

# Sulfhydryl groups as potential biomarkers of water pollution

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## Research Article

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# Abstract

Thiols represent a source of environmental pollution especially wastewater. The present work aims to evaluate the degradation of sulfur in two biological treatment plants in Tunisia: conventional plant of Rades Malienne, and vertical and horizontal flow from the Grombalia plant. We analyzed (1) wastewater properties, (2) the hydrosulfur (thiol) group, (3) membrane processes ultrafiltration technique and (4) characterization of the quality of wastewater from different plants. We used ultrafiltration membrane assisted ZnO and TiO<sub>2</sub> NPs application on real effluents from different biological treatment plants. STEP1 is found to be more loaded with sulphur. Application of AC-ZnO membrane gives 99.07% and 99.55% of sulfur removal from wastewater of STEP1 and STEP3. STEP3 is 50 times less charged on sulfur than STEP1. We suggested that when the sulphur content is high, this leads to an increase in mineral elements. This could be explained by the interactions between thiols and the major elements that cause mineral pollution.

## 1. Introduction

Water used for domestic, industrial or even agricultural purposes constituted a polluted effluent, and which is discharged into a sewer outfall (Missaoui et al. 2020). Wastewater includes domestic wastewater, runoff and industrial effluents (Chemingui et al. 2021). Domestic wastewater comes from the various domestic uses of water. They are divided into domestic water from bathrooms and kitchens and are generally loaded with detergents, grease solvents, organic debris, and black water. It is toilet waste, loaded with various nitrogenous organic materials (Chemingui et al. 2019).

Industrial water is very different from domestic wastewater. Its characteristics vary from one industry to another. In addition to organic, nitrogenous or phosphorus-containing materials, they can also contain toxic products, solvents, heavy metals, organic micropollutants and hydrocarbons (Missaoui et al. 2019). Some of them become the subject of pre-treatment before being discharged into collection networks. They are only mixed with domestic waste when they no longer present a danger for the collection networks and do not disrupt the operation of depollution stations (Guey et al. 2020). Storm water is the cause of significant pollution of waterways, especially during stormy periods. Rainwater is loaded with impurities when it comes into contact with the air (industrial fumes), and then, as it runs off, with residues deposited on city roofs and pavements (used oil, fuel, tire residues and heavy metals, etc.). In addition, when the sanitation system is said to be "unitary", rainwater is mixed with domestic wastewater. In the event of heavy rainfall, the constraints of preserving treatment facilities may require that this highly polluted mixture be discharged (relieved) into the natural environment. Finally, in urban areas, built surfaces make the soil impermeable and add the risk of flooding to that of pollution (Ben Moussa et al. 2020).

In general, there are four forms of water pollution (1) Chemical pollution, (2) Bacteriological pollution (3) Thermal pollution and (4) Radioactive pollution. Chemical pollution of mineral origin (Smiri et al. 2015) can be classified as due to (i) essential elements: N, P, Na, (ii) desirable elements: Fe, Mn, Zn, Cu and (iii)

toxic elements: Pb, Se, Hg, As, Cr, Sn, and Cd. Among the chemical pollutants of organic origin are detergents, pesticides, phenols, hydrocarbons and organic matter such as proteins and lipids. Water pollution can be identified and characterized using some parameters. Temperature is the most important parameter; it has direct influence on the behavior of the different substances present in water (Boelee et al. 2019). The coloration of water can be either of natural origin or associated with its pollution. The coloration of water is thus very often synonymous with the presence of dissolved compounds and correlatively the presence of solutes leads to a coloration that is not limited to the visible range (Abdulla and Farahat 2020). Unpleasant, foul-smelling ( $H_2S$ ), these two characteristics can be changed by the addition of industrial waste (Ladjel 2005). Suspended Solids (TSS) are the most important part of water pollution. High levels of them can prevent the penetration of light which decreases dissolved oxygen (Regsek 2002). Chemical parameters are biochemical oxygen demand ( $BOD_5$ ), chemical oxygen demand (COD) which are Phosphorus, Nitrogen and Sulfur components. These elements have an urban and industrial origin. Free colloidal sulfur and reducing sulfur compounds are generally found in natural mineral waters, but they can be concentrated in the water as a result of pollution or bacteria or germs that can lead to the reduction of sulfates (Leonov and Chicherina 2008).

