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Coagulation and advanced oxidation processes in the treatment of olive mill wastewater (OMW)

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ABSTRACT

This paper proposes the use of a combination of two treatment processes for the removal of organic pollutants from the olive oil mill wastewater (OMW). The two treatment processes are, a single coagulation stage followed by a single advanced oxidation, AOP, stage. For the AOP_s, the following processes were used; UV, O_3, O_3/UV and H_2O_2/UV depending on the operating time .Two coagulant Al^{3+} and Fe^{3+} ions were used in the experimental program conducted in this study. The concentration of the chemical oxygen demand (COD) was measured in the effluent of the treated wastewater for each experiment. The percent removal of the COD concentration achieved using the two coagulant Al^{3+} and Fe^{3+} ions at $pH = 9$, was 54% and 58%, respectively. In a comparison, the percent removal of the COD is found in the range of 10–39% using an advanced oxidation process alone. The percent removal of the COD concentration achieved using the combined processes, coagulation and AOP_s (O_3, O_3/UV and H_2O_2/UV), are 90%, 95% and 94%, respectively. In all experiments conducted, the percent removal of organic contaminants load was directly related to the concentration of organic compounds in the influent of the wastewater.

Keywords: Olive mill; Advanced oxidation; Coagulation; COD; Wastewater treatment

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1. Introduction

In the recent years, the governments of the Middle Eastern countries, especially Jordan, are concerned with the exploitation of their water sources, due to the severe shortage of water and the successive years of drought. Therefore, the local governments have directed their researchers to find best ways in exploitation of these water sources and for the treatment of the industrial wastewater to protect the water resources from contamination. The wastewater of olive oil mill (OMW) is one of the most important wastewater sources that must be treated. A high priority was given to deal with this type of wastewater mainly for two reasons; due to the difficulty of treating this type of waste, and due to the large volumes of wastewater that is annually generated from the OMWs. In year 2004, the volume of the generated wastewater exceeded 200,000 m^3 and approximately 95,000 ton of solid waste [1].

At the present, this kind of wastewater are thrown untreated, in rivers and valleys and finally are collected in dams. This practice leads to the contamination of surface water and groundwater resources.

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Purification difficulty of this wastewater is due to the presence of diverse mixture of organic and inorganic compounds such as: sugars, nitrogenous compounds, tannins, pectin, volatile acids, polyalcohol, oil and phenolic substances. These compounds are responsible for the high concentration of COD and biochemical oxygen demand (BOD) in the influent wastewater [2–6]. The untreated waste is very harmful to human and to the environment. For instance, it has been reported that phenols are considered toxic for some aquatic life forms in concentrations higher than 50 ppb and the ingestion of one gram of phenol can have fatal consequences in humans [7]. Therefore, it is urgent to continue the search for optimum treatment methods of this type of industrial waste to protect the water resource of these developing countries [8].

The treatments processes selected for different types of wastewater must guarantee compliance with the strict authorized discharge levels for the regulated contaminants in the effluent wastewater. In general, the elimination of the organic molecules from aqueous solution needs one or more of the following basic treatment techniques [9]: chemical oxidation, air desorption, liquid–liquid extraction, adsorption, reverse osmosis, ultra-filtration and biological treatment. The choice of method depends on the cost of the process, and on other factors like the concentration of contaminant and the volume of the wastewater to be treated. Nowadays, the most widely used methods in the treatment of industrial wastewater are the coagulation, flocculation, and advanced oxidation processes (AOPs).

2. Treatment processes

The following paragraphs include description of the conventional treatment processes typically used to treat industrial wastewater.

2.1. Coagulation and flocculation process

Coagulation and flocculation processes are an important part of water and wastewater treatment. The processes of coagulation and flocculation are employed to separate suspended solids (turbidity) from water. In the coagulation process, the colloidal particles are essentially coated with a chemically sticky layer that allows them to stick together and form a slime that is heavier than water. Under gravity, the slime settles out of water in a reasonable period of time in a clarifier. Salts such as aluminum sulfate (alum), or ferrous or ferric (iron) salts are typically used as coagulants. These salts make the suspended particles less stable in suspension, i.e., more likely to settle out. Flocculation is the physical process that makes the sticky particles comes together (causing collision) and stick together forming the slime. Flocculation agents such as natural synthetic polymers, and synthetic organic polymers, are used to form the flocculation [10,11].

