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Treatment of municipal wastewater of Fez city (Morocco) using a sequence of aerobic and Fenton processes

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ABSTRACT

The study aims to assess the efficiency of applying the Fenton process to municipal wastewater from Fez city (Morocco), previously pretreated by the aerobic process. Experiments were carried out on a lab scale with batch reactors. The aerobic pretreatment was operated in a suspended growth bioreactor and monitored periodically for several parameters. The process performance was evaluated based on chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and UV-Visible absorption spectra. The aerobic bioreactor showed a high efficiency, with removals up to 67% and 100% for COD and BOD_5, respectively. The Fenton process applied after aeration pretreatment successfully reduced the residual bio-resistant organics, and its efficiency was evaluated in terms of COD. Therefore, the integrated treatment of aeration and Fenton technologies, at optimal operating conditions of the Fenton process (pH = 3, contact time = 60 min, $FeSO_4$ dose = 3.57 mmol/L, and H_2O_2 dose = 14.71 mmol/L) achieved total COD, color and BOD_5 removals of 86%, 90.3%, and 100%, respectively. Accordingly, UV-visible absorption spectra underwent a significant decrease due to the removal of organic substances. Indeed, the final measured COD was 117.3 mg/L, which complies with national and international standards for liquid disposal or reuse. Therefore, the proposed treatment train could be promising for raw wastewater remediation and environmental protection.

Keywords: Municipal wastewater integrated process; Aeration; Fenton; Chemical oxygen demand; Biochemical oxygen demand; UV_{254nm}

1. Introduction

Recently, scientists have focused on wastewater treatment and reuse, which is becoming a real challenge in many developing countries that have passed tougher liquid discharge restrictions. Furthermore, numerous studies have proven that conventional wastewater treatment plants (WWTPs) methods fail to treat industrial wastewater [1,2].

A considerable amount of contaminants such as nutrients, heavy metals, and persistent organic compounds,

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usually from anthropogenic activities, can infiltrate the aquatic ecosystem and cause enormous disturbances. Only a few studies have attempted to identify recalcitrant compounds in surface and groundwater in Morocco [3]. Fez city is known for its various economic activities, especially in agriculture and industry domains. The latter include tanneries, textiles, metal refineries, and oil mills that have been identified as major sources of pollution. Industrialization, rapid population growth, and rural-urban migration exert various environmental pressures and cause water shortages. In addition, liquid waste generated by the various activities is discharged into the nearby Fez River, a tributary of the Sebou watershed, Morocco's natural water resource, which accounts for 30% of surface and groundwater resources [4].

Several studies have highlighted the pollution of the Fez River downstream, where contaminants (organics and heavy metals) have been figured out, threatening the soil and surface water [5]. On the other hand, there have been few attempts to treat Fez's wastewater using conventional methods. In our previous work, the wastewater was treated by adsorption of chemical oxygen demand (COD) and color on synthesized powdered activated carbon. The results showed that the COD and color removal rates under optimal treatment conditions were 72% and 83%, respectively [6]. In another work on similar wastewater, the authors have applied coagulation–flocculation–precipitation to reduce heavy metals, color, and COD [7]. Nevertheless, the one-step treatment methods used in these studies remain insufficient to treat raw wastewater highly loaded with dissolved organic matter and pathogenic bacteria, and thereby do not produce treated water that meets the prescribed limits. Besides, numerous studies on the issue of wastewater treatment have been carried out in the past decades, proposing effective and inexpensive methods. Among these, biological processes are well-known for their efficiency in removing biodegradable organic contaminants and using microorganisms under specific conditions. Their application as a pretreatment in a combined system involving advanced oxidation processes (AOPs) aims mainly at reducing the high content of biodegradable compounds [8,9]. In addition, several studies have favored chemical oxidation technologies as a pretreatment to improve the biodegradability index [10,11]. However, the main disadvantage of the latter design is the high consumption of chemicals in the case of highly biodegradable wastewater, which results in a significant increase in treatment cost, making the combination unsuitable for practical use.

In this context, the present study focuses on the problem of real wastewater treatment by combining biological and chemical actions, considering the process feasibility, simplicity, and cost perspectives. To our knowledge, the wastewater of Fez city has never been treated by this combination. The application to municipal wastewater is interesting from a practical point of view. Initially, we started with a thorough physico-chemical and bacteriological characterization of urban wastewater collected upstream of the Fez WWTP. Subsequently, the raw wastewater was pretreated by two separate processes with anaerobic and aerobic suspension growth systems, so that the high-performing system would be followed up with the Fenton oxidation technology. Overall treatment efficiency was ascertained by COD, color, and variation in UV-visible absorption spectra.

2. Material and methods

2.1. Chemicals and real wastewater sampling

H_2O_2 (30%), $FeSO_4·7H_2O$ (≥99.0%), H_2SO_4 (96%), NaOH, and $Na_2S_2O_3$ were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were analytical grade. Milli-Q water (resistivity ≥ 18 mΩ cm) was used for the preparation of aqueous solutions.

Plate Count Agar (PCA) was used as non-selective culture media. Tergitol 7-Triphenyl Tetrazolium Chloride (Tergitol 7-TTC), Chapman Agar, and Slanetz Agar were used as semi-selective media for bacteriological examination.

The raw wastewater used in this study was sampled only once in a dry period (May 2020), upstream of the municipal WWTP of Fez (Fig. 1). The sample was collected in a polyethylene bottle (25 L), transferred immediately to the laboratory, and stored according to standard methods.

