Chaos control in the cerium-catalyzed Belousov–Zhabotinsky reaction using recurrence quantification analysis measures

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Abstract

Chaos control in the Belousov–Zhabotinsky-CSTR system was investigated theoretically and experimentally by reconstructing the phase space of the cerium (IV) ions concentration time series and then optimizing recurrence quantification analysis measures. The devised feedback loop acting on the reactor inlet flow rate was able to experimentally suppress chaos and drive the system to an almost predictable state with approximately 93% determinism. Similar theoretical results have also been demonstrated in numerical simulations using the four-variable Montanator model as solved by the multistage Adomian decomposition method.

1. Introduction

Complex dynamic behaviors have been reported for a number of chemical reaction systems including the Belousov–Zhabotinsky (BZ) [1], the Briggs–Rauscher (BR) [2], the Bray–Liebhafsky (BL) [3], the chlorine dioxide–iodide [4] reactions, etc. Particularly, the BZ system has been extensively investigated and was found to exhibit limit cycle behavior, hysteresis and chaos under certain conditions in well-mixed, as well as unstirred, batch and continuous reactors [5,6]. In fact, a BZ reaction consists of simultaneous oxidation and bromination of an organic compound, such as malonic acid, by bromate ions catalyzed by the ions of a transition-metal, such as cerium or manganese, in a strongly acidic environment [7].

The first elaborate mechanism for the BZ reaction was proposed by Field, Körös and Noyes in 1972 [8], which is now widely accepted, and involves three main processes: (1) consumption of bromide ion, (2) autocatalytic reaction of bromous acid with oxidation of the catalyst, and (3) organic reaction with reduction of the catalyst. In 1974, Field and Noyes simplified the FKN mechanism by retaining only five key reactions and developed a mathematical model dubbed the Oregonator, named after the University of Oregon, where the research was conducted [9]. The Oregonator model is formulated as a system of coupled nonlinear ODEs, which captures the essential features of the FKN mechanism. Györgyi, Rempe and Field provided further insights into the BZ reaction in a continuous-flow, stirred tank reactor (CSTR) by developing an 11-state variable model with three adjustment parameters [10]. A simplified version of the latter model, with a substantially reduced computational burden, was then proposed by Györgyi and Field, which is now recognized as the four-variable Montanator model in deference to the University of Montana [11]. The four-variable Montanator model can satisfactorily account for chaos formation in
BZ-CSTR systems, which has been demonstrated by experiment [12,13].

The recurrence quantification analysis (RQA) has emerged as a powerful tool for investigation of the dynamics of a given system through means of a reconstructed phase space. The salient feature of the RQA is that it provides a wealth of useful information even in the case of short, non-stationary and extremely noisy data where previous time series analysis strategies fail to yield reliable results. Moreover, by using the RQA, one may partition the whole time history into consecutive epochs and thus better investigate the system behavior step by step [14,15]. For example, the RQA-based measures have been employed to successfully interpret electromyography data [16], data of human postural fluctuations [17], electroencephalographic time series [18], neuronal signals [19], cardiovascular variability signals [20,21], molecular dynamics simulation results [22], pressure signals of fluidized bed reactors [23–27], stock market time series [28]. For a review see [29].

Most recently, we have shown that a number of control designs, involving nonlinear, dislocated and speed feedback laws, can stabilize the periodic oscillations of the BZ reaction under batch conditions in theory [30]. Petrov et al. [31] have experimentally stabilized periodic oscillations in a BZ-CSTR system by perturbing the flow rates of cerium and bromate solutions into the reactor and monitoring according to the phase-portrait of the system. Our work is mainly different from their approach in that we here investigate the application of the RQA-based measures to feedback control the chemical chaos for the first time to the best of our knowledge. Moreover, as it will be discussed in the next parts, we have measured ceric ions concentration by means of a spectrophotometer instead of the potentiometric method. In what follows, we develop a systematic approach for controlling the BZ-CSTR chaos by means of two RQA-based measures, namely the recurrence rate and determinism. As it will be shown in the sequel, a feedback law that locally maximizes any of these measures can realize chaos suppression, both in theory and practice.

