THE USE OF THE MODIFIED SPLINE METHOD TO OPTIMIZE PHOTOCHEMICAL REACTORS

Hélio Gabardo Filho[1], Edson Tomaz[1], José Roberto Nunhez [1], Wilson de Figueiredo Jardim[2]

(1)Departamento de Processos Químicos, Faculdade de Engenharia Química, (2) Instituto de Química
Universidade Estadual de Campinas - UNICAMP, CEP 13083-970, Campinas, São Paulo, Brasil.
etomaz@feq.unicamp.br

1. Introduction

Several technologies have been developed in the last years to treat effluents. Among these, special attention has been given to Advanced Oxidative Processes (AOP). These processes are characterized for the generation of hydroxyls radicals that possesses a high oxidative power, capable of mineralizing the organic mass (Legrini et al., 1993).

There are several types of reactor being used for this process. However, among these, annular reactors are more adequate due to a higher efficiency in terms of power consumption per produced photon and, among annular reactor choices, the plug flow reactors stand out. (Smith, 1981).

The degradation phenol process has a peculiarity with relation to its degradation behavior: the reaction rate shows different behaviors due to the formation of some intermediate reactants, which allows the optimization of the system. The effluent treatment capacity is increased by making use of recycle (Levenspiel, 2000).

2. Methodology

The main parameter to be determined in an optimization process is the empirical reaction rate of the system. In order to determine it, a process for organic compounds degradation consisting of an annular reactor with an ultraviolet bulb placed concentrically and a storage tank for the mixture has been built. The organic compound is phenol and the chemical reagent to promote hydroxyls radicals generation is oxygen peroxide.

The monitoring of the degradation process was carried out through a series of sample collections from the storage tank which were analyzed for Total Organic Carbon (TOC).

It has been used initially a polynomial model to fit the experimental data. The model, however, proved inadequate for unwarranted inflexion points were obtained. Due to this, a more efficient model was used. The Modified Spline Method (MSM) by Nunhez et al. (1993, 2004) was used through the use of a windows based software named Power Spline, obtained at the main author homepage (www.feq.unicamp.br/~nunhez).

3. Results and Discussion

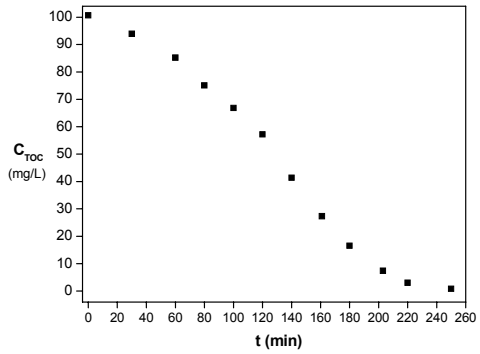

Figure 1 – Experimental phenol degradation with time measured using TOC content.

In order to determine the reaction rate of the system, a degradation batch experiment was performed initially with a phenol solution of C_{TOC}=100 m/L e C_{H2O2}= 600 mg/L using a bulb with an emitting power of 102 W and a reactor with a 2.7 cm of internal diameter. Figure 1 shows the results for TOC variation with time.

Using the results for TOC with time, a first fitting of the data was performed in order to obtain the first derivative of each experimental point, that is, the behavior of the reaction rate.

The photochemical reactor optimization is determined by the optimal recycle rate. The design reactor equation for a continuous system with recycle is a function of TOC concentration at the reactor entrance (C_{TOCi}), the TOC concentration at the outlet of the system (C_{TOCf}) and the reaction rate in relation to the TOC concentration TOC (r_{TOC}), where τ is the residence time, as shown in Equation 1.

$$\tau = -(R+1).\int_{C_{TOCi}}^{C_{TOCf}} \frac{dC_{TOC}}{-r_{TOC}} \quad (1)$$

The maximization of the feed entrance flow is linked to a reduction in the residence time and, this way, its determination is obtained by finding the minimum of Equation 1 in relation to the recycle determining, this way the value of R that minimizes τ. The minimization result is Equation 2, used to determine the optimum recycle rate:

$$\left.\frac{1}{-r_{TOC}}\right|_{C_{TOCi}} .\left(C_{TOCi} - C_{TOCf}\right) = \int_{C_{TOCf}}^{C_{TOCi}} \frac{dC_{TOC}}{-r_{TOC}} \quad (2)$$

A plot of se $1/-r_{TOC}$ versus C_{TOC} was built for each value of rate determined (r_{TOC}). Figure 2 shows this plot.

