

Use of an amorphous iron oxide hydrated as catalyst for hydrogen peroxide oxidation of ferulic acid in water

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Abstract

The abatement of ferulic acid (FA), a polyphenolic constituent of olive mill wastewater, is studied in the pH range 5.0–7.0 by using hydrogen peroxide and an amorphous iron oxide as catalyst. The effect of pH, catalyst load, hydrogen peroxide and substrate starting concentrations is assessed during the investigation. A suitable reaction scheme is developed and used to build a mathematical model which satisfactorily describes the system's behavior. Kinetic constants for the proposed scheme as well as the total active site concentration of the catalyst in the studied pH range are estimated.

The occurrence of internal mass-transfer limitation for the adopted granulometric fraction of the catalyst is demonstrated.

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1. Introduction

Among Fenton-derived processes, the mineral-oxide-catalysed Fenton is one of the most interesting mainly due to the fact that it does not require a strict control of pH and that the recovery and reuse of the catalyst (an iron oxide) are quite simple. Previous investigations [1–4] have already demonstrated that the use of an iron oxide suspended in the water to be treated in the presence of H₂O₂ allows one to achieve the abatement of different kind of pollutants. In particular some of the Authors [3] found that the system with goethite (one of the most used iron oxide for this process) and H₂O₂ is characterised by a certain selectivity with respect to the organic species to be removed. In fact as a result of testing a wide group of aromatic molecules it has been shown [5] that the oxidation of an organic species occurs only when the substrate is capable of adsorbing on the surface of the oxide. Therefore, only in the case in which at least two adjacent (ortho) functional groups are present on the aromatic ring an oxidation of the species is observed. In the present work the investigations are extended to the use of an amorphous iron

(III) oxide hydrated, which has been less frequently investigated. As a test molecule it is adopted ferulic acid (4-hydroxy-3-methoxycinnamic acid), an antioxidant species which is present in plant tissues [6] and has been reported as one of the main constituent of the polyphenolic fraction of olive oil mill wastewaters (OMW) [7]. These wastewaters are produced annually in great quantities in Mediterranean countries during the manufacturing of olive oil. There is a general consensus that the polyphenolic fraction is the main cause for the poor biodegradability of OMW and its removal has been studied by many researchers. In fact polyphenol removal from OMW or more generally from aqueous solution has been attempted by means of microorganisms [8], by Fenton's reagent [9], ozone [10] and by combined chemical and biological processes [11,12]. None of these attempts gave completely satisfactory results and a reliable solution for the treatment of OMW is still lacking.

Mineral-oxide-catalysed Fenton could represent a valid alternative to the other systems so far investigated due to its selectivity during the oxidation processes [5]. In fact in the case of the use of advanced oxidation processes (AOP) for the (pre)-treatment of a OMW it is important to consider that OH radicals attack not only the polyphenolic species but also the biodegradable molecules present in the wastewater which can be more conveniently removed by means of a biological process. In this

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sense the present work may be considered as a preliminary study before starting an investigation on the real OMW.

2. Experimental

An amorphous iron(III) oxide hydrated [20344-49-4] was used as a catalyst, which was sieved and treated in a drying oven at 120 °C for 2 h. The granulometric fraction (24–38 μm) with a surface area of 187 m^2/g has been used in the experiments.

For each run the catalyst has been added to 0.75 l of water in which ferulic acid (FA) was dissolved. The pH of the solution has been regulated, with perchloric acid and sodium hydroxide addition, in the range 5.0–7.0 and measured by means of an Orion 420A+ pH-meter. Oxidation experiments have been carried out in a batch stirred tank made of Pyrex glass (1.090 l) and equipped with a jacket for temperature control ($T=298\text{ K}$, stirrer speed = 380 rpm). As soon as hydrogen peroxide was added, the reaction started. During each run the pH was monitored by a handheld pH-meter, Piccolo Plus HI 1295 (Hanna Instruments) and regulated at initial value. Samples of liquid were collected from the reactor at different reaction times and filtered by membrane filter Millex HA (pore size 0.45 μm , Millipore) to remove the catalyst. Liquid samples were also analyzed by HPLC apparatus (Hewlett-Packard 1090) equipped with a UV-vis detector ($\lambda = 320\text{ nm}$) and a Synergi Hydro-RP 80A column, using a mobile phase (85:15 buffered aqueous solution:acetonitrile) flowing at 1.0 ml min^{-1} . The buffered aqueous solution was prepared with 4 ml phosphoric acid (85% by weight), 25 ml methanol in 1 l of HPLC water. The reactor and all glassware were cleaned with hydrochloric acid and washed several times with bidistilled water before use. All the reagents have been purchased from Aldrich.