The presence of sulfur in wastewater causes serious odor and corrosion problems in sewage systems. These troublesome sulfur compounds are also formed in nature in various reactions, mostly when substances that are not naturally present have been added. These compounds are undesirable because they often have a bad smell and are often toxic. Overall, sulfuric substances can cause neurological effects and behavioral changes, disruption of blood circulation, heart problems, eye problems, vision problems, reproductive problems, damage to the immune system, liver and kidney dysfunction, disruption of hormone metabolism, dermatological problems and skin problems. On the environment (García et al. 2020), sulphuric substances can also have a negative impact on the natural environment through changes in air and freshwater quality, soil modifications and wildlife disturbance and impacts related to the presence of dissolved sulfides on wastewater (Bhomick et al. 2017). During pre- and primary treatments, the presence of dissolved sulphides in wastewater causes serious odour and corrosion problems in the sewage system. Dissolved sulphide occurs as a mixture of hydrosulphide ion and hydrogen sulphide gas ( $H_2S$ ). In the presence of oxygen, the hydrogen sulphide is converted into sulphuric acid by sulphate oxidizing bacteria, which promotes corrosion. Hydrogen sulphide causes corrosion of copper, copper-based alloys such as brass; some bronzes; iron and silver and leads to formation of black metallic sulphides. It can indeed be catastrophic on the electrical equipment. During secondary treatment, the high concentration of sulphides in the activated sludge aeration tank also promotes the excessive growth of sulphide-containing filamentous bacteria, such as *Beggiatoa thiotrix*, which use sulphide as an energy source and oxidize into sulphur. The presence of these filamentous microorganisms reduces the compacting and settling capacity of the activated sludge, which is manifested by the phenomenon of sludge swelling. In general, the dissolved sulphides come from the anaerobic decomposition of organic matter containing sulphur and also from the reduction of inorganic sulphates. In an anaerobic environment the sulphate-reducing bacteria use the sulphate ion as a source

of oxygen for respiration, thus converting sulphates into dissolved sulphides. This occurs in the sediments of gravity sewers and primary treatment plants.

Wastewater treatment is a set of events that consist of purifying water either to recycle wastewater in the natural environment, or to transform natural water into drinking water (Boubakri et al. 2019) using many techniques such as membrane separations, biological treatment ... the role of wastewater treatment plants can be summarized in (1) water treatment, (2) possible valorization of treated water and sludge, and (3) protection of public health (Liwarska-Bizukojc et al. 2011). Wastewater treatment processes depend on the nature and importance of the pollution. Different processes can be implemented for the treatment of wastewater according to its characteristics and the desired degree of purification (Wang and Yang 2016). It is carried out at wastewater treatment plants (STEPs) where wastewater undergoes pre-treatment and different types of treatment: physical, biological and physico-chemical. Pre-treatments used for the removal of objects between 0.1 and 50 mm in size are (screening, sieving), grease and sand. A primary treatment is used for the removal of easily settleable suspended solids. A secondary treatment composed of a biological reactor for the elimination of organic ( $BOD_5$ ) or mineral biodegradable pollution ( $NH_3$ ,  $NO_3$  and P). Some plants are also equipped with tertiary treatment for the removal of microorganisms or residual phosphorus.

The elimination of organic matter implies the use of biological treatments involving living organisms, essentially bacteria (Rejsek 2002). These treatments are based on the capacity of microorganisms to oxidize mineral matter ( $NH_3$  ...) and the constituents of COD and BOD (aerobiosis) and to reduce oxygen-containing molecules such as  $NO_3$  (anoxia),  $SO_4$  and  $CO_2$  (anaerobic) on the other hand. They will thus make it possible to eliminate the biodegradable soluble pollution and part of the TSS. Biological wastewater treatment methods are divided into two categories (1) Intensive techniques (bacterial beds, biological discs, biofiltration or accelerated biological filtration, etc.) and (2) Extensive techniques such as extensive free culture techniques (natural lagooning, macrophyte lagooning and aerated lagooning) and extensive fixed culture techniques (horizontal flow reed planted filters, vertical flow planted filters and percolation infiltration).

A sub-surface horizontal flow planted filter is a large channel filled with gravel and sand on which aquatic vegetation is planted. As wastewater flows horizontally through the channel, the filter material filters out particles and microorganisms break down organic matter. The water level in a subsurface flow planted filter is kept 5 to 15 cm below the surface to ensure subsurface flow. The bed should be wide and shallow so that the water flow path is maximized. An intake area should be used to evenly distribute the flow. Primary treatment is essential to prevent clogging and ensure effective treatment. The bed should be lined with an impermeable liner (clay or geotextile) to prevent infiltration into the subsoil. Small, round, evenly sized gravel between 3 and 32 mm in diameter is generally used to fill the bed to a depth of 0.5 to 1 m. To limit clogging, the gravel should be clean and free of fine particles, the water to be treated should undergo primary treatment before entering the filter and the filter material should be replaced every 8 to 15 years. The efficiency of the filter removal is a function of surface area and cross-sectional area (Tilley et al. 2008). In horizontal-flow filters, the filter bed is distributed over the entire width and height of the bed