2.2. Analytical techniques

The physico-chemical characterization of raw and pretreated wastewater covered: pH, total alkalinity (TA), total dissolved solids (TDS), total suspended solids (TSS), ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), orthophosphate

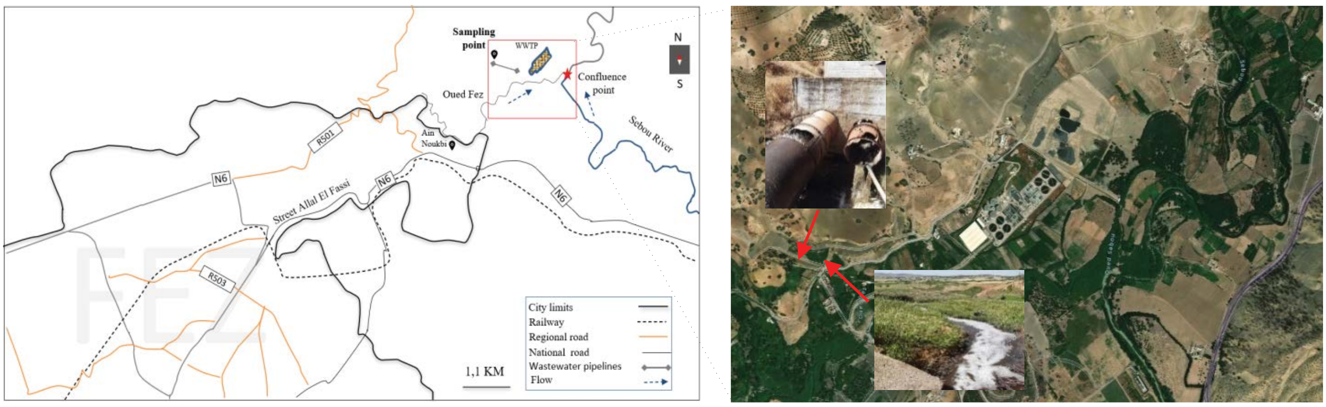

Fig. 1. Location of sampling point, upstream of the WWTP, northeast of Fez city, Morocco.

(PO_4^{3-}), sulfate (SO_4^{2-}) and chloride (Cl^-). Their analysis was carried out according to standard methods for water and wastewater examinations [12]. pH, turbidity, total salinity (TS), electrical conductivity (EC), and color measurements were conducted with a pH-meter (JENCO – Electronics LTD), turbidimeter (HI 88713 – ISO HANNA-Instruments), WTW inoLab, Cond Level 1, and VWR UV-6300PC spectrophotometer, respectively. COD and biochemical oxygen demand (BOD_5) were assessed using the ISCO RECOD and WTW OxyTop IS 6 reactors, respectively. Heavy metal concentration was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Activa, Jobinyvon).

The color index (CI) was calculated according to the method reported by Tizaoui et al. Eqs. (1) and (2) [13].

$$CI = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

$$SAC_{\lambda_i} = \frac{Abs\lambda_i}{x} \quad (2)$$

$Abs\lambda_i$ denotes the absorbance at wavelength λ_i, and x is the optical path of the spectrometer cuvette.

The ratio $Abs\lambda_i/x$ denoted as $SAC_{\lambda i}$ is the spectral absorption coefficient at wavelength λ_i.

The process performance was evaluated in terms of removal rates of COD, BOD_5, and turbidity using the following equation:

$$\text{Removal}(\%) = \frac{\left(\begin{array}{c}\text{Raw wastewater}\\ -\text{Treated wastewater}\end{array}\right)}{\text{Raw wastewater}} \times 100 \quad (3)$$

Bacteriological analysis of samples before and after biological treatment was performed by cultural techniques according to standard methods [14] and Moroccan interpretation criteria [15] as summarized in Table 1. Coliforms (C), fecal coliforms (FC), fecal streptococci (FS), revivable microorganisms (RM), and *Staphylococcus aureus* were all considered indicators of wastewater contamination. Several dilutions were prepared and analyzed by direct inoculation or filter concentration methods. Thereafter, incubation of the Petri dishes was performed under appropriate conditions. Colony counts were performed using a Colony Counter 560 Suntex and expressed as colony forming units (CFU) per sample volume.

2.3. Pretreatment of raw wastewater using aerobic and anaerobic processes

The raw wastewater was placed in two glass bioreactors with a capacity of 2 L. One underwent aeration (aerobic pretreatment); while the other bioreactor remained closed without aeration (anaerobic pretreatment). The two bioreactors were operated independently in batch mode at 25°C (gaseous products were removed continuously).

In the aerobic bioreactor, aeration was performed continuously during the processing period using an air blower with a flow rate of ca. 0.5 L/min to maintain the required dissolved oxygen. Aliquots were taken every 3 d to measure the evolution of several parameters, including turbidity, pH, TS, TA, TDS, EC, COD, BOD_5, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, UV-Visible spectra, and color index.

2.4. Sequential aeration and Fenton processes

Experiments were conducted in a batch system at pH 3 and room temperature. Initially, 25 mL of aerobically pretreated wastewater was introduced into opaque flasks

Table 1
Methods and results of bacteriological analysis of wastewater from Fez according to the Moroccan Standards NM 03.7.001

Microorganisms	Method	Medium	Incubation	Raw wastewater	Aerobic effluent
Coliforms (log10 CFU/100 mL)	ISO 9308-1 Membrane filtration	Lactose TTC agar with Tergitol-7	36°C ± 2°C during 21 ± 3 h	6.72	3.58
			36°C ± 2°C during 44 ± 4 h	6.97	3.70
Fecal coliforms (log10 CFU/100 mL)			44°C ± 0.5°C during 21 ± 3 h	6.42	3.41
Fecal streptococci (log10 CFU/100 mL)	ISO 7899-2 Membrane filtration	Slanetz and Bartley	36°C ± 2°C during 22 ± 2 h	2.48	0
			36°C ± 2°C during 44 ± 4 h	2.6	
Revivable microorganisms (log10 CFU/mL)	ISO 6222 Inoculation in agar culture medium	Plate count agar	36°C ± 2°C during 21 ± 3 h	6.58	3.65
			36°C ± 2°C during 44 ± 4 h	6.67	3.69
Staphylococcus aureus (log10 CFU/mL)	Inoculation in agar culture medium	Chapman's medium with mannitol	36°C ± 1°C during 44 ± 4 h	5.65	0

and placed under magnetic stirring. Afterward, a desired amount of $FeSO_4$, $7H_2O$ was added and the mixture was stirred vigorously for less than 2 min, then a volume of H_2O_2 was added to initiate the Fenton process and the mixture was stirred at 350 rpm. Upon sampling time, the supernatant was withdrawn and added into a centrifuge tube containing Na_2SO_3 (2 M) to stop the Fenton reaction, then a 5 min centrifugation at 2,000 rpm was done before analysis for COD, UV-Visible spectra, and CI.

In order to determine the optimal conditions for the Fenton process, three factors were investigated, including pH, iron dose, and hydrogen peroxide dose.

3. Results and discussion

3.1. Raw wastewater characterization

The bacteriological examination of the raw wastewater was performed, and the results are listed in Table 1. All investigated microorganisms were present in the raw wastewater. Coliforms (C), fecal coliforms (FC), and fecal streptococci (FS) were significantly above the threshold for water reuse, indicating the poor quality and high fecal contamination level of the wastewater [16,17].

