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# Application of Doehlert matrix to determine the optimal conditions for landfill leachate treatment by electro-Fenton process

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## Abstract

The degradation of recalcitrant organic matter present in landfill leachates (which are hazardous and heavily polluted wastewaters) has been studied by electro-Fenton process using a Pt anode and a carbon felt cathode. This process exhibits great oxidation ability due to the in situ production ability of hydroxyl radicals ($^{\bullet}OH$) at large extent from electrochemically assisted Fenton's reaction which takes place between electrogenerated $H_2O_2$ and $Fe^{2+}$ in homogeneous medium. $H_2O_2$ and $Fe^{2+}$ are generated by simultaneous reduction at the cathode of dissolved $O_2$ and added (at catalytic amount) $Fe^{3+}$ ions. $^{\bullet}OH$ thus generated react on organic pollutants until their mineralization. The optimal operating parameters for the mineralization of organic pollutants have been investigated by using Doehlert matrix. It has been demonstrated that under the optimal conditions determined by this method, electro-Fenton process can lead to an effective mineralization degree of 78% of landfill leachate solution after 8 h oftreatment. The obtained results show the efficiency of the electro-Fenton process to remove organic pollutants from aqueous medium.

*Keywords:*Landfill leachates, Electro-Fenton, Doehlert matrix, Hydroxyl radical, Mineralization.

## 1. Introduction

The degradation of the organic fraction of the municipal solid waste in landfill in combination with the percolation of rainwater [1-2] produces a liquid called leachate. The composition of this leachate depends on a variety of parameters, such as the type of waste, the climatic conditions, the mode of operation, and the age of the landfill [2].

Leachates, which are often defined as hazardous and heavily polluted wastewaters may contains large amounts of organic matter [3] as well as ammonia nitrogen, heavy metals, chlorinated organic and inorganic salts. They have been identified as potential sources of ground and surface water contamination when they are not properly treated [3].

The characteristics of the leachate vary with its composition, volume, and ratio of the biodegradable matter presents [4]. For this reason, young and old landfill leachate fractions have very different features. Calace et al. [5] reported that the young landfill leachate fractions present 70% low molecular weight distributions (<500Da), while the high molecular weight distribution (>10,000 Da) is 18%. Besides, the low and high molecular weight distributions are 28 and 67% respectively in old landfill leachate samples.

According to this result, easily biodegradable components of landfill leachate decrease and constituents having high molecular weights, that are biorecalcitrants, increase in the course of time.

These factors make leachate treatment difficult, so, they needed to be taken into account when different treatment processes are considered.

Alternative treatments have been reviewed [6, 7]. Briefly, leachate can be recirculated to the same landfill [8-10] or treated by different methods: aerobic or anaerobic biological methods and/or nitrification/denitrification, processes [11, 12] in order to remove organic matter and ammonium nitrogen. Biological processes can be effective for young leachate having high $BOD_5$/COD ratio [13]. They are, however, less effective with time due to the formation of biorefractory organic matter and consequently the decrease of $BOD_5$/COD ratio. Accordingly, a variety of physicochemical processes have been used to treat landfill leachates such as coagulation–flocculation [2], adsorption on activated carbon [14, 15], chemical oxidation [16,17], membrane filtration [18,19] and nanofiltration[20].

Recent progress in the removal of toxic and/or persistent organic compounds from polluted water has led to the development of advanced oxidation processes (AOPs). These processes involve chemical, photochemical or electrochemical techniques based on the activation of commonly used chemical oxidants such as $H_2O_2$, $O_3$ or $O_2$ leading to the formation of the highly powerful oxidizing agent, hydroxyl radicals $^{\bullet}OH$) [21-25]. These radicals react with organic pollutants and thus lead to their degradation by hydrogen abstraction reaction (dehydrogenation), electron transfer (oxido-reduction) or electrophilic addition to π systems (hydroxylation) reactions [21, 22].