3. Results and discussion

3.1. Oxidation of ferulic acid

Preliminary runs have been carried out at pH = 6.0 to evaluate the capability of the substrate to adsorb on the solid surface at different catalyst loads. The results shown in Fig. 1 indicate that FA does not adsorb on the surface of the used iron oxide. It has been also assessed that hydrogen peroxide is not capable of directly reacting with FA in the absence of the catalyst (data not shown).

Fig. 2 illustrates the effect of catalyst load on the oxidation of FA by means of H_2O_2 (symbols). As expected for a catalytic process, the reactivity of the system increases with increasing the catalyst load. Half-life times pass from 90 to 50 min for an iron oxide load by increasing from 100 to 150 mg/l .

In Fig. 3 the data of normalized concentrations versus reaction time, collected during the runs at different substrate starting concentrations, are also shown (symbols). As expected the increase of initial substrate concentration leads a higher system reactivity (for example, for a reaction time of 100 min the concentration decreases of $2.3 \times 10^{-5}\text{ M}$ and $1.4 \times 10^{-5}\text{ M}$, respectively, for the highest and lowest concentrated solutions). Further experiments have been carried out to assess the effect of changing the

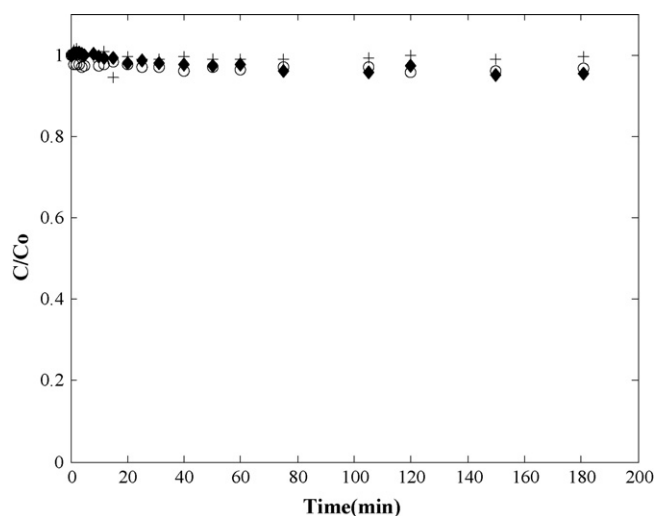


Fig. 1. Adsorption of ferulic acid at various catalyst loads. $[\text{FA}]_0 = 2 \times 10^{-5}\text{ M}$; pH = 6.0; (○), 50 mg/l ; (+), 100 mg/l ; (◆), 150 mg/l .

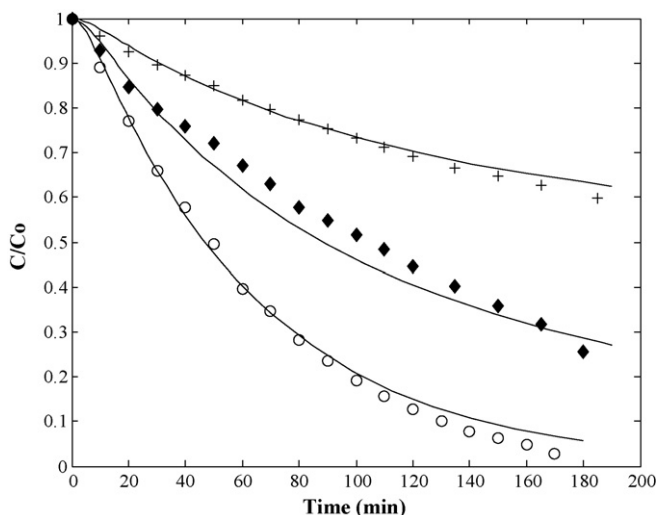


Fig. 2. Influence of catalyst load on FA oxidation. $[\text{FA}]_0 = 2 \times 10^{-5}\text{ M}$; $[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-5}\text{ M}$; pH = 6.0; (+), 50 mg/l ; (◆), 100 mg/l ; (●), 150 mg/l .

