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Adsorption and Desorption of Coenzyme Q 10 from Activated Carbons: Study of Kinetics

May 2003

ADSORPTION AND DESORPTION OF COENZYME Q_{10} FROM ACTIVATED CARBONS: STUDY OF KINETICS

by

Pierre Delacolonge

A Thesis

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Of Lehigh University

In Candidacy for the Degree of

Master of Science

in

Chemical Engineering

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This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science.

April 24, 2003

Date

Thesis Advisor

Chairperson of Department

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Abstract

In the process of recovering coenzyme Q_{10} (COQ_{10}) from soybean oil, process that can be carried out by packed bed or expanded bed chromatography, activated carbons act as efficient adsorbents. In this study, based on simple stirred tank experiments, four different activated carbons were tested for COQ_{10} adsorption. The two best activated carbons, APA and CAL, being selected, adsorptions and desorptions were performed at different initial COQ_{10} concentrations, in order to calculate the rate constants associated to those processes, for each adsorbent. It was found that CAL is more efficient than APA from the adsorption prospect only, but that desorption seems, on the contrary, to be facilitated by the use of APA. It could also be noted that regardless of the activated carbon, the desorption process resulted in much smaller rate constants than adsorption.

Keywords: Adsorption, Activated Carbon, Coenzyme Q_{10}

1. Introduction

Coenzyme Q_{10} (COQ_{10}), also known as ubiquinone 10 or ubidecarenone, consists of a variable polyprenyl tail covalently bound to a quinone ring. Constituent of various cellular membranes, it is an endogenous cellular antioxidant, and above all an essential component of the mitochondrial electro transport chain, playing in this way a dramatic role in respiration. As it is a natural and quite plentyful component in soybean oil, COQ_{10} is expected to be recovered from this oil, through packed bed or expanded bed chromatography. For that matter, adsorption at a solution-carbon interface is a common technique: it is widely used on a large scale for water treatment, decolorizing, gold recovery, etc. Apart from those well-established applications, more recent interest is shown in the removal of pollutants and for the treatment of radioactive waste. Previous studies showed that, with COQ_{10} as an adsorbate, activated carbons are the most efficient adsorbents compared to silicas and other particular adsorbents.

This paper reports the study of the kinetics of adsorption of COQ_{10} on activated carbon and of desorption in hexane. It relies on simple stirred tank experiments.

2. Material and Methods

Four different Calgon Corporation (Pittsburgh, U.S.A.) activated carbons were used for this study: CAL 12*40 (high activity process carbon), APA 12*40, CPG LF 12*40 (acid-washed carbons) and WPX Pulv. (powdered activated carbon). The adsorbate employed was ubidecarenone (Nisshim Flour Milling Co., Tokyo, Japan), dissolved in crude soybean oil from Central Soya (Bellevue, U.S.A.). Desorption was conducted using hexane (Fisher Scientific). All experiments were run in a 100 mL beaker with continuous stirring.

The COQ_{10} concentration of the solution during adsorption and desorption was calculated using a high precision liquid chromatography column at a wavelength of 275 nm.

3. Adsorption

3.1 Choice of activated carbons

After testing four different activated carbons for adsorption of COQ_{10} (Figures 1, 2, 3 and 4), it was noted that the adsorbents that best fitted the operation were activated carbons APA and CAL. Thus the following studies are based on those two adsorbents.

3.2 Theoretical study of adsorption

The COQ_{10} concentration in the oil (C), the fraction of free sorbent active sites (1-θ) and the fraction of occupied sites (θ) are the three variables used to describe the adsorption kinetics. The adsorption of a solute A on a solid sorbent S can be written as:

$$S(s) + A \Leftrightarrow S - A(s) \qquad (1)$$

with the following kinetics:

$$\frac{-d[A]}{dt} = \frac{-dC}{t} = k_1 \cdot C^{n_1} \cdot (1-\theta)^{n_2} - k_2\theta^{n_3} \qquad (2)$$

Considering that at t = 0, θ = 0 and (1- θ) = 1, equation (2) yields:

$$(\frac{-dC}{dt})_0 = k_1 C_0^{n_1} \qquad (3)$$

Calculating the slope of the adsorption curve at t = 0 for different initial concentrations (experiment 1 and 2), one can find n_1 using:

$$n_1 = \frac{\ln\left(\frac{(-dC/dt)_0^1}{(-dC/dt)_0^2}\right)}{\ln\left(\frac{C_0^1}{C_0^2}\right)} \quad (4)$$

