

*Numerical models for reactions catalysed by homogeneous mediators: the case of Fenton's reagent**

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A numerical model has been developed to describe the behaviour of a batch reactor in which Fenton's reagent is used for hydroxylating aromatic hydrocarbons under conditions of electrochemical regeneration. The test reaction considered is the conversion of benzene into phenol. Comparison is made with previously published experimental results.

Nomenclature

A	electrode area, m^2
a_i	parameter defined by Equation 21
C_i	concentration of species, i , in the bulk solution, $mol\ m^{-3}$
c_i	local concentration of species, i , in the diffusion layer, $mol\ m^{-3}$
K_i	effective mass-transfer coefficient, $m\ s^{-1}$
k_j	rate constant of reaction j
R_j	rate of reaction j , $mol\ m^{-3}\ s^{-1}$
r_i	rate of change of concentration of species i due to chemical reaction, $mol\ m^{-3}\ s^{-1}$

t	time, s
V	reactor volume, m^3
x	distance from the cathode surface, m
x^*	maximum thickness of the diffusion layer, m
τ	period of diffusion layer renewal, s

Subscripts

1	oxygen
2	Fe^{3+}
3	hydrogen peroxide
4	Fe^{2+}
5	benzene
6	phenol
7	biphenyl

1. Introduction

Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron which generates hydroxyl radicals capable of oxidizing various organic substrates [1]. This reagent has traditionally been prepared by simple mixing of the pre-formed constituents, though in that case the progress of the reaction is difficult to control and the yields are generally low [2-10]. A number of authors [11-17] have pointed out that the formation or regeneration of this reagent by cathodic reaction is a convenient way of moderating the rate at which the hydroxyl radicals are formed, thus minimizing the importance of a number of undesirable side reactions. In the present work,

numerical calculations are used to explore some of the possibilities of this reagent when used under conditions of electrochemical regeneration. The particular reaction chosen is the oxidation of benzene to phenol. This reaction is relatively simple and is one for which certain experimental data have been published.

2. The reaction scheme

The reaction scheme shown in Fig. 1 is based on the work of Walling and his colleagues [1, 9, 10]. Their papers have also provided most of the values of the rate constants used in this work. Even though the reaction with benzene is a relatively simple one, eleven homogenous reactions

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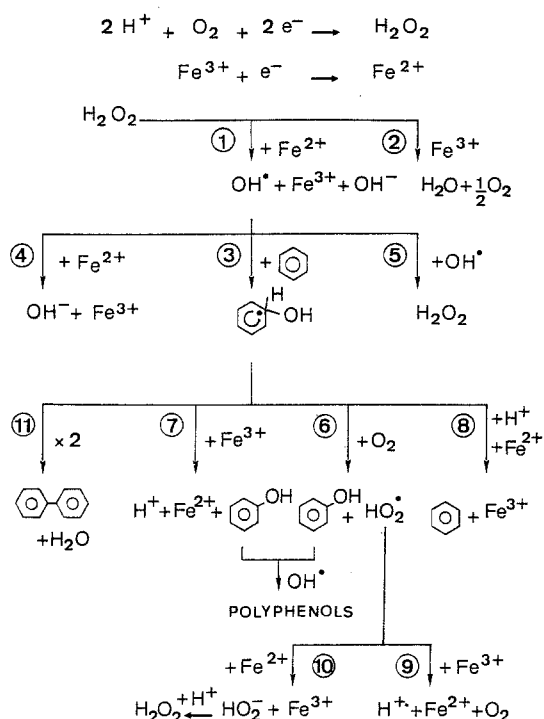
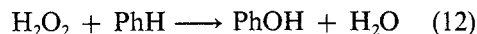


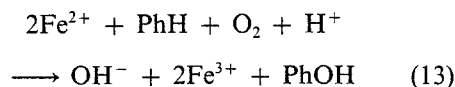
Fig. 1. Reaction scheme.

