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Removal of phenolic compounds from olive mill wastewater by a Fenton-like system $H_2O_2/Cu(II)$—thermodynamic and kinetic modeling

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ABSTRACT

The degradation of olive mill wastewater was investigated by a Fenton-like process using Cu (II) as a catalyst and hydrogen peroxide as an oxidant. Phenolic compounds degradation increased from 43% at 30˚C to 62% at 50˚C after 65 min treatment. Nonlinear regression methods allowed to accurately describe the experimental results and among the tested models, namely Lewis, Page-modified, Henderson/Pabis, and diffusion models, the most appropriate was found to be the Lewis model. The degradation was found to follow a first-order kinetic and the activation energy was 21 kJ/mol.

Keywords: Olive mill wastewater treatment; H_2O_2/Cu^{2+}; Polyphenols; Microwave; Nonlinear regression; Activation energy

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1. Introduction

In Algeria, olive mill wastewater (OMW) does not undergo any treatment and are often dumped in nature. This leads to a negative impact on the environment which results in plugging soil, pollution of surface, and the release of odors. These environmental problems are attributed to the richness of the effluent in organic matter, especially polyphenols [1].

Although there is no perfect solution for the treatment of vegetable water, some processes seem to be more effective than others. Time and technical constraints drive the choices made by researchers. The available methods of treatment to eliminate the pollution load of OMW can be classified as physical, chemical, and/or biological, with advantages and disadvantages for each of these methods. The search for alternative or complementary treatment methods have led to the emergence of new technologies. Among these technologies, the so-called advanced oxidation processes (AOP) are booming.

The oxidation of organic compounds is one of the recent processes which led to the advancement in the treatment of wastewater. AOP are based on the production and the use of a very reactive and non-selective oxidizer, the hydroxyl radical. Its mode of action is based on the substitution of hydrogen atoms, electron transfer or electrophilic addition. Complex organic molecules are either processed in more advanced oxidation products than the original compounds or completely mineralized into CO_2 and H_2O.

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Depending on the mode of production of hydroxyl radicals, AOP include a variety of types of oxidation in homogeneous or heterogeneous phases. Regarding the former processes, the following systems can be quoted: Fe(II)/H_2O_2 (Fenton reaction) [2], O_3/OH (ozonation) [3], O_3/H_2O_2 (peroxonation) [4], H_2O_2/UV (photolysis of H_2O_2) [5], Fe(II)/H_2O_2/UV (photo-Fenton), while regarding heterogeneous phases TiO_2/UV [6], ZnO/UV [7], etc. In addition, some other advanced processes involving electricity can be cited, such as the electro-Fenton and sonolysis oxidation processes [8].

Fenton's reagent H_2O_2/Fe(II) has been extensively studied for the remediation of organic matter in different types of wastewater, industrial and agricultural waste, surfactants, and polluted soils. These applications are limited by the need to operate at acidic pH. To overcome these problems, the degradation process by H_2O_2/Cu (II) system has been chosen. The latter, unlike the H_2O_2/Fe(II) system, gives good results in a wide pH range [9].

In the present work, the treatment of OMW by an advanced oxidation process based on H_2O_2/Cu (II) system was carried out. The evolution of the rate of phenolic compounds during processing at different temperatures has been followed and the kinetic process has also been examined. To our knowledge, no mathematical model has been proposed to study the degradation of organic matter in OMW by H_2O_2/Cu (II) system. For this reason, four models have been proposed and tested to fit experimental data.

2. Materials and methods

2.1. OMW characterization

Fresh OMW was obtained from an olive oil continuous processing plant located in Tizi-ouzou (northern Algeria). OMW was collected in a closed plastic container and stored at 4°C. Experiments were conducted on the decanted and diluted OMW characterized by pH 4.7, the COD and the total polyphenol amounts were 74 g/L and 20.56 g/L, respectively. All used chemicals were of analytical grade.

2.2. Treatment procedure

Tests were performed in a 500 mL vessel surrounded by a glass cylindrical jacket, allowing water-cooling of the reactor at natural pH according to Rivas et al. [10] and Gulkaya et al. [11]. In all experiments, the treated volume of OMW solution was 100 mL. A 10 mL of H_2O_2 (12 M) and 10 mL of copper (0.5 g/L) were added according to the optimal conditions found by Iboukhoulef et al. [12]. The mixture was stirred at a given agitation speed of 400 rpm (conventional method). The choice of the temperature is important because at 20°C the reaction is slow, while beyond 50°C hydrogen peroxide decomposes into H_2O and O_2 [11,13]. The following range of temperatures was therefore tested, 30, 35, 40, and 50°C. Phenolic compounds were quantified by means of the Folin–Ciocalteu colorimetric method [14]. Gallic acid was used for the calibration, and the results of duplicate analyses are expressed as gallic acid equivalent with $R^2 = 0.997$.

