Use of parallel, parameterized metaheuristics for the determination of the kinetic constants of a chemical reaction in heterogeneous phase

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Abstract. The reaction in the human stomach when neutralizing acid with an antacid tablet is simulated and the evolution over time of the concentration of all chemical species present in the reaction medium is obtained. The values of the kinetic parameters of the chemical reaction can be determined by integrating the equation of the reaction rate. There is a classical optimization problem that can be approached with metaheuristic methods. The use of a parallel, parameterized scheme for metaheuristics facilitates the development of metaheuristics and their application to the problem.

Keywords: Chemical reaction, kinetic constants, parameterized metaheuristic schemes, parallel metaheuristic schemes

1 Introduction

This work focuses on the estimation with metaheuristic methods of the kinetic parameters of a chemical reaction. A chemical reaction in heterogeneous phase that takes place in a batch stirred tank reactor is studied [1], and the processes occurring in the human stomach when neutralizing the acid with an antacid tablet is simulated. It is a reaction combined with mass transfer of carbonate ions present in the solid phase upon contact with an acid solution. The solid phase consists of an antacid tablet, which contains a certain amount of calcium carbonate. The reaction medium represents the approximate pH of the human stomach (with values between 3 and 4). The kinetic parameters of the reaction are determined using the Euler numerical method.

We have a classical optimization problem consisting of the estimation of the kinetic parameters that best fit with the experimental data for a given reaction mechanism. The optimization problem can be broached with metaheuristic methods [2, 3]. The use of a unified parameterized scheme for metaheuristics facilitates the development of metaheuristics and their application by reusing the basic functions, and the parallelism accelerates the solution in large simulations. The scheme has been applied successfully to different problems [4, 5]. The shared-memory, parameterized metaheuristic scheme is used and adapted here

to the problem of estimation of the kinetic parameters in a chemical reaction, so better solutions and in a shorter execution time can be achieved.

2 A problem of determination of the kinetic constants of a chemical reaction in heterogeneous phase

When chemical reactions occur in heterogeneous phase the variables that affect the reaction rate are not only temperature, pressure or composition. The mass transfer rate becomes important and should be included in the terms of the reaction rate. When reaction rates in complex systems are compared or combined, we have to take into account that if the change of property is effected by several parallel paths mutually independent, the overall rate is simply the sum of all individual rates. The kinetic of dissolution of calcium carbonate is a function of the concentration of the various carbonate species in the solution and, therefore, a function of the partial pressure of carbon dioxide and pH. A model for the dissolution of calcium carbonate was developed in [6]. Depending on the value of the pH, there are four different ways in which the dissolution of calcium carbonate occurs: by reaction with acetic acid, by reaction with carbonic acid, and by the hydrolysis reaction (the fourth path may be neglected in the pH range considered). Therefore the variation of moles of calcium over time is:

$$\frac{1}{V}\frac{dN_{Ca^{2+}}}{dt} = -k_1 a^{n_1}\left[H_3O^+\right]^{n_2} - k_2 a^{n_3}\left[H_2CO_3\right]^{n_4} - k_3 \tag{1}$$

where k_1, k_2 and k_3 are the combined reaction rate constants, n_1, n_2, n_3 and n_4 are the reaction orders, and a is the area of the tablet, which is known for each increase of time. The integration of the equation for a certain value of time, t_j, gives the increase of calcium in the solution as a function of the concentrations of protons and carbonic acid.

The values of the parameters can be approached with metaheuristics. An individual is represented by a real vector of size seven. The ranges of values for the constants are set following empirical criteria. Every time we have to evaluate the fitness of an individual, we must solve the whole chemical system. The calculation of the fitness function is presented in algorithm 1, where we have a loop of N time intervals that calculates the value of each variable of the chemical problem for next time instant $i + 1$ depending on the value of the variable in the previous instant i.

3 A unified parameterized scheme of metaheuristics

For the application of different metaheuristics to an optimization problem, a good option is to use a common scheme for several techniques [7]. We study its adaptation and application to the estimation of kinetic parameters. In order to simplify the experimentation, functions are reused in the unified parameterized scheme in algorithm 2, where S, SS, $SS1$ and $SS2$ represent the sets generated at each stage of the algorithm, $ParamX$ are the metaheuristic parameters

Algorithm 1 Calculation of the fitness function for an individual

Calculate Fitness(k_1, k_2, k_3, n_1, n_2, n_3, n_4):
for $i = 0 \rightarrow N$ **do**
Calculate at instant i: $\left[Ca^{2+}\right], a, \left[H_3O^+\right], \left[HCO^-\right], \left[H_2CO_3\right], pH_{cal}, \Delta\left[Ca^{2+}\right], \left[CH_3COOH\right], \left[CH_3COO^-\right]$
$Fitness = Fitness + (pH_{exp,i} - pH_{cal,i})^2$
end for

specific to each function, and $ThreadsX$ the number of threads used for the application of each function in parallel. Using as basic metaheuristics Genetic algorithm (GA), Scatter Search (SS), GRASP (GR) and Tabu Search (TS) we obtain 20 metaheuristic parameters which allow us to experiment with different hybridations/combinations, and the selection of appropriate values for the parallelism parameters gives short execution times.