The physico-chemical characterization of the Fez wastewater is summarized in Table 2. The result revealed some differences from our previous work, especially for COD, BOD_5, EC, TDS, TS, and TSS which exceeded the strict requirements for liquid discharge or reuse [6]. Indeed, raw wastewater is characterized by a high biodegradability index, a slightly alkaline pH, and a yellow color due to humic compounds. Furthermore, several heavy metals such as Cu, Mn, Zn, Fe, and Cr were present in the wastewater with concentrations varying from 0.1 to 2.7 mg/L. Obviously, the concentration of total chromium was higher than the Moroccan Standards for Liquid Disposal (MSLD) and the Moroccan Standards for Liquid Reuse (MSLR), which can be explained by the anthropogenic activities of the tanning industry in Fez. In addition, this wastewater was characterized by a low concentration of anions, that is, nitrate (2.4 mg/L) and sulfate (278 mg/L).

According to the reported literature on wastewater classification, the municipal wastewater of Fez could be categorized as high-strength wastewater, requiring adequate treatment processes [18].

As it was highly biodegradable wastewater, biological processes were applied as a pretreatment to reduce the huge amount of biodegradable organic matter. Therefore,

Table 2
Physico-chemical characteristics of municipal wastewater from the city of Fez-Morocco before and after biological pretreatment

Parameter	Raw wastewater	Anaerobically wastewater	Aerobically wastewater	MSLD*	MSLR**
T (°C)	24 ± 0.5	22	22	<30	35
pH	7.61 ± 0.05	7.12	8.7	5.5–9.5	6.5–8.4
EC (μS/cm) at 25°C	2,770 ± 8	3.020	2,620	2.700	1.000
TS (mg/L)	1,300 ± 3	1,500	1,200	NA	NA
TDS (mg/L)	1,108 ± 7	1,180	1,051	NA	NA
TA (mg·$CaCO_3$/L)	520 ± 20	620	335	NA	NA
Turbidity (NTU)	130 ± 4	17	2.51	NA	NA
TSS (mg/L)	1,937 ± 18	1.184	80	150	<50
COD (mg·O_2/L)	843 ± 45	440	281	250	100
BOD_5 (mg·O_2/L)	400 ± 10	200	0	120	20
BOD_5/COD	0.5 ± 0.03	1	0	NA	NA
CI	0.05	0.04	0.03	NA	NA
$A_{254\text{ nm}}$	0.48	0.3	0.29	NA	NA
NH_4^+ (mg/L)	20 ± 2	32.9	0	NA	NA
NO_3^- (mg/L)	10.4 ± 0.4	4.15	140.2	NA	30
NO_2^- (mg/L)	1.45 ± 0.18	0.29	0.5	NA	NA
Cl^- (mg/L)	710 ± 14	690	720	NA	15–350
SO_4^{2-} (mg/L)	278 ± 9	88.4	344	600	250
PO_4^{3-} (mg/L)	32.5 ± 2.4	84.9	15.7	NA	NA
Cu (mg/L)	0.1 ± 0.01	0	0	2	0.2
Mn (mg/L)	0.2 ± 0.01	0.09	0.1	2	0.2
Zn (mg/L)	0.3 ± 0.01	0.4	0.08	5	2
Fe (mg/L)	1.3 ± 0.01	0.73	0.1	5	5
Cr (mg/L)	2.7 ± 0.01	2.2	0.31	2	1

*MSLD: Moroccan Standards for Liquid Disposal;
**MSLR: Moroccan Standards for Liquid Reuse, according to FAO and Water Reuse Standard for Irrigation, Land Watering, Morocco;
NA: Not available.

the treatment would be economically feasible with reduced chemical consumption.

In the following section, the raw liquid waste from Fez was subjected separately to anaerobic and aerobic biological pretreatment processes. The study aims to examine the evolution of wastewater characteristics in the aerobic and anaerobic environment, in order to establish the best configuration with the Fenton process.

3.2. Anaerobic and aerobic pretreatment of raw wastewater

3.2.1. Anaerobic pretreatment

The anaerobic pretreatment was periodically monitored for turbidity, COD, and BOD_5 until a steady state was reached, and the result is plotted in Fig. 2. As shown in Fig. 2, the pretreatment period lasted 38 d, during which a rapid increase in turbidity removal efficiency to 78% was achieved in the first 3 d, followed by a steady increase to 89% on day 18, where it remained constant. In the same way, COD elimination showed 31% in the first 3 d, then progressively increased to a maximum of 48% on day 29. However, BOD_5 did not show removal even after 18 d, beyond that, a drastic removal of 50% was ascertained on day 21, and after that, no further removal was observed. These removals could be explained by the presence of anaerobic bacteria, responsible for the biodegradation of organic compounds under anaerobic conditions [19]. In addition, the reduction in chromium concentration was not sufficient to meet the MSLD and MSLR requirements (Table 2).

The UV-Visible spectra recorded on days 3, 6, and 38 are displayed in Fig. 3. A slight drop in absorbance values between the beginning and end of the pretreatment period was noticed. According to Komatsu et al. [20], the residual organic matter after anaerobic pretreatment could be attributed to the high content of hydrophobic and aromatic substances. El Mrabet et al. [8] have found a similar trend in UV-Visible spectra when applying the anaerobic process to complex wastewater.

The variation of inorganic nitrogen concentrations during the anaerobic pretreatment was investigated and the result is plotted in Fig. 4. The ammonium concentration attained 1.9 mM after the first week of the pretreatment due to the ammonification mechanism [21]. Similar results have been found by Fatma et al. [22] when nitrogen species were monitored in the anaerobic process applied to leachates diluted with municipal wastewater.

