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Optimization of the Degradation of Hydroquinone, Resorcinol and Catechol Using Response Surface Methodology

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Abstract

A clay catalyst (montmorillonite and kaolinite) was prepared and used to degrade three phenolic compounds: hydroquinone, resorcinol and catechol obtained from the treatment the Olive Mill Wastewater (OMW) generated in the production of olive oil. The operating conditions of the degradation of these compounds are optimized by the response surface methodology (RSM) which is an experimental design used in process optimization studies. The results obtained by the catalytic tests and analyses performed by different techniques showed that the modified montmorillonites have very interesting catalytic, structural and textural properties; they are more effective for the catalytic phenolic compound degradation, they present the highest specific surface and they may support iron ions. We also determined the optimal degradation conditions by tracing the response surfaces of each compound; for example, for the catechol, the optimal conditions of degradation at pH 4 are obtained after 120 min at a concentration of H_2O_2 equal to 0.3 M. Of the three phenolic compounds, the kinetic degradation study revealed that the hydroquinone is the most degraded compound in the least amount of time. Finally, the rate of the catalyst iron ions release in the reaction is lower when the Fe-modified montmorillonites are used.

Keywords

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1. Introduction

All over the world, domestic and industrial discharges and agricultural pollution have greatly contributed to deteriorating surface and groundwater quality. These pollutants have an important impact on the environment and human health. Significant efforts have been made to reduce pollutant discharges by promoting clean technologies in industrial sectors and by cleaning up waste gas and waste water before discharging them into the environment [1].

The latest advances in water treatment have been achieved in the oxidation of organic compounds [2] [3] including phenolic compounds which are harmful to the environment and to human health [4] [5].

For example, the Advanced Oxidation Process (AOP) is based on the *in situ* formation of highly reactive chemical entities such as hydroxyl radicals (OH·). These radicals possess a high power of oxidation of organic molecules to CO_2 and H_2O [6] compared to conventional oxidants like Cl_2, ClO_2 or O_3. These radicals are able to mineralize, partially or totally, most phenolic compounds. The AOP includes oxidation processes in the following:

- Homogeneous phase: Fe^{2+} (Fe^{3+})/H_2O_2, O_3/OH^- and O_3/H_2O_2 [7]-[9],
- Photochemical processes: UV alone, H_2O_2/UV, H_2O_2/Fe^{2+}(Fe^{3+})/UV, photo-Fenton, TiO_2/UV, O_3/UV [10]-[14],
- Direct electrochemical processes [15] [16],
- Indirect electrochemical processes [17]-[20].

Concerning the Fenton reagent (Fe^{2+} (Fe^{3+})/H_2O_2), applications are limited and they are destined specifically for industrial waste water treatment and contaminated soils depollution. The main limitations of this system include the need to operate at acidic pH (pH approximately 3), the need to use large quantities of chemical reagents and the formation of ferric hydroxide [21].

By using iron supported on clays, through different procedures such as impregnation, intercalation or insertion, in the catalytic oxidation, the effectiveness of this system is significantly increased and the doses of reagents are reduced [1] [22]. This study has several objectives. Initially, this study aims to improve the degradation of three phenolic compounds, namely, hydroquinone, resorcinol and catechol using Fenton-type catalysts. This study also aims to optimize the degradation operating conditions of the response surface methodology (RSM) and to study the degradation kinetics by three types of catalyst (pillared montmorillonite, intercalated montmorillonite and impregnated kaolinite). Finally the study investigates the catalytic performance of solid catalysts by characterizing them with different techniques.

2. Experimental

2.1. Materials and Instrumentation

Two commercial clay products, montmorillonite K10 and kaolinite powder, were provided by Aldrich and Parachimic, respectively. Iron (III) solution was prepared by dissolving iron hydrochloric hexahydrate ($FeCl_3$, $6H_2O$; 99%; Merck) in purified water and for the catalytic test hydrogen peroxide solution (>30 wt%, CHEMIPHARMA) was used.