3. Results and discussion

3.1. Phenolic compounds degradation

The evolution of the rate of phenolic compounds expressed as the ratio (C/C_0) in OMW treated with H_2O_2/Cu (II) system is given in Fig. 1. C_0 and C are the concentrations of phenolic compounds (g/L) at the initial time and a given time t.

Examination of the results showed a rapid degradation of phenolic compounds of OMW at the beginning of treatment; it can be also noted that this degradation increased significantly with the temperature of the system. After 65 min of reaction, 43 and 62% of the phenolic fraction were degraded at 30 and 50°C, respectively. These results are in agreement with those found by Lucas and Peres [5] during the degradation of organic matter of OMW by H_2O_2/Fe (II) system. With the same system, Bautista et al. [15] showed that the carbon removal increased with the

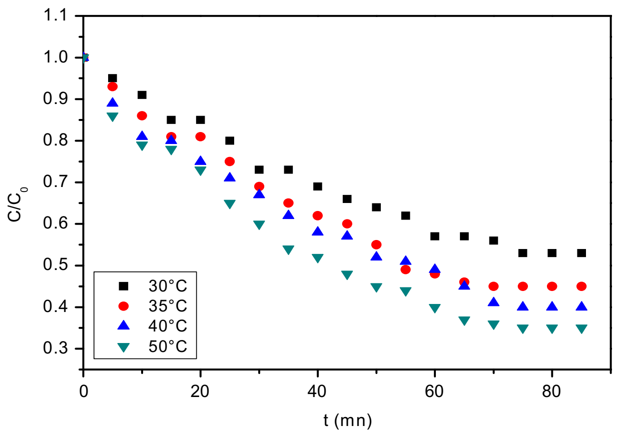

Fig. 1. Degradation of phenolic compounds: OMW + (H_2O_2: 12M) + (Cu (II): 0.5 g/L) + magnetic stirring (400 rpm).

temperature of the reaction mixture in the treatment of water resulting from the cosmetic industry.

These results indicated that the increase in temperature promoted the oxidation phenomenon by H_2O_2/Cu system. However, the efficiency of this treatment remains low compared with that obtained under microwave irradiation; the process assisted by microwave leads to higher elimination rate in a very short reaction time [12].

3.2. Mathematical modeling

Some mathematical models used to describe the falling rate period of drying can be used to monitor the treatment of OMW [16]. The models selected for this study are those of Lewis, Page-modified, Henderson/Pabis and diffusion. All these models are first written as a function of dimensionless ratio $(C-C_\infty)/(C_0-C_\infty)$, where C_∞ is the concentration at time $t=\infty$. Constants for each model were determined using the nonlinear regression method (Statistica 7). The selected models are given in Table 1.

To evaluate the goodness-of-fit of the experimental results by the models, the values of the coefficient of determination (R^2), chi-square (χ^2), and the mean square error (MSE) were determined. The best fit corresponds to the highest value of R^2 and the smallest χ^2 and MSE. The equations to determine the values of these criteria are:

To simplify the formulas, the following parameter was considered: $R = C/C_0$.

$$\aleph^2 = \frac{\sum_{i=1}^{18} (R_{\text{exp}} - R_{\text{The}})^2}{N - z} \tag{1}$$

$$\text{MSE} = \left(\frac{1}{N}\sum_{i=1}^{18} \left(R_{\text{the}} - R_{\text{exp}}\right)^2\right)^{\frac{1}{2}} \tag{2}$$

R_{exp}: experimental value, R_{the}: calculated value, N: number of observations ($N = 18$), Z: number of constants.

The values of the constants of the mathematical models for the considered temperatures are given in Table 2.

The comparison of experimental results with those calculated by the different models used is displayed in Fig. 2(a–d). All models seem to lead to good fits, showing a good accuracy between experimental and calculated values.