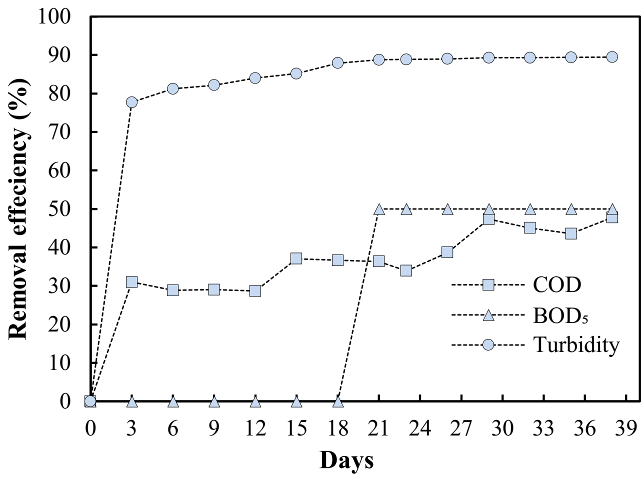

Fig. 2. Evolution profile of turbidity, COD, and BOD_5 removal during the anaerobic process at 25°C.

Furthermore, nitrite concentration was almost negligible, while nitrate concentration decreased during the first two weeks of anaerobic pretreatment, corresponding to 63% removal which is higher than the removal that has been found by Manrique Losada (25%) [10]. These removals could be justified by the conversion of nitrate to nitrogen gas through anaerobic denitrification by microorganisms [Eq. (4)]. The addition of external organic carbon was found to be crucial for denitrification [23].

$$NO_3^- + COD_{(\text{organic matter})} \rightarrow N_2 + CO_2 + H_2O + OH^- + \text{New cells} \quad (4)$$

The evolution of orthophosphate, sulfate, and chloride concentrations during anaerobic pretreatment is represented in Fig. 5. The orthophosphate concentration increased from 32.5 to 85 mg/L during the processing period, respectively, probably due to the hydrolysis of organic phosphorus by specific microorganisms. It was found that the orthophosphate trend is dependent on nitrate concentration [24,25]. During same period, sulfate concentration gradually decreased from 0.28 to 0.07 g/L, probably due to the high activity of sulfate-reducing bacteria [26]. The chloride concentration remained unchanged at 0.69 g/L throughout the pretreatment period.

The variation of TDS, EC, pH, TA, and TS during the anaerobic pretreatment is depicted in Fig. 6. It can be seen that pH, TS, and EC remained almost constant during the experiment. Moreover, TDS increased moderately at the beginning as some ionic species were released, while TSS was removed by 39% (Table 2).

3.2.2. Aerobic pretreatment

Aerobic pretreatment was monitored periodically for turbidity, COD and BOD_5 until a steady state was reached, and the result is plotted in Fig. 7. As shown in Fig. 7, turbidity removal increased up to 88% during the first three days of the pretreatment period and reached stability with 98% removal on day 18. In the same way, COD removal followed the same trend with up to 47% removal in the first three days and reached a steady state on day 21 with a maximum COD reduction of 67%. In addition, BOD_5 removal increased up to 50% after the first two weeks before achieving a complete removal at the end of the pretreatment period. These eliminations could be interpreted by the role of aerobic germs in the degradation of organic substances involving metabolic mechanisms, as well as by air stripping [Eq. (5)] [27]. A similar COD reduction of 62% has been reported by Changotra et al. [28] for biodegradable wastewater from the effluent treatment plant. According to Trapido et al. [29] biological pretreatment of high-strength raw wastewater removed 67%–73% and 92%–94% of the initial COD and BOD_5, respectively. However, in these studies,

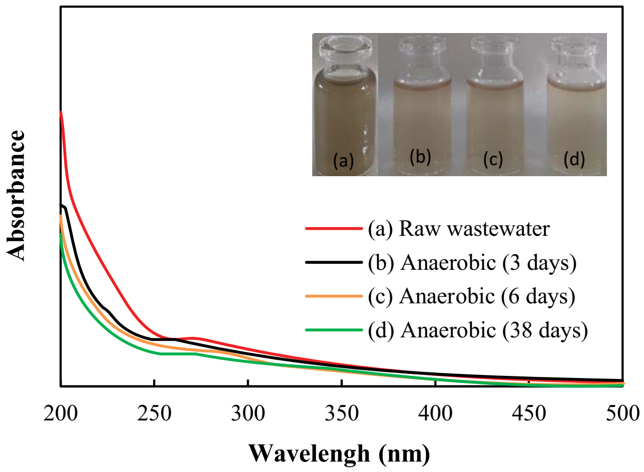

Fig. 3. UV-Visible spectra of raw and pretreated wastewater from the anaerobic system (diluted ×5).

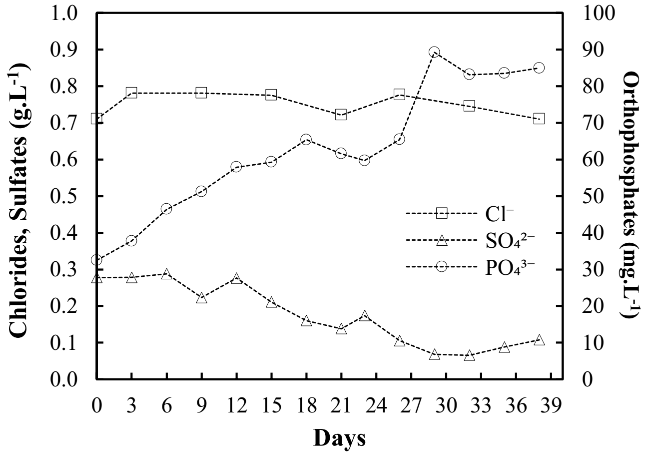

Fig. 5. Evolution profile of sulfate, chloride, and orthophosphate concentrations during the anaerobic process at 25°C.

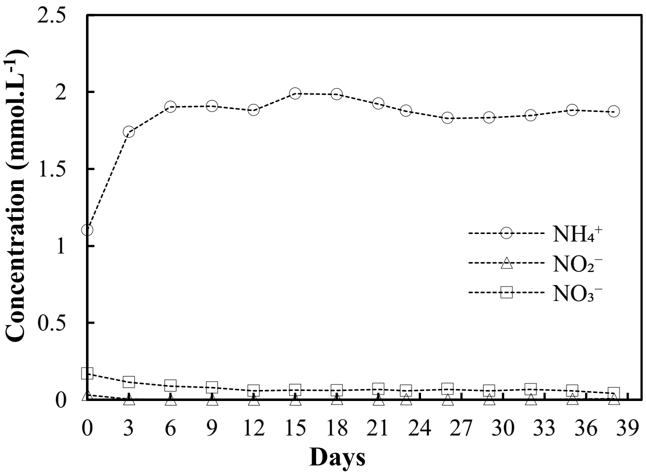

Fig. 4. Evolution profile of inorganic nitrogen concentration during the anaerobic process at 25°C.