Using Figure 5, for APA, a value of 1.7 is obtained for n_1. For CAL, Figure 6 gives a value of 2.1. Consequently, it can be assumed that the actual value of n_1, which has to be common to the two sets of experiments, is 2, corresponding to an adsorption kinetics of order 2 with respect to the free adsorbate concentration C. Furthermore, assuming the most likely first order dependency on the other variables, as it was seen in other studies, equation (2) can be rewritten as:

$$\frac{-dC}{dt} = k_1 \cdot C^2 \cdot (1-\theta) - k_2 \cdot \theta \quad (5)$$

Knowing that θ is related to C:

$$\theta = \frac{C_0 - C}{C_0 - C_e} \quad (6)$$

with C_e being the equilibrium COQ10 concentration, θ can be replaced in equation (5) After integration,

$$C = \frac{C_0 + k_1 C_e t}{1 + k_1 t} \quad (7)$$

Differentiating equation (7) allows finding a linear equation of the square root of the inverse of –dC/dt with respect to t:

$$\sqrt{\frac{1}{(-dC/dt)}} = \sqrt{\frac{1}{k_1(C_0 - C_e)}} + \sqrt{\frac{k_1}{(C_0 - C_e)}} \cdot t \quad (8)$$

From equation (8), calculating the slope S of the straight line obtained, a value for the adsorption rate constant k_l can be found:

$$k_1 = S^2 \cdot (C_0 - C_e) \tag{9}$$

3.3 Results and comments

Figures 5 and 6, respectively for Activated Carbon APA and CAL, were used to calculate the value of the derivative dC/dt. The plot of the straight lines used to find adsorption rate constants is shown in Figures 7 and 8.

The results for k_l are displayed in Table 1.

From this table, it can be seen that the adsorption rate constant on Activated Carbon APA has an approximate value of 0.1 h^{-1}, while the adsorption rate constant on Activated Carbon CAL is about 0.16 h^{-1}. However, the constant is, in each case, a little stronger when the initial COQ_{10} concentration in the oil gets bigger.

Based on the values obtained for this study, considering the single adsorption process, it can be concluded that CAL provides more efficient adsorption than APA.

4. Desorption

4.1 Theoretical Study of Desorption

The desorption process consists in the same equilibrium as adsorption:

$$S - A(s) \Leftrightarrow S(s) + A \tag{10}$$

Similarly to equation (5) for adsorption, desorption kinetics follow the equation:

$$\frac{-dC}{dt} = k_2'\theta - k_1'C^2(1-\theta) \tag{11}$$

with C now being the COQ_{10} concentration in the solvent used for desorption, hexane, and θ now being defined by:

$$\theta = \frac{C}{C_e} \tag{12}$$

After integration,

$$C = \frac{k_1'C_e t}{k_1't - 1} \tag{13}$$

and differentiating this expression:

$$\sqrt{\frac{1}{(dC/dt)}} = \frac{1}{\sqrt{k_1'C_e}} - \sqrt{\frac{k_1'}{C_e}} \cdot t \tag{14}$$

From equation (14), calculating the slope S of the straight line obtained, a value for the desorption rate constant k_1' can be found:

$$k_1' = S^2 \cdot C_e \tag{15}$$

4.2 Results and comments

The method used for adsorption was repeated in the case of desorption: values of derivatives were obtained from Figures 9 and 10, and a plot of those values versus time is shown in Figures 11 and 12.

The results for k_1' are displayed in Table 2.

This table shows that desorption rate constants are 0.009 h^{-1} for Activated Carbon APA and 0.006 h^{-1} for CAL. It is noticeable that the reaction constant is now bigger for APA. If the adsorption process on APA was the slower one, here desorption seems easier than for CAL, which would make of APA the activated carbon that would first be retained for this kind of operation. However, it must be noted that the differences between the two activated carbons are not really significant, given the fact that the desorption rate constants are still small in both cases (about ten to twenty times smaller than adsorption rate constants).