The most commonly used AOPs for the removal of persistent organic pollutants from water are those based on the Fenton reaction. Among the different Fenton and Fenton-like technologies currently available, indirect electrochemical treatment, namely electro-Fenton process, has appeared to be quite efficient in eliminating organic pollutants from aqueous media [26-30]. This technology uses the Fenton reaction (Eq. (1)) as the source of hydroxyl radicals in which the Fenton reagent, the mixture of $H_2O_2$ and $Fe^{2+}$, is generated electrochemically (Eq. (2)) and/or regenerated throughout the process (Eq. (3)) [22, 31]. Because hydroxyl radical production does not involve the use of harmful chemical reagents which can be hazardous for the environment, this process is environmentally friendly for wastewater treatment and seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutants [21, 22]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + {}^{\bullet}OH \qquad (1)$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$
$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^- \qquad (3)$$

In this study, we applied the electro-Fenton process to the treatment of Tunisian landfill leachate, whose characteristics are reported in Table 1. Thus, the planning of the experimental work for investigating the influence of the principal experimental parameters such as current intensity ($I$), electrolysis time ($t$) and the pH of the solution ($pH$) were chosen as main operating parameters to optimize the removal of chemical oxygen demand (COD) of the leachate solution using the experimental design methodology. Therefore, the optimal conditions for the degradation of organic compounds present in Tunisian landfill leachate were studied by the use of Doehlert matrix [32-35].

**Table 1.** Main physico-chemical characteristics of Tunisian landfill leachate.

| **Parameters** | **Value** |
|---|---|
| $COD_0$ (mg/L) | 10200 |
| pH | 8.15 |
| Conductivity | 39.70 à 23°C |
| [Fe] (mmol/L) | 0.135 |

The “Doehlert uniform shell design” used in this study consists of a set points uniformly distributed in space filling. For two variables, the Doehlert design consists of one central point and six points forming a regular hexagon and therefore situated on a circle. In three dimensions, it can be viewed in as a cube-octahedron.

The total experimental domain is explored through a minimum number of experiments which depends on the number of factors studied: indeed, $k$ factors will require a minimum of $k^2 + k + 1$ experiments. It allows an optimal organization of experiences and, consequently reduction of time and cost [35].

The experimental response of interest associated to a Doehlert matrix (for 3 variables) is represented by a quadratic polynomial model:

$$\mathbf{Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3} \quad (4)$$

where$Y$: experimental response; $X_i$: coded variable; $b_i$: estimation of the principal effect of the factor $i$ for the response $Y$; $b_{ii}$: estimation of the second effect of the factor $i$ for the response $Y$; $b_{ij}$: estimation of the interaction effect between factor $i$ and $j$ for the response $Y$.

The coefficients of this model are calculated in the experimental region (Table 2), using the least squares method:

$$B = (X^{\mathrm{T}}X)^{-1}X^{\mathrm{T}}Y \qquad (5)$$

With $B$, the vector of estimates of the coefficients; $X$, the model matrix; $Y$, the vector of the experimental results and $X^T$: transposed matrix from the matrix of the model A.

The experimental values $U_i$ are calculated from the coded variables $X_i$ using the following formula:

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \times \alpha \qquad (6)$$

where:

$U_{i,0} = \dfrac{U_{i,\max} + U_{i,\min}}{2}$ is the value of $U_i$ at the centre of the experimental region;

$\Delta U_i = \dfrac{U_{i,\max} - U_{i,\min}}{2}$ is the step with $U_{i,\max}$ and $U_{i,\min}$, maximum and minimum values of the effective variable $U_i$, respectively and $\alpha$ is the maximum coded value of $X_i$: $X_1 = 1$; $X_2 = 0.866$; $X_3 = 0.816$.

## 2. Experimental details

### *2.1. Sampling*

Leachate samples were taken with polyethylene bottles from the discharge of BorjChakir (Tunisia). Samples taken were preserved in refrigerator at 4 °C.