The phenolic compounds were analysed by a standard HPLC instrument Younglin Acme 9000 (Eclipse column type C-18 5 μm 4.6 × 250 mm, wavelength: 254 nm, at an injection volume of 20 μL, mobile phase: methanol-water: 60/40). XRD (X'PERT Pro Philps Analytical diffractometer), surface area analysis by volumetric adsorption of nitrogen (ASAP 2000 Micromeritics), and atomic absorption spectroscopy (Novo 400 Analytikjena) were performed to characterize the resultant powders.

2.2. Catalyst Preparation

We used two types of clay to prepare the catalysts: a swelling (montmorillonite) and a non-swelling clay (kaolinite) which were prepared according to protocols I and II (**Figure 1** and **Figure 2**) corresponding to the intercalation of montmorillonite, its bridging and the impregnation of kaolinite.

2.3. Catalytic Conditions

The catalytic test is done by preparing phenolic compounds solutions ([phenolic compound] = 50 mol·L^{-1})
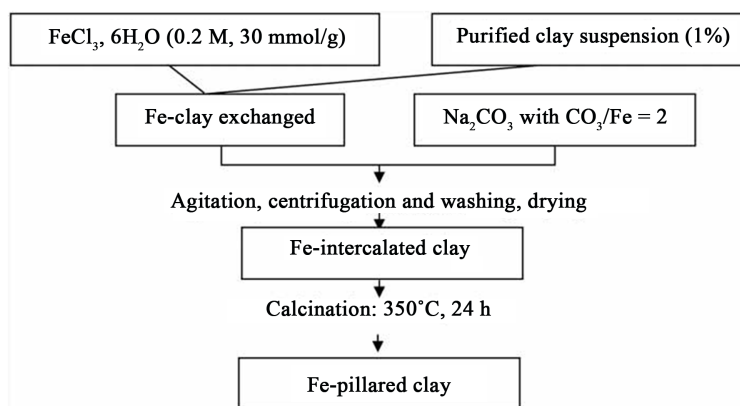
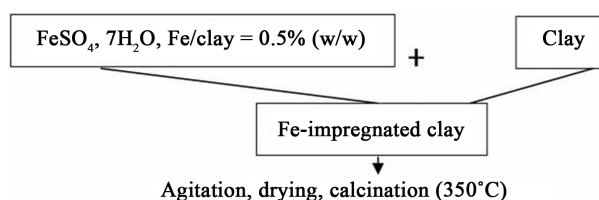Figure 1. Preparation protocol of Fe-modified montmorillonite.

Figure 2. Preparation protocol of Fe-impregnated kaolinite.

changing the pH values (the pH were adjusted with NaOH or HCl) and adding Fe-powder (0.3 g) to the different prepared solutions using magnetic stirring to maintain a uniform suspension.

After 10 min, varying concentrations of H_2O_2 were added into the reactor and time logged.

2.4. Investigation of Iron Release Conditions

After the three phenolic compounds degradation test ([phenolic compound] = 50 mol·L^{-1}, ambient temperature and pressure, pH = 6, catalyst mass = 0.3 g, 2 mL of [H_2O_2] = 0.26 M, solution volume = 200 mL), the solution was recovered and analyzed by atomic absorption to determine the amount of iron leached from the catalysts.

3. Result and Discussion

3.1. Optimization of Degradation of Phenolic Compounds by RSM

The general practice for optimizing the operating conditions for this process consists of varying one parameter and keeping the other ones constant. The major disadvantage of this single variable optimization is the disregard of interactive effects between the variables. In order to overcome this problem, optimization studies have been carried out using RSM. The theory behind RSM has been reviewed [23] [24].

This technique is an integration of experimental strategies, mathematical methods and statistical inference to determine the optimal level giving the most interesting response. RSM reduces the number of experimental trials needed to evaluate multiple parameters and their interactions and is therefore less laborious and time consuming than other approaches. RSM has been widely applied for optimizing processes in different domains such as the chemical process, geotechnical engineering and animal science research [25]-[27]. The phenolic compounds degradation is governed by several physicochemical factors. The selected factors and their corresponding ranges can be found in Hamzaoui, Jamoussi, M'nif and Missaoui Ines [28] [29].