5. Conclusion

This study, being mainly focused on kinetics, can be seen as a prelude to a scale-up of the COQ_{10} adsorption-desorption process. It would be necessary to study the thermodynamics for a complete knowledge of the process. Besides, in order to make COQ_{10} recovery profitable, an important part of the scale-up study would be to find a way to increase desorption efficiency, in view of the small rate constant values found in this study.

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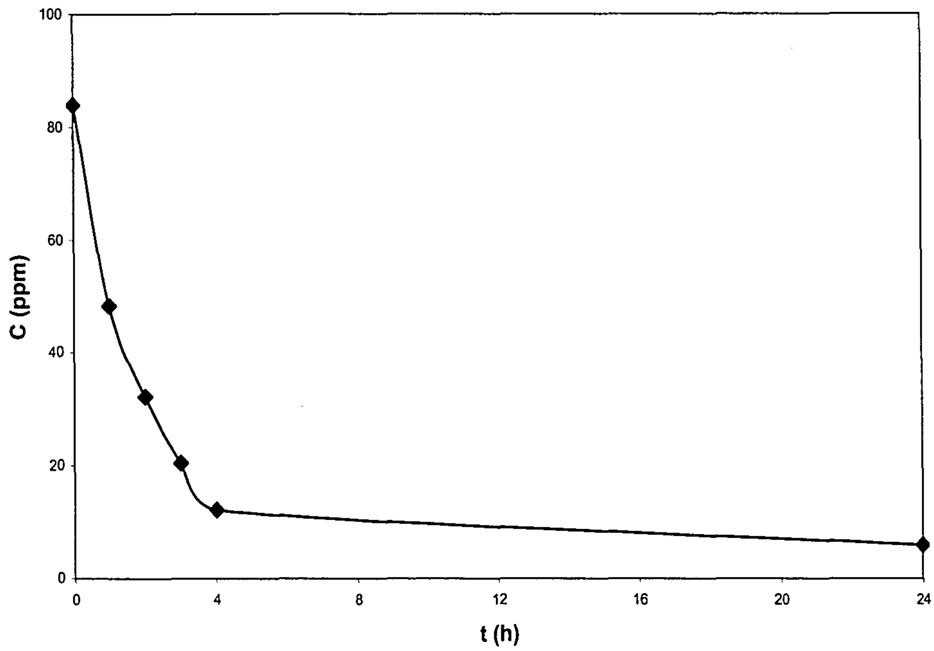
Figure 1.



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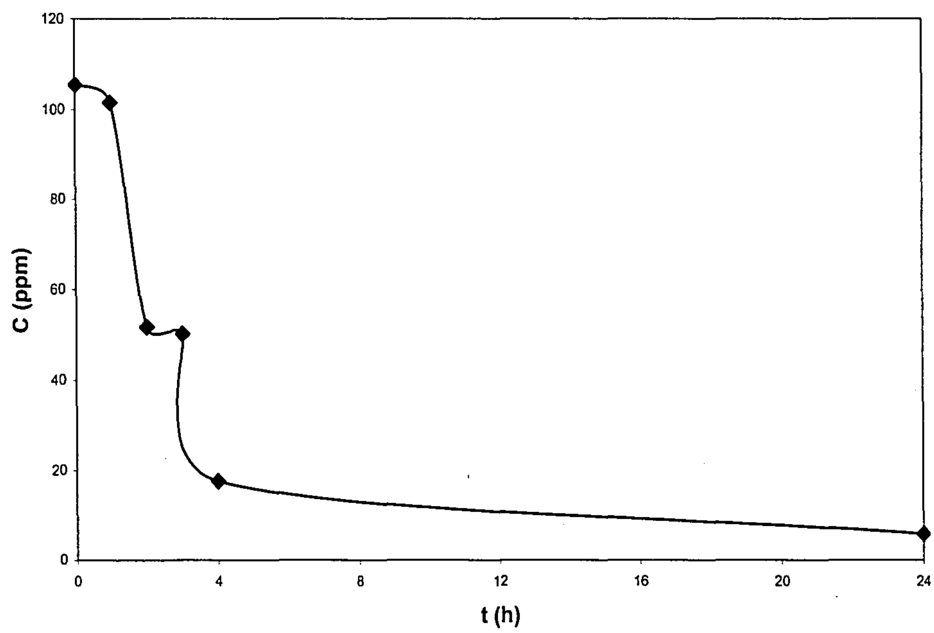