have been taken into account in our calculations. The major steps in the sequence of useful reactions are: first, the reaction (1) between hydrogen peroxide and ferrous iron to form the hydroxyl radical; second, the addition (3) of this radical to the benzene to form a hydroxycyclohexadienyl radical; third, the oxidation (6, 7) of the latter radical to phenol. The final oxidation step can be performed either by ferric ions (7) or by oxygen (6) if it is present. The reaction with oxygen is much more rapid than that with Fe^{3+} [15, 18]; it gives rise to hydroperoxy radicals which are either oxidized (9) or reduced (10), depending on the relative concentrations of $\text{Fe}^{2+}/\text{Fe}^{3+}$.

When oxygen is present, two different overall reactions are possible, depending on which reaction, either 9 or 10, is the last in the sequence. With reaction 9:



With reaction 10:



When no oxygen is present, only the overall reaction 12 occurs, together with the side reactions 2, 4, 5, 8 and 11. In either case, electrochemical reactions can be used to regenerate the Fe^{2+} [16], and if oxygen is present it can be reduced to form the hydrogen peroxide [11, 15].

Eleven homogeneous reactions are considered:

$$\begin{array}{l}
 R_1 = k_1 [\text{H}_2\text{O}_2][\text{Fe}^{2+}] \\
 R_2 = k_2 [\text{H}_2\text{O}_2][\text{Fe}^{3+}]/[\text{H}^+] \\
 R_3 = k_3 [\text{OH}^\bullet][\text{PhH}] \\
 R_4 = k_4 [\text{HO}^\bullet][\text{Fe}^{2+}] \\
 R_5 = k_5 [\text{HO}^\bullet]^2 \\
 R_6 = k_6 [\text{HOPhH}][\text{O}_2] \\
 R_7 = k_7 [\text{HOPhH}][\text{Fe}^{3+}] \\
 R_8 = k_8 [\text{HOPhH}][\text{H}^+] \\
 R_9 = k_9 [\text{HO}_2^\bullet][\text{Fe}^{3+}] \\
 R_{10} = k_{10} [\text{HO}_2^\bullet][\text{Fe}^{2+}] \\
 R_{11} = k_{11} [\text{HOPhH}]^2
 \end{array} \quad (14)$$

In setting up the equations describing the reaction kinetics, the usual steady-state assumption concerning the concentrations of the radicals has been used. The rates of formation of the various stable species are as follows.

$$\begin{array}{l}
 \text{O}_2: \quad r_1 = \frac{1}{2}R_2 - R_6 + R_9 \\
 \text{Fe}^{3+}: \quad r_2 = R_1 + R_4 - R_7 + R_8 - R_9 + R_{10} \\
 \text{H}_2\text{O}_2: \quad r_3 = -R_1 - R_2 + R_5 + R_{10} \\
 \text{Fe}^{2+}: \quad r_4 = -r_2 \\
 \text{PhH}: \quad r_5 = -R_3 + R_8 \\
 \text{PhOH}: \quad r_6 = R_6 + R_7 \\
 \text{PhPh}: \quad r_7 = R_{11}
 \end{array} \quad (15)$$

The values of the rate constants used in our calculations are shown in Table 1. Of the eleven reactions considered, precise information concerning the rate constant has been found for only eight of them. For those reactions for which no reference is given, the rate constants have been estimated in the following way. The rate constant for reaction 11, which is diffusion-controlled, has been calculated from the Smoluchowski equation [20], for which the