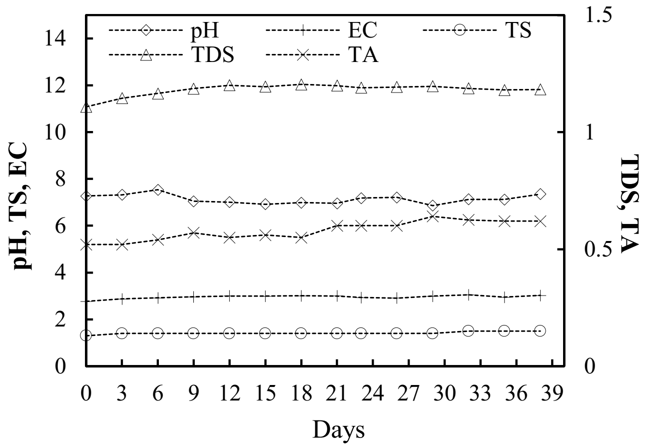

Fig. 6. Evolution profile of pH, TS, EC (mS/cm), TDS (g/L), and TA (g·$CaCO_3$/L) during the anaerobic process at 25°C.

the use of pre-selected germs, as well as the provision of nutrients (appropriate COD:N:P ratio) with the biomass inoculum may be responsible for the high abatement yields. El Mrabet et al. [8] attempted to treat stabilized leachate using intensive aeration, and removals of up to 40% and 31% were achieved for COD and BOD_5, respectively. In addition, initial chromium and TSS concentrations were reduced by 88.5% and 96%, respectively, resulting in final effluent concentrations well below the MSLD and MSLR thresholds (Table 2). This result is in agreement with other work reported elsewhere [30].

In order to evaluate the effect of aeration on the composition of raw wastewater, Fig. 8 describes the evolution of the absorbances of compounds in the effluent during the processing period. The decrease in UV-Visible absorption spectra during aeration is remarkable, especially in the wavelength range 250–300 nm, indicating the removal of organic matter with unsaturated double bonds characterizing hydrocarbons, benzene, and humic acids. A similar finding has been reported elsewhere [8].

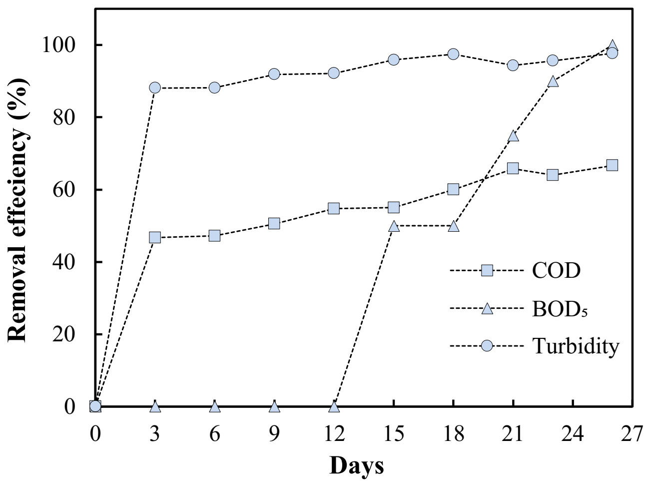

Fig. 7. Removal evolution profile of turbidity, COD, and BOD_5 during the aerobic process at 25°C.

The variation of inorganic nitrogen concentrations during aerobic pretreatment was investigated and the result is plotted in Fig. 9. The first transformation that occurred during the aeration process corresponded to the complete oxidation of ammonium with an initial concentration of 1.1 mM to nitrite, achieving a maximum concentration of 8.1 mM. The latter showed the second transformation to nitrate species, achieving a maximum concentration of 2.31 mM from the 15th day of the pretreatment period. These transformations are attributed to the nitrification mechanism by ammonia and nitrite oxidizing bacteria present in raw wastewater sludge [Eqs. (6) and (7)] [31].

$$\text{Organic matter} + O_2 \rightarrow CO_2 \uparrow + NH_3 \uparrow + \text{biomass} \quad (5)$$

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (6)$$

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \quad (7)$$

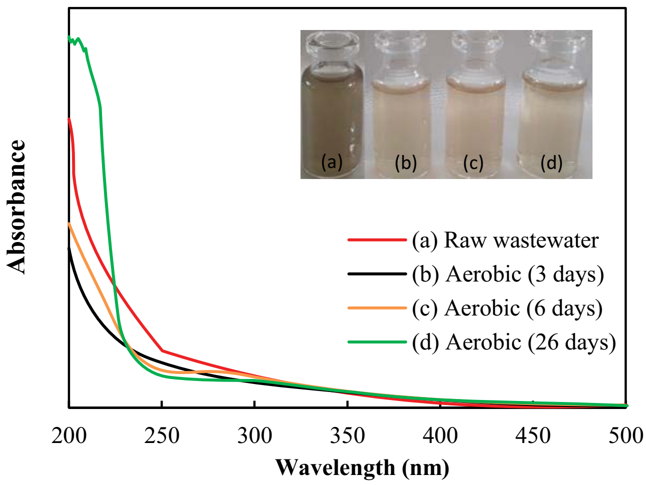

Fig. 8. UV-visible spectra of raw and pretreated wastewater from the aerobic process (diluted ×5).

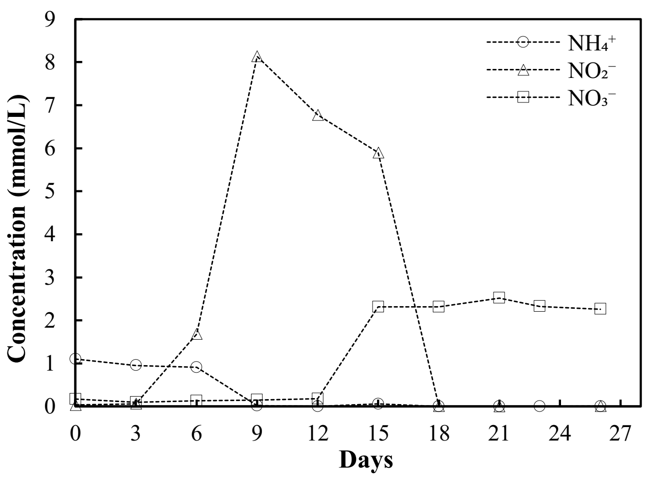

Fig. 9. Evolution profile of inorganic nitrogen concentration during the aerobic process at 25°C.