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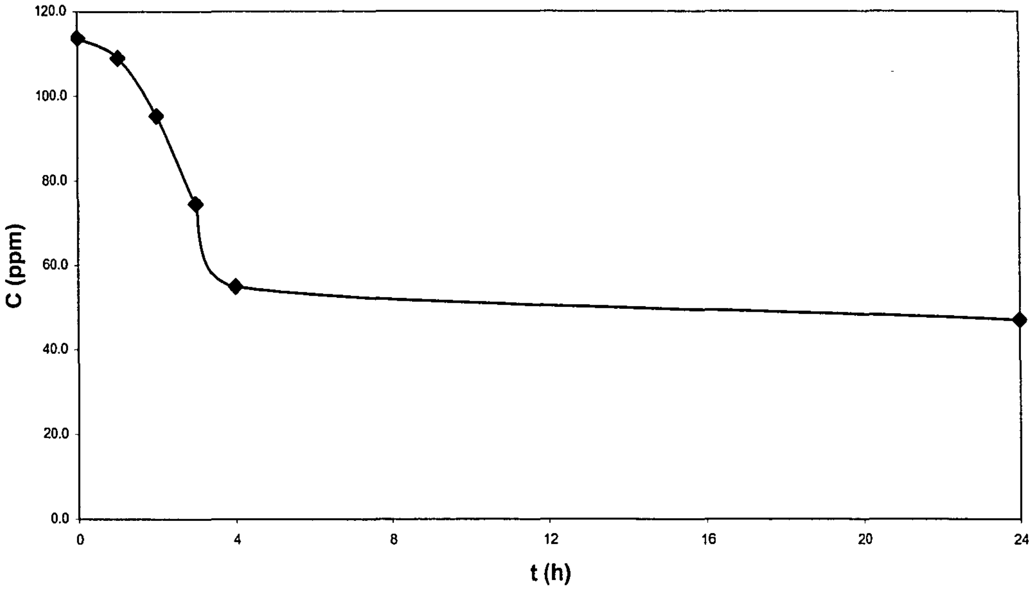

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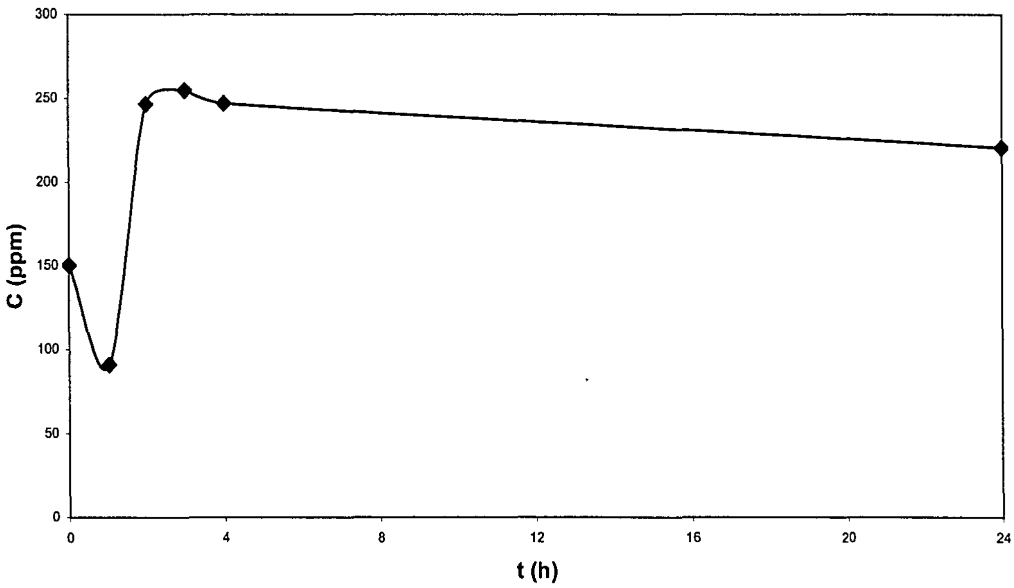