Table 1. Values of rate constants used

Reaction	Rate constant	Reference
1	$0.076 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[1]
2	$4 \times 10^{-5} \text{ s}^{-1}$	[9]
3	$4.3 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[18]
4	$3 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[1]
5	$5.3 \times 10^9 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[1]
6	$5 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[18]
7	$50 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-
8	$7.6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-
9 and 10	$k_9 = 0.1k_{10}$	[9, 19]
11	$9 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-

diffusion coefficient of the cyclohexadienyl radicals was estimated from the Wilke–Chang correlation. On the basis of the rate constant for reaction 11 given in Table 1, the rate constants for reactions 7 and 8 were determined from experimental observations published by Walling and Johnson [10]. These authors performed experiments, in the absence of oxygen, in which a small quantity of H_2O_2 was added to a system containing excess Fe^{2+} and various concentrations of the substrate, benzene. They measured the amount of Fe^{2+} consumed and the results are given in terms of $R = \Delta c_4 / 2\Delta c_3$ for different benzene concentrations (their Fig. 1). Since reactions 7, 8 and 11 consume different amounts of Fe^{2+} , the values of R make it possible to determine the relative importance of these three reactions. Using the values of the other rate constants given in Table 1, the experiments of Walling and Johnson were simulated and the value of R determined; the values of the rate constants for reactions 7 and 8 were adjusted until the calculated and experimental values of R were in agreement. Fig. 2 shows the calculated and experimental values for R as a function of the benzene concentration. The calculated curves were obtained using the rate constants given in Table 1.

3. Published experimental results

The mathematical model has been used to simulate the experimental results observed by Tomat and Vecchi [11]. Their work was performed in a bench-scale reactor with a volume of 30 ml aqueous phase and 0.5 ml benzene. They used

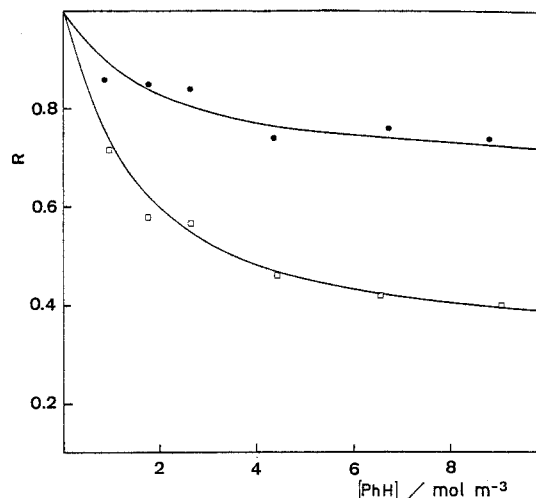


Fig. 2. Plot of the ratio $R (= \Delta c_4 / 2\Delta c_3)$ for different benzene concentrations (after [10]). Initial concentrations: (●) Fe^{2+} , 19 mol m^{-3} ; Fe^{3+} , 0; (□) Fe^{2+} , 19 mol m^{-3} ; Fe^{3+} , 40 mol m^{-3} . The curves are calculated for $k_7 = 50 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_8 = 71.6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, assuming initial $[\text{H}_2\text{O}_2]$ of 2 mol m^{-3} and $k_{11} = 9 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

various concentrations of H_2SO_4 and Fe^{3+} in the aqueous phase and their reaction mixture was kept saturated with oxygen (concentration assumed to be 1 mol m^{-3}). In our calculations only the H_2SO_4 concentration of 100 mol m^{-3} has been considered.

Their initial solutions contained neither Fe^{2+} nor hydrogen peroxide, both of these species being formed by electrolysis. It has been assumed that the electrochemical reactions were performed under conditions of mass-transfer control. In this system the Fe^{3+} and the oxygen diffuse to the electrode where they are reduced to Fe^{2+} and H_2O_2 . These species diffuse back towards the bulk solution while at the same time reacting to give hydroxyl radicals which attack the benzene to form phenol. The rate of phenol formation is highest near the electrode, and the phenol also diffuses towards the bulk solution where it is partly taken up by the organic (benzene) phase.

