Modelling Kinetics of Photocatalytic Reactions

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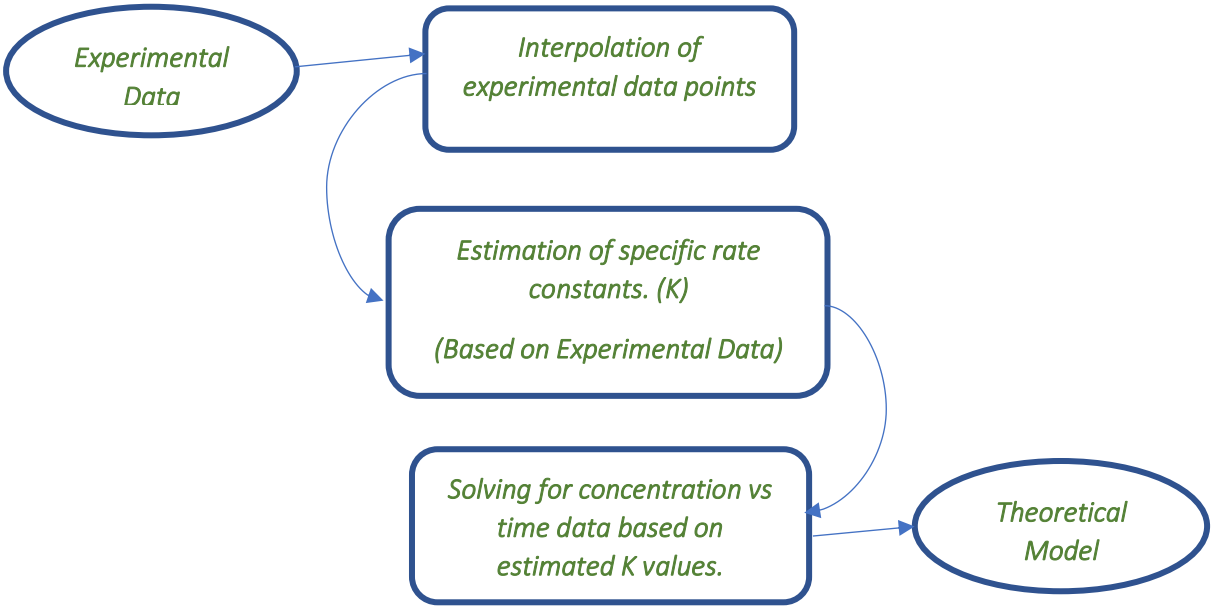
Introduction:

This study has two primary aims. Firstly, to implement numerical techniques learnt in the classroom to a larger, practical system. Secondly, to provide an introduction to the free-radical driven kinetics of photocatalytic reactions.

Two different publications based on kinetics of photocatalytic reactions were studied[1,2], and one of these[1], has been successfully modelled. The mathematical modelling was done on MATLAB 2019a. The details of the study and the model are discussed in the following sections.

Description of the Model:

- ***Primary Algorithm:***
- The publications used as references are a source of experimental data and proposed mechanism of the set of catalytic reactions.
- Based on this given data, the following flowchart summarises the algorithm used.



The results obtained have been discussed in the following sections.

- ***About the MATLAB model:***
- The following pre-defined functions based on numerical techniques were called in the model:
    - *Spline:*
        - A cubic interpolation tool, used for interpolating between experimental data points. It provides creates data points for an accurate nonlinear regression.
        - In our study, we have used it to obtain intermediate component concentrations by increasing datapoints in the time series.

    - *lsqnonlin:*
        - A data-fitting tool, being used to estimate the approximate specific rate constants (k values). This is done by comparing the experimental and numerically obtained values of the variables of importance, and then minimizing this difference.
        - The task is simplified by providing lower and upper bounds to this function based on reported values in the publication.

    - *Ode15s:*
        - The estimated k values are plugged back into the system of ordinary differential equations. We provide the initial concentrations of the chemical species and ODE Solver returns the array of concentration data evolved in the timespan specified.
        - Ode15s is a stiff ode solver. The same procedure can be repeated to using a non-stiff ode solver (ode45) to give almost the same results, as there are no sudden changes in the concentration data.

- ***Reactions Modelled:***
- As presented in the publication, the following reaction system is studied. This is one of the two possible mechanisms, the second proposed mechanism being an autocatalysis reaction.

$$H_2O + h^+ \xrightarrow{k_1} OH^\bullet$$

$$O_2 + e^- \xrightarrow{k_2} O_2^{\bullet -}$$

$$h^+ + e^- \xrightarrow{k_3} h^+e^-$$

$$A + OH^\bullet \xrightarrow{k_4} B$$

$$B \xrightarrow{k_5} C$$

$$C \xrightarrow{k_6} D$$

  However, in this case, the concentration of water, electrons and holes is assumed to be much greater than the concentration of the chemical species, and is safely assumed to be constant with time.