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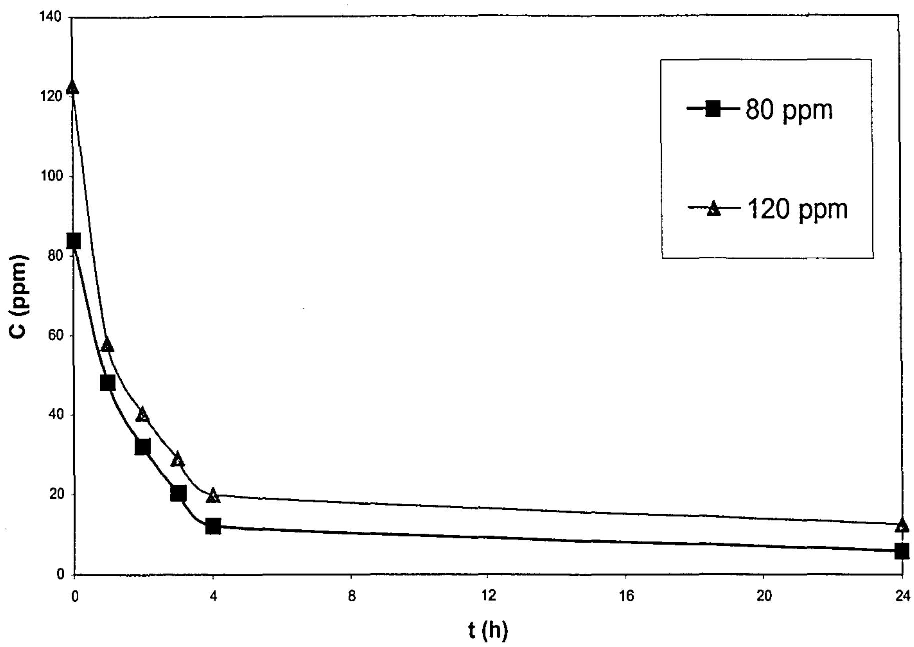

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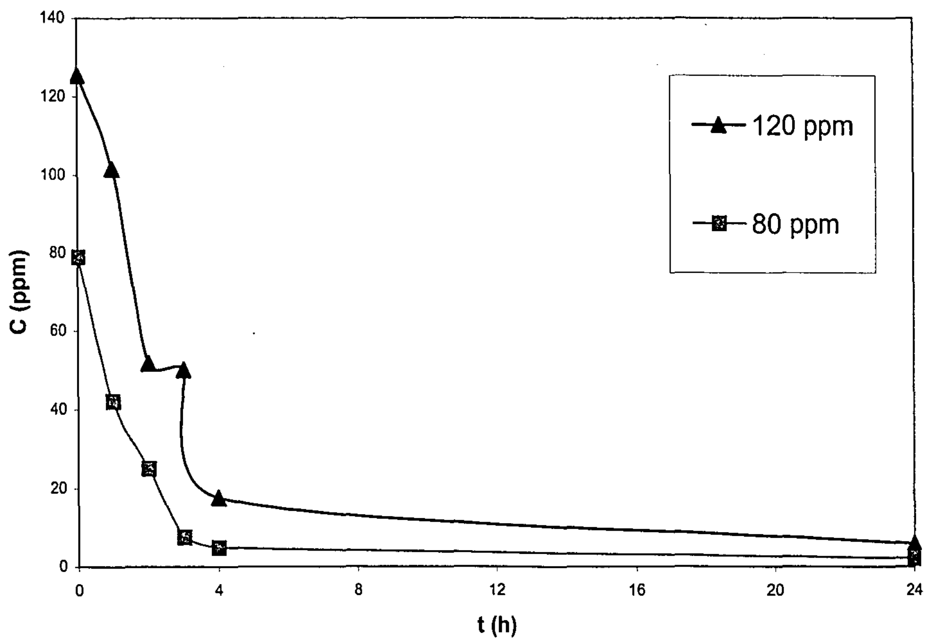

