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Optimal design of multi-stage bioreactors for degradation of phenolic industrial wastewater: Theoretical analysis

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Abstract

An analytical relationship for the optimum design of continuous stirred tank reactors (CSTR's) in series performing phenol degradation was derived. The optimal design is based on the minimum overall reactor volume required for a certain degree of phenol removal. It is assumed that cell growth kinetics follow the Haldanes kinetics model with respect to phenol and with no oxygen limitation. The effect of operating parameters such as phenol inlet feed concentration, phenol removal efficiency and number of CSTR's in series on the optimum design are investigated. The design equations compared the volume required for a certain percentage of phenol removal for the optimum design and the equal volume design which is currently practiced design criteria. This study shows that the optimum design (variable volume reactors) is more efficient than equal volume design at relatively high inlet feed substrate concentration, high substrate conversion and increasing the number of reactors. The percentage of degree reduction in the total volume using the optimum design compared to equal size reactors can be up to 80 % depending on the operating parameters. Up to five CSTRs in series and PFR are described in this study. Experimental and kinetic data used in this optimization problem were collected from the literature.

Keywords: Phenol degradation, Haldanes model, Substrate inhibition, CSTRs in series, bioreactor optimization, PFR

Introduction

Phenol is a common constituent of many industrial effluents, such as chemical, petroleum refineries, petrochemical, pharmaceutical, metallurgical, and textile industries. Phenol is water soluble and very toxic chemical. It is listed as priority pollutant by the US Environmental Protection Agency (Annaduri et al. 2000). Because of the high toxicity of phenolic compounds to human and marine life, stringent restrictions have been imposed on the concentration of these compounds in the wastewater discharged into the environment. Biological treatment is a favorable method for phenol degradation. It can be applied to wastewater with high concentration of phenol. Other methods of treatment such as physiochemical methods have drawbacks such as the production of other products more toxic than phenol such as chlorophenol (Hughes and Cooper 1996) also these methods require other processing steps (Kobayashi and Rittmann 1982) and they are proven to be costly.

CSTR's in series is commonly used in biological treatment of industrial wastewater such as activated sludge basins which are cascade connected. This arrangement of reactors offer number of advantages for degradation of phenol such as increased stability to the treatment plant when subjected to pulse load of phenol and also enhanced degree of phenol degradation by an adopted activated sludge recycle. Colvin and Rozich (1986) studied phenol degradation in a two-stage CSTR's . The second stage operated at high phenol concentration. Hobson and Millis (1990) optimized the degradation of phenolics by a mixed culture of microorganisms growing in a two stage chemostat. Cells exhibited inhibition kinetics at high concentrations of phenolics. The viability decreased with increasing dilution rate, or with increasing phenol concentration. Banerjee (1996) studied the removal of phenol and thiocyanate from wastewater in 4 stages of rotating biological contactors. Phenol was mostly removed in the first and second stage, while thiocyanate removal was greater in the last two stages. Bae et al (1995) has performed phenolic degradation in three CSTRs with mixed culture and recycle, but till now no one has gone up to level of five CSTRs in series with a plug flow reactor.

Biological treatment of industrial wastewater by activated sludge CSTR's in series is usually carried out in equal–size reactors. A number of investigators have studied the optimum design of CSTR's in series performing different cell growth kinetics (Wall and Hill 1992; Hill and Robinson 1989; Scuras et al. 2001) and enzymatic reactions (Abu-Reesh 1996; Abu-Reesh 2000).

The objective of this work is to derive an analytical performance relationship for the optimum design of N-CSTRs in series for degradation of phenol. The optimal design was based on the minimum overall reactor volume required for a certain degree of substrate conversion and the total number of reactors. The

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intermediate phenol concentration at different operating conditions in the multi-stage reactor, correspond to the optimum design and to the equal size design criteria were determined. The effect of substrate conversion, substrate concentration in the feed to the first reactor and number of reactors on the total dimensionless residence time was also determined.