- ***Discussions, Challenges and Scope of improvement:***
- The relevant experimental data reported in the publication[1] was: an estimate of the K-values, the required time-span, and the time-evolution plots of the product and reaction concentration (*Figure 7(a)*).

- Thus, experimental data was generated based upon this plot, using our best judgement.

- Arbitrary guesses were provided for the specific rate constants, based on the reported values. The *'lsqnonlin'* function was then called to optimise the arbitrary guesses. The arbitrary guess values were successfully optimised to fit the reported plot Figure 7(a).

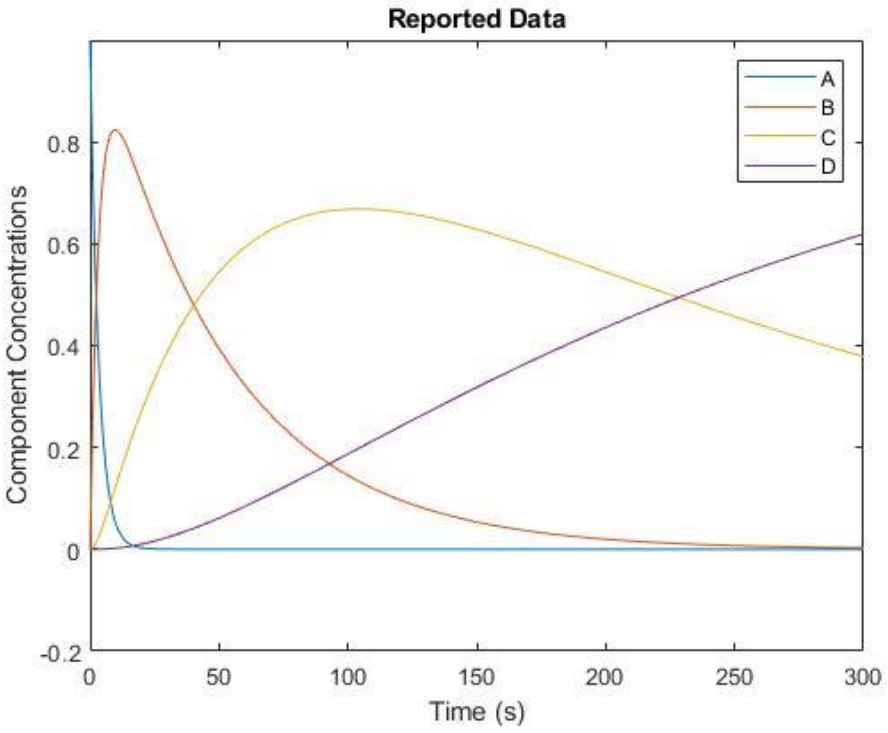
- Since the model generates experimental data points based on the plots reported in the publication, the experimental k values can be altered to study the effect of varying concentrations of species at t = 0s.

- Usually, only the reactant or the primary product component data are reported in a publication. However, our model currently optimizes, experimental data for all the species involved. This feature can be altered in the code, to specifically optimize only the required species.

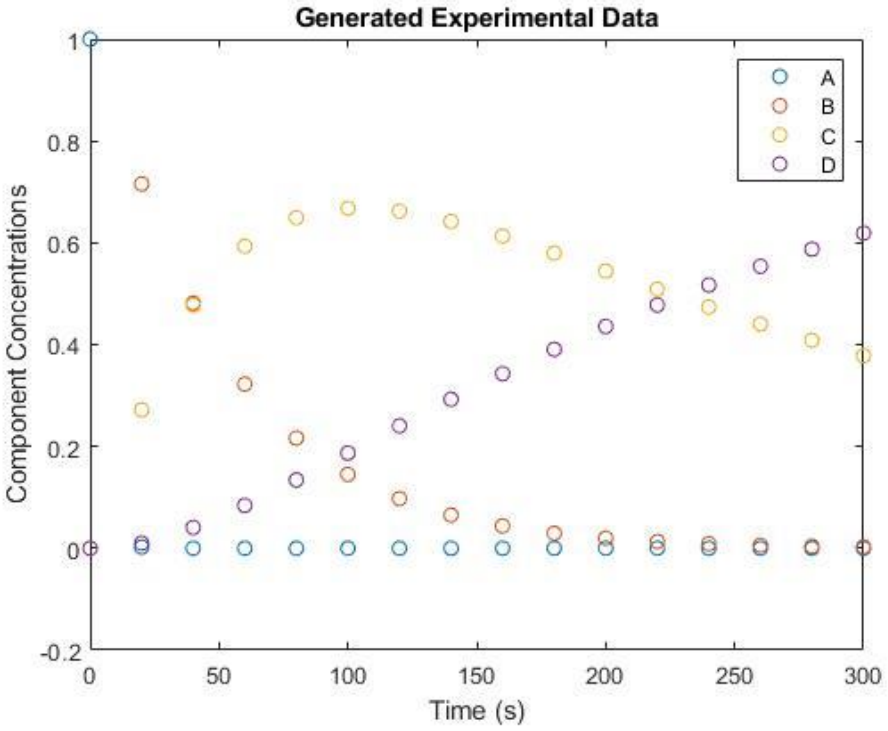
- Currently, the model is set to predict models only for a timespan of 300s. A simple improvement to this would be the to allow the user to input the time-span required.