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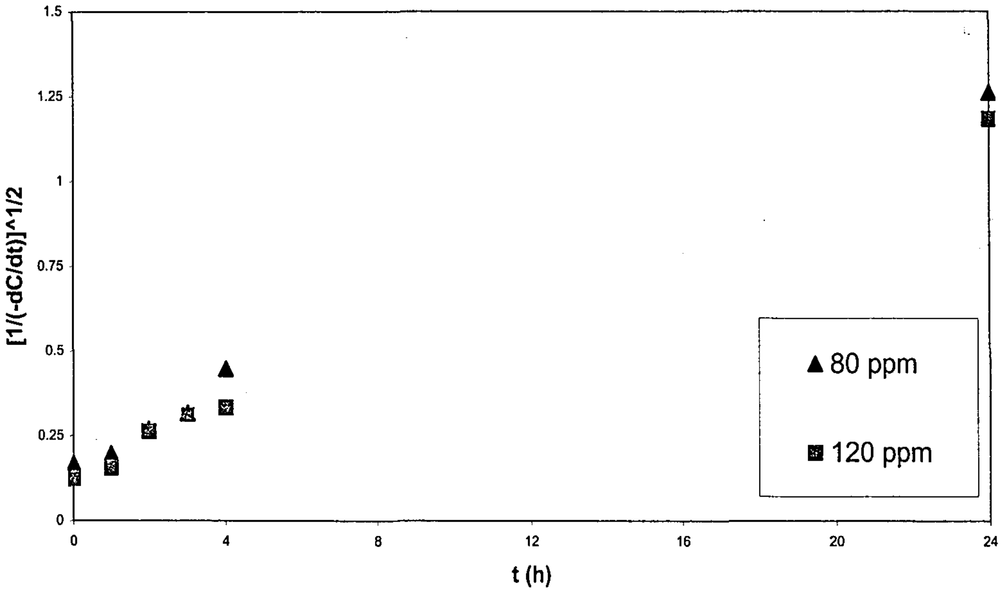

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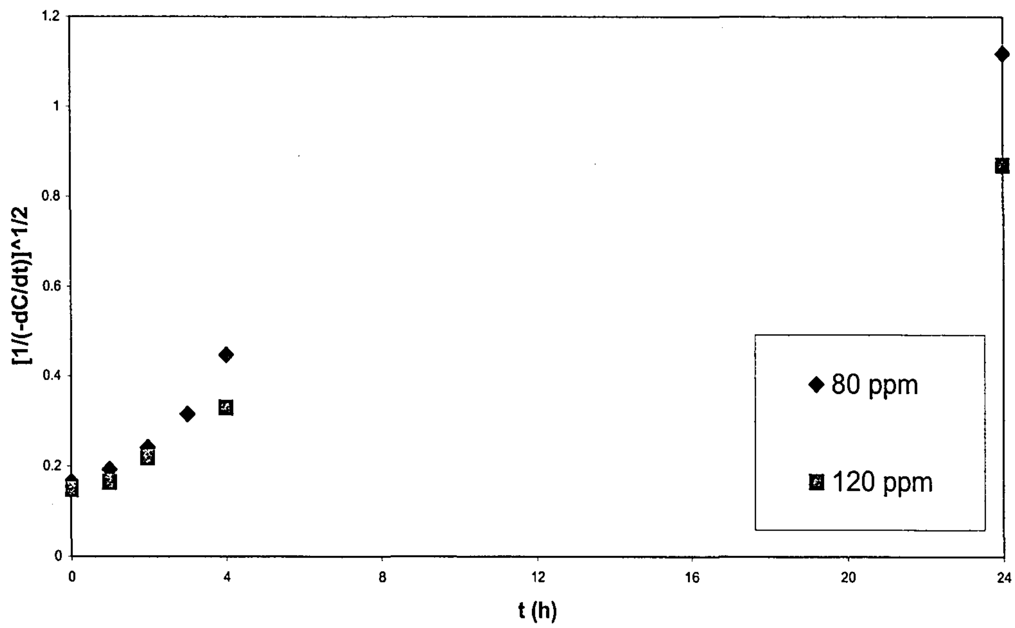