3.1.1. Central Composite Design

The applied optimization approach is based on a central composite design and RSM, this method is one of the most important experimental designs used in process optimization studies [30]. In order to describe the nature of the response surface in the optimum region, a central composite design with five coded levels was performed (−1.68, −1, 0, 1, 1.68) and three factors (t: time (min), C: concentration of H_2O_2 (mol·L^{-1}) and pH)) were selected

and processed simultaneously through the central composite design.

In general, central composite designs need a total of ($2^k + 2k + N_0$) runs where k is the number of studied factors, 2^k are the points from the factorial design, 2k the face-center points and N_0 the number of experiments carried out at the center (**Figure 3**). As usual, the experiments were carried out in random order to minimize the effect of systematic errors.

The parameter levels and coded values are given in **Table 1**. Fifteen experiments were performed corresponding to the three variables central composite design (**Table 2**). An example of the graphical representations of the distribution of these experimental points is given in **Figure 4** [30]. The measured response was defined as degradation rate in %.
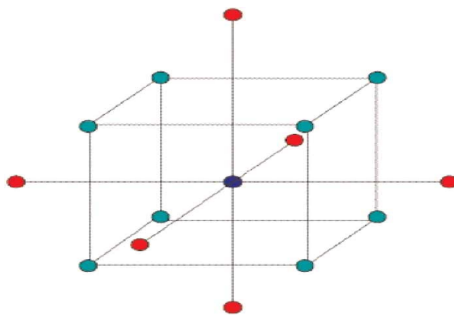

Figure 3. Spatial representation of a complete centred composite design with three factors.

Table 1. Parameter levels and coded values used in the experimental design.

Parameters	Code	$+\alpha = +1.68$	$+1$	0	-1	$-\alpha = -1.68$
Time (min)	X_1	12.8	40	80	120	147
Concentration of H_2O_2 (mol·L^{-1})	X_2	0	0.02	0.11	0.2	0.26
pH	X_3	0.64	2	4	6	7.36

Table 2. Experimental design and response value.

| Experimental number	Time (min)	Concentration of H_2O_2 (mol·L^{-1})	pH	Degradation rate (%) of		
				Hydroquinone	Resorcinol	Catechol
1	120	0.2	6	85.66	0.86	3.92
2	40	0.2	6	86.73	4.16	28.48
3	120	0.02	6	79.50	0	84.08
4	40	0.02	6	100.00	0	86.35
5	120	0.2	2	60.31	0	18.10
6	40	0.2	2	77.21	50.12	15.40
7	120	0.02	2	57.74	39.89	3.62
8	40	0.02	2	100.00	60.43	53.83
9	80	0.11	4	58.10	33.96	48.55
10	147	0.11	4	51.10	25.81	48.51
11	12.8	0.11	4	53.57	33.73	48.63
12	80	0.26	4	67.82	0	10.36
13	80	0	4	60.20	69.20	67.82
14	80	0.11	0.64	60.82	44.30	64.71
15	80	0.11	7.36	72.02	48.75	22.33
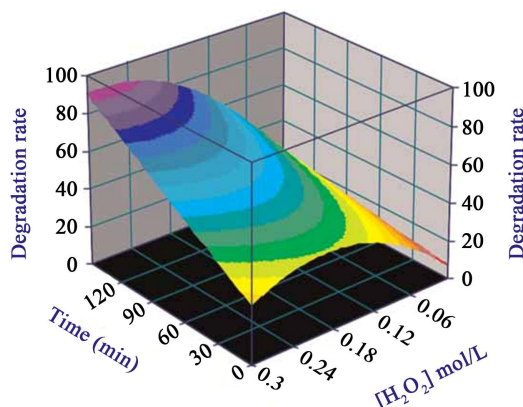
Figure 4. Three-dimensional plots for catechol degradation as a function of [H$_2$O$_2$] and time, pH = 4.

3.1.2. Determination of Optimal Conditions

The quadratic response surface for the three factors involved generates a four-dimensional response surface, which can be illustrated in a three-dimensional (3D) response surface. For this, we used the software MAPLE 9.5. The surfaces were obtained by varying an experimental factor each time while keeping the third constant at its central value.