### *2.2. Electrochemical apparatus and procedures*

Electrolyses were performed at room temperature with an AX 320 Metrixpotiensiostat/galvanostat in a 400 mL undivided cylindrical glass cell of internal diameter of 8 cm equipped with two electrodes. The working electrode was a carbon felt piece of 132 cm$^2$ (Carbone-lorraine) placed on the inner wall of the cell covering the totality of the internal perimeter. The counter electrode was a platinum grid (4.5 × 3.1 cm) placed on the centre of the cell. Prior to the electrolysis, compressed air was bubbled for 10 min through the solution to ensure its saturation in $O_2$. Electrolyses were carried out under current controlled conditions. The current remained constant during electrolysis. The initial pH of solutions was adjusted by sulphuric acid and its value was measured by a pH glass electrode calibrated with standard buffers at pH values of 4, 7 and 9.

### *2.3. Analytical method*

The mineralization degree of treated leachates was assessed in term of chemical oxygen demand (COD) and was determined by standard dichromate reflux method. Potassium dichromate was added into sample solutions in concentrated $H_2SO_4$ medium and the solution was heated to 170 °C for two hours under reflux. COD values (in mg/L) of the samples are then determined by the instrument C214 multiparameter bench photometer Henna.

## 3. Results and Discussion

### *3.1. Treatment of the landfill leachate*

The optimal conditions of the current intensity (*I*), the electrolysis time (*t*) and the pH of the solution (*pH*) for the mineralization of the organic matter of landfill leachates (in term of solution COD removal) were studied. Referring to the previous work [35], the experimental region investigated is represented in Table 2. The Doehlert matrix for 3 factors is composed by 13 experiments as reported in Table 3. The levels of the independent variables (effective variables $U_i$) were calculated according to the following relations:

$$U_1 = 3\,X_1 + 5 \qquad (7)$$

$$U_2 = \frac{350}{0.866}\,X_1 + 650 \qquad (8)$$

$$U_3 = \frac{1}{0.816}\,X_3 + 3 \qquad (9)$$

***Table 2.*** Experimental region investigated for the Tunisian landfill leachate.

| **Variables** | **Factors ($U_i$)** | **Unit** | **Experimental region** | |
|---|---|---|---|---|
| | | | Minimum value | Maximum value |
| $X_1$ | $U_1$: time | h | 2 | 8 |
| $X_2$ | $U_2$: current intensity | mA | 300 | 1000 |
| $X_3$ | $U_3$: pH | - | 2 | 4 |

***Table 3.*** Experimental design and results of the Tunisian landfill leachate.

| **Experimental n°** | **Time (h)** | **I (mA)** | **pH** | **COD (%)** |
|---|---|---|---|---|
| 1 | 8 | 650.0 | 3 | 55 |
| 2 | 2 | 650.0 | 3 | 19 |
| 3 | 7 | 1000.0 | 3 | 61 |
| 4 | 4 | 300.0 | 3 | 27 |
| 5 | 7 | 300.0 | 3 | 41 |
| 6 | 4 | 1000.0 | 3 | 56 |
| 7 | 7 | 766.7 | 4 | 49 |
| 8 | 4 | 533.3 | 2 | 31 |
| 9 | 7 | 533.3 | 2 | 34 |
| 10 | 5 | 883.4 | 2 | 46 |
| 11 | 4 | 766.7 | 4 | 33 |
| 12 | 5 | 416.6 | 4 | 29 |
| 13 | 5 | 650.0 | 3 | 42 |

The experimental design and results are represented in Table 4. Replicates at the central level of the variables are performed in order to validate the model by means of an estimate experimental variance. The experiment at the centre (experiment number 13) was carried out three times in order to obtain an estimation of the experimental error (Table 4).

***Table 4.***Repeated experiments in the centre of the investigated region.

| **Experimental n°** | **Time (h)** | **I (mA)** | **pH** | **COD (%)** |
|---|---|---|---|---|
| 13 | 5 | 650 | 3 | 42 |
| 14 | 5 | 650 | 3 | 41 |
| 15 | 5 | 650 | 3 | 42 |

According to these obtained results, the coefficients of the polynomial model were calculated using the NEMROD Software [36]:

$$\text{COD (\%)} = 42.4 + 14.8\, X_1 + 14.6\, X_2 - 0.7\, X_3 - 6.4\, X_1^2 + 4.3\, X_2^2 - 6.5\, X_3^2 - 5.0\, X_1X_2 + 7.7\, X_1X_3 - 0.4\, X_2X_3 \qquad (10)$$

The COD removal ratio being defined as fellows:

$$\%COD\ removal = \frac{COD_0 - COD_t}{COD_0} \times 100 \qquad (11)$$

In order to interpret these results, the predicted contour plots (curve of constant response) and the three-dimensional representation of the same plots are given in Figures. 2, 3 and 4.