Methodology

The growth kinetics is assumed to follow Haldanes equation which is the most widely used kinetic equation to describe substrate inhibition by phenol (Tang and Fan 1987). Assuming no oxygen limitations, the specific growth rate is described by:

$$\mu = \mu_{\max} \frac{S}{K_s + S + \frac{S^2}{K_i}} \quad (1)$$

Where, S is the substrate (phenol) concentration, K_s is the substrate saturation constant and K_i is the substrate inhibition constant. This equation reduces to Monod kinetic model when K_i goes to infinity. For N-CSTR's in series, substrate balance on the i^{th} reactor assuming steady state well mixed reactors gives:

$$F(S_{i-1} - S_i) = \mu_i X_i \frac{V_i}{Y_x} \quad (2)$$

Where, F is the liquid volume flow rate, X is the cell concentration, V is the reactor volume. Y_x is the cell yield coefficient. Cell concentration in the i^{th} reactor can be related to the substrate concentration by the cell yield coefficient, Y_x (X_o assumed to have a value of 10 mg/l).

$$X_i = X_o + Y_x(S_o - S_i) \quad (3)$$

By substituting Eq (1) and (3) into (2), the mean residence time in the i^{th} reactor is given by:

$$\tau_i = \frac{(S_{i-1} - S_i)\,(K_s + S_i + S^2/K_i)\,Y_x}{\mu_{\max}\, S_i\, [X_o + Y_x(S_o - S_i)]} \quad (4)$$

By using dimensionless variables, the dimensionless residence time θ_i is given by:

$$\theta_i = \frac{(\alpha_{i-1} - \alpha_i)\,(K_s^* + \alpha_i + K_i^*\,\alpha_i^2)}{\alpha_i\,(A - \alpha_i)}$$

i=1,2,……, N (5)

Where $\alpha_i = \frac{S_i}{S_o}$, $K_s^* = \frac{K_s}{S_o}$, $K_i^* = \frac{S_o}{K_i}$,

$\theta_i = \mu_{\max}\tau_i$, $A = \frac{X_o}{Y_x\, S_o} + 1$

To find the conditions for optimum design (minimum overall reactor volume):

$$\frac{\partial}{\partial S_i}\left[\sum_{i=1}^{N}\theta_i\right] = 0$$

i =1,2,…….., N-1 (6)

Only two terms of Eq (6) have α_i (i.e i^{th} and (i+1)th) as given by

$$\frac{\partial}{\partial \alpha_i}\left[\frac{(\alpha_{i-1} - \alpha_i)\,(K_s^* + \alpha_i + K_i^*\,\alpha_i^2)}{\alpha_i(A - \alpha_i)} + \frac{(\alpha_i - \alpha_{i+1})\,(K_s^* + \alpha_{i+1} + K_i^*\,\alpha_{i+1}^2)}{\alpha_{i+1}(A - \alpha_{i+1})}\right] = 0$$

i =1,2,…N-1 (7)

Equation 7 represents N-1 equations with N-1 unknowns (i.e. α_1 to α_{N-1}). α_o by definition should be equal to 1 and α_N is related to the substrate conversion, δ by the relation $\delta = 1 - \alpha_N$. Equation (7) can be simplified to give α_{i-1} as a function of α_i and α_{i+1}.

$$\alpha_{i-1} = \frac{A\,(\frac{K_s^*}{\alpha_i} + 1 + K_i^*\alpha_i) + (K_i^*\alpha_i - \frac{K_s^*}{\alpha_i})(A - \alpha_i) - (\frac{K_s^*}{\alpha_{i+1}} + 1 + K_i^*\alpha_{i+1})(\frac{(A - \alpha_{i+1})^2}{(A - \alpha_{i+1})})}{(\frac{K_s^*}{\alpha_i} + 1 + K_i^*\alpha_i) + (K_i^* - \frac{K_s^*}{\alpha_i^2})\,(A - \alpha_i)}$$

i =1,2,…..N-1 (8)

By knowing α_N and α_o, the intermediate dimensionless substrate concentrations that correspond to the optimum design can be calculated using Fortran program (guessing α_{N-1} and moving backwards to satisfy the condition of α_o = 1).

Plug flow reactor (PFR)

The residence time for PFR is determined by integration of the Haldanes kinetic equation (Fogler 2006). The dimensionless residence time is given by:

$$\theta_{PFR} = \tau_{PFR}\,\mu_{\max} = (\frac{K_s^*}{A} + 1 + K_i^*\,\mathrm{A})\,\ell\mathrm{n}\left(\frac{\mathrm{A} - \alpha_L}{\mathrm{A} - 1}\right) - \frac{K_s^*}{A}\,\ell n\alpha_L - K_i^*(1 - \alpha_L) \quad (9)$$

Where, α_L is the dimensionless substrate concentration at the PFR exit.

