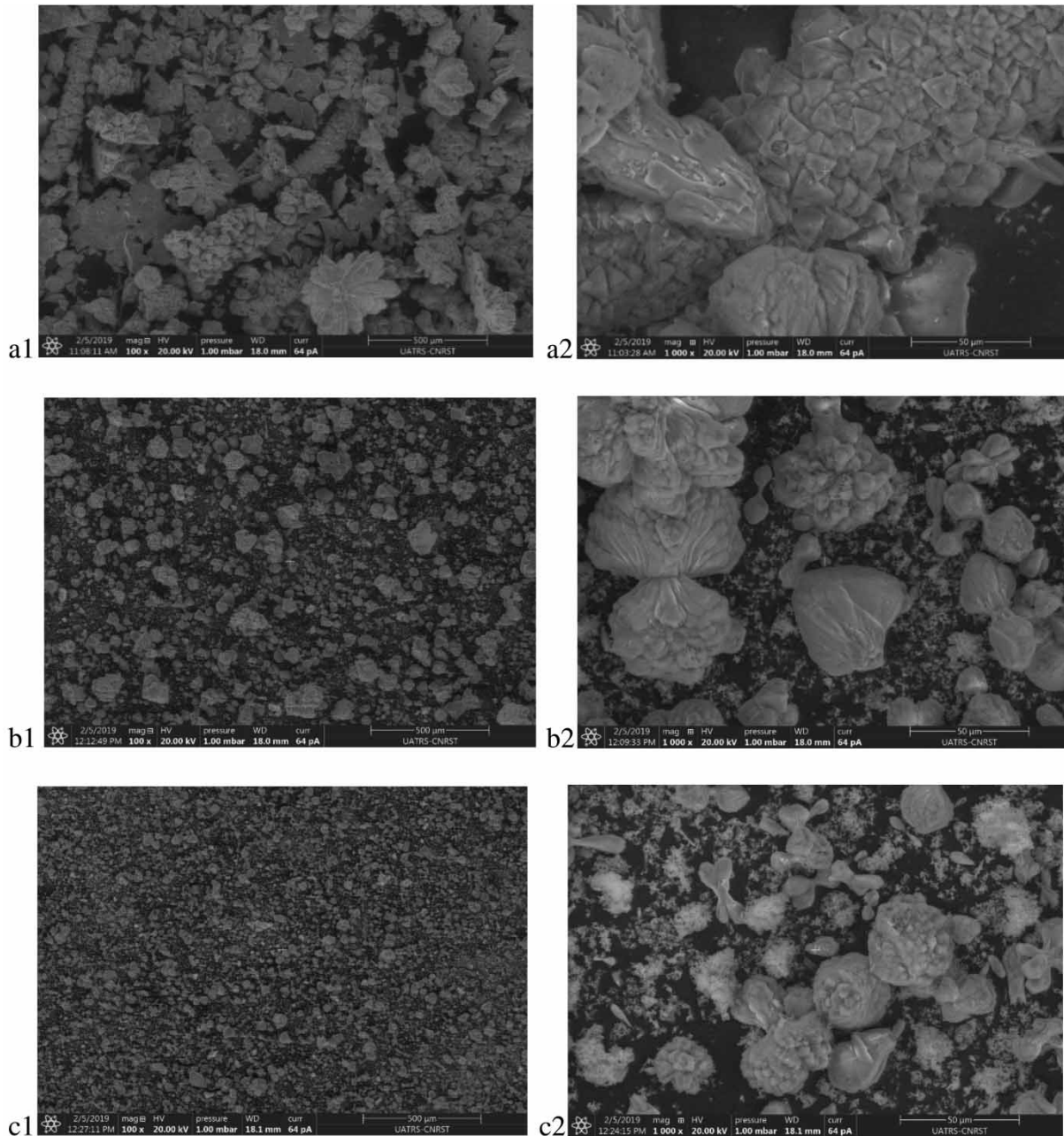


Figure 8 | SEM micrograph of the precipitated material collected in the post-aeration tanks: (a1) control (x100), (a2) control (x1000), (b1) $16.5\ \text{L}/(\text{h L}_{\text{reactor}})$ (x100), (b2) $16.5\ \text{L}/(\text{h L}_{\text{reactor}})$ (x1000), (c1) $33\ \text{L}/(\text{h L}_{\text{reactor}})$ (x100), (c2) $33\ \text{L}/(\text{h L}_{\text{reactor}})$ (x1000).

triangular forms (Figure 8(a1) and (a2)). In the presence of aeration, the structure of crystals was similar to flower and chromosome forms (Figure 8(b1), (b2), (c1) and (c2)).

The average atomic composition of the clogging material sampled in the irrigation pipeline and of the precipitates formed in the aeration/sedimentation tanks after 30 days of treatment is reported in Table 7. Statistical t-tests (significance level 0.05) were applied for each element, to assess the differences in composition between the pipeline clogging material and the precipitates formed in the tanks at different aeration intensities. In comparison with the precipitates formed in the irrigation pipeline, the aeration treatment resulted in consistent and statistically significant decreases in the content of P and – to a lower extent – Ca, the major constituents of the deposits formed in the irrigation pipeline. Aeration also resulted in statistically significant decreases in Mn, Si, Al, Mg and Fe. These results confirm the effectiveness of post-aeration in reducing the TWW clogging potential.

Implications for the decrease of clogging in irrigation pipelines and devices

The findings of this work provide interesting implications in the perspective of decreasing the clogging of irrigation equipment.