The evolution of orthophosphate, sulfate, and chloride concentrations during the aerobic pretreatment is represented in Fig. 10. In contrast to the anaerobic pretreatment, the orthophosphate concentration decreased from 32.5 to 15.7 mg/L during the aeration process. This result is consistent with research that has been conducted on two wastewaters from two different treatment plants, where the authors observed a similar trend after aeration, whether intensive or extensive [32]. During the same period, sulfate concentration showed a slight increase from 0.28 g/L up to 0.34 g/L, probably due to the minor reduction of sulfur-containing organic matter by sulfate-reducing bacteria [26]. In addition, the chloride concentration remained almost unchanged at 0.72 g/L throughout the aeration process.

The variation of TDS, EC, pH, TA, and TS during aerobic pretreatment is depicted in Fig. 11. As can be seen, TDS declined moderately possibly due to the precipitation of some inorganic solids [33]. The pH and TA variated conversely, the former increased from 7.6 to 8.7, whereas the latter declined to an average of 0.33 g·$CaCO_3$/L. These changes could be explained by the assimilation of

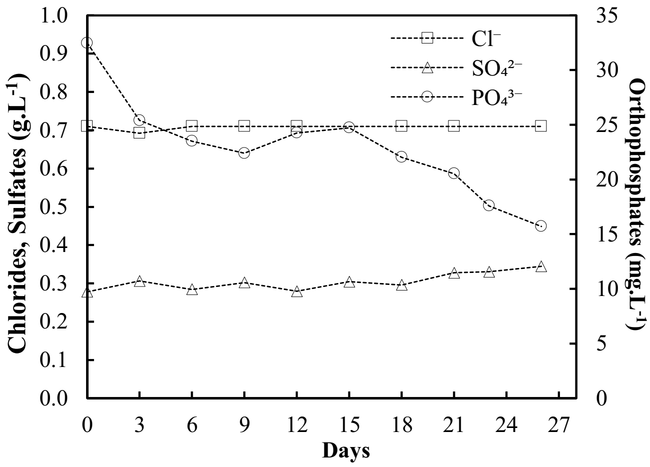

Fig. 10. Evolution profile of sulfate, chloride, and orthophosphate concentration during the aerobic process at 25°C.

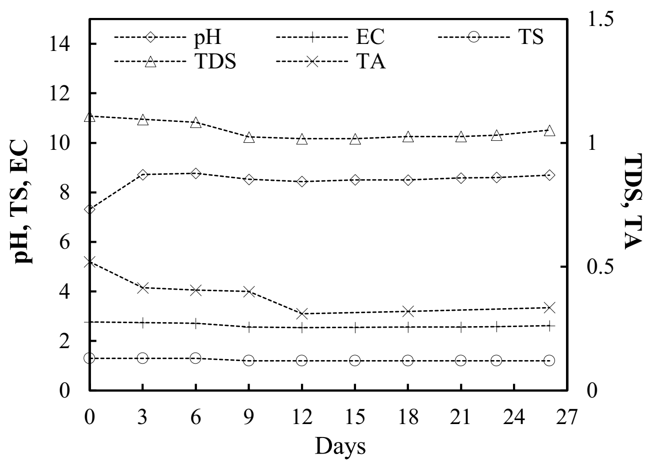

Fig. 11. Evolution profile of pH, TS, EC (mS/cm), TDS (g/L), and TA (g·$CaCO_3$/L) during the aerobic process at 25°C.

HCO_3^- substrate and organic acids (i.e., volatile fatty acids) by the microorganisms, as well as the air stripping of CO_2 [34]. TS and EC remained almost constant throughout the aeration experiment.

3.3. Sequential treatment of aeration-Fenton processes

Because the aeration method is widely used in most wastewater treatment plants and based on the results obtained in terms of investigated parameters, aerated wastewater was preferentially selected for further treatment. The application of Fenton oxidation to aerated wastewater was carried out in a batch system, in which the Fenton-induced reaction is represented as follows [Eq. (8)]:

$$Fe^{2+} + H_2O_2 + COD_{bio-resistent} \rightarrow Fe^{3+} + HO^{\bullet} + OH^- + CO_2 + H_2O + COD_{biodegradable} \quad (8)$$

Experiments were repeated in duplicate and operational parameters were optimized, including pH, iron dose, and hydrogen peroxide dose.

3.3.1. Effect of initial pH on COD removal and UV-visible spectra

A series of experiments was performed to define the optimal initial pH giving high COD removal. The result is displayed in Fig. 12. Clearly, the COD abatement increased from 27% to 52% when pH was varied from 2 to 3. Beyond pH 3, the COD elimination declined to 15% and 37% at pH 4 and 6, respectively. It is well known that Fenton oxidation technology is most effective in the acidic pH range between 3 and 4 [35].

The UV-visible absorption spectra corresponding to the pH effect are shown in Fig. 13. Indeed, a significant decrease in absorbances and color (insert image) was observed at pH = 3, wherein degradation of a wide range of organic compounds occurred, typically at the 254 nm wavelength. These results confirm that the optimal pH for the Fenton process applied to aerobic effluent is pH 3.

3.3.2. Effect of [Fe^{2+}] on COD removal and UV-visible spectra

The evolution of COD removal rate as a function of the [Fe^{2+}]/[H_2O_2] molar ratio is plotted in Fig. 14. As it is clear, increasing the iron dose in the Fenton process had a positive effect on COD removal. The latter increased from 6.4% to 57% when the [Fe^{2+}]/[H_2O_2] ratio was varied from 0 to 0.3.