Destabilization of a colloidal suspension results in joining of minute particles by physical and chemical processes which neutralize the forces that keep the colloids apart. Cationic coagulants provide positive electric charges to reduce the negative charge layer (zeta potential) of the colloids. When the coagulant added to the water, numerous species of hydroxyl metallic complexes are formed. These metallic complexes are hydrolysis products that tend to polymerize. The general expressions for these complexes are $\mathrm{Me_q(OH)_p}^{z+}$ such as $\mathrm{Fe_2(OH)_2}^{4+}$ and $\mathrm{Al_7(OH)_{17}}^{4+}$. The complexes are polyvalent, possess high positive charge and adsorbed to the surface of the negative colloids [12,13].

Currently, there is no such economically feasible and easy solution to the treatment of the waste water of OMW. Physical and chemical methods, such as flocculation, coagulation, filtration, lagoon of evaporation and burning systems, partially solve the problem [14,15]. Biological treatment of OMW is difficult because of the presence of phenolic chemicals, which possess antibiotic characteristics [16]. In wastewater handling, in general, coagulation precedes chemical or biological processes. Coagulation is a pretreatment stage for the removal of suspended solids, foam, and high molecular weight compounds. Coagulation is also used for the removal of turbidity, water clarification and reduction of organic load (COD, BOD) [17].

2.2. AOP

The AOPs [18–20] involve the generation of highly reactive free radicals (especially hydroxyl radicals) in sufficient quantity to effect water purification. Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules. The attack by hydroxyl radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization. Because the hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The AOP with UV radiation and ozone is initiated by the photolysis of ozone. As shown in the chemical reaction listed below, the photodecomposition of the ozone leads to two hydroxyl radicals, which do not act as they recombine producing hydrogen peroxide [21]

$$\mathrm{H_2O_2 + O_3 \xrightarrow{hv} 2HO^{\bullet} + O_2}$$

Therefore, this system contains three components to produce OH radicals and/or to oxidize the pollutant for subsequent reactions: UV radiation, ozone and hydrogen peroxide. The addition of H_2O_2 to the UV/O_3 process accelerates the decomposition of ozone resulting in increased rate of OH radicals generation.

The AOP is a very powerful method that allows a considerable reduction of the TOC. Trapido et al. [22] reported that the combination of ozone with UV radiation and hydrogen peroxide was found to be more effective for the degradation of nitrophenols than single ozone stage or the binary combinations. He also reported that at low pH value, the reaction rate was increased and the ozone consumption was decreased. Contreras et al. [23] demonstrated that the addition of H_2O_2 to UV/O_3 system slightly improves the rate of TOC removal in a solution of nitrobenzene.

This paper proposes the use of a combined process, a single coagulation stage followed by a single oxidation stage to remove the organic pollutants in the OMW. Two kinds of aluminum ferrous or ferric (iron) salts are used in coagulation and flocculation process. No articles have been found in the literature about the oxidation of the organic compounds by means of this combined process.

3. Material and methods

3.1. Collection of samples

Wastewater samples were obtained from an olive oil production plant located in City of Irbid, in the northwestern part of the Country of Jordan. In a first step, the main physicochemical characteristics and features of the OMW were determined. The following are the results of the general characteristics: pH = 5.56, BOD = 38.05 g/dm^3, COD = 117.1 g/dm^3, total phenolic compounds (TP) = 2.7 g/dm^3 (determined by the Folin–Ciocalteau method) [24], and total solids concentration (TS) = 29.3 g/dm^3. Prior to conducting the experimental treatment, the OMW were centrifuged for 3 min and filtered to remove the suspended solids.

Because of the high COD concentrations, OMW were diluted with distilled water approximately 10% (v:v) to give initial COD concentrations of approximately 12 g/dm^3. The experiments were conducted in a mixed batch reactor (a five- liter cylindrical vessel).

3.2. Coagulation of samples

The next step of treatment that coagulant $Al_2(SO_4)_3 \cdot nH_2O$ were added in a dose of 60 mg/dm^3 on various levels of pH. Then we accomplished a rapid mixing for a 1 min followed by a slow mixing for another 15 min. Afterwards, a sedimentation process along with COD testing was accomplished. A different type of coagulant was used such as $FeCl_3$ and $Fe_2(SO_4)_3 \cdot nH_2O$ in a ratio of 1:1 and a 50 mg/dm^3 as a dose with two modes of mixing (rapid and slow), then it followed by sedimentation and COD testing. The optimum dosage of coagulant was determined by a Jar test method. $FeCl_3$, $Fe_2(SO_4)_3 \cdot nH_2O$, $Al_2(SO_4)_3 \cdot nH_2O$ and CaO (Sigma).