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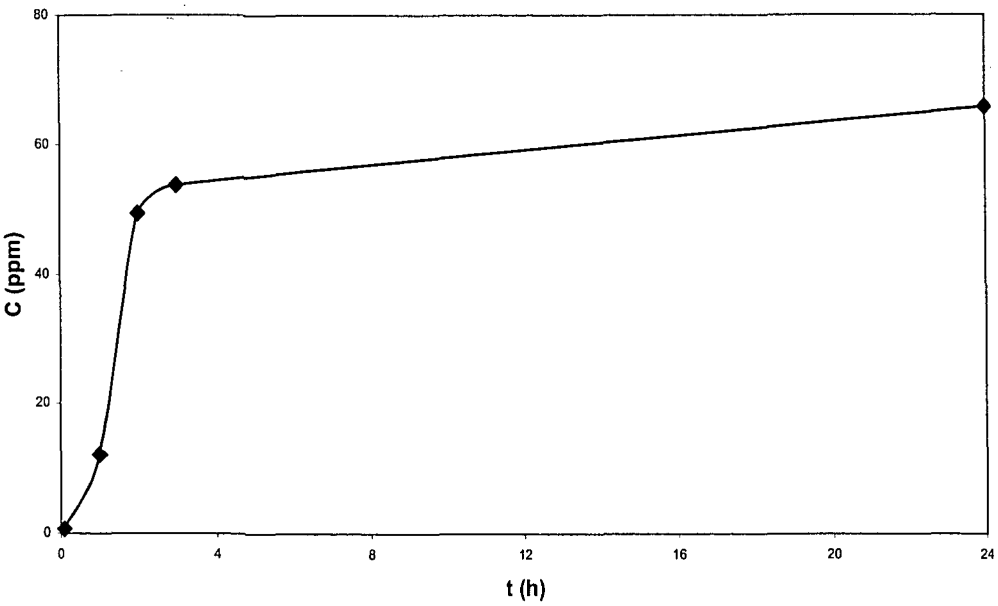

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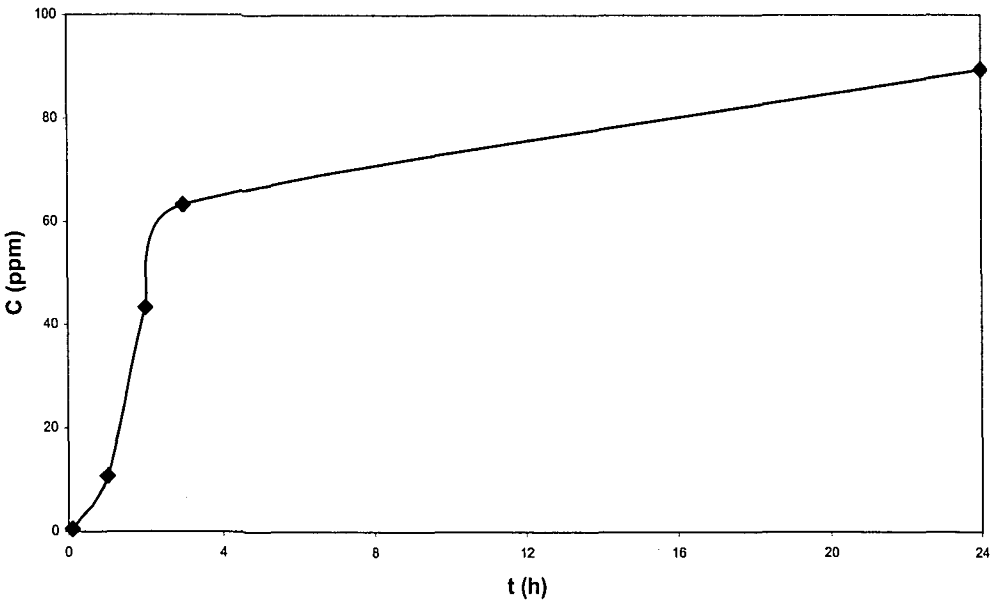