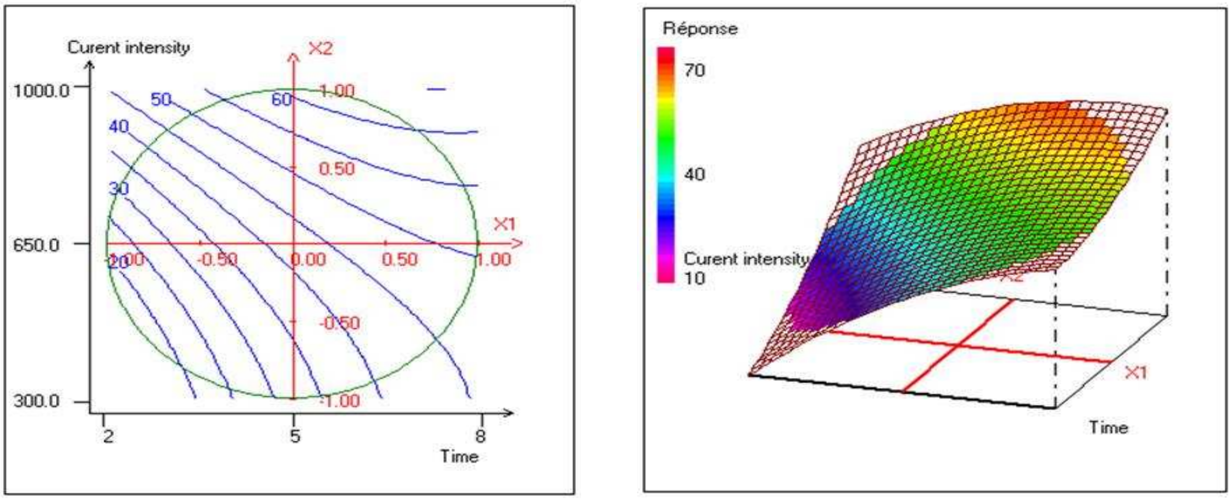

**Figure 1**. (a) Contour plots of COD removal versus electrolysis time (h) and current intensity (mA); (b) Corresponding three-dimensional plot, obtained from Dohelert matrix using the data of Table 2.