3.3. Advanced oxidation samples

The second treatment process was the advanced oxidation AOPs, wherein its effect on COD concentration at pH = 5.67 were studied. Ultraviolet radiation devices typically have stainless steel tube with a mercury vapor lamp, running inside along the length of the tube. An ultraviolet light type AQOAPRO (USA), the lamp power is 14 W and emits radiation basically at 253 nm was used in the experimentation of this study.

Initially, the OMW was treated with UV radiation with determining COD on different period of time (15, 30, 45, 60, 90 min.). Then we repeated the previous step with ozonation process (O_3). The ozone gas stream was then fed into the reacting medium with a constant flow rate of 40 dm^3/h. afterwards; the treating process was with both UV and O_3. Finally, H_2O_2 (2% Conc.) was added to the OMW in a dose of 2 ml/dm^3 with UV. Then the COD was measured on different times. The stage three studied the COD removal from OMW using the effect of the AOPs after the coagulation process, under the same conditions of the previous steps at pH = 8. In the fourth stage, the AOPs were used before the coagulation.

The treatment processes are achieved in 4 L stirred tank reactor as shown in Fig. 1. In order to evaluate the reduction of organic pollutants content, the percentage of COD removal is calculated as

$$\% \text{ COD} = \frac{\text{COD}_\text{i} - \text{COD}_\text{f}}{\text{COD}_\text{i}},$$

where the subscripts i and f indicate initial and final state, respectively. The following chemicals were used in determination of COD: $K_2Cr_2O_7$, H_2SO_4,$HgSO_4$,-$Fe(NH_4)_2\ (SO_4)_2$ (Sigma).

4. Results and discussion

4.1. Coagulation

All experiments were generated at a 10% solution of the OMW. In order to observe how COD removal changes with variation of pH, the value of pH was varied from 5.6 to 9 as presented in Fig. 2. Also, different type of coagulants were used, $Al_2(SO_4)_3$ and $FeCl_3+Fe_2(SO_4)_3$.

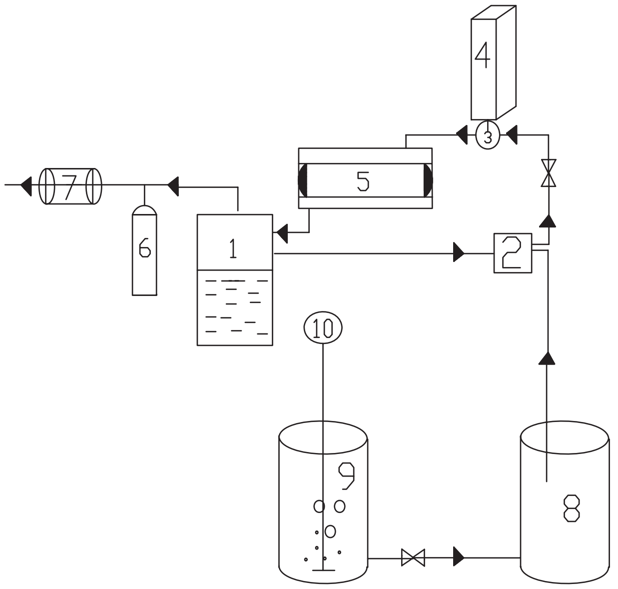

Fig. 1. Experimental setup: (1) chemical oxidation tank, (2) peristaltic pump, (3) diffuser valve, (4) ozone generator, (5) UV emitting device (6) KI trap (7) ozone destruction (8) sedimentation unit (9) p^H adjustment, and coagulation unit (10) mixer.

For each value of pH, the percentage of the COD removal was measured. The results obtained for each coagulant and for CaO, were plotted as shown in Fig. 2. It has been observed that the percentage of COD removal depends on the treatment process for both types of coagulants. In general, the plot of COD removal versus pH demonstrates decreasing trend. At pH = 6, the aluminum provided 14% COD removal vs. 16% for iron. For pH = 9, the corresponding value are 54% (Al^{3+}) vs. 58% (Fe^{3+}).