Critical dimensionless substrate concentration, $\alpha_{critical}$

Hill and Robinson (1989) used the concept of critical dimensionless substrate concentration $\alpha_{critical}$ to determine if there is advantage of using multi-stage reactors compared to one CSTR. If α_1 approach α_2, $\alpha = \alpha_{critical}$ and is given by:

$$\alpha_{critical} = \frac{\sqrt{K_s^{*2} + AK_s^*[1 + K_i^*(A-1)]} - K_s^*}{(1 + A\,K_i^*)} = f(K_s, K_i, A) \quad (10)$$

It is clear from Eq (10) that the critical dimensionless substrate concentration depends on the dimensionless substrate saturation constant and the dimensionless substrate inhibition constant in addition to the cell concentration in the feed to the first reactor. The required substrate conversion determines whether one or multiple reactor should be used to minimize the total reactors volume.

If $\alpha_N \le \alpha_{critical} < 1$ One reactor is preferred
If $\alpha_N < \alpha_{critical}$ Multiple reactors are preferred

CSTR's of equal size in series

The volume of reactors of equal size was obtained and compared with the optimum volume required to achieve the same degree of substrate conversion. By applying equation (5) for reactors i and i+1 and equating θ_i and θ_{i+1}, the intermediate substrate concentrations α_i can be obtained as a function of α_{i+1} and α_{i-1}, which satisfies the conditions of equal size reactors. The relation is given by:

$$\alpha_{i-1} = \left(\frac{K_s^* + \alpha_{i+1} + K_i^* \alpha_{i+1}^2}{K_s^* + \alpha_i + K_i^* \alpha_i^2}\right)\left(\frac{A - \alpha_i}{A - \alpha_{i+1}}\right)\left(\frac{\alpha_i - \alpha_{i+1}}{\alpha_i + 1}\right)\alpha_i + \alpha_i$$

i=1,2,….N-1 (11)

A FORTRAN computer program was also used to calculate the intermediate α_i for equal size reactors. The total residence time can be calculated as given by:

$$\theta_{tot,eq} = N\,\theta_{eq} \quad (12)$$

The total residence time in case of equal size reactors and optimum (minimum θ) size were compared. The percentage reduction in total volume using minimum volume design as compared to equal volume design was calculated:

$$\% \text{ Reduction in total volume} = \frac{(\theta_{tot,eq} - \theta_{tot,opt})}{\theta_{tot,eq}} X100 \quad (13)$$

Comparison was made between the required volumes of the two design criteria.

Results and discussions

Kinetic and stoichiometric coefficients for phenol degradation were obtained from the literature as shown in Table 1. From the design equations above, it is clear that the optimum configuration of N-CSTRs in series depend on the substrate concentration in the feed to the first reactor, the substrate conversion and the number of reactors in series. Up to 5 CSTRs in series and a PFR were used in this study. Using So=50 mg/l as the substrate concentration in the feed to the first reactor, Figures 1a and 1b show the effect of substrate conversion on the total optimum dimensionless residence time for low substrate conversion (Fig 1a) and for high substrate conversion(Fig. 1b). It is clear from the two figures that the higher the conversion, the higher the residence time needed to achieve this conversion. Also increasing the number of reactors has advantage only at high substrate conversion. At low substrate conversion (Fig 1a) the optimum configuration is one CSTR. Using high inlet substrate concentration (So=500 mg/l) the effect of the substrate conversion on the total optimum dimensionless residence time is shown in Figure 1c. It is clear from this figure that one CSTR is the optimum reactor configuration and increasing the number of reactors increases the total dimensionless residence time. This is expected for substrate inhibition kinetics such as the case of phenol degradation. High substrate concentration such as in the case of PFR (or large number of CSTRs in series N) will results in low phenol degradation rate and , therefore, high residence time.

Table 1: Kinetics and stoichiometric coefficient used for phenol degradation (Tang and Fan 1987)

K_s (Substrate saturation constant)	10.948 mg/l
K_i (Substrate inhibition constant)	113 mg/l
Y_x (yield coefficient)	0.496 mg cells/mg substrate