by a distribution system at one end of the basin, and then flows in a mainly horizontal direction through the substrate. In most cases, the feed is continuous because the organic load is low. The most commonly used variety is the reed *Phragmites Australis* because of its fast growth rate of root development and its resistance to soil saturation conditions, planting can be done with seeds, young shoots or rhizomes with a density of about 4 per m<sup>2</sup> (Matamoros et al. 2016). Figure 1 (STEP 2) shows a schematic diagram of a horizontal flow planted filter used for wastewater treatment. The principle of the vertical filters consists of admitting the wastewater, without preliminary treatment, on a gravel massif planted with reeds (*Phragmites Australis*). The purifying bacteria are fixed on the grains of sand, on the rhizomes of the reeds and the surface layer of mud. They develop and degrade the pollution. The filter planted with reeds is generally composed of two stages: the first retains the solid particles and starts the treatment, the second refines the purification. The device is fed in a sequential way due to the presence of a flush tank placed at the head to ensure a homogeneous supply over the entire surface of the filter. This system has a good yield on organic matter and partially treats nitrogen. The process is recommended for a population of 50 to 1000 population equivalents, globally 10 m<sup>2</sup>/eqh. Operation and maintenance are simple and can be entrusted to the municipal employee (Sylla 2020). Figure 1 (STEP3) shows a schematic diagram of a vertical flow planted filter used for wastewater treatment. Membrane separation process consists of a semi-permeable membrane for the separation of species from a feed mixture (Kahloul et al. 2019a). The different membrane processes are distinguished by the chemical nature and structure of the membrane, the implementation and mode of operation, the type of force, and the size of the solutes to be treated. Frontal filtration consists of bringing the solution to be filtered perpendicularly to the membrane. The retained molecules concentrate on the membrane surface, which causes a decrease in flow (Kahloul et al. 2019b). When cross-flow filtration is performed (Tangential filtration), the feed water is recycled. When recirculating the water, the flow is parallel to the membrane. Only a small part of the feed water is used for the production of permeate, most of the water leaves the module. Therefore cross-flow filtration has a high energy cost because all the water fed to the system has to be supplied under pressure. The speed of the water supplied to the system parallel to the membrane is relatively high. The purpose of this flow is to control the thickness of the cake. The flow forces are high, allowing suspended solids to be carried away in the water. Tangential operation can provide stable flow rates, but still requires cleaning of the installations from time to time. This mode of filtration is expensive, hence the interest of immersed membranes which combine both tangential and frontal modes (Fradj et al. 2019).

## 2. Materials And Methods

**2.1. Case study on actual effluents from different plants** There are 03 sampling points (1) The 1<sup>st</sup> sampling point is located at the exit of the water from the Rades Malienne treated by secondary treatment and noted STEP1. (2) The 2<sup>nd</sup> sampling point is located at the exit of the waters of the Grombalia treated by horizontal-flow filters and noted STEP2 and (3) The 3<sup>rd</sup> sampling point is located at the exit of the water of Grombalia treated by vertical-flow filters and noted STEP3 (Figure 2).

**2.2. Conservation, transport and storage of samples** In order to avoid any contamination of samples, all equipment used for analysis is first decontaminated of all organic matter by following a procedure by a chemical treatment (bath of 10% hydrochloric acid) for at least 4 hours followed by an abundant rinsing with pure water. Samples should be placed in plastic bottles that have been thoroughly washed and rinsed with water to be examined. The samples collected are stored in vials and kept at a temperature of 4°C.

**2.3. Wastewater properties analyses** pH is measured according to the Nernst equation (Rejsek 2002). The conductivity of water is proportional to the dissolved salt content, measured as previously described (Lagnika et al. 2014). Suspended matter (TSS) (Vidmar et al. 2016), Turbidity (Rejesk 2002). Chemical Oxygen Demand (COD) is the amount of oxygen consumed by materials existing in the water and oxidizable under the defined operating conditions. The amount of oxygen (mg/L), used by the oxidation reactions, is estimated from the measurement of the reagent residue after 2 hours, as described previously (Zhu et al. 2020). Ion chromatography used to quantify the concentration of the anions  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $(PO_4)^{3-}$  and  $SO_4^{2-}$  and of the cations  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  (Joachim 2004; Minet et al. 2010; Almuktar et al. 2018). Total organic carbon (TOC) is the amount of carbon bound in an organic component. It is often used as a non-specific indicator of water quality, determined using InnovOx ES rapid TOC determination method (Fritz and Gjerde 2000). Metals were determined using Atomic flame absorption method (Slaveykova and Hoenig 1997). The nature of chemical elements present in samples as well as their mass concentration were analyzed using fluorescence spectrometry (Pearson et al. 2017). We determined thiols using spectrophotometer UV/Visible at 412 nm as previously described (Diez et al. 2001; Steehler 2008).

## 3. Results And Discussion

### 3.1. Ultrafiltration membrane assisted ZnO and TiO<sub>2</sub> NPs application on real effluents from different biological treatment plants

**3.1.1. Wastewater properties from different biological treatment plants** To evaluate the wastewater, three outlet samples from each of the wastewater treatment plants (STEP) were vacuum- filtered through a 0.45 µm filter, and the dissolved phase is analyzed during screening. Indeed, the first STEP1 of Rades Malienne is surrounded by various industrial, hospitals and domestic activities. The STEP2 and STEP3 of Grombalia are surrounded by agricultural activities which discharge their effluents into the wastewater collection networks. The concentrations for all these molecules and the physicochemical parameters such as TSS concentrations, concentrations of major elements ( $Ca^{2+}$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ...) and heavy metal concentrations from different stations are presented in Tables 2, 3 and 4. The tables give the values before and after UF treatment.

3.1.1.1. Monitoring of pH and conductivity parameters: pH indicates a slight alkalinity of WW due to presence of organic matter. According to Figure 3, a slight variation in conductivity can be seen in the majority of samples after removal through the membranes. The values vary in a range from a minimum

of 4.22 ms/cm to a maximum of 5.57 ms/cm at the outlet of the STEP. After treatment with UF, it is 1.96 ms/cm to 2.34 ms/cm. This variation is due to the change in the concentration of dissolved salts in the water of different STEPs. After membrane treatment, the conductivity almost stabilizes.