4. Mathematical model

In the reactor used by Tomat and Vecchi [11] the cathode was a pool of mercury on which floated a magnetic stirrer. This means that at each passage of the stirrer bar, the interface between

the mercury and the aqueous phase is renewed and all the species formed at the interface are projected into the bulk of the aqueous phase. This operation can be represented by a penetration model in which it is assumed:

(i) that a diffusion layer forms at the electrode surface and progressively spreads into a stagnant liquid phase,

(ii) that the mass transfer by diffusion is limited to a thin layer, of maximum thickness x^* , so that beyond this layer, concentrations vary only as a result of homogeneous reactions,

(iii) that periodically this layer is completely re-mixed with the bulk solution.

This is certainly an idealized view of the process, as it neglects any convective effects near the interface and assumes perfect mixing with the bulk phase. However, among the models simple enough to be usable, it is the one that most closely corresponds to the physical situation. The renewal period is half the rotation period of the stirrer; a value of 0.25 s has been assumed.

To describe the formation of the diffusion layer, the equation to be solved is the diffusion-reaction equation:

$$\begin{aligned} \partial c_i / \partial t &= D_i \partial^2 c_i / \partial x^2 + r_i(c_1, c_2, \dots, c_5) \\ \text{where } i &= 1, 2, \dots, 7 \end{aligned} \quad (16)$$

The boundary conditions are the following.

(a) The concentrations of all species are uniform at the beginning of each stirrer cycle,

$$\text{at } t = t_{k-1}, c_i = C_i(k-1) \text{ for all } x > 0$$

(b) The electrode reactions are limited by mass transfer, so the concentrations of the oxidized species at the electrode surface are zero,

$$\text{at } x = 0, c_i = 0 \text{ for } i = 1, 2$$

(c) The diffusive flux of the oxidized species towards the electrode is equal to the diffusive flux of the corresponding reduced species away from the electrode,

$$\begin{aligned} \text{at } x = 0, D_i \partial c_i / \partial x &= -D_{i-2} \partial c_{i-2} / \partial x \\ \text{for } i &= 3, 4 \end{aligned}$$

(4) For the other species the diffusive flux at the electrode is zero,

$$\text{at } x = 0, D_i \partial c_i / \partial x = 0 \text{ for } i = 5, 6, 7$$

(5) Sufficiently far from the electrode, concentration changes are due only to homogeneous reactions,

$$\text{for } x > x^*, \partial c_i / \partial t = r_i(c_1, c_2, \dots, c_5)$$

The system of Equation 16 has been integrated using a finite-difference technique, the modified Crank-Nicholson method [21]. The reaction term is calculated explicitly, because of the great complexity of the reaction scheme, and is incorporated into the discretized version of Equation 16 before it is solved. Thirty-one grid points are used in the space coordinate together with 15 time steps whose size varies according to the step number, n .

$$\Delta t_n = (2n - 1)\Delta t_1$$

$$\text{for steps } n = 1, 2, \dots, 15$$

At the end of this integration (cycle k), concentration profiles such as those shown in Fig. 3 are obtained for the various species. These profiles are integrated and the new bulk concentrations, $C_i(k)$, are calculated after re-mixing of the reaction layer. The difference between these concentrations and the bulk concentrations at the beginning of the cycle, $C_i(k-1)$, can be used to calculate an overall rate of change

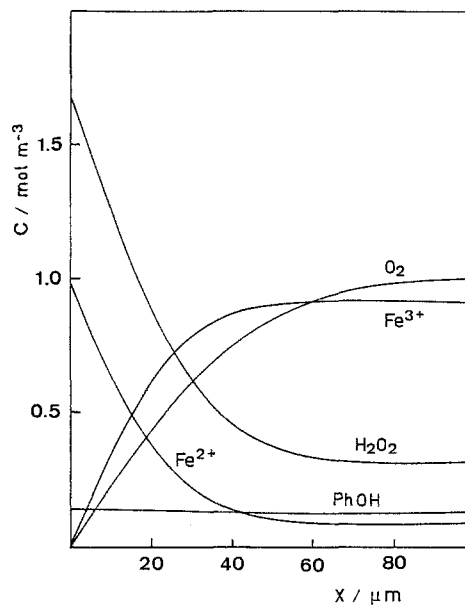


Fig. 3. Concentration profiles at the end of a stirrer cycle. $[\text{Fe}^{3+}]$, 1 mol m^{-3} ; time, 120 s.

of concentration

$$dC_i/dt = [C_i(k) - C_i(k-1)]/\tau,$$

$$\text{for } i = 1, 2, \dots, 7$$

where τ is the period of diffusion-layer renewal.