Results:

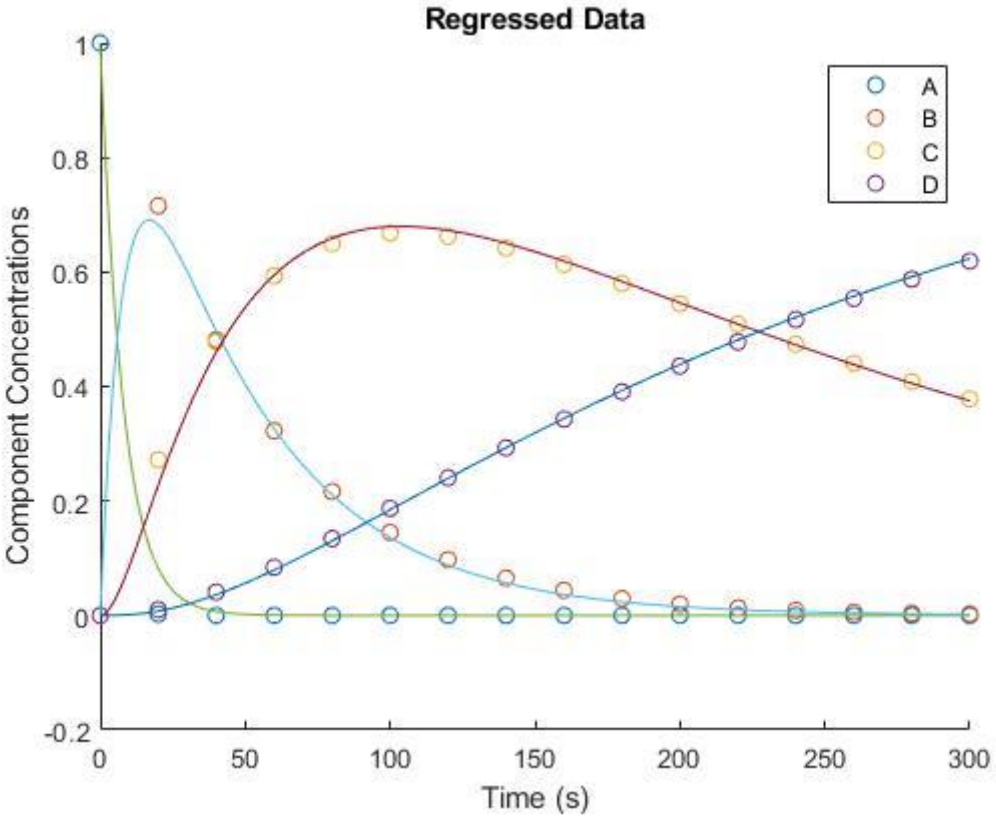
- The following figures show the output of the model. The first figure depicts the Figure 7(a) from the publication, with the four components A, B, C, D.



- Using this reported data, the following figure has been generated for the experimental data points created.



These data points are used to optimise the specific reaction constants. As mentioned before, in this study we have optimised all the four species. However, in case experimental data were available for only the reactant and the desired product, the optimization would have been limited to those species alone.



Conclusions:

Through the means of this study, a successful model was developed for a system of free radical catalysed reactions. An in-depth study with a simultaneous improvement of the model, which could accommodate more than one reaction cycles, would be an ideal follow-up.

References:

1. Tsuchiya, N., Kuwabara, K., Hidaka, A., Oda, K., & Katayama, K. (2012). Reaction kinetics of dye decomposition processes monitored inside a photocatalytic microreactor. Physical Chemistry Chemical Physics, 14(14), 4734-4741.
2. Vinu, R., & Madras, G. (2007). Kinetics of simultaneous photocatalytic degradation of phenolic compounds and reduction of metal ions with nano-TiO2. Environmental science & technology, 42(3), 913-919.