3.1.1.2. Turbidity and suspended solids (TSS): Turbidity is a very important physical parameter for wastewater quality control. According to the Figure 4, very high values can be found at the vertical and horizontal flow treatment plant of 94.78 NTU and 71.98 NTU, then it decreased after UF treatment (Figure 5). This decrease is due to the degradation of organic matter in the treated water, with an average of 45.72 NTU. These recorded turbidity levels largely exceed the acceptable limit value for water intended to be discharged into the receiving environment ( $> 5$  NTU), these exceedances show that the wastewater is loaded with TSS and colloids. It is noticeable that the decrease in turbidity and TSS after ultrafiltration treatment at different types of membranes that the ZnO-modified AC membrane gives a good result in removing colloidal materials. Turbidity results are confirmed by the TSS results, which is more important in the vertical basin than the others (Table 1).

3.1.1.3. Total organic carbon: TOC level varies from 34.3 mg/L in WW of STEP1, 142 mg/L in WW of STEP2 and 168 mg/L in WW of STEP3. TOC level of water treated with AC-ZnO membrane is about 10.6 mg/L and 31.3 mg/L for AC-TiO<sub>2</sub> membrane treatment. We note that the ZnO-modified membrane removes organic carbon better than the other membrane (Figure 6).

3.1.1.4 Heavy Metals: Results presented in Tables 1, 2 and 3 show that heavy metals levels found in urban and rural wastewater have a strong variation between stations. Lead and manganese levels are important in the STEP1 while zinc is higher in the STEP3. After membrane treatment, there is a decrease in heavy metals contents, but AC and AC-ZnO membranes give better results.

3.1.1.5. Determination of the major ionic elements: Sulphates are bound to the major cations: calcium, magnesium and sodium. Except those of lead, barium and strontium, we note a high content of chlorides and sulfate in the three stations (STEP1  $>$  STEP2 and STEP3), with a high content of calcium Figure 7. Chlorides exist in almost all waters with variable concentrations. Most of the organic phosphorus come from the waste products of protein metabolism and its elimination in the form of phosphates in the urine by humans. Phosphorus is not inherently toxic to terrestrial and aquatic fauna and flora. Sulphated, phosphated waters have a high salinity with a variable metallic composition. As a result, the station of Rades is loaded with the toxic mineral elements than that of the station of Grombalia. STEP1 has a higher sulphur concentration than the other stations (Table 5). Sulfur, nitrate, nitrite, chlorine and other heavy metals levels such as lead and manganese are higher in the Rades station (STEP1) than the Grombalia stations (STEP2 and STEP3) when the sulfate ( $\text{SO}_4^{2-}$ ) is important, and involved in accumulation of certain heavy metals. Zinc is found to be high in the Grombalia stations (STEP2 and STEP3) where the sulphate level is low, in the opposite of the STEP1. When sulphate is found in large quantities, it is combined with heavy metals forms complexes and caused mineral pollution. On the other hand, organic carbon and suspended matter is not important when there is a significant amount of sulfur,

which indicates that there is no organic pollution. If there is a high level of sulfur, it is a sign of finding mineral pollution.

**3.1.2. Membrane application for water treatment under optimal conditions** We have reminded in the synthetic part that the ability to remove thiol (-SH) gives best results at optimal P pressure and pH. So, during membrane treatment we work under these optimal conditions (P = 2 bars, pH= 10).

3.1.2.1. Determination of concentration  $C_0$  of thiol (-SH): We have three samples with different concentrations of thiol (-SH). To know their concentrations, we used the calibration curve of DTT concentration as function of absorbance (OD) at 412 nm. The results are shown in Table 6.

3.1.2.2. Study of membrane retention of thiol (-SH): According to Figure 8, it can be seen for the 3 effluents that the treatment by membrane modified with nanoparticles gives a higher retention rate by the AC-ZnO membrane in a short time and also by the AC-TiO<sub>2</sub> membrane but in a long time. It finds that STEP 3 has the highest retention rate of 99.55% by AC-ZnO compared to STEP1 and STEP2. According to results of Table 5 and Figure 7, we find that the Rades plant has a higher sulfur content of 343.14 mg/L compared to the other plants and poses water pollution. After applying membrane ultrafiltration process, we find that there is a 99.07% removal of sulfur by AC- ZnO (Table 7). Wang et al. (2009) found that the maximum flow of a hybrid membrane of CA mixed with ZnO NPs was improved by 111.1%. Thus, according to the results the nanoparticles strongly affect the properties of the cellulose acetate (CA) membrane. The contact angle decreased by the addition of additives which considerably improves the hydrophilicity of the CA membrane. On the other hand, membrane water flow increased after use of nanomembrane compared with the AC membrane and more precisely by the nano-ZnO gives better results. Wu et al (2010) claimed that the hydrophilicity, water flow, thermal stability and mechanical strength of hybrid membranes were improved by the addition of TiO<sub>2</sub> and ZnO.