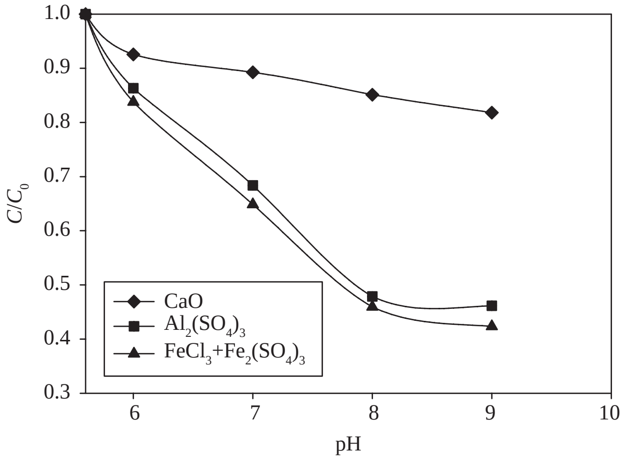

Fig. 2. The change in values of %COD (C/C_0) during pH adjustment and coagulation process of OMW. The coagulants are $Al_2(SO_4)_3$ and $FeCl_3 + Fe_2(SO_4)_3$.

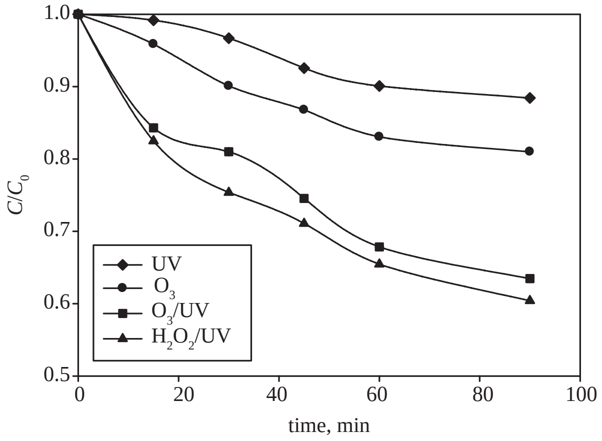

Fig. 3. The change in values of %COD (C/C_0) during AOP_s degradation of OMW at pH = 5.6.

It can be seen that as pH increases, the COD removal is decreases. A maximum value of 58% is reached at pH = 9, which provides the most considerable flocculent of $Fe(OH)_3$. Aluminum ions coagulant behaved differently, the maximal (54%) COD removal from the solution was observed at pH = 9. This can explained, by the fact that under high pH values, $Al(OH)_3$ dissolves in water and forms $[Al(OH)_n]^{-(n-3)}$.

4.2. AOPs

The efficiency of the AOPs was investigated by varying the contact time. The results for COD removal vs. contact time are shown in Fig. 3. The maximum COD removal at pH = 5.6, was about 10% by UV, 19% by O_3, 37% by O_3/UV and 39% by H_2O_2/UV.

The reduction in COD using the O_3/UV and H_2O_2/UV are reasonably satisfactory. We observed that the COD concentration decreases continuously as time increases. Our results are in good qualitatively agreement with those found by Adhoum and Monsoer [25]. The degradation of organic compounds decreased rapidly at the first 45 min. So, it could be concluded that AOPs are good oxidizing agent in the specific destruction of organic compounds of OMW [26,27].

4.3. Combination of coagulation and AOPs

The performance of the combined OMW degradation processes were studied vs the performance of the two conventional single treatment processes. The first tested combined process consisted of the use iron coagulant as a pretreatment stage followed by AOPs. The following AOP methods were studied at pH = 8: O_3, O_3/UV, and H_2O_2/UV. The pH of 8 is the closest to the specifications of treated wastewater. Fig. 4 shows the COD removal in each AOP method. The total COD

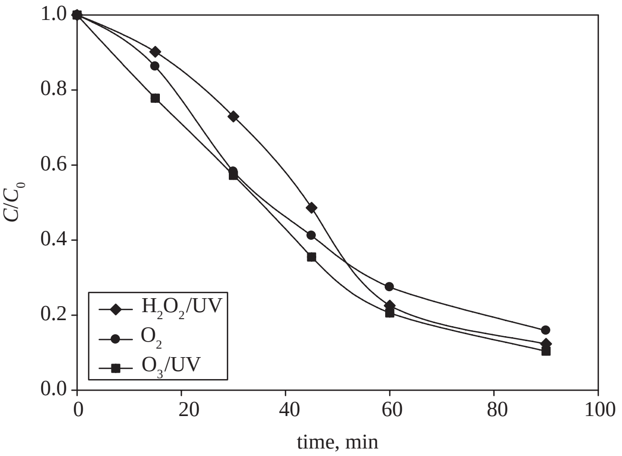

Fig. 4. The change in values of %COD (C/C_0) during AOP$_s$ degradation of OMW after coagulation with $FeCL_3$ + $Fe_2(SO_4)_3$ at pH = 8.