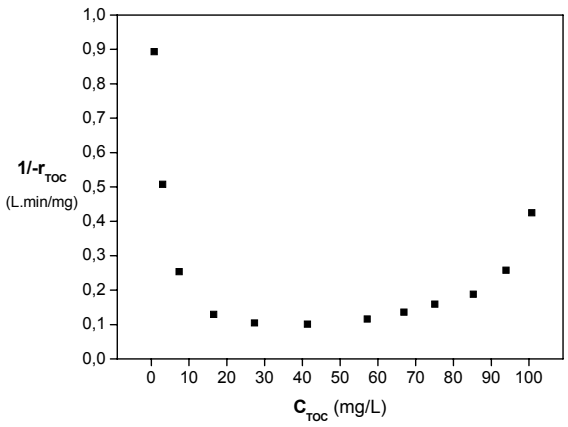

Figure 2 – Inverse of the reaction rate with time.

The optimum recycle rate is determined by the value of $C_{TOCi,}$ which satisfies Equation 2. Therefore a new fitting was performed using the software Power Spline®. Figure 3 shows the result of this fitting. An advantage of the MSM in these fittings is that it can guarantee the concavity of the curve even for imprecise data,

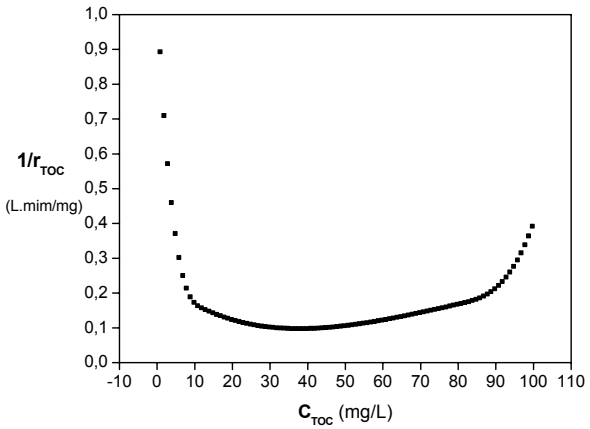

Figure 3 – Fitting of the inverse of the reaction rate with time using the Power Spline software.

By assuming that the operating values of the initial and final phenol concentration for a continuous process is (C_{TOC0}=90 mg/L and C_{TOCf}=5 mg/L, respectively), Equation 2 was used to determine the value of C_{TOCi} that satisfies the equality. The determined value, for this case is 61,1 mg/L.

The optimum recycle rate is given by Equation 3, using the value of de C_{TOCi} determined by Equation 2 and the values of C_{TOCo} e C_{TOCf}. The value for this case is 51% of the flow at the outlet should return to the reactor.

$$R = \frac{C_{TOC_0} - C_{TOC_i}}{C_{TOC_i} - C_{TOC_f}} = \frac{90{,}0 - 61{,}1}{61{,}1 - 5{,}0} = 0{,}5159 \qquad (3)$$

The residence time was also determined using Equation 1. The time needed to reduce the TOC concentration from 90 mg/L to 5 mg/L is 10.6 min. Since the net reactor volume is 245 ml, the feed flow determined is 23,1 mL/min and the recicle is 11,9 mL/min. This way the continuous system can be operated at its efficiency peak, allowing for a maximum operating capacity for the effluent treatment system.

4. Conclusions

Experimental optimization data for a continuous photochemical reactor has been presented in this paper. It has been observed that the presence of a recycle increases the capacity of the effluent treatment system, augmenting this way the viability of the process, since it lower costs for the mineralization of the organic carbon (C removed/kWh).

The methodology is based on an Equation used for the determination of the empirical reaction rate used for the design of a continuous annular reactor with recycle.

It was necessary to use an efficient method to fit the data to guarantee that the fitting was coherent with the phenomena. The MSM, incorporated inside the Power Spline software, proved adequate for the fitting since it has the capability of guaranteeing the concavity of the data fitting where no unwarranted inflexion should be present (this capability is only for strictly concave or convex curves). The polynomial fitting proved inadequate for it introduced inconsistent oscillations. Therefore this work presents a new fitting technique and proposes its use to properly fit reaction rates.

5. Bibliography

(Legrini et al., 1993) Legrini, O., Oliveros, E., Braun, A.M. Chem. Rev. Data 1993, 93, 671-698.
(Smith, 1981) Smith, J. M., Eds. Chemical Engineering Kinetics; Mc. Graw Hill: New York, 1981.
(Levenspiel, 2000) Levenspiel, O., Eds. Engenharia das Reações Químicas; Ed. Edgard Blucher ltda: São Paulo, 2000.
(Nunhez et al., 1993) Nunhez, J.R., Mori, M., Davila, S.G. Computers chem. Engng. Data 1993, 17, 1091-1099.
(Nunhez et al., 2004) Nunhez, J.R., Costa, C.B.B., Guirardello, R. Fluid Phase Equilibria. Data 2004, 220, 171-180.