## 4. Conclusion

The presence of sulfur in wastewater creates serious problems for human health and the environment. We analyzed wastewater from ONAS plant of Rades (STEP1) and Grombalia (STEP2 and STEP3). STEP1 is found to be more loaded with sulphur. Using AC-ZnO membrane, almost 99.07% of sulfur element is removed. STEP3 is 50 times less charged than STEP1. The retention reaches 99.55%. The decrease of retention in STEP1 can be explained by the interaction of the sulphur elements with other metals which become more charged after the formation of metal complexes. It is concluded from this study that when the sulphur content is high, this leads to an increase in mineral elements. This could be explained by the interactions between thiols and the major elements that cause mineral pollution.

## Declarations

### Compliance with Ethical Standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethics approval and consent to participate** This article does not contain any studies with human participants or animals performed by the author involved.

**Consent to Publish** Not applicable

**-Authors Contributions** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Moez Smiri, Zahrah Alhalili, Chourouk Romdhani and Soumaya Elarbaoui. The first draft of the manuscript was written by Moez SMIRI and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**-Availability of data and materials** They are all publically available.

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## Tables

**Table 1.** Turbidity classes as a function of visual water quality of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

Turbidity NTU Water Quality	
NTU < 5	Colorless water
5 < NTU < 30	Slightly colourless water
NTU > 50	Cloudy water

**Table 2.** Physico-chemical characteristics of STEP1 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO<sub>2</sub> membranes.

	Water STEP1			
	Before treatment	After membrane treatment		
		AC	AC-ZnO	AC-TiO <sub>2</sub>
pH	6.85	7.57	7.56	7.95
EC (ms/cm)	4.22	1.92	2.26	1.96
TOC (mg/L)	34.4	9.36	14	4.20
TSS (mg/L)	108.46	70.62	53.21	81.34
Turbidity (NTU)	4.55	3.63	2.83	4.07
Ca (mg/L)	280.56	106.33±15.17	168.29±9.82	138.17±7.73
Pb (mg/L)	0.540	0.159	0.278	0.333
Zn (mg/L)	0.319	0.209	0.233	0.265
Mn (mg/L)	0.315	0.274	0.281	0.301
Cd (mg/L)	Undetectable	Undetectable	Undetectable	Undetectable

**Table 3.** The physico-chemical characteristics of STEP2 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO<sub>2</sub> membranes.

	<b>Water STEP2</b>			
	<b>Before treatment</b>	<b>After membrane treatment</b>		
		<b>AC</b>	<b>AC-ZnO</b>	<b>AC-TiO2</b>
<b>pH</b>	7.54	7.64	7.53	7.75
<b>EC (ms/cm)</b>	4.54	2.21	2.31	2.23
<b>TOC (mg/L)</b>	143	13.2	31.3	2.06
<b>TSS (mg/L)</b>	290	190.52	164.09	201.33
<b>Turbidity (NTU)</b>	71.98	57.04	40.03	60.71
<b>Ca (mg/L)</b>	200.4	4.06 ± 1.36	64.25±7.71	36.36±10.18
<b>Pb (mg/L)</b>	0.503	0.209	0.316	0.443
<b>Zn (mg/L)</b>	0.743	0.223	0.638	0.261
<b>Mn (mg/L)</b>	0.290	0.205	0.238	0.268
<b>Cd (mg/L)</b>	Undetectable	Undetectable	Undetectable	Undetectable

**Table 4.** Physico-chemical characteristics of STEP3 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO<sub>2</sub> membranes

	<b>Water STEP3</b>			
	<b>Before treatment</b>	<b>After membrane treatment</b>		
		<b>AC</b>	<b>AC-ZnO</b>	<b>AC-TiO2</b>
<b>pH</b>	7.3	7.94	7.63	7.71
<b>EC (ms/cm)</b>	5.57	2.25	2.34	2.33
<b>TOC (mg/L)</b>	168	10.4	23.9	7.81
<b>TSS (mg/L)</b>	410.67	201.33	294.13	389.01
<b>Turbidity (NTU)</b>	91.78	60.34	55.27	70.32
<b>Ca (mg/L)</b>	80.16	40.25 ± 0.99	24.38±1.49	160.04±16.57
<b>Pb (mg/L)</b>	0.463	0.264	0.338	0.444
<b>Zn (mg/L)</b>	1.775	0.247	0.352	0.362
<b>Mn (mg/L)</b>	0.273	0.215	0.232	0.262
<b>Cd (mg/L)</b>	Undetectable	Undetectable	Undetectable	Undetectable

**Table 5.** Major ionic elements of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

**Table 7:** Major ionic elements found at the three stations

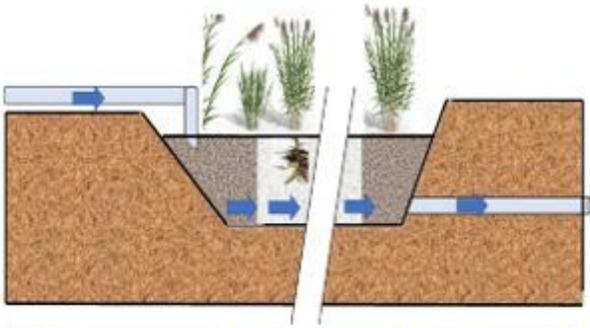
Major elements (mg/l)	Cl <sup>-</sup>	NO <sup>2-</sup>	NO <sup>3-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>
STEP1	476.46	16.44	18.72	41.22	343.14
STEP2	273.06	0.42	6.96	8.4	59.94
STEP3	228.78	-	-	45.54	7.92