Firstly, the characterization of the clogging deposits indicates that the addition to the Agadir municipal wastewater of highly saline industrial wastewater (EC 24 dS/m, P 113 mg/L) deriving mainly from fish processing industries contributes significantly to the formation of clogging deposits in the irrigation pipelines. This finding indicates that, in the perspective of TWW reuse for irrigation, it is generally recommended to collect and treat separately saline industrial wastewater.

The aeration post-treatment proposed in this work appears to be a promising option for the reduction of the TWW clogging potential, thanks to the reduction of organic matter, bicarbonates and calcium. The proposed post-treatment is expected to lead not only to a decrease of the maintenance costs associated with the cleaning or replacement of pumps, filters and irrigation devices, but also to an increase in irrigation uniformity and efficiency, helping thus to save water and improve crop yield. Post-aeration thus represents an interesting alternative to decarbonize TWW and improve its re-usability for agricultural purposes.

The proposed post-aeration technology is characterized by a low investment cost, a null consumption of chemicals and a high technological simplicity, which makes it suitable for implementation in rural contexts where the reuse

Table 7 | Comparison of the composition of the clogging material sampled in the irrigation pipeline and of the precipitates formed in the aeration/sedimentation tanks after 30 days of treatment, determined by EDS analyses (atomic percentages)

| Parameter | Clogging material from irrigation pipeline % content | Precipitates collected from the aeration tanks | | | | | |
|-----------|---|--|-----------------------|---|-----------------------|---|-----------------------|
| | | Control (no aeration) | | 16.5 L/(h L _{reactor}) aeration | | 33 L/(h L _{reactor}) aeration | |
| | | % content | p_{t-test}^a | % content | p_{t-test}^a | % content | p_{t-test}^a |
| O | 63 ± 3 | 60 ± 3 | 3.0·10 ⁻¹ | 67 ± 3 | 2.1·10 ⁻¹ | 66 ± 3 | 3.2·10 ⁻¹ |
| Ca | 20 ± 1 | 22 ± 1 | 8.0·10 ⁻² | 17 ± 1 | 1.7·10 ^{-2*} | 17 ± 1 | 1.7·10 ^{-2*} |
| P | 7.7 ± 0.4 | 3.1 ± 0.2 | 4.3·10 ^{-5*} | 1.4 ± 0.1 | 9.8·10 ^{-6*} | 1.5 ± 0.1 | 1.1·10 ^{-5*} |
| Mn | 3.5 ± 0.2 | b | 4.1·10 ^{-6*} | b | 4.1·10 ^{-6*} | b | 4.1·10 ^{-6*} |
| Si | 3.5 ± 0.2 | 3.3 ± 0.2 | 2.2·10 ⁻¹ | b | 4.1·10 ^{-6*} | b | 4.1·10 ^{-6*} |
| Al | 1.0 ± 0.1 | b | 6.5·10 ^{-5*} | b | 6.5·10 ^{-5*} | b | 6.5·10 ^{-5*} |
| Mg | 0.84 ± 0.08 | 0.39 ± 0.04 | 1.1·10 ^{-3*} | 0.44 ± 0.04 | 1.9·10 ^{-3*} | b | 6.5·10 ^{-5*} |
| Fe | 0.35 ± 0.04 | b | 6.5·10 ^{-5*} | b | 6.5·10 ^{-5*} | b | 6.5·10 ^{-5*} |
| S | b | 0.29 ± 0.03 | 6.5·10 ^{-5*} | b | c | b | c |
| K | b | 0.18 ± 0.02 | 6.5·10 ^{-5*} | b | c | b | c |
| Ni | b | 0.48 ± 0.05 | 6.5·10 ^{-5*} | b | c | b | c |

Application of a t-test (significance level 0.05) to assess statistical differences between compositions.

^aProbability that there are no statistically significant differences between the % content of each monitored element in the precipitates formed in the aeration/sedimentation tanks after 30 days and the corresponding % content in the clogging material sampled in the irrigation pipeline. The probabilities lower than the significance level (0.05), corresponding to statistically different % contents, are indicated with an asterisk.

^bBelow detection limit.

^ct-test not applicable.

of TWW often takes place. On the other hand, post-aeration presents the drawback of a rather high energy consumption. However, this study showed that – in a country characterized by high solar irradiation – the required electric energy can be obtained from a relatively low surface of solar panels.

Lastly, this study – conducted in collaboration with the Agadir basin authority and Ocean Golf Course management – revealed that TWW users still have a relevant reluctance towards TWW reuse for irrigation, and that the results of field studies of TWW post-treatment and reuse for irrigation can significantly contribute to reduce such reluctance, thus leading to an increase of TWW reuse for irrigation and ultimately to an increase in water security.

CONCLUSION

This study showed that the peculiar composition of the clogging deposits produced by the Agadir TWW, featuring a combination of $\text{Ca}(\text{PO}_4)_3(\text{CO}_3)_{0.5}$, CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$, is associated with the relevant discharge of highly saline, P-rich industrial wastewater in the Agadir sewer system.

The studied aeration post-treatment, even though characterized by a high energy consumption, resulted in a significant reduction of the TWW clogging potential.

Further research is needed in order to assess (i) the effectiveness of post-aeration at shorter retention times than those tested in this work and for TWWs characterized by a different composition, and (ii) the actual long-term reduction of clogging phenomena attainable in pipelines and irrigation devices thanks to TWW post-aeration.

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CONFLICT OF INTEREST

The authors report no conflicts of interest. The authors are responsible for the content and writing of the paper.

RESEARCH DATA

Research data relative to this article have been deposited in the AMS Acta Institutional Research Repository of the University of Bologna (doi:10.6092/unibo/amsacta/6393).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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