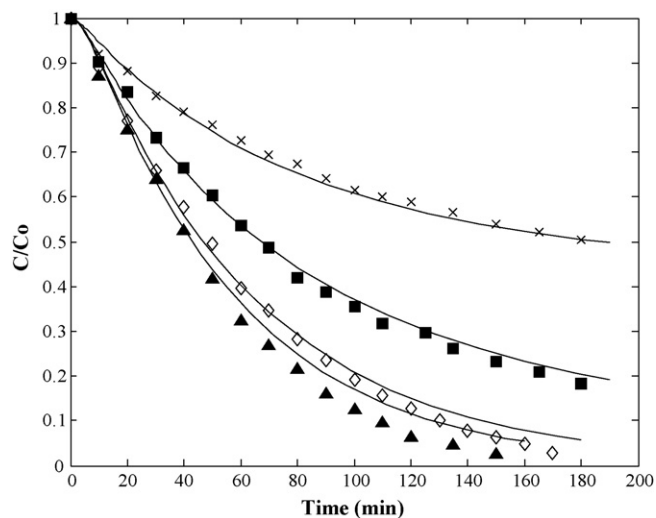


Fig. 3. Influence of starting concentration of ferulic acid ($[\text{FA}]_0$). $[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-5}\text{ M}$, pH = 6.0; $[\text{Cat}] = 150\text{ mg/l}$; (▲), $1.6 \times 10^{-5}\text{ M}$; (◇), $2 \times 10^{-5}\text{ M}$; (■), $4 \times 10^{-5}\text{ M}$; (×), $6 \times 10^{-5}\text{ M}$.

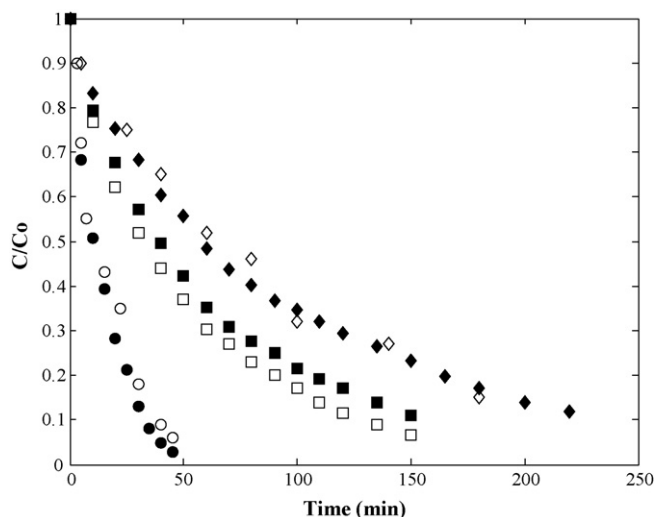


Fig. 4. Influence of pH and of radical scavenger on FA oxidation. ($[FA]_0 = 2 \times 10^{-5}$ M; $[H_2O_2]_0 = 1 \times 10^{-3}$ M; $[Cat] = 150$ mg/l; empty symbols with radical scavenger (1×10^{-3} M), full ones without radical scavenger: (●), pH=5.0; (▲), pH=7.0.

initial hydrogen peroxide concentration. The results of this set of runs (data not shown) indicate that the changes in hydrogen peroxide concentrations do not have a significant influence on the reactivity of the system. Only a reduction of 30% in half-life times was observed for a large increase of the oxidant concentration (from 0.5 to 4 mM). On the other hand, the behaviour of the system is greatly influenced by the pH of the solutions (Fig. 4, symbols), where the highest value of reactivity was recorded at the lowest pH. Additional runs have been performed in the presence of *tert*-butanol, a well known radical scavenger to assess the mechanism of the reaction. No significant differences have been observed during these experiments with respect to the runs where no radical scavenger was used, thus ruling out the intervention of a radical mechanism at least in the liquid bulk (see Fig. 4). According to the results reported above it can be stated that the iron oxide, used in this study, shows a behaviour quite different from that of the crystalline goethite. In fact the oxidation of FA does not proceed through a preventive adsorption on the solid surface as found in the case of goethite for other substrates [3,5]. In order to clarify the mechanism that supports the process, additional runs have been carried out on two different substrates, vanillic (4-hydroxy-3-methoxybenzoic acid) and *p*-coumaric acids (*E*)-3-(4-hydroxyphenyl)-2-propenoic acid), which have some common structural fragments with ferulic acid in their molecules (Fig. 5) and both are incapable of adsorbing on the solid surface. Surprisingly the results of these runs indicate that both these species are completely unreactive in the experimental