**Table 6.** Determination of concentration of thiol (-SH) of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

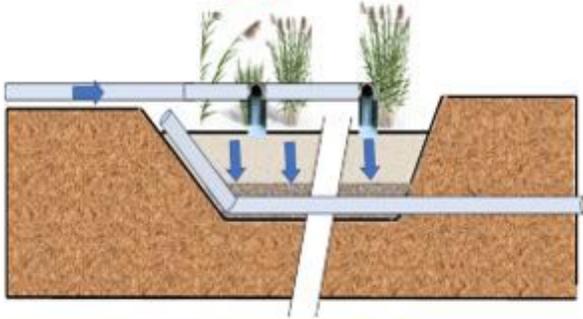
	Absorbance	Concentration C <sub>0</sub> (mM)
STEP1	12*10 <sup>-3</sup>	1.4
STEP2	25*10 <sup>-3</sup>	2.7
STEP3	47*10 <sup>-3</sup>	3.57

Due to technical limitations, Table 7 is only available as a download in the supplementary files section.

## Figures



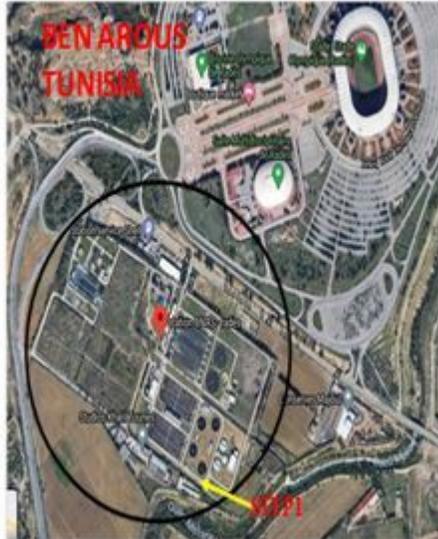
**STEP2**



**STEP3**

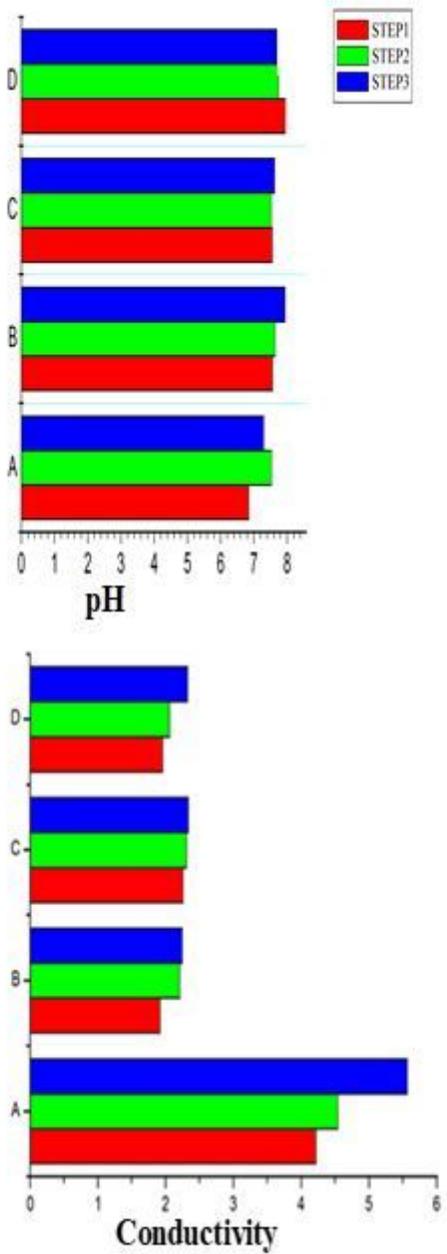
**Figure 1**

Diagrams and photos of horizontal flow (STEP2) and vertical flow (STEP 3) planted filter used for wastewater treatment.