The sub-routine calculating dC_i/dt can be considered the equivalent of a system of ordinary differential equations:

$$dC_i/dt = F_i(C_1, C_2, \dots, C_5)$$

$$\text{for } i = 1, 2, \dots, 7$$

Such a system can be integrated numerically using different techniques, e.g. the Runge-Kutta method. Here, the Runge-Kutta method was used for the first three steps and thereafter a 4th order Adams predictor-corrector method was used. The step size in these calculations was 10 s. In this way it is not necessary to calculate every cycle of formation and re-mixing of the diffusion layer, but only about one cycle in ten or fifteen.

5. Discussion

In Fig. 3 the concentration profile for phenol is quite flat, i.e. the concentration at the electrode at the end of a stirrer cycle is only slightly higher than in the bulk. At first sight this might be surprising, considering that the rate of phenol formation is about an order of magnitude higher at the electrode than in the bulk, but this can be explained by the fact that the stirrer period is so short that there is little time for the phenol to accumulate. No profile has been drawn for the biphenyl because its concentration in this case, as in all our calculations, is extremely low.

Fig. 4 shows the calculated variation in time of Fe^{2+} and H_2O_2 concentrations in the bulk solution for two different values of the initial Fe^{3+} concentration. At 3 mol m^{-3} the H_2O_2 concentration rises continuously over the whole 15 min; on the other hand, the Fe^{2+} concentration initially rises, passes through a maximum then slowly declines. Thus hydrogen peroxide is present in an ever increasing excess. At a higher Fe^{3+} concentration (5.6 mol m^{-3}), the situation is reversed. Obviously the ideal situation would be one in which both Fe^{2+} and hydrogen peroxide are consumed at the same rates at which they are generated.

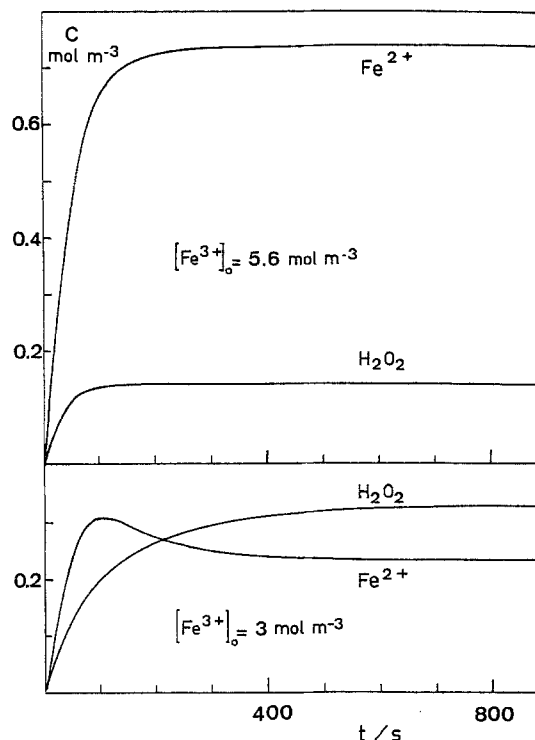


Fig. 4. Bulk concentrations of H_2O_2 and Fe^{2+} as functions of time.