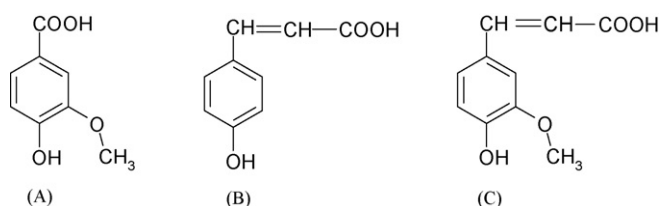


Fig. 5. Structures of vanillic acid (A), *p*-coumaric acid (B) and ferulic acid (C).

conditions adopted for FA oxidation. Thus, these results show that the presence of both structural fragments (exocyclic double bond and ortho hydroxyl-methoxy groups) on the same ring is required in order to promote the reaction of FA with hydrogen peroxide which is adsorbed on the surface of the iron oxide.

Moreover, these results indirectly support the occurrence of a non-radical mechanism of reaction. In fact the selectivity shown by the system does not agree with the activation of a radical mechanism with the formation of unselective species such as OH radicals. This behaviour is in agreement with the results obtained by others using a different iron oxide (ferrihydrite) for atrazine removal by means of hydrogen peroxide [13].

On the basis of the previous results, the following reaction scheme can be proposed:



where * is an active site on the iron oxide surface and P_1 and P_2 are the reaction products.

According to this scheme, the disappearance of the substrate is the result of a reaction between dissolved FA with the H_2O_2 adsorbed on the surface (Reaction (r_3)). It is also suggested that the adsorbed hydrogen peroxide undergoes a decomposition reaction which does not produce any species, capable of oxidating the substrate (Reaction (r_2)).

Following the proposed scheme a set of mass-balance equations on FA, hydrogen peroxide and the active sites has been written.

$$\frac{d[H_2O_2]}{dt} = -(k_1 + k_2)[H_2O_2][*][Cat] \quad (1)$$

$$\frac{d[H_2O_2]_{ads}}{dt} = k_1[H_2O_2][*][Cat] - k_3[FA][H_2O_2]_{ads} \quad (2)$$

$$\frac{d[*]}{dt} = -k_1[H_2O_2][*] - k_2[H_2O_2][*] + \frac{k_3}{[Cat]}[FA][H_2O_2]_{ads} \quad (3)$$

$$\frac{d[FA]}{dt} = -k_3[FA][H_2O_2]_{ads} \quad (4)$$

$$\frac{d[P_1]}{dt} = +k_2[H_2O_2][*][Cat] \quad (5)$$

$$\frac{d[P_2]}{dt} = +k_3[FA][H_2O_2]_{ads} \quad (6)$$

where [*] is the concentration of active site (mol/mg) and [Cat] is the catalyst load (mg/l).

The Eqs. (1)–(6) are numerically solved by using appropriate starting conditions ($[FA] = [FA]_0$; $[*] = C_{L0}$; $[H_2O_2] = [H_2O_2]_0$; $[H_2O_2]_{ads} = [P_1] = [P_2] = 0$ where C_{L0} is the concentration of total active sites of the catalyst).