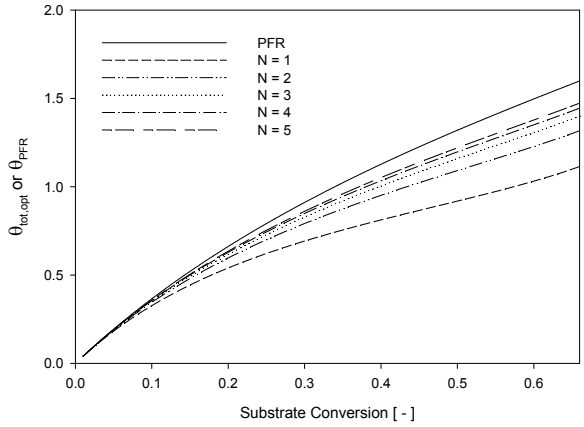

Figure 1a: Effect of substrate conversion on the total optimum dimensionless residence time (So=50 mg/l) (low substrate conversion)

Using 90 % substrate conversion, Figures 2a and 2b show the effect of inlet substrate concentration to the first reactor on the total optimum dimensionless residence time. Figure 2a shows that using more than one CSTR in series is beneficial only at very low So. At high So as shown in Figure 2b, one CSTR is the optimum configuration required to achieve 90% substrate conversion. Increasing the number of reactors increases the total dimensionless residence time. The highest residence time achieved using PFR. At 99% substrate conversion , Figure 2C shows the effect of So on the total optimum dimensionless residence time. It is clear from this figure that CSTRs in series is beneficial especially at low So. At high So, about 2 CSTRs in series, are the optimum reactors configuration needed to achieve 99% conversion.

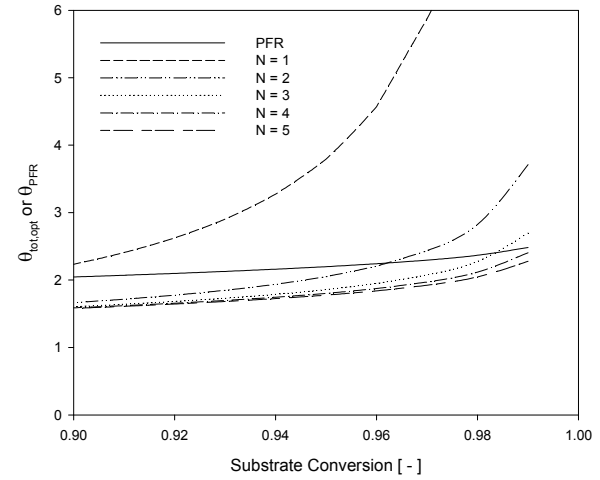

Figure 1b: Effect of substrate conversion on the total optimum dimensionless residence time (So=50 mg/l) (high substrate conversion)

The volume of reactors of equal size was obtained and compared with the optimum volume of reactors required to achieve the same degree of substrate conversion. Figures 3a-d shows the effect of

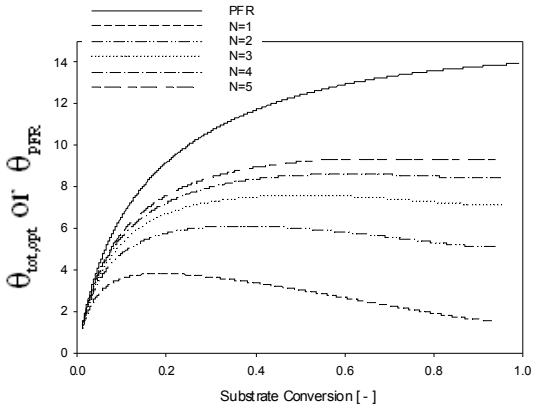

Figure 1c: Effect of substrate conversion on the total optimum dimensionless residence time (So=500 mg/l)

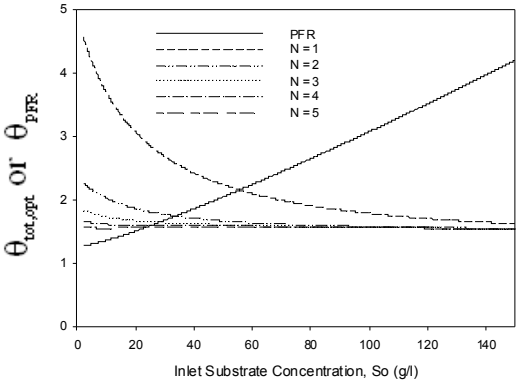

Figure 2a: Effect of inlet substrate concentration on the dimensionless residence time (S conversion=90%) (low inlet substrate concentration)

