Investigation of pipes and sprinklers scaling at the golf course turf irrigated by treated wastewater of Mzar plant in Agadir-Morocco

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Abstract: In Agadir city, the reuse of treated wastewater for irrigation of green spaces has faced the problem of scaling of the pipes of these waters. This research paper aims at studying the phenomenon of scaling caused by the treated wastewater from the Mzar sewage treatment plant in the city of Agadir in south-west of Morocco. These waters are used in the irrigation of golf turf “Ocean”. The formation of solid deposits in the irrigation systems has decreased their lifetime, and consequently, a loss of load and performance is occurring. Thus, the sprinklers used in golf turf irrigation are plugged in the first weeks of the beginning of their operation. The wastewater used for the irrigation of the golf was analyzed at various points using physicochemical measurements: in the golf entry, at the tarpaulin and the exit of the sprinklers. The samples of treated wastewater and obtained scale were studied. The characterization of the scale samples formed in the passageways of the treated wastewaters has been performed by X-ray fluorescence spectrometry, X-ray diffraction, thermogravimetric analysis, differential thermal analysis and scanning electron microscopy. The results of the physicochemical analysis of the waters show that they are full of bicarbonates (653 mg/L), chloride (478 mg/L), nitrate (412 mg/L), sodium (425 mg/L) and in calcium (199 mg/L). Their pH is slightly alkaline. The analysis of the scale reveals that it is rich in calcium and phosphorus. It is formed of calcium carbonate (CaCO₃), silica (SiO₂), calcium silicate (Ca₂SiO₄), hydroxyapatite (Ca₁₀P₆O₁₉H₂), calcium carbonate-apatite(Ca₁₀ (PO₄) ₆CO₃) and silicate calcium and magnesium (Ca₃MgSi₃O₁₂).

Keywords: Scaling water; wastewater; scale; irrigation; Agadir.

1. Introduction

The region of Souss Massa in the south-west of Morocco is known for its semi-arid climate and its minimal water resources. In order to mitigate this water deficit, the development master plan for this region recommends resorting to unconventional resources. The reuse of treated wastewater to reduce this water deficit is now inevitable. Infrastructures have been made to serve the golf and green spaces of the city of Agadir by treated wastewater from Mzar station in the city. The average flow of treated wastewater is 30000 m³/d 1-2. Nevertheless, this reuse of treated water has encountered the problem of scaling of water pipelines. This phenomenon has created technical economic and environmental problems.

This study aims, on the one hand, to examine the physical and chemical quality of the treated wastewater used for irrigation of golf turf. On the other hand, it aims identifying and characterizing the scale deposits assembled at the level of the pipes and sprinklers of the "Ocean" golf.

2. Materials and methods

2.1. Site of the study and sampling

The sewage treatment plant of wastewaters Mzar is located at approximately 4 km in the south of Agadir city on the left coast of Oued Souss on the coastal dunes of Mzar. Its western limit is about 1500 m from the sea.

The "ocean" golf, which was opened in January 2010, is located at 11 km from the city center of Agadir in the forest of Bensergao (Figure 1). Its total area is 100 hectares, of which 75 hectares are grassed. It has a storage tank of treated wastewater 15,000 m³ of capacity and 1.5 m of the depth off. The flow of daily watering rate ranges from 3000 to 4000 m³.
The studied scale was collected inside the golf at three different points. Figure 2 shows a sprinkler clogged up by scale and Figure 3 shows the scale taken from the sprinkler.

**Figure 1.** Location of the Mzar’s sewage treatment plant and the "Ocean" golf

**Figure 2.** Sprinkler clogged by the scale

**Figure 3.** Golf Sprinkler scale

### 2.2. Methods of analysis

#### 2.2.1. Physicochemical analyzes
Calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$) ions were determined by the atomic absorption method, while sodium (Na$^+$) and potassium (K$^+$) ions by flame spectrophotometry, chloride (Cl$^-$) by Mohr method, sulfates (SO$_4^{2-}$) by gravimetry, nitrates (NO$_3^-$) by visible spectrophotometry and bicarbonate by volumetry.