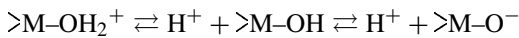
The kinetic constants of the reactions (r_1) – (r_3) and the concentration of total active sites have been also estimated by means of this mathematical model and adopting a proper optimization

procedure (a Matlab code that utilize a least square procedure) for the analysis of the data collected during the experimental runs. In particular, since it was necessary to estimate four parameters (three kinetic constants k_1, k_2, k_3 and the term C_{L0}), a pool of 10 different oxidation runs has been considered simultaneously in the optimization procedure. Table 1 illustrates the best values estimated for the parameters along with a statistical index for runs at pH=6.0. In Figs. 2 and 3 the concentrations of FA predicted by the model at varying operating conditions (catalyst load and initial substrate concentration) are plotted as continuous lines, by using the best estimated values for k_1, k_2, k_3 and C_{L0} . The low uncertainties associated to the best estimates of the unknown parameters and the values calculated for the adopted statistical index indicate a good adequacy of the proposed model.

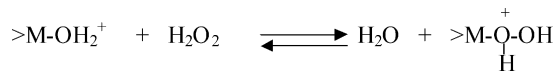
The experimental campaign was then extended at pH 5.0 and pH 7.0. Also at these pH values no adsorption of the substrate on catalytic surface was observed. For these runs the four parameters have been estimated by the proposed model. The results are shown in Tables 2 and 3, respectively.

It is noteworthy to observe that the reliability of the model at all investigated pH values is satisfactory. Moreover, the C_{L0} values, estimated by the model, decrease by pH increasing according to the reactivity of the substrate recorded during the experiments (see Fig. 4).

This result can be explained by considering that the surface of iron oxide presents active sites which assume different forms according to the pH [14]:



The $>M-OH_2^+$ form prevails at low pH whereas $>M-O^-$ dominates at high pH. If it is assumed that $>M-OH_2^+$ makes the adsorption of H_2O_2 possible:



it is clear that, by increasing the pH, the concentration of active sites decreases and so does the reactivity.

In order to evaluate the occurrence of mass-transfer limitation, the existence of external and internal resistances has been considered.

3.2. External mass-transfer limitation

By means of the following relationship [15]:

$$Sh = 2 + 0.6Re^{1/2} Sc^{1/3} \tag{7}$$

among Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers, the mass-transfer liquid–solid coefficient k_L has been estimated ($2.17 \times 10^{-2} \text{ cm s}^{-1}$). To calculate the Reynolds number a characteristic velocity has been estimated from that of the stirrer. By keeping the diameter of the stirrer (D) fixed at 7.51 cm, the circumference, described by its edge during the rotation, can then be calculated ($2\pi D/2$) and hence the characteristic velocity can be derived:

$$v = \frac{2\pi D}{2} \text{ rpm} \tag{8}$$

Table 1
Estimated values of kinetic constants and initial active site concentration at pH=6.0

[FA] ₀ (M)	[H ₂ O ₂] (M)	[Cat] (mg/l)	k_1 (M ⁻¹ s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)	k_3 (M ⁻¹ s ⁻¹)	C_{L0} (mol/mg)	R^2
1.6×10^{-5}	1×10^{-3}	150				$2.86 \times 10^{-10} \pm 4.28 \times 10^{-12}$	0.998
2×10^{-5}	1×10^{-3}	150					0.995
4×10^{-5}	1×10^{-3}	150					0.979
6×10^{-5}	1×10^{-3}	150					0.985
2×10^{-5}	5×10^{-4}	150					0.993
2×10^{-5}	2×10^{-3}	150	$1.49 \pm 2.24 \times 10^{-2}$	$2.11 \times 10^{-1} \pm 7.40 \times 10^{-3}$	92.2 ± 3.22		0.989
2×10^{-5}	4×10^{-3}	150					0.996
2×10^{-5}	1×10^{-3}	50					0.987
2×10^{-5}	1×10^{-3}	100					0.979
2×10^{-5}	1×10^{-3}	200					0.979

Table 2
Estimated values of kinetic constants and initial active site concentration at pH = 5.0

[FA] ₀ (M)	[H ₂ O ₂] (M)	[Cat] (mg/l)	k_1 (M ⁻¹ s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)	k_3 (M ⁻¹ s ⁻¹)	C_{L0} (mol/mg)	R^2
2×10^{-5}	1×10^{-3}	150					0.985
4×10^{-5}	1×10^{-3}	150					0.973
6×10^{-5}	1×10^{-3}	150					0.987
2×10^{-5}	2×10^{-3}	150	$7.30 \pm 1.46 \times 10^{-1}$	$1.11 \pm 2.78 \times 10^{-2}$	197.52 ± 10.86	$4.28 \times 10^{-10} \pm 1.92 \times 10^{-11}$	0.995
2×10^{-5}	4×10^{-3}	150					0.991
2×10^{-5}	1×10^{-3}	50					0.888
2×10^{-5}	1×10^{-3}	100					0.982
2×10^{-5}	1×10^{-3}	200					0.960