The visualization of these surfaces allows studying of the influence of each parameter and determining the optimal operating conditions to degrade the phenolic compounds, the subject of this study. An example of a graphical representation of the experimental points distribution of catechol degradation as a function of [H$_2$O$_2$] and time at Ph = 4 is given in **Figure 4**. The measured response was defined as the degradation of phenolic compound in %.

3.2. Characterization of Fe-Modified Clays

3.2.1. Textural Characterization

Measurement of specific surface S$_{BET}$ (Brunauer, Emmett and Teller method): We noted that the natural or modified montmorillonite presents a surface with high specificity compared to that of the kaolinite (**Table 3**).

This can be explained by the fact that the montmorillonite is a swelling clay and its surface is formed by the internal basal surface, the external basal surface, and the external lateral surface, in addition to the surface of the pillars. This is unlike the non-swelling kaolinite which is characterized only by an external basal surface and an external lateral surface as shown in **Figure 5** [31].

We also found that the S$_{BET}$ of intercalated montmorillonite doubled from 142 to 327 m^2/g compared to that of natural montmorillonite which is probably due to the intercalation of iron polycations between the clay layers. As for the S$_{BET}$ of pillared montmorillonite, we observed that it is less than the intercalated one. These results corroborate those obtained by Baccar, Batis and Ghorbel [32] who attributed this decrease to the formation of pillars of iron oxides after calcination.

3.2.2. Structural Characterization

Chemical analysis: **Table 4** shows that the impregnated kaolinite contains a small amount of iron because the iron is impregnated on a low specific surface, in contrast to montmorillonite in which the iron can be set between its layers. In addition, the high quantity of iron in the two modified montmorillonites revealed that both clays were intercalated by iron ions. The mass percentage of iron (42.41% w/w) in pillared montmorillonite is higher than in the intercalated montmorillonite (33.7% w/w). This is probably due to the loss of water by intercalated montmorillonite therefore the mass percentage of iron increases relative to the total mass of the calcined clay.

X-ray diffraction: **Figure 6** shows the XRD patterns of the Fe-modified montmorillonite.

The X-ray diffractogram of intercalated montmorillonite presents the 001 ray (peaks due to regular stacking of montmorillonite layers) whose position corresponds to a distance between the layers of d001 = 10.24 Å. This ray on the diffractogram of pillared montmorillonite moves to d001 = 9.12 Å.
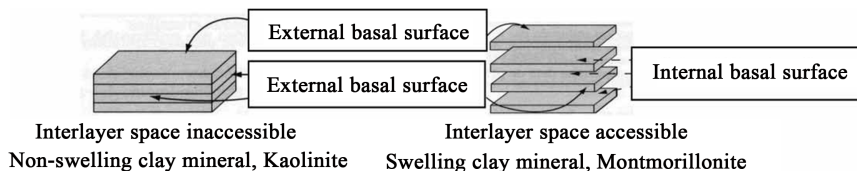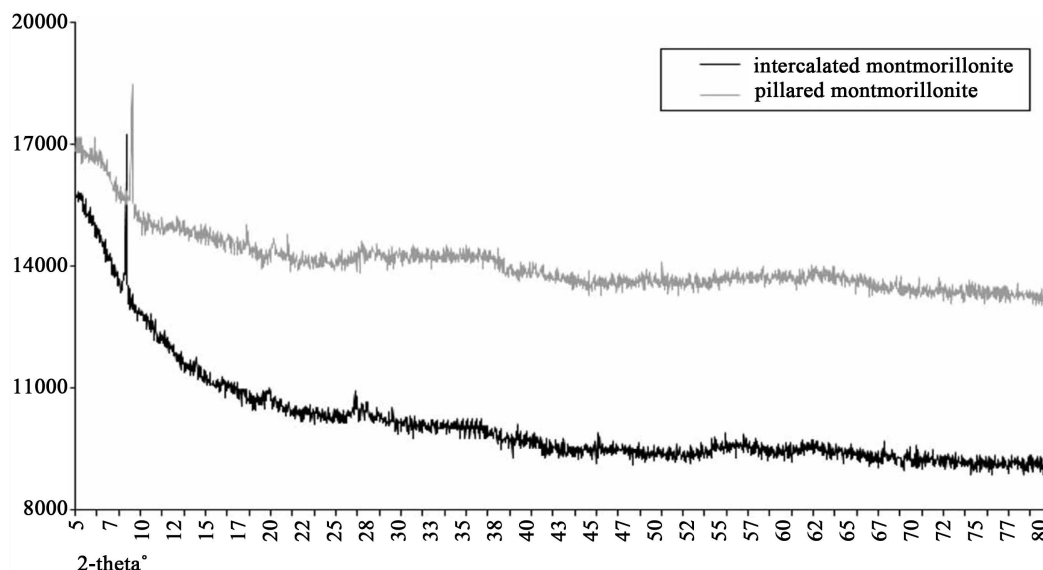
Figure 5. Structure of kaolinite and montmorillonite.