It is possible to calculate approximately what conditions are necessary for this situation to be attained. Firstly, it is assumed that the side reactions are of little importance (under conditions of electrochemical regeneration this is true). Then

$$R_1 = R_3 = R_6 = R_9 + R_{10} \quad (18)$$

Also the rates of formation of H_2O_2 and Fe^{2+} in the bulk solution are given respectively by

$$dC_3/dt = -R_1 + R_{10} + a_1 C_1$$

$$= -R_9 + a_1 C_1 \quad (19)$$

$$dC_4/dt = -R_1 + R_9 - R_{10} + a_2 C_2$$

$$= -2R_{10} + a_2 C_2 \quad (20)$$

where

$$a_i = AK_i/V \quad (21)$$

The condition for maximum yield is that

$$dC_3/dt = dC_4/dt = 0 \quad (22)$$

that is

$$a_1 C_1 = R_9 \quad (23)$$

$$\frac{1}{2}a_2C_2 = R_{10} \quad (24)$$

From the ratio of Equations 23 and 24, it is possible to show that the Fe^{2+} concentration is given by

$$C_4 = K_2C_2^2/(20K_1C_1) \quad (25)$$

and from the sum of Equations 23 and 24 it can be shown that the H_2O_2 concentration is given by

$$C_3 = \left(\frac{20K_1C_1A}{k_1K_2C_2V} \right) \left(\frac{K_1C_1}{C_2} + \frac{K_2}{2} \right) \quad (26)$$

Thus Equations 25 and 26 give the concentrations of H_2O_2 and Fe^{2+} required for the system to give a maximum current yield.

The effective mass-transfer coefficients are calculated for the two species being reduced at the electrode; this quantity is taken as the flux of reduced species reaching the bulk solution divided by the concentration of oxidized species in the bulk solution. In this way the effect on mass transfer of reactions occurring in the diffusion layer can be made evident. Fig. 5 shows the variation of these coefficients as a function of the initial Fe^{3+} concentration. Although the coefficient for the iron varies little, the transfer coefficient for oxygen decreases sharply at high iron concentrations. This reflects the fact that as the iron concentration increases, the fraction of hydrogen peroxide consumed in the diffusion layer increases and the fraction reaching the bulk solution is reduced.

The instantaneous current yield is shown in

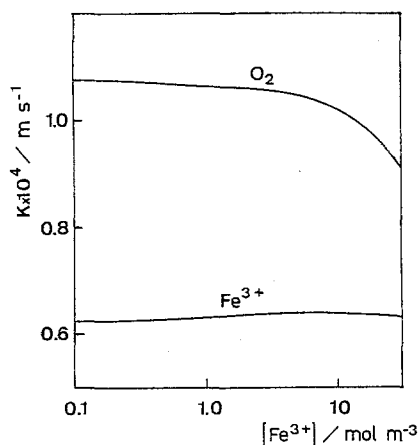


Fig. 5. Effective mass-transfer coefficients as a function of initial Fe^{3+} concentration.

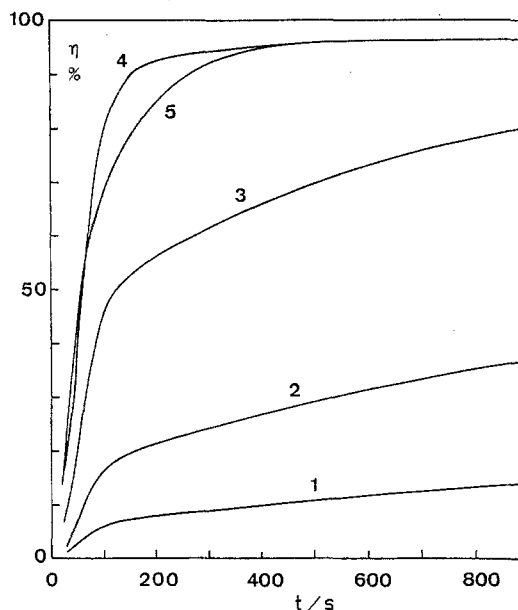


Fig. 6. Instantaneous current yield as a function of time. Initial Fe^{3+} concentrations in mol m^{-3} : (1) 0.1; (2) 0.3; (3) 1.0; (4) 3.0; (5) 10.0.