#### 2.2.2. X-ray Fluorescence Spectrometry Analysis
X-rays are electromagnetic radiation ranging approximately between 0.1 and 50 Å. They are emitted by the bombardment of the surface of a solid by cathode rays. The scale was analyzed using XRF spectrometer Axios. The applied voltage is 60 kV with a current intensity of 125 mA and 4000 W power.

#### 2.2.3. X-ray diffraction analysis
The use of X-ray diffraction (XRD) spectroscopy is an essential step in accurately identifying the scale structure formed during the scaling process. The diffractometer used for these measurements is a goniometer with direct optical encoding connected to a computer and using a copper anticathode Kα ($\lambda = 1.5406$ Å), with an absolute angular accuracy of 0.0025 and a reproducibility lower than 0.0001 degrees. The Scan is adopted with a step of 0.06682°.

#### 2.2.4. Differential thermal and gravimetric analysis
Differential thermal analysis is a technique that measures the temperature difference between a sample and a reference according to time and/or temperature. Thermogravimetric analysis is a technique that measures the mass variation of a sample when it is subjected to temperature variation programming, under a controlled atmosphere. The thermal and gravimetric analysis of the scale was carried out by a thermogravimetric analyzer (TGA) apparatus combined with differential thermal analysis (DTA) of the type Shimadzu DTG-60, under air with 10°C/min, from 0°C to 1100°C. The flow rate used is 10 mL/min.
2.2.5. Scanning electron microscopy analysis
Scanning electron microscopy (SEM) is used to gain visual mastery of the objects: the morphology of the grain boundaries and the porosity. It also allows highlighting the textural state of a powder or a material. The scale samples were dehydrated, treated and then placed on the slide. The micrographs of the scale are obtained by scanning electron microscope FEI Quanta 200 equipped with an EDX probe. The surface microanalysis is carried out with a resolution of 3.5 nm and optical magnification of 20-106 times.

According to these results, treated wastewaters are slightly rich in alkaline pH of 8.3 at the level of the sprinkler. These waters have high contents of bicarbonate ions HCO$_3^-$, sodium Na$^+$, nitrate NO$_3^-$, chloride Cl$^-$ and sulphate SO$_4^{2-}$. These contents widely exceed the values fixed by the Moroccan norms relating to the reuse of wastewaters for the irrigation of the public green spaces.

The water used to irrigate golf turf "Ocean" has a slight amount of alkaline pH, which has the effect of promoting the formation of scale. The average value of the electrical conductivity highlights strong mineralization of these waters. Similar results were obtained on the treated waters of Mzar station. Inside the Golf, a slight variation of the pH and the contents of calcium, bicarbonate, sulphate and chloride were noticed.

The treated water thus presents favorable conditions for the formation of chemical deposits in their passageways. All the sprinklers of the Golf are thus clogged up in the first weeks of the beginning of their operation. To overcome this problem, filters were installed upstream and downstream of the pipes. Few hours after this operation, filters are clogged and must be disassembled for cleaning.

3. Results and discussion

3.1. Physicochemical analysis of treated wastewater
The physicochemical parameters of the wastewater related to the scaling phenomenon were determined by taken water samples at three points: the golf entrance, the tarpaulin and from the sprinklers. The obtained results are summarized in Table 1.

### Table 1. Physicochemical parameters of treated wastewater

|       | Golf entrance | Tarpaulin | Sprinkler | Moroccan norms |
|-------|--------------|-----------|-----------|----------------|
| T(°C) | 27.90        | 27.90     | 27.50     | 35.00          |
| pH    | 7.80         | 7.80      | 8.30      | 6.50-8.50      |
| EC (mS/cm) | 2.82   | 2.86      | 2.90      | 12.00          |
| Ca$^{2+}$ (mg/l) | 199.00 | 196.00    | 201.00    | -              |
| Mg$^{2+}$ (mg/l) | 55.10   | 49.30     | 51.00     | -              |
| K$^+$ (mg/l) | 36.00   | 38.00     | 37.00     | -              |
| Na$^+$ (mg/l) | 414.00  | 431.00    | 430.00    | 69.00          |
| HCO$_3^-$ (mg/l) | 635.00 | 659.00    | 665.00    | 518.00         |
| PO$_4^{3-}$ (mg/l) | 5.70   | 6.10      | 4.60      |                |
| SO$_4^{2-}$ (mg/l) | 216.00  | 235.00    | 220.00    | 250.00         |
| NO$_3^-$ (mg/l) | 428.00  | 402.00    | 405.00    | 30.00          |
| Cl$^-$ (mg/l) | 458.00  | 484.00    | 493.00    | 105.00         |