Figure 6. X-ray diffraction of Fe-modified montmorillonite.

Table 3. Specific surface area values.

Samples	S_{BET} (m^2/g)
Natural montmorillonite	142
Intercalated montmorillonite	327
Pillared montmorillonite	290
Natural kaolinite	11
Impregnated kaolinite	11

Table 4. Values of iron amount in clay.

Samples	Intercalated montmorillonite	Pillared montmorillonite	Impregnated kaolinite
Iron amount (% w/w)	33.7	42.41	7.99

This slight decrease from 10.24 to 9.12 Å in the distance between the layers in the two clays reveals that the large polycations of iron inserted between the layers after calcination become pillars of iron oxides which are less bulky.

The X-ray diffractogram of the Fe-impregnated kaolinite (Figure 7) shows the rays of iron oxide that confirms their setting on kaolinite.

3.2.3. Investigation of Iron Release

We notice in Table 5 that the presence of leached iron in the solution induces the degradation of phenolic compounds according to homogeneous catalysis in addition to the heterogeneous catalysis. In fact the first catalysis is the result of the leached iron in the solution and the second one is caused by iron supported by clays.
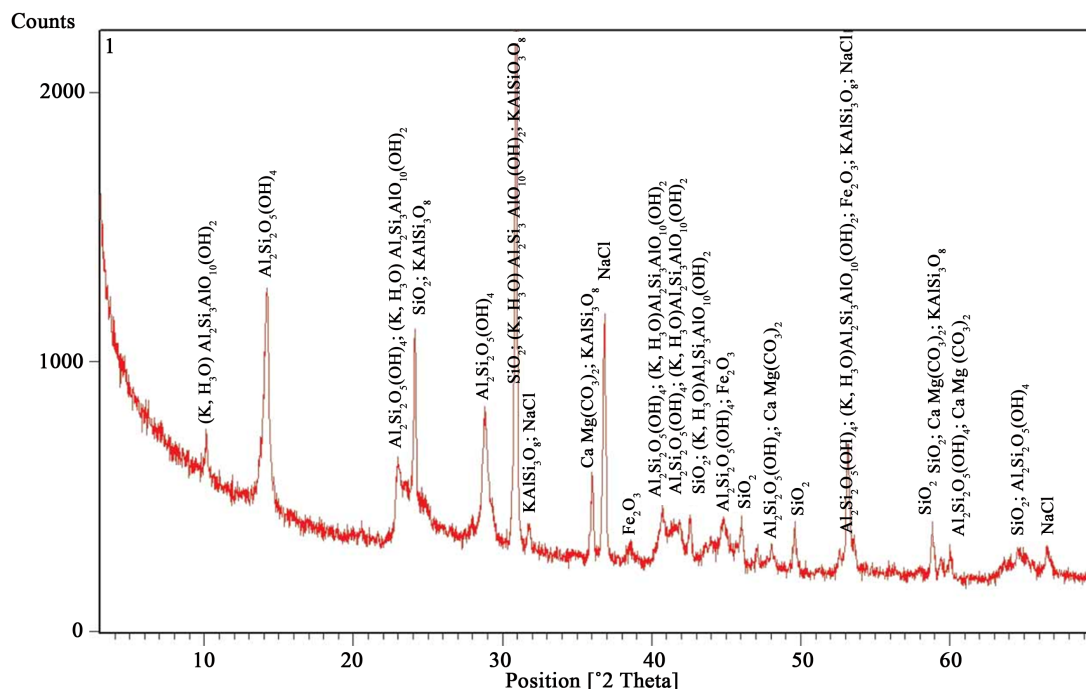
Figure 7. X-ray diffraction of Fe-impregnated kaolinite.