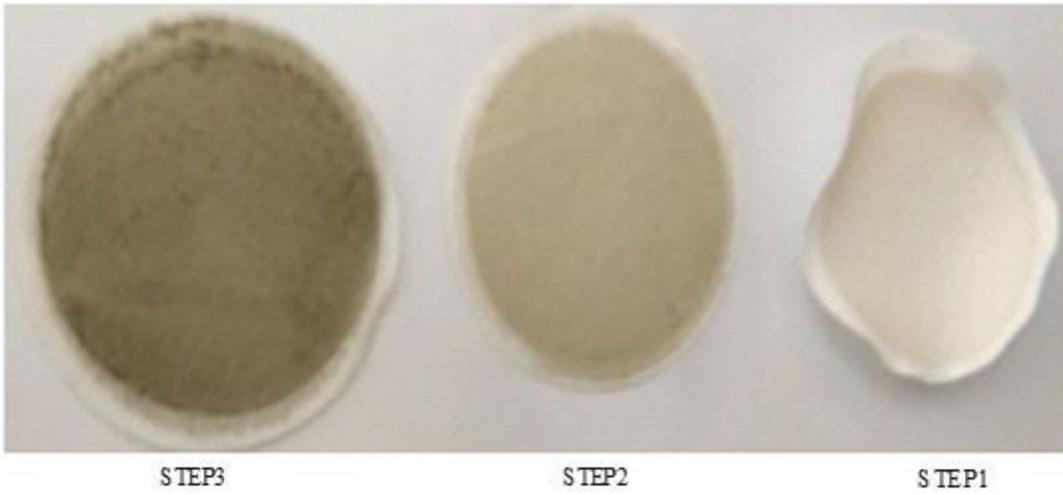
**Figure 2**

Wastewaters treatment plant from Rades Malienne secondary treatment (STEP1), Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).



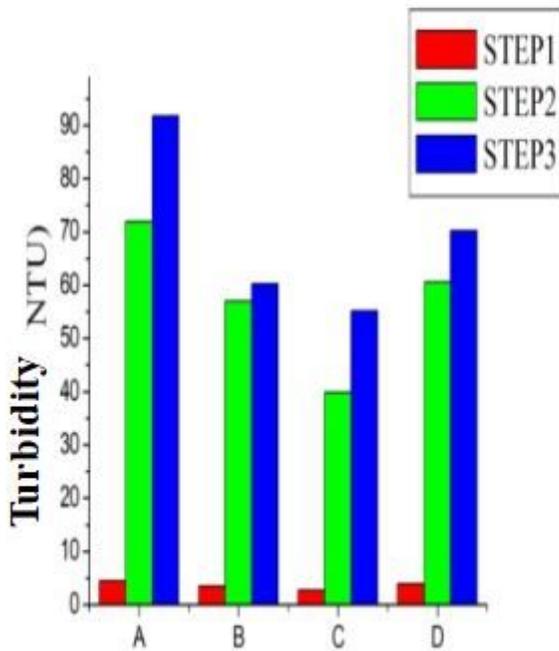
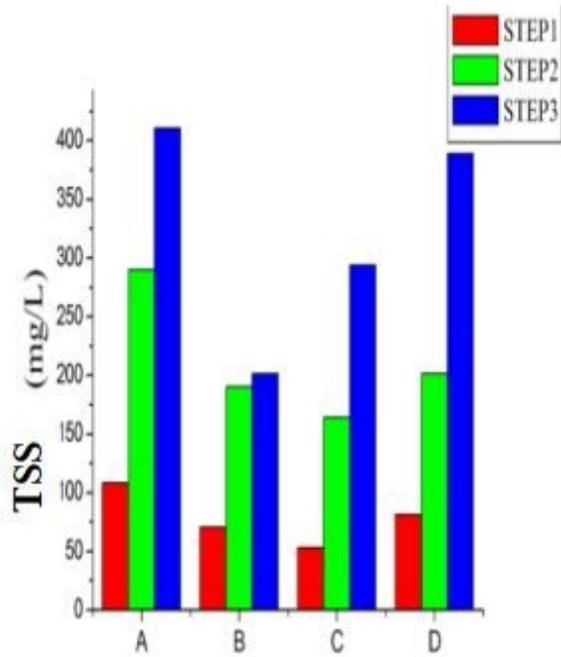
**Figure 3**

Variation of pH and conductivity of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3). (A) WW before treatment, (B) WW treated with AC, (C) WW treated with AC-ZnO, (D) WW treated with AC-TiO<sub>2</sub> membranes.



**Figure 4**

TSS of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).



**Figure 5**

Variation of turbidity and suspended solids (TSS) of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3). (A) WW before treatment, (B) WW treated with AC, (C) WW treated with AC-ZnO, (D) WW treated with AC-TiO<sub>2</sub> membranes.

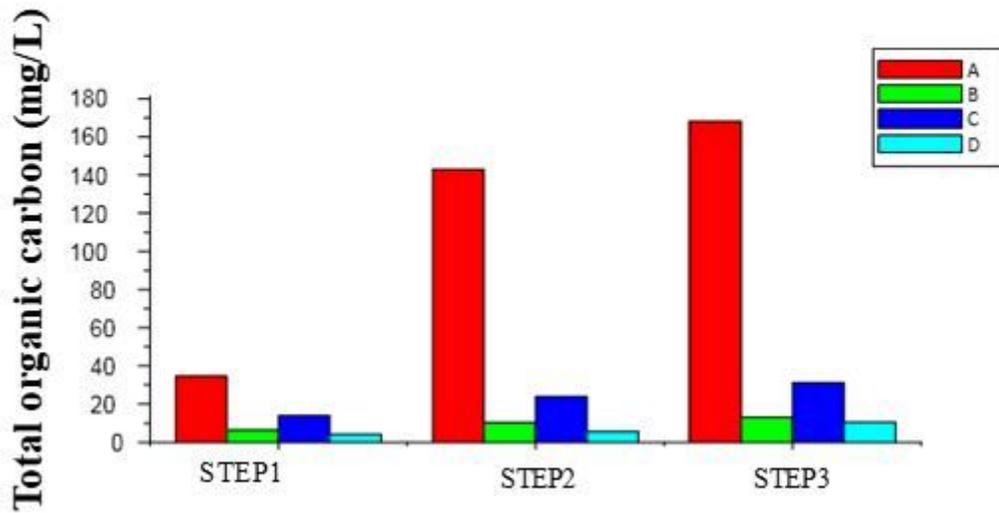


Figure 6

Variation of total organic carbon (TOC) of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3). (A) WW before treatment, (B) WW treated with AC, (C) WW treated with AC-TiO<sub>2</sub> membranes, (D) WW treated with AC-ZnO.