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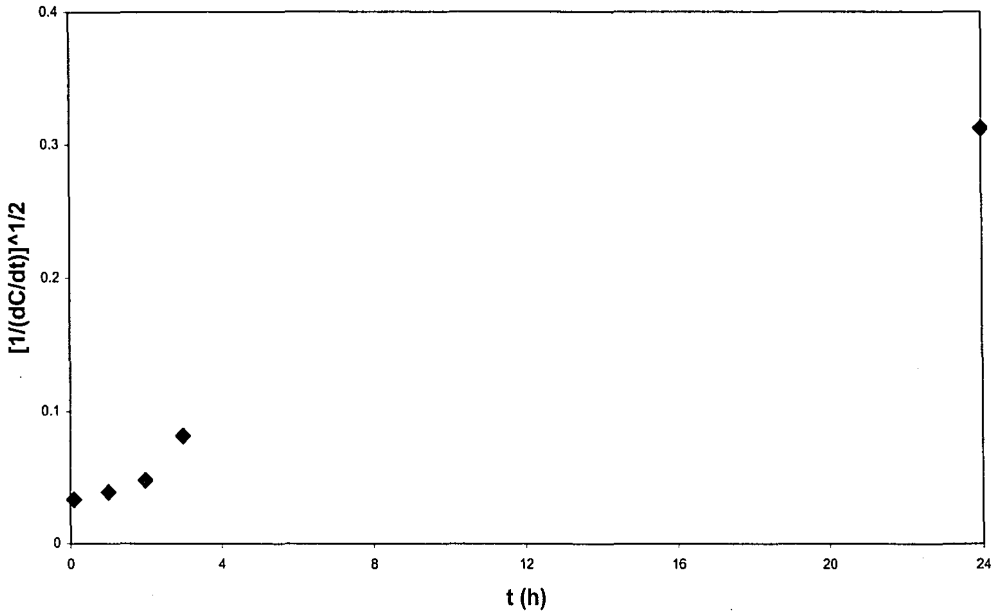

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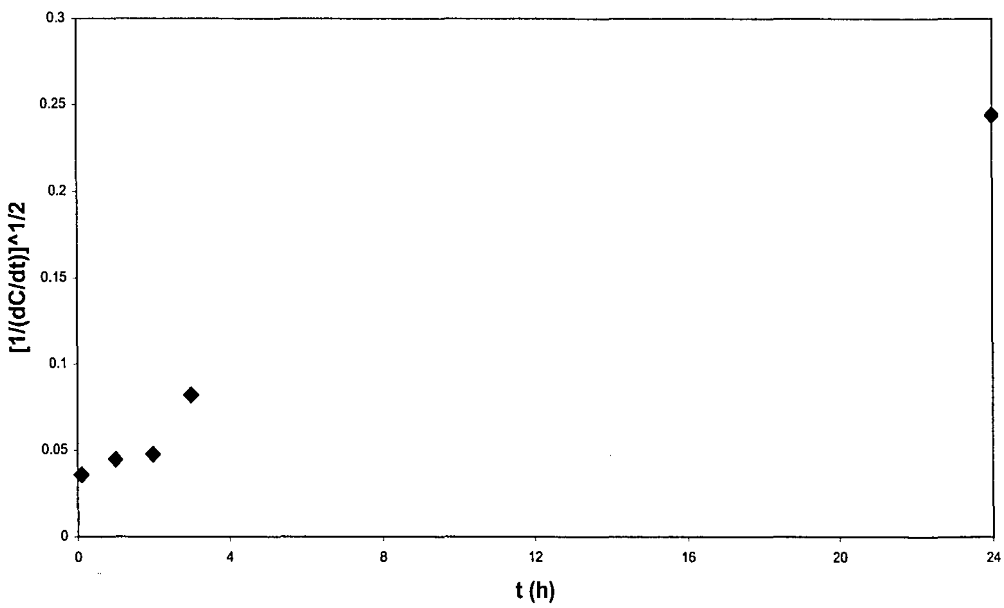

Table 1.

	APA		CAL	
	Co = 80 ppm	Co = 120 ppm	Co = 80 ppm	Co = 120 ppm
Slope	0.0451	0.0433	0.0392	0.0298
k1	0.11	0.1	0.14	0.18

Unit of S is [$h^{-1/2}ppm^{-1/2}$]

Unit of k_1 is [h^{-1}]

Table 2.

	APA	CAL
S	0.0117	0.0086
k_1'	0.009	0.006

Unit of S is [$h^{-1/2}ppm^{-1/2}$]

Unit of k_1' is [h^{-1}]

Vita

Pierre Delacolonge, son of Mr. François Delacolonge and Mrs. Geneviève Delacolonge, was born in Villefranche sur Saône, France, in September 12th 1980. He attended Lycée Claude Bernard (Villefranche sur Saône, France), Lycée La Martinière-Monplaisir (Lyon, France) and the Ecole Nationale Supérieure d'Ingénieurs en Génie Chimique (ENSIGC, Toulouse, France) where he got his bachelor's degree in Chemical Engineering.

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