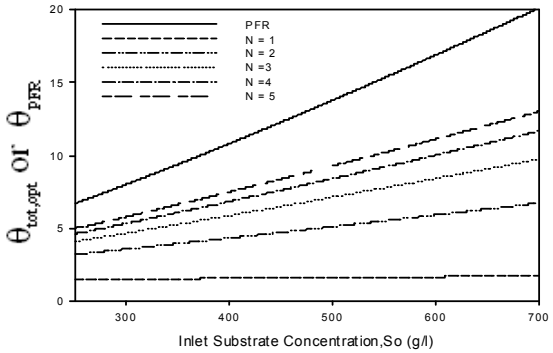

Figure 2b: Effect of inlet substrate concentration on the dimensionless residence time(S conversion=90%) (high inlet substrate concentration)

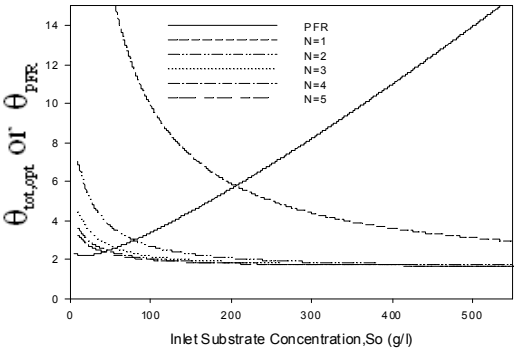

Figure 2c: Effect of inlet substrate concentration on the dimensionless residence time(S conversion=99%)

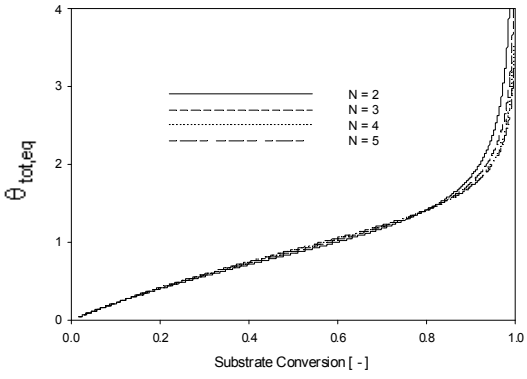

Figure 3a: Effect of substrate conversion on the dimensionless residence time of equal CSTRs in series (So = 30 mg/l)

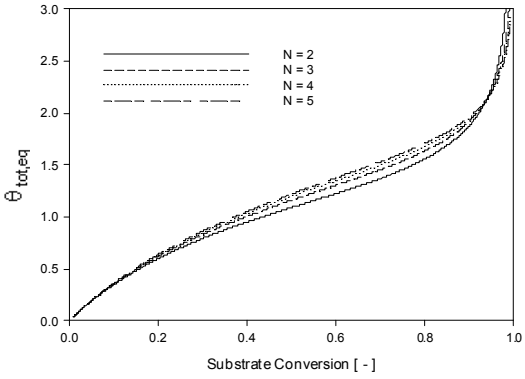

Figure 3b: Effect of substrate conversion on the total dimensionless residence time of equal CSTRs in series (So = 50 mg/l)

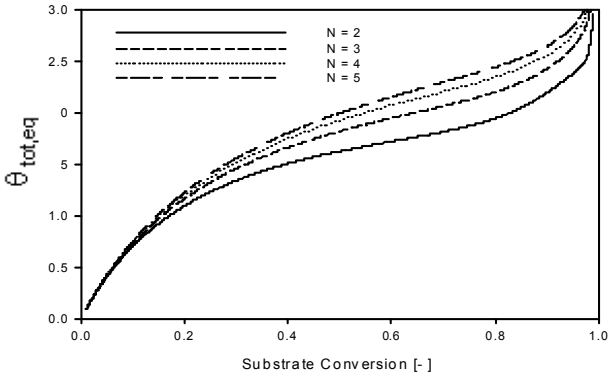

Figure 3c: Effect of substrate conversion on the total dimensionless residence time for equal CSTRs in series (So = 100 mg/l)

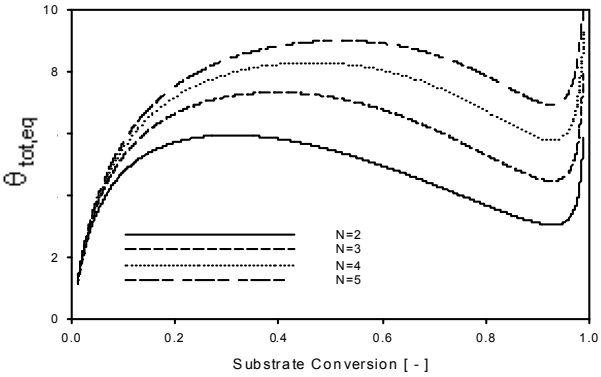

Figure 3d: Effect of substrate conversion on the total dimensionless residence time for equal CSTRs in series (So = 500 mg/l)