removal by coagulation pretreatment and O_3 was 90%, which is higher than any of the two single processes, under the same operating conditions. With O_3/UV oxidation the COD removal was 95%, By H_2O_2/UV oxidation and coagulation pretreatment, COD removal of 94%. The value of COD was reduced from 12.1 to 0.5 g/dm^3. This value is acceptable to Jordan standards and specification for treated industrial wastewater [28].

The second tested combined process consisted of the use of aluminum as coagulant at pH = 8, for pretreatment followed by AOPs. As seen from Fig. 5 the COD removal of 88%, 94% and 91% was achieved by using the following AOP processes: O_3, O_3/UV and H_2O_2/UV, respectively. These results are higher values than that achieved by either single process under the same conditions. This suggests that coagulation pretreatment process enhances the subsequent advanced oxidation.

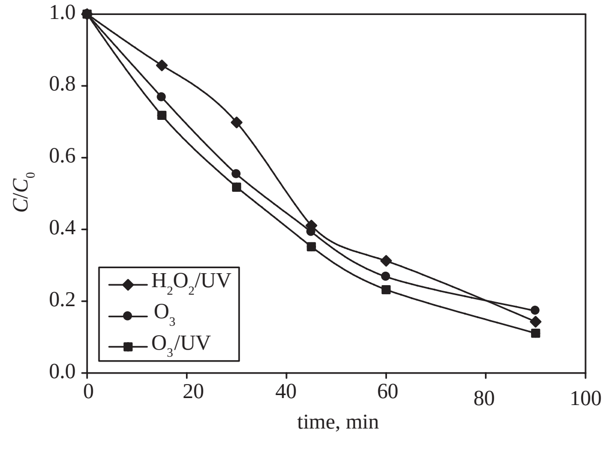

Fig. 5. The change in values of % COD (C/C_0) during AOP$_s$ degradation of OMW after coagulation with $Al_2(SO_4)_3$ at pH = 8.

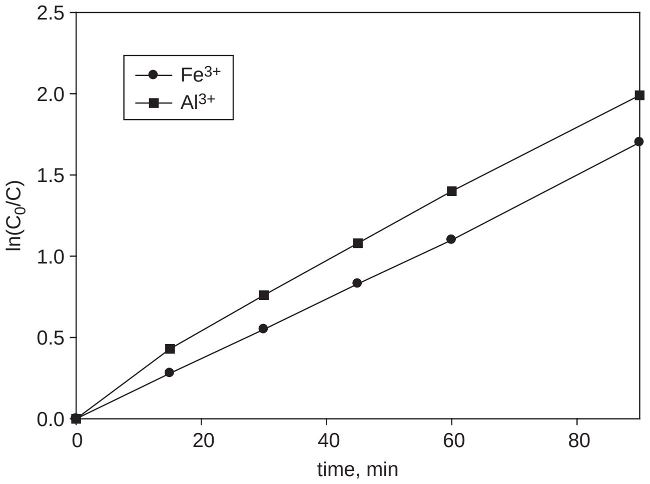

Fig. 6. Ozonation of OMW after coagulation. Determination of apparent kinetic constants of pseudo order reaction.

The oxidation by AOPs of the dissolved organic substance contained in OMW is a complex process. However, the total consumption of ozone by the organics can represented by a simple irreversible reaction in the form:

$$\text{Organics} + O_3 \longrightarrow \text{Non-Organic Compound.} \tag{1}$$

By assuming that this reaction follows pseudo-first order kinetics with respect to the organic compounds concentration, the reduction in concentration can be obtained by the following equation

$$dC/dt = -kt, \tag{2}$$

which can be integrated between $t = 0$ and $t = \text{i}$, yielding:

$$\ln C/C_0 = -kt. \tag{3}$$

Fig. 6 shows plot of $\ln(C/C_0)$ vs. time. The correlation coefficient R^2 was found 0.974 and 0.952 for $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, respectively. In contrast, the curve fitting of the experimental data using the linearized equation of second-order kinetic model (it does not plot in Fig. 6) has lower values of correlation coefficients than the first order. This confirms the applicability of the first-order kinetic model to the advanced oxidation of OMW trend agrees with the results of Glaze [19].