In order to confirm the previous results, Fig. 15 depicts the variation of UV-Visible absorption spectra as a function of the initial iron doses. In agreement with the result obtained for COD removal, the variation of the UV-visible spectrum was insignificant when only H_2O_2 was added. However, an obvious reduction of absorbances was observed when the initial [Fe^{2+}]/[H_2O_2] molar ratio

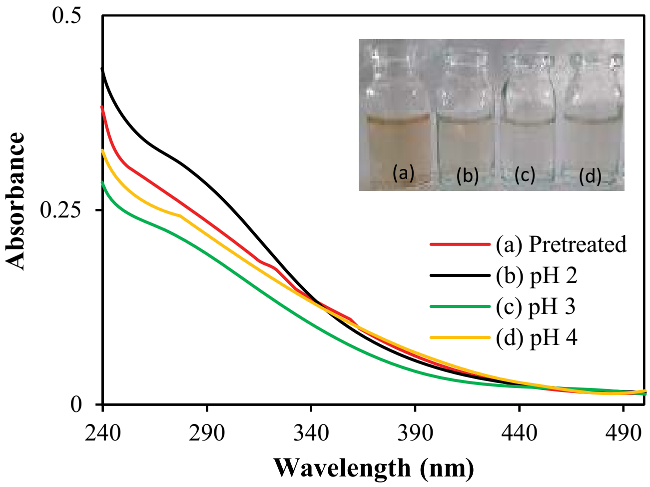

Fig. 13. Effect of initial solution pH on UV-Visible absorption spectra in the Fenton process applied to the pretreated wastewater by aeration at 25°C (diluted ×5).

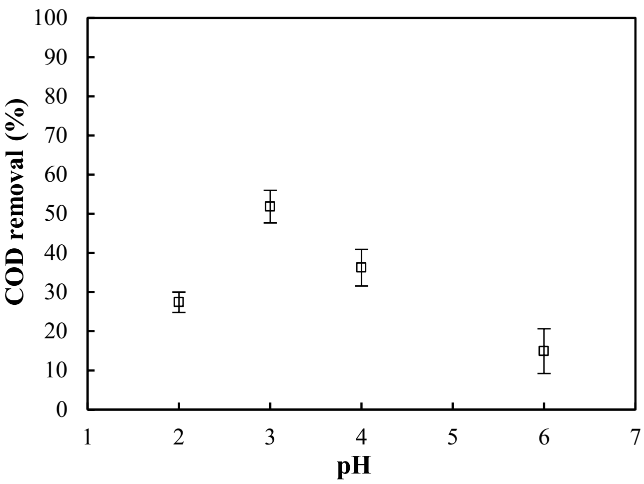

Fig. 12. Effect of initial solution pH on COD removal in the Fenton process applied to the pretreated wastewater by aeration ([Fe^{2+}] = 3.57 mmol/L; [H_2O_2] = 14.71 mmol/L; $[DCO]_i$ = 281 mg·O_2/L; T = 25°C; 60 min contact time).

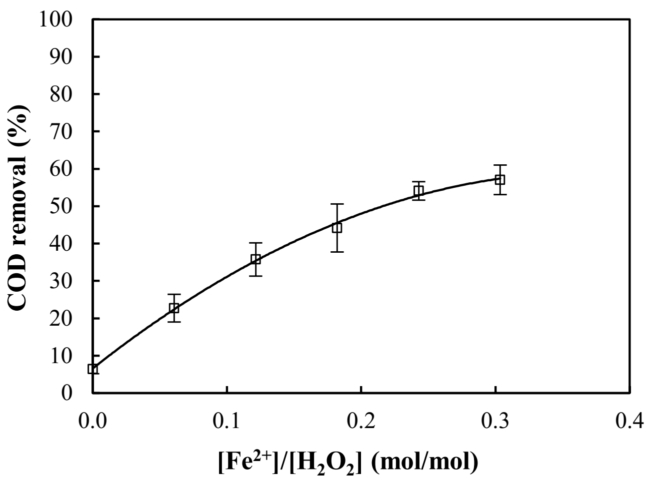

Fig. 14. Effect of initial Fe^{2+}/H_2O_2 molar ratio on COD removal in the Fenton process applied to the pretreated wastewater by aeration ([H_2O_2] = 14.71 mmol/L; $[DCO]_i$ = 281 mg·O_2/L; pH = 3; T = 25°C; 60 min contact time).

was increased from 0 to 0.12 and 0.24. The same trend was noticed for color removal (insert image), where pretreated wastewater discoloration was more pronounced as iron loading increased. A similar result has been found by other researchers [36]. Thus, increasing iron load promotes the generation of $HO^{\cdot}$ radicals, which in turn promotes the degradation of organic compounds.

3.3.3. Effect of $[H_2O_2]$ on COD removal and UV-visible spectra

The effect of initial H_2O_2 dose on COD removal in the Fenton process is discussed in Fig. 16. H_2O_2 dosages ranged from 0 to 29.41 mmol/L at a constant catalyst concentration (3.57 mmol/L). The result showed that increasing the $[H_2O_2]/[COD]$ ratio (w/w) from 0 to 1.8 enhanced the COD removal from 25.4% to 58.3%. Thereafter, treatment efficacy decreased slightly to 52.1% when the ratio increased to 3.6. Thereby, excessive H_2O_2 may cause free radical scavenging, recombination, and catalyst oxidation [Eqs. (9)–(12)] as has been reported elsewhere [37]. According to many studies, increasing the catalyst dose is more favorable to the process performance than increasing the oxidant dose [38,39].

In order to confirm the results obtained previously, Fig. 17 shows the effect of the H_2O_2 dose on the UV-visible absorbances. Clearly, a significant reduction of organic matter with more or less complex structures caused a substantial decrease in absorbances within the UV-visible range, as well as an obvious discolorization of the final effluent (inset image). Similarly, other researchers have also confirmed that color reduction is proportional to H_2O_2 loading [36]. Therefore, for the optimal dose of catalyst (3.57 mmol/L) and oxidant (14.71 mmol/L), A_{254nm} and color removal reached 74.86% and 83.36%, respectively.

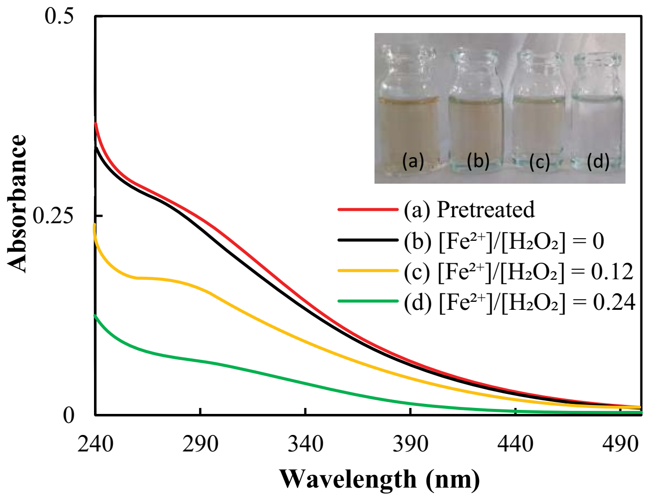

Fig. 15. Effect of Fe^{2+}/H_2O_2 molar ratio on UV-Visible absorption spectra of wastewater pretreated by aeration at 25°C (diluted ×5).