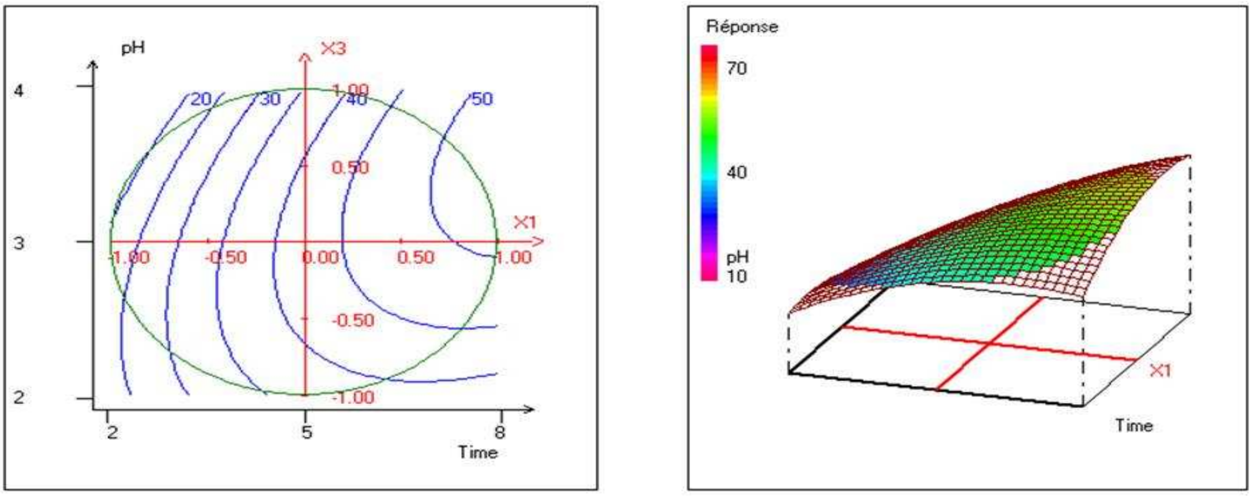

**Figure 2.** (a) Contour plots of COD removal versus electrolysis time (h) and pH of the treated landfill leachate solution; (b) Corresponding three-dimensional plot, obtained from Dohelert matrix using the data of Table 2.

The analysis of the isoresponse curves at the chosen experimental field delimited by a circle show that the maximum of COD removal ratio was obtained with longer electrolysis time and a high value of the current intensity. Indeed, a high applied current accelerates the $H_2O_2$electrogeneration and $Fe^{2+}$ generation rates according to reactions (2) and (3).

Regarding the pH of the solution, the maximum of COD removal ratio was obtained for pH values between 2.5 and 3.5. Indeed, for a pH value upper 3, the concentration of free ferric ion ($Fe^{3+}$ and $Fe(OH)^{2+}$) in the solution decreases due to its precipitation in the form $Fe(OH)_3$ inhibiting thus its regeneration by reaction (3). At pH = 3, the predominant iron species in the solution are $Fe^{3+}$ and $Fe(OH)^{2+}$[37]. The lower pH values (pH < 2.5) disadvantage also the degradation kinetics because the formation of the peroxonium ion ($H_3O_2^+$) [38] according to the Eq. (12), enhancing thus its stability and reducing its reactivity in the Fenton reaction:

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (12)$$

Consequently, the following optimal working conditions are predicted: $I$ = 1000 mA, $t$ = 8 h, $pH$ = 3.

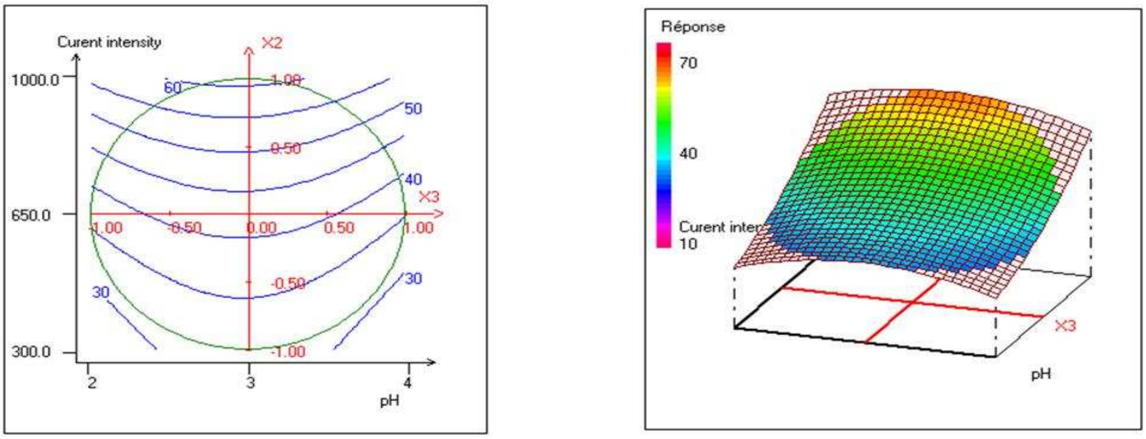

**Figure 3.** (a) Contour plots of COD removal versus current intensity (mA) and pH of the solution; (b) Corresponding three-dimensional plot, obtained from Dohelert matrix of Table 2.

On the basis of these results, the removal of organic matter present in the landfill leachate was investigated as function of the treatment time and results are depicted in Figure.4. This Figure shows that a significant amount of organic matter, i.e. 78% of initial COD was removed after 8 hours of electro-Fenton treatment under optimal operating conditions of $pH$ = 3 and $I$ = 1000 mA for a treatment time of 8 h.