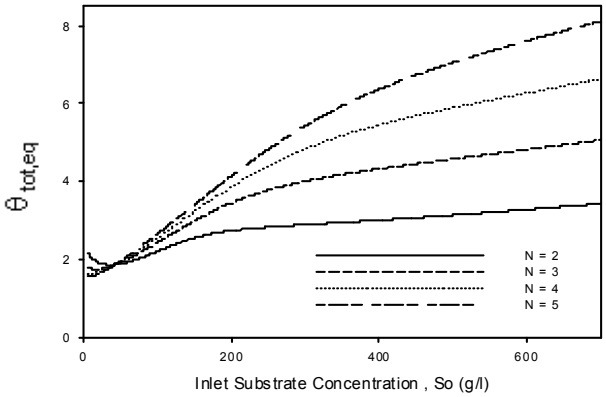

Figure 4a: Effect of inlet substrate concentration on the total dimensionless residence time of equal CSTRs in series (S conversion= 90%)

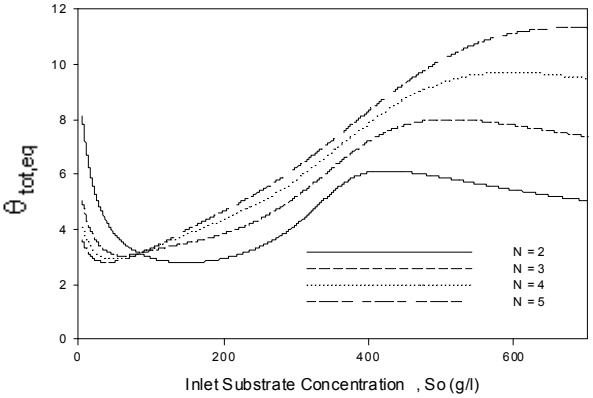

Figure 4b: Effect of inlet substrate concentration on the total dimensionless residence time of equal CSTRs in series (S conversion= 99%)

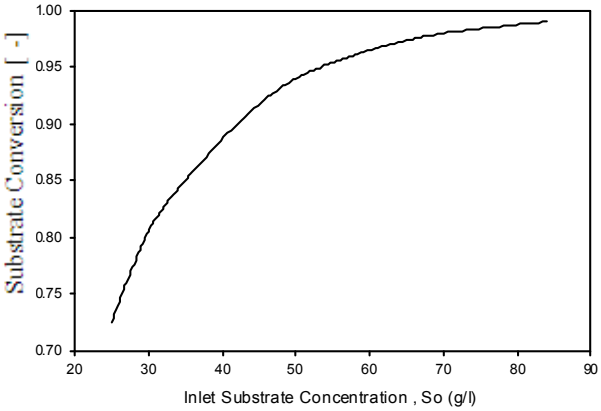

Figure 4c: The effect of inlet substrate concentration on the substrate conversion above which CSTRs in series reactors is beneficial compared to single CSTR (i.e crossover point)

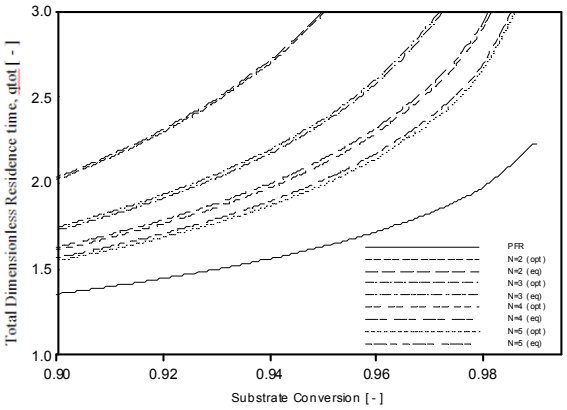

Figure 5a: The effect of substrate conversion on the total dimensionless residence time for optimum and equal CSTRs in series . PFR is shown for comparison (So= 10 mg/l)