3.2. Chemical analysis of scale
The results of the chemical analysis of the scale taken at the entrance of the golf course inside the tarpaulin and at the level of the sprinklers are collected in Table 2.

The chemical analysis of the studied scale reveals that the rates of dry matter and organic matter vary slightly from one point to another. They range from 76% to 78% and from 3.15% to 3.75% respectively. At the three sampling points, the pH is alkaline, and the electrical conductivity has higher values.

The chemical compositions of scales collected at the entrance to the golf course, inside the tarpaulin and at the watering sprinklers are relatively similar. The major oxides in these scales are CaO (35%) and P$_2$O$_5$ (18%). These samples are completely and rapidly dissolved in the acid medium. Other elements and other oxides are present but with very low contents compared to the content of CaO and P$_2$O$_5$. Their iron contents are respectively 0.26%, 0.24% and 0.038%.

### Table 2. Chemical properties of scale taken at different points of the "Ocean" Golf Course

|       | Golf entrance | Inside the tarpaulin | Sprinklers |
|-------|--------------|----------------------|-----------|
| Dry matter (%) | 78.00  | 78.32    | 76.00     |
| Humidity (%) | 22.00  | 21.68    | 24.00     |
| Organic matter (%) | 3.75  | 3.20     | 3.15      |
| EC (µS/cm) | 7.95   | 7.52     | 8.20      |
| pH | 9.32     | 9.29     | 9.40      |
| N (%) | 0.47    | 0.56     | 0.50      |
3.3. X-ray fluorescence analysis

The product collected at the sprinkler is moist and reddish. It was dried in an oven at 105°C for 24 hours and then ground to obtain a fine and homogeneous powder. This drying gave a mass loss of 24%. The product color changed and became light brown.

| Element | MgO (%) | CaO (%) | Na2O (%) | Fe (%) | Cu (mg/Kg) | Mn (mg/Kg) | Zn (mg/Kg) |
|---------|---------|---------|----------|--------|------------|------------|------------|
| P2O5 (%) | 17.92   | 19.27   | 16.95    |        | 206.00     | 470.00     | 280.00     |
| Cl (%)  | 0.34    | 0.31    | 0.37     |        | 44.00      | 395.00     | 88.00      |
| K2O (%) | 0.02    | 0.02    | 0.02     |        | 31.00      | 278.16     |            |
| MgO (%) | 1.10    | 1.03    | 0.93     |        |            |            |            |
| CaO (%) | 31.83   | 34.07   | 38.92    |        |            |            |            |
| Na2O (%)| 0.27    | 0.23    | 0.32     |        |            |            |            |
| Fe (%)  | 0.26    | 0.24    | 0.04     |        |            |            |            |

The qualitative analysis by X-ray fluorescence spectrometry made it possible to identify the chemical elements in the scale sample. Calcium and phosphorus are the significant elements in the scale. They have two intense peaks (Figure 4).

![Figure 4. X-ray fluorescence spectrum of deposited scale](image)

They are followed by the magnesium and silicon elements. Other elements such as oxygen, carbon, sulfur, iron and sodium are also present with peaks of very low intensities. The quantitative analysis (XRF) of scale are shown in Table 3.
Table 3. Elemental composition of deposited scale

|       | Ca     | P      | Mg   | Si   | Na   | Fe   |
|-------|--------|--------|------|------|------|------|
| % Mass| 71.92  | 25.85  | 0.89 | 0.73 | 0.24 | 0.38 |
| % Atomic| 66.25 | 30.82  | 1.35 | 0.96 | 0.38 | 0.25 |

The scale contains 72% of calcium, 26% of phosphorus incomplete weight. The other elements Mg, Si, Na and Fe are present with mass percentages lower than 1. In the calcined product, calcium oxide (CaO) is the major compound with a level of 38.92% followed by phosphorus pentoxide (P₂O₅) with a percentage of 16.95% in weight. Other trace oxides have been detected such as magnesium oxide MgO (0.93%), sulfuric oxide SO₃ (0.39%), sodium oxide Na₂O (0.32%) and iron oxide Fe₂O₃ (0.038%).