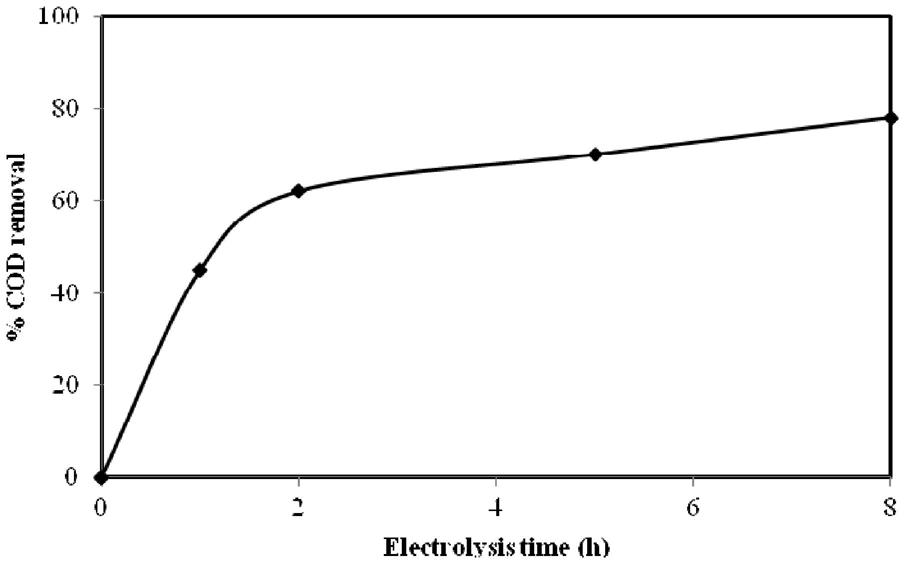

**Figure 4.** Variation of COD removal with electrolysis time during constant current electrolysis of 1000 mA at $pH = 3$.

Figure 4 shows that the COD removal rate (from the Tunisian landfill leachates of BorjChakir) is very high at the beginning of the treatment (during two first hours), whereas it begin slow at longer treatment time. This phenomenon can be explained by contribution of two different factors:

(i) Enhancement of the parasitic reactions consuming $^{\bullet}OH$, the concentration of organic matter being low, the wasting reactions such as reactions (13) and (14) becomes competitive with the reaction between $^{\bullet}OH$ and organic matter.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (13)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \qquad (13)$$

(ii) Formation of recalcitrant oxidation by-products such as short-chain carboxylic acids and their complexes with Fe(III) which are recalcitrant to mineralization by $^{\bullet}OH$ which increases the mineralization ability of the process.

On the other hand the mineralization degree of 78% can be considered a very good result, since at this level of treatment the initial aromatic pollutants which are in the origin of the toxicity were already destroyed by ring opening reactions leading to the formation of short-chain carboxylic acids as showed previously by several reports [22, 26-31] and the remaining carbon content of the solution is composed of these non-toxic and biodegradable compounds. The total mineralization of electro-Fenton treated solution can then achieved by biological treatment if wanted, but such a solution can also be introduced to the natural water system.

## Conclusion

In the electro-Fenton process, the Fenton's reagent was electrochemically generated in aqueous solution, thereby leading to an efficient and continuous $^{\bullet}OH$ production. This system was successfully applied to the removal of organics matter of landfill leachate. The experimental design methodology was used in this work to determine the optimal operating conditions for the efficient mineralization of the organic matter contained in landfill leachate. The use of Doehlert matrix permitted to determine the optimal conditions for treatment of Tunisian landfill leachates of BorjChakir as $I$ = 1000 mA, treatment time = 8 h and $pH$ = 3. Application of these operating conditions yielded a mineralization degree of 78% in term of COD removal, the residual COD being composed of non-toxic and biodegradable short-chain carboxylic acids.

These results show that the electro-Fenton process is a viable environmentally friendly technology for the efficient treatment of landfill leachates and can be generalized to remediation of wastewaters because the strong oxidizing agent generated by the process is a non-selective reagent.

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