A visual inspection shows that the Lewis (Fig. 3(a)), the Page-modified (Fig. 3(b)), and the diffusion (Fig. 3(d)) models had the majority of the

Table 1
Selected models

Lewis[a]	$\frac{C}{C_0} = \frac{C_\infty}{C_0} + \left(1 - \frac{C_\infty}{C_0}\right) e^{-kt}$	(4)
Page-modified[a]	$\frac{C}{C_0} = \frac{C_\infty}{C_0} + \left(1 - \frac{C_\infty}{C_0}\right) e^{-(kt)^y}$	(5)
Henderson/Pabis[a]	$\frac{C}{C_0} = \frac{C_\infty}{C_0} + \left(1 - \frac{C_\infty}{C_0}\right) b \cdot e^{-kt}$	(6)
Diffusion[a]	$\frac{C}{C_0} = \frac{C_\infty}{C_0} + \left(1 - \frac{C_\infty}{C_0}\right) \left[b \cdot e^{kt} + (1-b) e^{kct}\right]$	(7)

Note: C_0: concentration of phenolic compounds at initial time (g/L); C_∞: concentration of phenolic compounds at equilibrium (g/L); k: kinetic constant (min^{-1}); t: time of degradation (min); b, c, y: constant.

[a] For all models.

Table 2
Constant values and value of R^2, χ^2, and MSE for the various considered models

Model	T (℃)	30	35	40	50
Lewis	K	0.0155	0.0181	0.0210	0.0260
	C_∞/C_0	0.3326	0.2647	0.2671	0.2488
	R^2	0.993	0.988	0.99	0.99
	χ^2	0.00018	0.00043	0.00035	0.00008
	MSE	0.01257	0.01947	0.01776	0.00880
Page-modified	K	0.1230	0.1350	0.1470	0.1620
	y	0.1247	0.1363	0.1452	0.1611
	C_∞/C_0	0.3326	0.2647	0.2670	0.2488
	R^2	0.993	0.988	0.99	0.99
	χ^2	0.00019	0.00045	0.00038	0.00044
	MSE	0.01250	0.01940	0.01770	0.01920
Henderson/Pabis	K	0.0160	0.0180	0.0187	0.0242
	b	1.0081	1.0033	0.9637	0.9735
	C_∞/C_0	0.3463	0.2688	0.2184	0.2300
	R^2	0.993	0.988	0.992	0.991
	χ^2	0.00018	0.00045	0.00029	0.00039
	MSE	0.01230	0.0190	0.01580	0.0180
Diffusion	K	0.0220	0.02035	0.3369	0.0239
	b	−27.079	−61.374	0.0684	0.0547
	c	0.9802	0.9910	0.0225	0.0159
	C_∞/C_0	0.4391	0.3584	0.1424	0.2043
	R^2	0.992	0.988	0.993	0.99
	χ^2	0.00023	0.00050	0.00028	0.00046
	MSE	0.01345	0.01980	0.01148	0.01900

points aligned on the first bisector, while the adjustment given by the model of Henderson/Pabis was worse because it has more points that deviate from the bisector.(Fig. 3(c)).

The values of the coefficient of determination (R^2), the chi-square (χ^2), and the mean square deviations (MSE) calculated for each model and for each temperature are collected in Table 2. To identify the model that led to the best results, the range of variations of these criteria are compiled in Table 3. All models showed no difference in the variation of the coefficient of determination (R^2 ranged 0.988 and 0.993). Only the chi-square and MSE can be helpful to identify the most relevant model. The Lewis model seems to be the most appropriate to describe the degradation of phenolic substances, since it led to the lowest values of χ^2 and MSE, 0.00008–0.00043 and 0.00880–0.01947, respectively. It should be noted that the Lewis model corresponds to the first-order kinetic model. The rate constant found at 30℃ using this model was $k = 0.0155$ mn^{-1}. This value was in the range of values reported in the literature since lower than that given by Lucas and Peres ($k = 0.052$ mn^{-1}) [5] in the treatment of OMW by $H_2O_2/Fe(II)$ and superior to that found by Badawy et al. ($k = 0.0085$ mn^{-1}) [17] in the removal of organophosphorus pesticides from wastewater by $H_2O_2/Fe(II)$.

3.3. Activation energy

The values of the constant K calculated by the Lewis model can allow to identify the parameters of the Arrhenius equation:

$$K = A \cdot e^{-\mathrm{Ea/RT}} \tag{3}$$

where K is the kinetic constant, Ea is the activation energy (J/mol), A is the frequency factor (min^{-1}), R is the gas constant (J/mol K), and T is the absolute temperature (K).