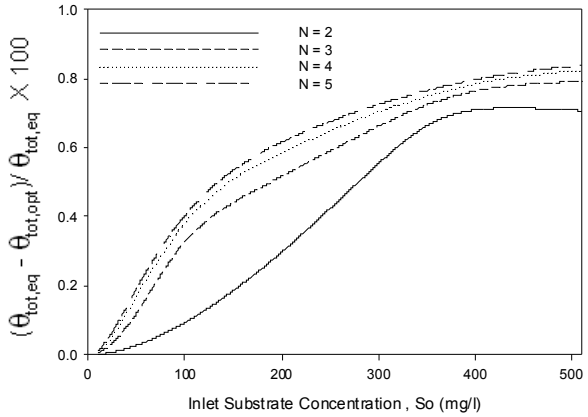

Figure 5b: Effect of inlet substrate concentration on the degree reduction in total volume using optimum volume design as compared to equal volume design for reactors connected in series (S conversion =99%).

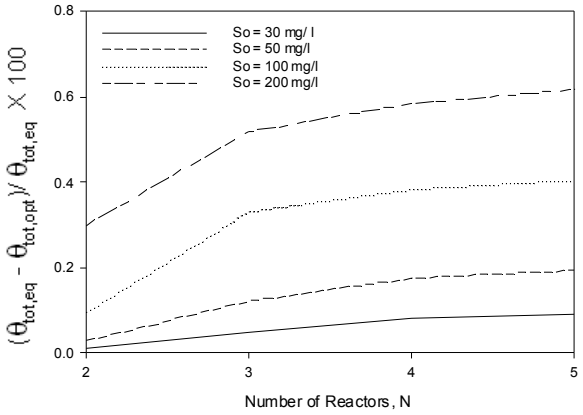

Figure 5c: Effect of inlet substrate concentration on the degree reduction in total volume using optimum volume design as compared to equal volume design for reactors connected in series (S conversion = 99%).

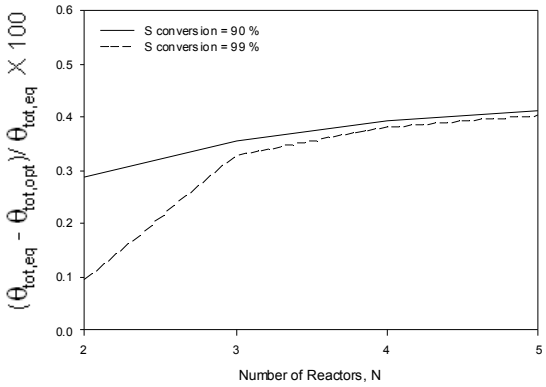

Figure 5d: Effect of substrate conversion on the degree reduction in total volume using optimum volume design as compared to equal volume design for reactors connected in series (So = 100 mg /l).

substrate conversion on the dimensionless residence time for equal CSTRs in series using So of 30, 50, 100 and 500 mg/l respectively. It is clear from the figures that increasing the substrate conversion increases the total residence time for the first 3 figures (3 a, b, c). In Fig 3d, the total residence time pass through maximum and minimum points. In Fig 3a (So=30 mg/l) and in Fig3b (So=50 mg/l) staging of CSTRs is preferred only at high substrate conversion i.e. at substrate conversion above the crossover point. In Figures 3a and 3b, the crossover points are at substrate conversions of 0.802 and 0.938 respectively. In Figures 3c (So=100 mg/l) and 3d (So=500 mg/l), no crossover points were observed, therefore, Increasing the number of CSTRs in series is not recommended.

The effect of inlet substrate concentration to the first reactor on the total dimensionless residence time of equal CSTRs in series is shown in figures 4a and 4b for substrate conversions of 90 and 99% respectively. Crossover points were observed at So of 35 and 84 mg/l using 90% and 99 % substrate conversion respectively. The crossover point location depends on the substrate conversion and the substrate concentration in the feed to the first reactor as shown in Figure 4c. It is clear from this figure that at high inlet substrate concentration, the crossover point is observed at high substrate conversion, i.e using CSTRs in series has advantage only at high substrate conversion. The dimensionless residence time versus substrate conversion (high) for both the optimum design and the equal volume reactors design is shown in figure 5a using low substrate concentration in the feed to the first reactor (So= 10 mg/l) . Using these conditions, No significant difference in the residence time was observed between the two design criteria. The percentage reduction in total volume (residence time) using the optimum design compared to equal volume design depends on So, S conversion and number of reactors N. Figure 5b shows the effect of So on the percentage degree reduction in total volume between the two design criteria for 99% conversion. The percentage degree reduction in total volume increased with increasing So and N. This is also clear in Figure 5c. The effect of substrate conversion (Fig 5d) is appreciable only for two CSTRs in series where high degree reduction is obtained at lower conversion.