5. Conclusions and Recommendations

The present work showed that over the range of operating conditions tested, single-advanced oxidation achieved a moderate reduction in the removal of COD. A higher removal levels were obtained using single coagulation process. The combination of the two processes, however, achieved higher COD removal efficiencies than either single stage treatment process under the same operating conditions. The test results confirmed that pseudo-first order kinetics with respect to the organic compounds concentration can be used to model the reduction of the COD concentration. Thus the kinetic parameters are helpful for the design of the treatment plant reactors.

References

[1] N. Adhoum and L. Monsoer, Chem. Eng. Process, 43 (2004) 1281.
[2] M. Hamdi, A Rev.. Bioproc. Eng., 8 (1993) 209.
[3] D.M. Gonzales, E. Moreno, Q.J. Sarmiento and R.A. Cormenzana, Chemosphere, 20 (1990) 423.
[4] D.J. Perez, E. Esteban, M. Gomez and F. Gallardo-Lara, Environ. Sci. Health, B 21, 4 (1986) 349.
[5] M.M.A. Rodriquez, J. Perez, A. Ramos-Cormenzana and J. Martinez, J. Appl. Bacteriol., 64 (1988) 219.
[6] Marco S. Lucas and José A. Peres, J. Hazard. Mater. 168 (2009) 1253.
[7] J. García, F. Diez and J. Coca, Ing. Quím., 238 (1989) 151.
[8] RSS, Wastewater from olive mills: reducing environmental impacts (Jordan). Royal Scientific Society (RSS), Environmental Research centre (ERC), Amman, Jordan (1997).
[9] R. Weber and E. Smith, Environ. Sci. Technol., 20 (1986) 970.
[10] A. Safrzadeh-Amiri, J.R, Boiton and S.R. Caer, J. Adv. Oxid. Technol., 1 (1996) 18.
[11] E.A. Vik, D.A. Carlson, A.S. Eikum and E.T. Gjessing, Water Res., 18 (1984) 1355.
[12] Walid K. Lafi, Benbella Shannak, Mohammad Al-Shannag, Zaid Al-Anber and Mohammad Al-Hasan, Sep. Purif. Technol., 70 (2009) 141–146.
[13] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo′ and C. Sáez, Chemosphere, 67 (4) (2007), 832.
[14] S. Sglik, L. Ersoy and S. Imre, Eur. J. Lipid Sci. Technol. 104 (2002) 212.
[15] N. Zouari, J. Chem. Technol. Biotechnol., 73 (1998) 297.
[16] E. Oktav, F. Sengul, A. Ozer, H. Kumbur and O. Zeren, Proceeding of the National Industry-Environment Symposium and Exhibition, Mersin, 25–27 April, Mersin, p.111, 2001.
[17] C. Volk, M. Lechevallier, K. Bell, E. Ibrahim, D. Verges and G. Amy, Water Res., 12 (2000) 3247.
[18] W. Glaze and D. Chapin, Ozone Sci. Eng., 9 (1987) 335.
[19] W. Glaze and J. Kang, Ind. Eng. Chem. Res., 28 (1989) 1580.
[20] W. Glaze, Y. Lay and J. Kang, Ind. Eng. Chem. Res., 34 (1995) 2314.
[21] G. Peyton and W. Glaze, Environ. Sci. Technol., 22 (1988) 761.
[22] M. Trapido, Y. Veressinina, and J. Kallas, Ozone Sci. Eng., 23 (2001) 333.
[23] S. Contreras, M. Rodríguez, E. Chamarro, S. Esplugas and J. Casado, Water Sci. Technol., 44 (2001) 39.
[24] J.D. Box, Water Res., 17 (1983) 511.
[25] N. Adhoum and L. Monser, Chem. Eng. Process., 43 (2004) 1281.
[26] A.S. Stasinakis, Global NEST Journal, 10 (2008) 376.
[27] Walid K. Lafi and Z.Al-Qodah, J. Hazard. Mater., B137 (2006) 489.
[28] Water Authority, Jordanian specification for Industrial wastewater, Jordan (2004).