Table 5. Iron amount leached.

Samples	Intercalated montmorillonite	Pillared montmorillonite	Impregnated kaolinite
Iron amount leached (mol·L^{-1})	0.415	1.619	58

We also note that the kaolinite leached a significant amount of iron (58 mg·L^{-1}). Thus, it does not yet support iron ions on its compact surface and these are not trapped between its layers. Both prepared montmorillonites released lesser amounts of iron (1.69 and 0.415 mg·L^{-1}) because iron ions were trapped between layers of clay. In summary, the catalysts prepared by swelling clays such as montmorillonite are more efficient than those prepared with compact structure clays.

3.3. Kinetics of Catalytic Degradation of Phenolic Compounds

The apparent degradation rate was determined by plotting the curve of $\ln([C]_0/[C])$, as a function of time. $[C]_0$ is the phenolic compound concentration at t = 0 and the [C] is the phenolic compound concentration at t. The equation was found to be first order.

The phenolic compounds degradation rate constants histogram (**Figure 8**) reveals that hydroquinone is the most degraded compound in the least amount of time and that modified montmorillonite is more efficient to degrade the phenolic compound than impregnated kaolinite; this is probably due to its interlayer structure which maintains iron ions between layers and to its high surface specificity compared to kaolinite.

3.4. Determination of Optimal Degradation Conditions

We traced the response surfaces of each compound by repeatedly varying two experimental factors and keeping the third constant at its central value (the pH was chosen at 4, the central value of time was 80 min and the H$_2$O$_2$ concentration was 0.11 M). For catechol (**Figure 4**), the optimal degradation conditions at pH 4 are obtained after 120 min with a concentration of H$_2$O$_2$ equal to 0.3 M. If we fix the H$_2$O$_2$ concentration at 0.11 M, the optimal conditions are obtained after 120 min and at pH less than 1.6. When the time of reaction is equal to 80 min, the optimal degradation is obtained at pH less than 3.2 and at a H$_2$O$_2$ concentration more than 0.12 M.
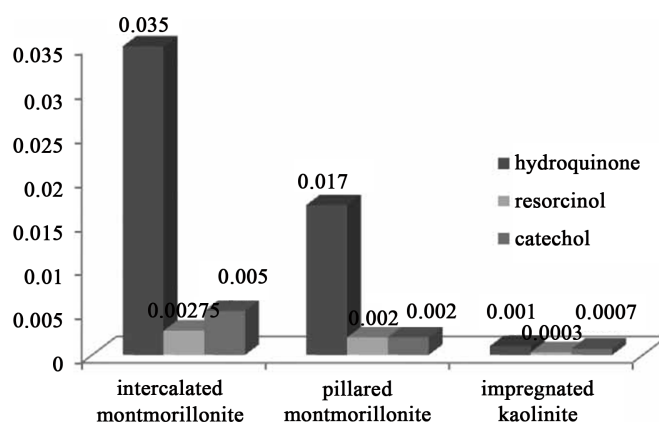
Figure 8. Histogram of rate constants of phenolic compounds degradation.

4. Conclusions

This study clearly shows the following:

-The use of the RSM allows the visualization of degradation response surfaces of each compound, the study of the influence of each parameter (pH, H_2O_2 concentration and time reaction) and the determination of the optimal operating conditions to degrade the selected phenolic compounds.

-The results obtained from the catalytic tests and analysis performed by different techniques show that the modified montmorillonites have very distinct catalytic, structural and textural properties; they are more effective for the catalytic phenolic compound degradation, they present the highest surface specificity and they may support iron ions.

-The kinetic degradation of three phenolic compounds supports the fact that hydroquinone is the most degraded compound in the least amount of time.

-The control of the release of iron ions by the catalysts performed by atomic absorption spectroscopy shows that the rate of the catalyst iron ions release in the reaction when the Fe-modified montmorillonites are used is lower than when Fe-modified kaolinite is used.

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