The Arrhenius equation written as $\ln K = \mathrm{f}\ (1/\mathrm{T})$ provides a straight line with a slope (−Ea/R) and intercept ln$A$ (Fig. 4). The value of the activation energy found (21 kJ/mol) was close to that given by Lucas and Peres [5] (28.2 kJ/mol) in the treatment of OMW by $H_2O_2/Fe(II)$ system, while this value was

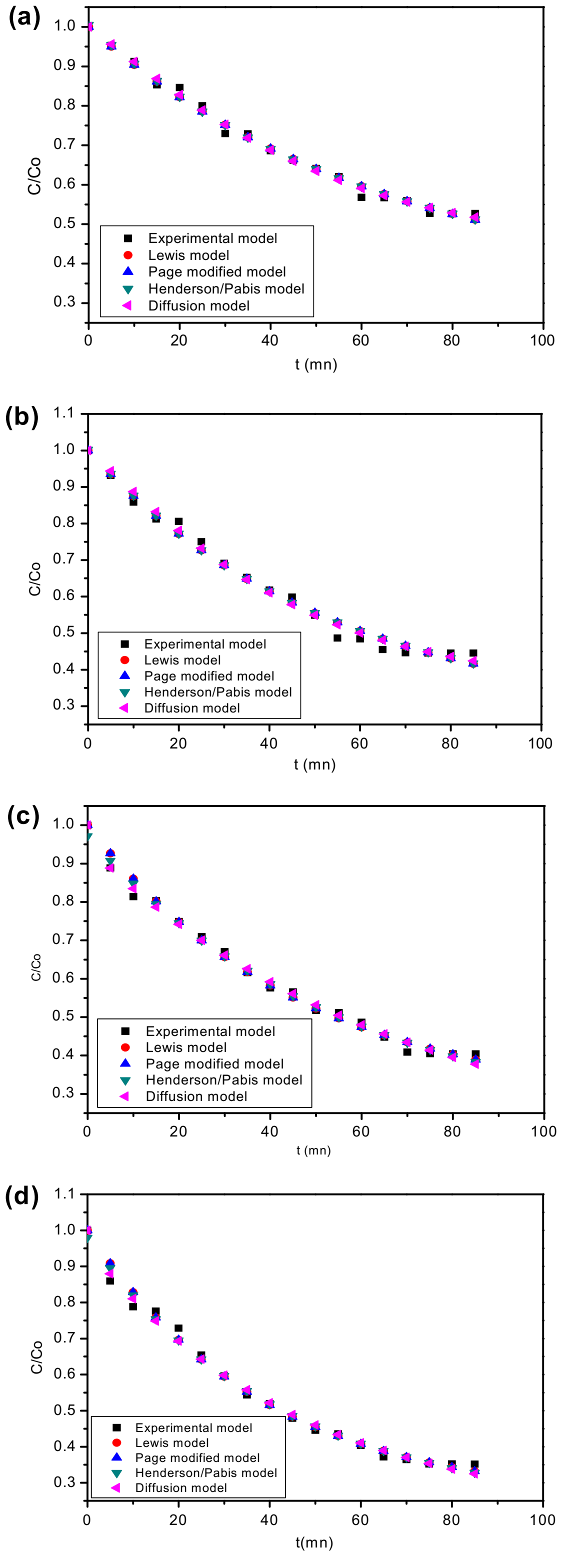

Fig. 2. Time-courses of the experimental and calculated values of phenolic compounds for the various tested temperatures. (a) 30˚C; (b) 35˚C; (c) 40˚C; and (d) 50˚C.