Table 3
Estimated values of kinetic constants and initial active site concentration at pH = 7.0

[FA] ₀ (M)	[H ₂ O ₂] (M)	[Cat] (mg/l)	k_1 (M ⁻¹ s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)	k_3 (M ⁻¹ s ⁻¹)	C_{L0} (mol/mg)	R^2
2×10^{-5}	1×10^{-3}	150					0.998
4×10^{-5}	1×10^{-3}	150					0.980
6×10^{-5}	1×10^{-3}	150					0.962
2×10^{-5}	2×10^{-3}	150	$3.95 \pm 5.93 \times 10^{-2}$	$4.19 \times 10^{-1} \pm 1.05 \times 10^{-2}$	121.2 ± 3.03	$1.02 \times 10^{-10} \pm 1.02 \times 10^{-12}$	0.985
2×10^{-5}	4×10^{-3}	150					0.988
2×10^{-5}	1×10^{-3}	50					0.984
2×10^{-5}	1×10^{-3}	100					0.994

with rpm (380 rpm) equal to the number of rotations per minute of the stirrer. The characteristic length L necessary to calculate both the Reynolds and Sherwood numbers has been assumed to be equal to the mean particles diameter (31 μm). This value has been compared with that calculated for the kinetic constant of the superficial reaction:

$$k_S = \frac{k_{\text{obs}} \times k_L}{k_L a - k_{\text{obs}}} = 6.78 \times 10^{-6} \text{ cm s}^{-1} \quad (9)$$

where k_{obs} is the observed pseudo-first order kinetic constant derived from the concentration–time data of the most reactive run (pH = 5.0, catalyst load: 200 mg/l, $[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-3} \text{ M}$, $[\text{FA}]_0 = 2 \times 10^{-5} \text{ M}$) and the term ‘ a ’ is the specific surface area (cm^{-1}).

From the comparison of k_L and k_S , it is evident that no external mass-transfer limitation occurs being $k_L \gg k_S$.

3.3. Internal mass-transfer limitation

According to the Weisz-Prater criterion [16], a modified Thiele Modulus is:

$$\phi = \frac{(-R_{\text{obs}})L^2}{D_{\text{eff}}C_S^0} \quad (10)$$

where R_{obs} is the observed rate of reaction for the most reactive run (moles consumed/time \times volume of catalyst); L is the length of the pores which can be estimated as one third of the average particle radius; D_{eff} is the effective diffusivity; C_S^0 is the initial concentration of ferulic acid in the liquid bulk. The above-mentioned parameters are calculated at $\phi = 45$.

The modified Thiele Modulus ϕ can be related to the Thiele Modulus Φ by means of the following relationship: $\phi = \eta\Phi^2$. Being $\phi = \eta\Phi^2 \gg 1$ the catalyst efficiency η results lower than 1 and, in particular, $\eta \cong (1/\Phi)$. Therefore, it can be concluded that $\phi \cong \Phi \cong 45$. This calculation confirms that the internal mass-transfer limitation is not negligible for the adopted granulometric fraction of the catalyst.

4. Conclusion

The oxidation FA has been studied by means of an iron oxide hydrated and hydrogen peroxide in the pH range 5.0–7.0. The present investigation indicates that although FA does not adsorb on the surface of the catalyst, the reactivity of the system increases by decreasing the pH of the solution. The results, obtained during this work, support the view of a non-radical reaction mechanism, at least in the liquid bulk. It also suggested that in order for the substrate to react with the adsorbed H_2O_2 , a particular molecular structure is required. A kinetic model has

been developed and used for the analysis of the experimental data at the investigated pH values. The model allows one to calculate the kinetic constants for the proposed reaction scheme as well as the total active site concentration of the catalyst in the pH range studied. For the adopted granulometric fraction of the catalyst the occurrence of internal mass-transfer limitation has also been demonstrated.

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