Algorithm 2 Unified parallel, parameterized scheme of metaheuristics

Initialize(S,$ParamIni$,$ThreadsIni$)
while (not EndCondition(S)) **do**
SS=Select(S,$ParamSel$,$ThreadsSel$)
$SS1$=Combine(SS,$ParamCom$,$ThreadsCom$)
$SS2$=Improve($SS1$,$ParamImp$,$ThreadsImp$)
S=Include($SS2$,$ParamInc$,$ThreadsInc$)
end while

4 Computational results

The simulation of the processes in the dissolution of an antacid tablet has been completed with the parallel, parameterized scheme of metaheuristics. Metaheuristics were applied to several series of experimental data with different configurations of chemical variables. The four basic metaheuristics considered and 11 hybridations are applied. Figure 1 shows the value of the objective function in successive iterations for each method, for a combination of the chemical variables, which is representative of the other experiments. We see that metaheuristics including GA have lower fitness values and generally more iterations to the optimum. On the other hand, we have GRASP, TS, SS and their combinations, with higher fitness and, finally, GR+TS+GA with intermediate values of fitness.

In figure 2 we can see the evolution of the experimental and calculated pH and concentrations of different chemical species given by the model with the optimum kinetic constants for the problem considered. The values obtained are: $k_1 = 6.41 \cdot 10^{-5}$, $k_2 = 9.68 \cdot 10^{-2}$, $k_3 = 8.87 \cdot 10^{-7}$, $n_1 = 0.749$, $n_2 = 1.59 \cdot 10^{-2}$, $n_3 = 3.25$ and $n_4 = 1.10$. The pH calculated in the simulation is not far from the

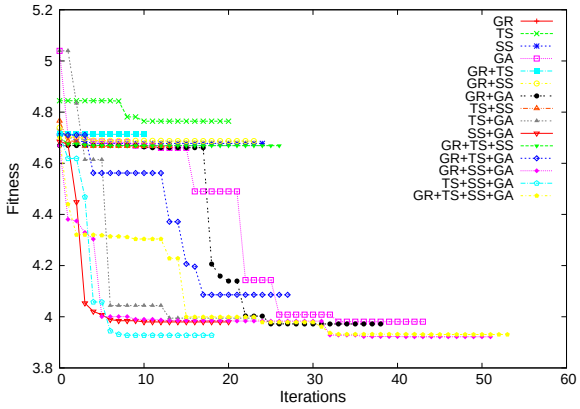

Fig. 1. Optimum values obtained by different metaheuristics in successive iterations for one problem size.

experimental one, and the prediction made by the kinetic model is acceptable. The simulation times give us a rough idea of the speed with which carbonate acts in the stomach, helping to predict effects against heartburn. This can be used to design more efficient pills and with relatively low experimental costs.

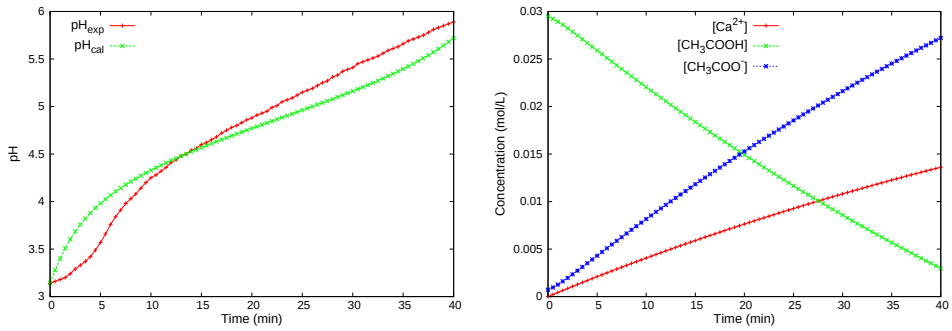

Fig. 2. (a) Evolution of pH over time. Experimental and calculated values; (b) Evolution of the concentration of acetic species and calcium. Calculated values.

5 Conclusions and research lines

The kinetic constants of a chemical reaction in heterogeneous phase have been determined satisfactorily using a shared-memory, parameterized scheme for metaheuristics. The best results in terms of fitness function are obtained by combining

metaheuristics: specifically the quaternary combination GR+GA+SS+TS and, in general, metaheuristics including GA.

Some future research lines we are working or plan to work on are: Application of hyperheuristics to obtain the best combination of parameters for the kinetic problem so as to facilitate the collection of the best metaheuristic or combination [8]. Application of the same methodology to other optimization problems of chemical parameters and processes. The shared memory scheme [5] is being adapted to message passing and GPUs.

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