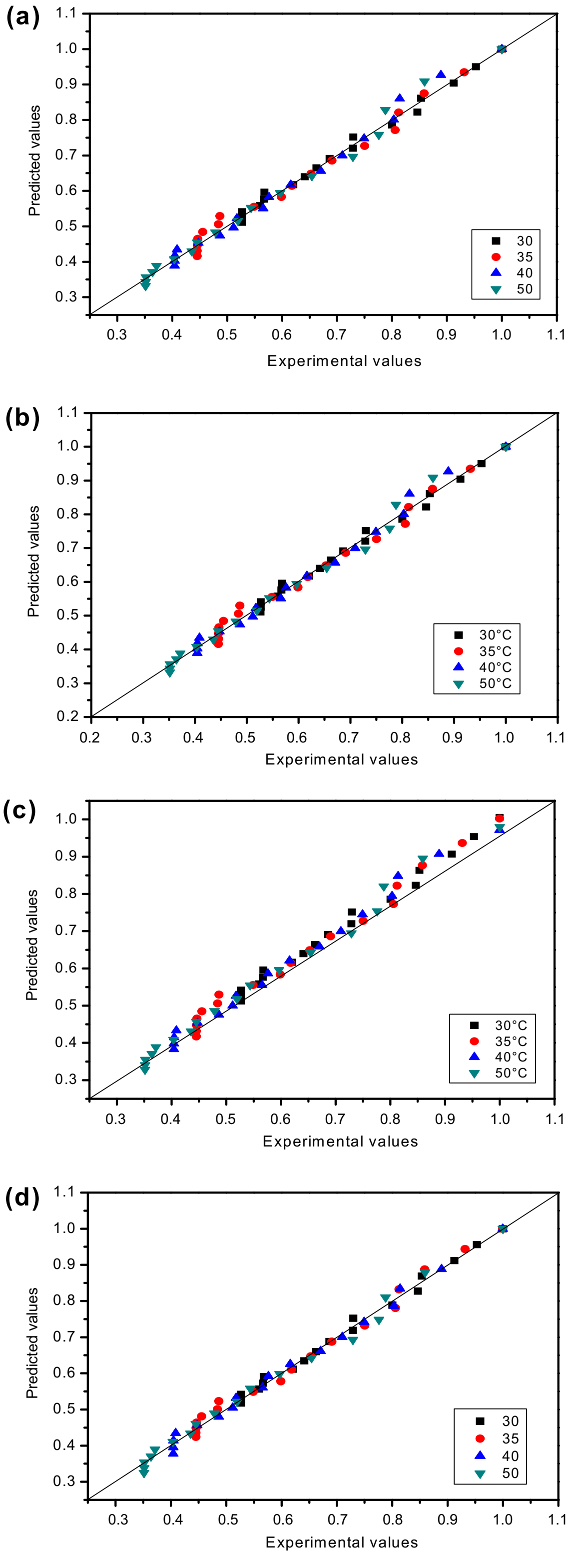

Fig. 3. Comparison between experimental and calculated values for the various considered models: (a) Lewis model; (b) Page-modified model; (c) Henderson/Pabis model; and (d) diffusion model.

Table 3
Comparison of criteria for the various models

Model	R^2	χ^2	MSE
Lewis	0.988–0.993	0.00008–0.00043	0.00880–0.01947
Page-modified	0.988–0.993	0.00019–0.00045	0.01250–0.01940
Henderson/Pabis	0.988–0.993	0.00018–0.00045	0.01230–0.01900
Diffusion	0.988–0.993	0.00023–0.00050	0.01148–0.01980

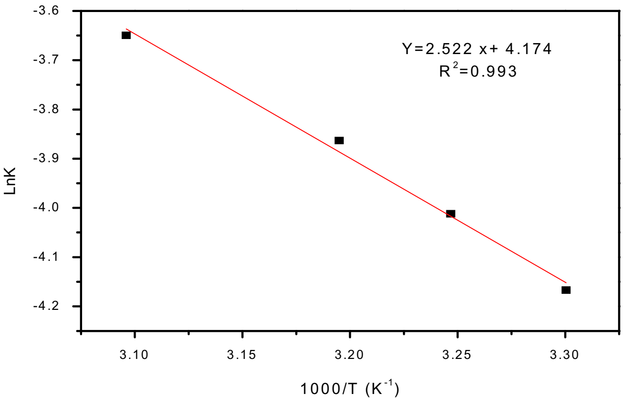

Fig. 4. Determination of the activation energy.

2.4-fold smaller than that obtained by Bautista (50.7 kJ/mol) using H_2O_2/Fe(II) system for the treatment of water from the cosmetic industry [15].

4. Conclusion

The results showed that the treatment of OMW by H_2O_2/Cu(II) system by the conventional method depends on the reaction temperature. Indeed, the removal yield of polyphenols increased from 43% at 30˚C to 62% at 50˚C after 65 min treatment. Nonlinear regression method allowed to accurately describe the experimental results and among the tested models the most appropriate was found to be the Lewis model. The degradation was found to follow a first-order kinetic and the activation energy determined from the Arrhenius equation was found to be 21 kJ/mol.

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