Conclusions

For biological treatment of phenolic wastewater using CSTRs in series, increasing the number of reactors has advantage (lower volume) only at low inlet substrate (phenol) concentration and for high percentage of substrate conversion. At high inlet substrate concentration, the minimum volume is achieved using one reactor. This is expected due to phenol inhibition. The transition (crossover point) occurs at certain inlet substrate concentration, S_o depending on the substrate conversion. The higher the substrate conversion, the higher the S_o at which the transition occurs. At low inlet substrate concentrations and very high substrate conversion, comparison of the optimum and equal volume CSTRs in series showed that the optimum design (variable volume reactors) is more efficient than equal volume design specially at relatively high S_o and increasing the number of reactors. The findings of this optimization problem can be further extended to other compounds with similar kinetics of biodegradation to phenol.

Acknowledgements

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Nomenclature

A	constant defined as $\left(\frac{X_o}{S_o Y_x}+1\right)$
F	liquid flow rate, l/h
K_s	Monod constant, g/l
K_s^*	dimensionless Monod constant
K_i	substrate inhibition constant, g/l
K_i^*	dimensionless substrate inhibition constant
N	number of CSTRs in series
S	substrate concentration, g/l
V	reactor volume, l
X	cell concentration, g/l
Y_x	cell yield coefficient, g cells/g substrate

Greek Symbols

α	dimensionless substrate concentration
τ	residence time, h
θ	dimensionless residence time
μ	specific growth rate, h^{-1}
μ_{max}	maximum specific growth rate, h^{-1}
δ	degree of substrate conversion

Subscripts

i	refer to the i^{th} reactor
L	refer to the plug flow reactor exit
N	refer to the n^{th} reactor
o	initial
tot	total
eq	equal
opt	optimum

Abbreviations

CSTR	continuous stirred tank reactor
PFR	plug flow reactor

References

Abu-Reesh IM (1996) Optimal design for CSTRs in series using reversible Michaelis-Menten reactions. Bioprocess Eng 15(5):257-264

Abu-Reesh IM (2000) Optimal design for CSTRs in series performing enzymatic lactose hydrolysis. Bioprocess Eng 23:709-713

Annaduri G, Mathalai Balan S and Murugesan T (2000) Design of experiments in the biodegradation of phenol using immobilized Pseudomonas pictorum (NICM-2077) on activated carbon. Bioprocess Eng 22(2):101-107

Bae BH, Autenrieth RL, Bonner JS (1995) Kinetics of multiple phenolic compounds degradation with a mixed culture in a continuous-flow reactor. Water Environmental Research 67(2):215-223

Banerjee G (1996) Phenol and thiocyanate based wastewater treatment in RBC reactor. J Environ Eng ASCE 122(10) : 941-948

Colvin RJ and Rozich AR (1986) Phenol growth kinetics of heterogeneous populations in a two-stage continuous culture system. J Water Pollut Control Fed 58(4):326-332

Fogler HS (2006) Elements of Chemical Reaction Engineering, 4th ed. Prentice Hall

Hill GA and Robinson CW (1989) Minimum tank volumes for CFST bioreactors in series. Can J Chem Eng 67:818-824

Hobson MJ and Millis NF(1990) Chemostat studies of a mixed culture growing on phenolics. J Water Pollut Control Fed 62(5):684-691

Hughes SM and Cooper DG (1996) Biodegradation of phenol using the self-cycling fermentation(SCF) process. Biotechnol Bioeng 51:112-119

Kobayashi H and Rittmann BE (1982) Microbial removal of hazardous organic compounds. Environ Sci Technol 16:170-183

Scuras SE, Jobbagy A and Grady Jr CPL (2001) Optimization of activated sludge reactor configuration : Kinetics considerations. Water Research 35(18):4277- 4284

Tang WT and Fan LS (1987) Steady state phenol degradation in a draft-tube, gas–liquid–solid fluidized-bed bioreactor. AICh E Journal 33:239–249

Wall JB and Hill GA (1992) Optimum CFST bioreactor design : Experimental study using batch growth parameters for *S. cerevesiae* producing ethanol. Can J Chem Eng 70:148-152