Fig. 6 as a function of time for different values of the initial Fe^{3+} concentration. After an initial rapid increase in yield, a pseudo-stationary phase is attained where the yield varies more slowly. The initial phase corresponds to the time required for the concentrations of the Fe^{2+} and H_2O_2 in the bulk solution to reach sufficiently high concentrations for the bulk to become productive.

In Fig. 7 the instantaneous current yield after 15 min operation is shown as a function of initial Fe^{3+} concentration. Also shown are the bulk concentrations of Fe^{2+} and H_2O_2 at the same point in time, while the dashed curves give the 'ideal' values for these concentrations calculated from Equations 25 and 26. It can be seen that the maximum yield occurs where the curves for the effective concentrations most closely coincide with those giving the ideal concentrations. The individual points are experimental mean current yields obtained by Tomat and Vecchi [11] after the passage of 550 coulombs (after about 6 h). The yields obtained by Tomat and Vecchi are much lower than the calculated yield, except at low iron concentrations, and the maximum yield occurs at an iron concentration about an order of magnitude lower than calculated. The lower

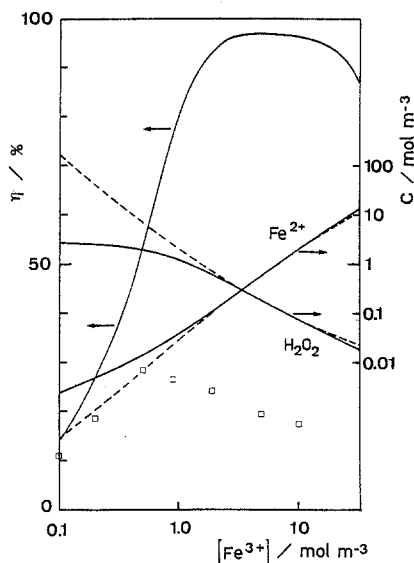


Fig. 7. Instantaneous current yield after 15 min operation and bulk concentrations of Fe^{2+} and H_2O_2 as functions of initial Fe^{3+} concentration. The broken lines indicate the ideal concentrations of Fe^{2+} and H_2O_2 calculated from Equations 25 and 26.

yields can be explained by the difference in time scales. The phenol formed in their system was allowed to accumulate in the reaction mixture and was thus exposed to further hydroxylation, giving catechol and hydroquinone [22]. The effect of further hydroxylation has not been included in our calculations because of the paucity of published data concerning this reaction, but it can be expected to modify considerably the yields obtained [23]. This was also the interpretation that Tomat and Vecchi made of the decrease in yield with time that they observed [11]. As the position of the maximum depends on the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio, there are at least three effects which could explain this difference.

(i) Oxygen solubility in the reaction mixture might have been much lower than the value of 1 mol m^{-3} estimated by Tomat and Vecchi.

(ii) The electrode kinetics for the reduction of oxygen are extremely complex and the assumption of mass-transfer-controlled reaction giving a 100% yield of hydrogen peroxide may not be a satisfactory approximation.

(iii) The presence of hydroquinone and catechol in the reaction mixture would alter the relative concentrations of the various reactants in such a way as to give a maximum yield at a lower iron concentration.

6. Conclusion

The calculations reported here have shown that Fenton's reagent, when used under conditions of electrochemical regeneration, should be capable of giving a high current yield and good selectivity. In fact the amount of reagent lost in the various side reactions is quite low and the main reason for any lowering of the yield is the excessive formation of either Fe^{2+} or H_2O_2 . It has also been found that, in order to make a clear judgment as to the accuracy of the model presented here, more experimental results would have to be obtained with an apparatus in which the phenol could be continuously extracted from the reaction mixture.

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