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{9}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{10}$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \tag{11}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \tag{12}$$

Overall, the removal of $A_{254\ nm}$, COD, color, and BOD_5 from the raw municipal wastewater of Fez city reached maximums of 84%, 86%, 90.3%, and 100%, respectively, using a combination of aeration and Fenton processes under optimal operating conditions.

Table 3 summarizes some of the reported work using integrated treatment involving biological and Fenton technologies. As the table shows, the removal rate of COD

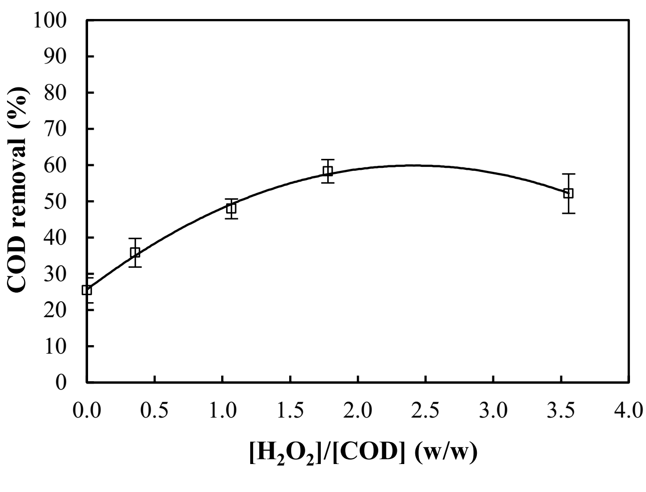

Fig. 16. Effect of initial H_2O_2/COD mass ratio on COD removal in the Fenton process applied to the pretreated wastewater by aeration ($[Fe^{2+}]$ = 3.57 mmol/L; $[DCO]_i$ = 281 mg·O_2/L; pH = 3; T = 25°C; 60 min contact time).

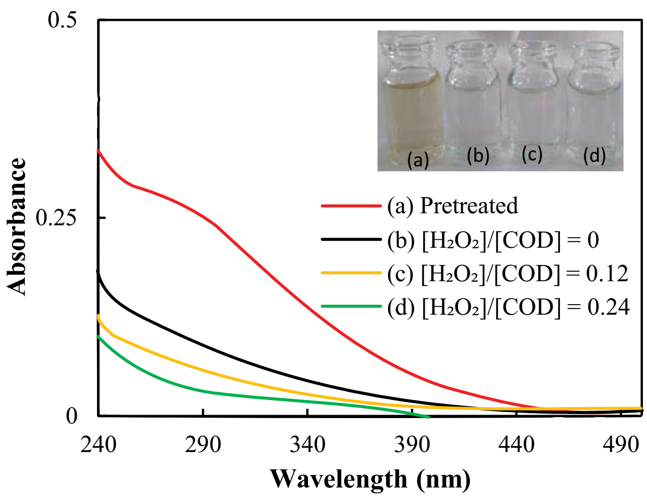

Fig. 17. Effect of initial H_2O_2/COD mass ratio on UV-Visible absorption spectra in the Fenton process applied to the pretreated wastewater by aeration at 25°C (diluted ×5).

Table 3
Comparative study of COD removal from different wastewaters using sequential biological – Fenton processes

Wastewater	Treatment scheme	COD removal (%)	References
Domestic + Industrial	Aerobic + Fenton	86	Present study
Leachate	Aerobic + Fenton	73	[8]
Industrial	Aerobic + Fenton	78	[29]
Industrial	Aerobic + Fenton	80	[41]
Industrial	Anaerobic + Fenton	61	[42]
Domestic		93	
Industrial	Anaerobic + Fenton	54	[36]
Domestic + Industrial		42	

depends primarily on the complexity of the original wastewater. In the case of leachates, the combined treatment was sufficient to meet even local standards for safe disposal. For industrial wastewater, COD removal rates ranged from 54% to 80% when the same treatment sequence was applied. In the case of domestic sewage, the COD removal rate reached 93% due to its highly biodegradable organic content. In contrast, for a mixture of industrial and domestic wastewaters, integrated treatment resulted in the lowest COD removal of 42%, likely due to the complexity of the mixture [36]. Indeed, the treatment scheme adopted in the current study improved the COD abatement by up to 86%, which is one of the highest COD removal efficiencies obtained using the Fenton process as a post-treatment of biologically pretreated municipal wastewater.

As a result, the average COD concentration recorded in the treated effluent after the sequential treatment aeration-Fenton was 117.3 mg·O_2/L which complies with national and international standards for safe disposal to the natural environment and water reuse. Hence, the resistant fraction after the advanced oxidation processes is ascribed to easily biodegradable simple organic acids [40]. In addition, it is worth mentioning that Fenton technologies are conducive to successful bacterial inactivation, as has been proven in numerous studies [35].

4. Conclusion

In the current study, the sequential treatment of aeration and Fenton processes was investigated for municipal wastewater collected upstream of the WWTP of Fez. The aeration pretreatment showed significant removal efficiencies in terms of color, COD, and BOD_5, reaching 40.2%, 67%, and 100%, respectively. In addition, the application of the Fenton process to the aerated pre-treated wastewater enhanced the reduction of residual COD and UV-visible absorption spectra. Thus, overall removals of up to 90.3% color, 86% COD, and 100% BOD_5 were achieved under optimal operating conditions for Fenton oxidation (pH = 3, contact time = 60 min, [Fe^{2+}] = 3.57 mmol/L and [H_2O_2] = 14.71 mmol/L). Indeed, the final COD concentration in the treated wastewater was about 117.3 mg/L, which complies with Moroccan standards for effluent discharge. The processing time of the integrated treatment used in this study was limited by the duration of the aeration pretreatment since only the raw sewage microorganisms were involved. Therefore, a reduction in processing time could be achieved by using activated sludge or a specific inoculum. Consequently, the combined process involving aeration followed by the Fenton processes could be an attractive alternative to remove bio-resistant compounds from the municipal wastewater of the city of Fez, thus preventing the contamination of the Sebou River in Morocco.

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