3.4. X-ray diffraction analysis

To identify and analyze the scale structure formed at the sprinklers, X-ray diffraction analysis allowed obtaining the results shown in Figures 5 and 6.

Figure 5. X-ray diffractogram of the scale taken from the sprinklers

Figure 6. X-ray diffractograms of the compounds present in the scale

The broad peaks observed in Figure 5 indicate low crystallinity of the scale samples. It is seen that the samples' scale contain different minerals. The highest intensity peak refers to calcium carbonate, calcium silicate and hydroxylapatite. Many other chemical compounds are presents at a low percentage. Figure 6 shows X-ray diffractograms of some of those compounds.
3.5. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

The thermal behavior of the scale collected on watering sprinklers of turf is followed by DTA and TGA techniques. The result of which is shown in Figure 7.

The DTA curve shows two endothermic and two exothermic peaks. The TGA curve shows four mass losses. The most significant mass loss is recorded before 450°C. Between 0°C and 200°C, the mass loss is of the order of 12% and it is due to the evaporation of water adsorbed on the crystals of scale. This is illustrated on the DTA curve by an endothermic peak centred at 95°C. Between 200°C and 440°C, the TGA curve recorded a mass loss of about 8%, which can be attributed to the departure of strongly bound intercrystalline water. In the temperature that ranges from 440 to 740°C, the DTA curve presents a marked endothermic peak at a temperature of about 725°C which illustrates the process of carbonate decomposition and departure of CO₂. At this decomposition corresponds to a mass loss of about 6%. A fourth mass loss was measured between 740 and 1000°C. It is weak in the order of 3% and may be due to decomposition of another carbonate or a morphological transformation of the compounds present in the scale. This transformation is illustrated by an exothermic peak around 950°C.

3.6. Scanning Electron Microscope analysis

The scanning electron microscope (SEM) analysis of the scale sample deposited in the sprinklers is given in Figure 8.

It shows that the scale collected consists of crystals of various forms. Corresponding to the different compounds present in the scale and confirming the results obtained by the previous analysis techniques. It includes rhombohedral crystals of calcium carbonate of calcite-type, irregular forms of calcium silicate polymorphs and hydroxyapatite.

4. Conclusion

The results of the physicochemical analysis of the treated wastewater of the Mzar treatment plant, intended for the irrigation of the turf of the “Ocean” Golf show that all factors are favorable for the formation of scale in the passageways of these waters.
The formation of scale has caused difficulties in the irrigation system. The scale analysis collected at the level of the sprinklers by X-ray fluorescence shows that it is rich in calcium Ca (72%) and phosphorus P (26%). Other elements such as O, Mg, Fe, S and Si are present with percentages less than 1. In the calcined product. Calcium oxide (CaO) is the primary compound with a level of 38.92% followed by phosphorus pentoxide (P$_2$O$_5$) with a percentage of 16.95% in weight. Other trace oxides have been detected.

X-ray diffraction scale analysis shows the presence of calcium carbonate, silica calcium, silicate hydroxyapatite, calcium and phosphate carbonate, calcium silicate and magnesium. The various analysis techniques used in this study allowed to characterize the scale deposited by the treated wastewater and show that it is a mixture of chemical compounds. Indeed, the scale deposits are the result of various actions of chemical, Physical or mechanical origin. This explains how hard it is to find adequate protection for this type of encrustations deposited by liquid effluents charged with various substances. However, this physicochemical characterization will undoubtedly make it possible to decide on the appropriate and effective treatment to put an end to scaling of the irrigation circuits by using purified water.

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