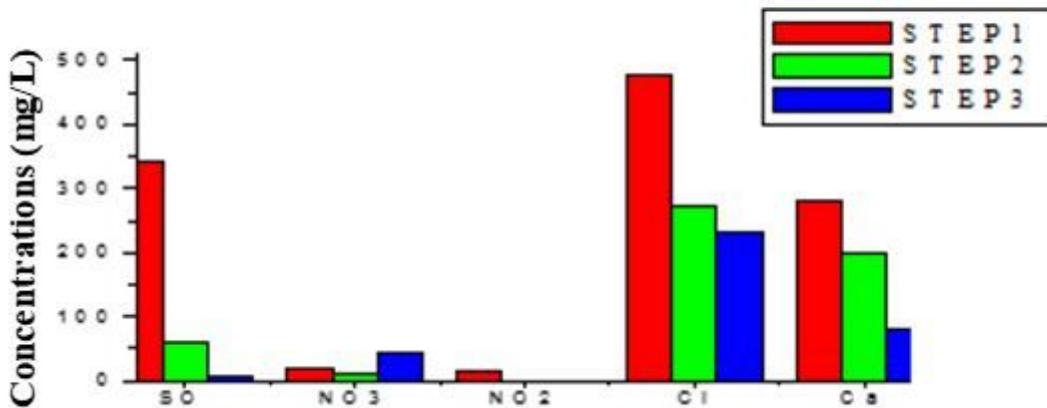
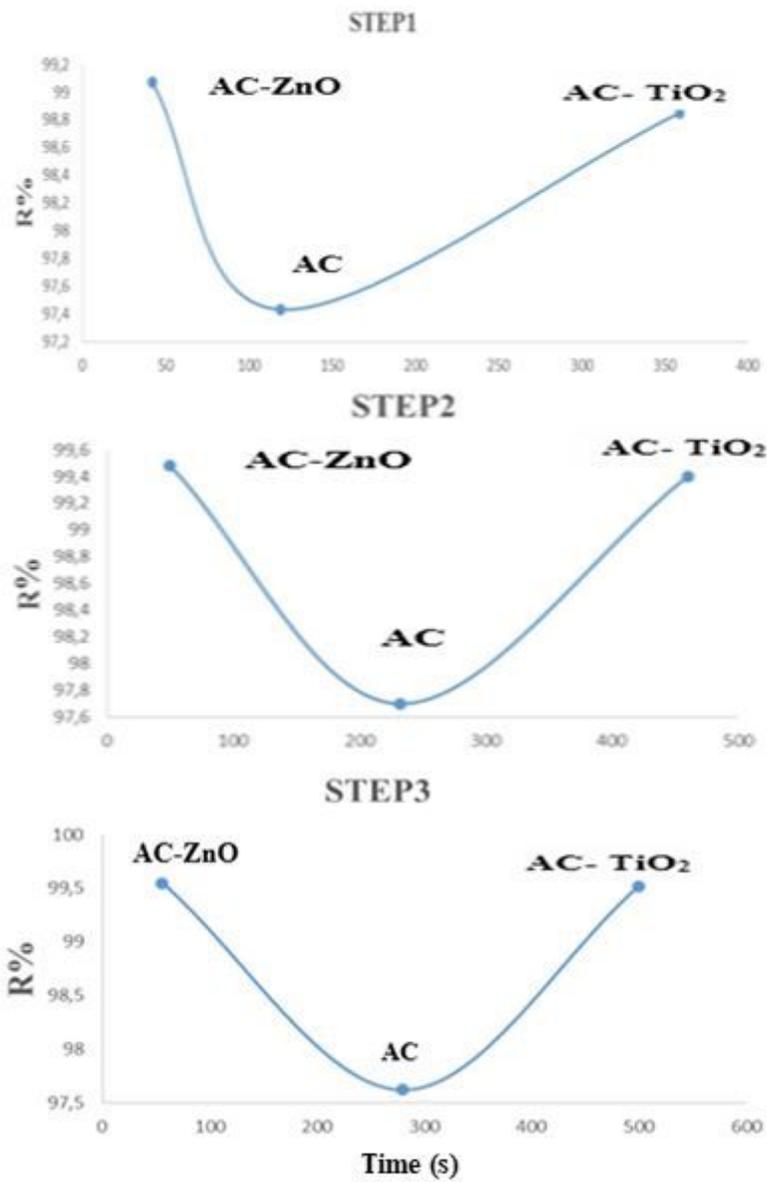


Figure 7

Change in major components of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).



**Figure 8**

Sulphur removal rate with AC, AC-ZnO and AC-TiO<sub>2</sub> membranes from wastewaters (WW) of Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).