2. The four-variable Montanator model

The four-variable Montanator model is a powerful tool for the analysis of mathematical models, especially those involving chaotic dynamics. As indicated in [33], certain popular numerical methods, such as finite difference schemes and Euler’s method, might lead to grossly erroneous outcomes known as ghost solutions in the treatment of stiff ODEs, or sometimes even non-stiff ODEs, unless an

<table>
<thead>
<tr>
<th>Reaction steps</th>
<th>Kinetic rate expressions (\text{M}^{-1}\text{s}^{-1})</th>
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<tr>
<td>(\text{Br}^- + \text{HBrO}_2 + [\text{H}^+] \rightarrow 2\text{BrMA})</td>
<td>(r_1 = 2.0 \times 10^6[\text{H}^+])</td>
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<tr>
<td>(\text{Br}^- + (\text{BrO}_3^- + 2[\text{H}^+]) \rightarrow \text{BrMA} + \text{HBrO}_2)</td>
<td>(r_2 = 2.0[\text{BrO}_3^-][\text{Br}^-])</td>
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<tr>
<td>(2\text{HBrO}_2 \rightarrow \text{BrMA})</td>
<td>(r_3 = 3.0 \times 10^3[\text{HBrO}_2]^2)</td>
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<tr>
<td>(0.5\text{HBrO}_2 + (\text{BrO}_3^- + [\text{H}^+]) \rightarrow \text{HBrO}_2 + \text{Ce}^{4+})</td>
<td>(r_4 = 6.2 \times 10^4[\text{H}^+]\left([\text{Ce}]<em>{\text{iox}} - [\text{Ce}]</em>{\text{red}}\right)[\text{BrO}<em>3^-]</em>{\text{red}})</td>
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<td>(\text{HBrO}_2 + \text{Ce}^{4+} \rightarrow 0.5\text{HBrO}_2)</td>
<td>(r_5 = 7.0 \times 10^4[\text{HBrO}_2][\text{Ce}^{4+}])</td>
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<td>(\text{Ce}^{4+} + [\text{MA}] \rightarrow (\text{products}))</td>
<td>(r_6 = 0.3[\text{MA}][\text{Ce}^{4+}])</td>
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<td>(\text{BrMA} + \text{Ce}(\text{IV}) \rightarrow \text{Br}^-)</td>
<td>(r_7 = 3.0 \times 10^3[\text{BrMA}][\text{Ce}^{4+}])</td>
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<tr>
<td>(\text{BrMA} \rightarrow \text{Br}^-)</td>
<td>(r_8 = 2.4 \times 10^3[\text{BrMA}][\text{MA}]_{\text{iox}})</td>
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extremely small step-size is chosen. In fact, these solution techniques can induce spurious chaos or, in contrast, even suppress authentic chaotic oscillations in numerical simulations. Surprisingly, even a more sophisticated numerical solver such as a popular variable step-size, explicit Runge-Kutta (4,5) scheme, i.e. the Dormand–Prince pair [34], is not guaranteed to yield correct results for chaotic problems [35]. Consistently, we have obtained unphysical results, i.e. negative values for concentrations, when solving system (1) by MATLAB’s standard integrator ode45, which is based on the Dormand–Prince algorithm.

Recently, a semi-analytical, semi-numerical method, namely the multistage Adomian decomposition method (MADM) has been proposed to analyze dynamical systems. The MADM is an explicit time-marching version of the classic Adomian decomposition method (ADM) that advantageously provides the functional form of the solution over each time interval by representing the nonlinear terms using the Adomian polynomials instead of a priori incorporating a crude linearization as in purely numerical schemes. In actual practice, the MADM has provided the physical solution as compared with experimental data, whereas several well-known standard numerical methods have yielded grossly inaccurate solutions or even spurious, unphysical values. Furthermore, the MADM ensures at least the same or higher level of accuracy as obtained by other numerical methods, such as the Runge-Kutta techniques when these are effective, but with comparatively larger step-sizes.

In what follows, we present the fundamentals of the ADM, and subsequently the MADM, for solving a system of first-order nonlinear ODEs subject to initial conditions.

Without loss of generality, let us consider the following system of first-order nonlinear ODEs:

\[
\begin{align*}
\dot{y}_1 &= f_1(t,y_1,\ldots,y_n), \\
\dot{y}_2 &= f_2(t,y_1,\ldots,y_n), \\
& \vdots \\
\dot{y}_n &= f_n(t,y_1,\ldots,y_n),
\end{align*}
\]

(4)

where the prime denotes differentiation with respect to time \( t \).

The \( i \)-th ODE of the system (4) can be rewritten in Adomian’s operator-theoretic notation as

\[
L y_i = f_i(t,y_1,\ldots,y_n), \quad i = 1, 2, \ldots, n,
\]

(5)

where \( L \) is the first-order linear differential operator, i.e. \( d(\bullet)/dt \), and its inverse is \( L^{-1} = \int_0^t (\bullet) dt \). Applying the inverse operator \( L^{-1} \) to both sides of Eq. (5), we obtain

\[
y_i = y_i(0) + \int_0^t f_i(t,y_1,\ldots,y_n) dt, \quad i = 1, 2, \ldots, n.
\]

(6)

According to the ADM, the solution \( y_i \) in the former equation is decomposed as

\[
y_i = \sum_{j=0}^{\infty} y_{ij},
\]

(7)

where its components are computed by the system of coupled recursion schemes

\[
\begin{align*}
y_{i0} &= y_i(0), \\
y_{ij} &= \int_0^t \Theta_{ij}(y_{10},\ldots,y_{1j},y_{20},\ldots,y_{2j},\ldots,y_{n0},\ldots,y_{nj}) dt, \quad j \geq 1
\end{align*}
\]

(8)

where \( \Theta_{ij} \) denotes the multivariate Adomian polynomials that compose the nonlinearity \( f_i(t,y_1,\ldots,y_n) \). In other words, the nonlinearity comprises the Adomian polynomials

\[
f_i(t,y_1,\ldots,y_n) = \sum_{j=0}^{\infty} \Theta_{ij}(y_{10},\ldots,y_{1j},y_{20},\ldots,y_{2j},\ldots,y_{n0},\ldots,y_{nj}).
\]

(9)

A set of innovative algorithms for faster generation of the multivariate Adomian polynomials has been recently developed by Duan [36]. Obviously, it is often impossible to identify a closed-form solution from Eq. (4). For these cases, one has to accept a truncation error and approximate the solution as \( \tilde{y}_i = \sum_{j=0}^{m} y_{ij} \). The ADM has been applied in various branches of science and engineering as a reliable tool for analysis of functional equations; in this regard, see [37–51].

Despite its many distinct advantages, the classical ADM may yield solutions with a finite region of convergence which is, after all, a possibility with all series methods. For certain problems, the region of convergence may not be adequate for engineering purposes, particularly with unbounded domains [52]. The MADM applies a time-marching concept to extend the region of convergence and hence offers the solution of system (4) by the following algorithm:

(I) \( t_* = 0 \) (for initial value problems) and choose a time step-size \( h \).

(II) Calculate \( y_i = \sum_{j=0}^{m} y_{ij} \) through the following recurrence relation:

\[
\begin{align*}
y_{i0} &= y_i(t_*), \\
y_{ij} &= \int_{t_*}^{t_*+h} \Theta_{ij}(y_{10},\ldots,y_{1j},y_{20},\ldots,y_{2j},\ldots,y_{n0},\ldots,y_{nj}) dt, \quad j \geq 1
\end{align*}
\]

(III) \( t_* = t_* + h \) and repeat steps 2 and 3 until the intended point in time is reached.

(IV) Select an absolute error value \( E \) for the obtained solution.

If \( \sum_{j=0}^{\infty} |y_i - f_i(t,y_1,\ldots,y_n)| \geq E \), then decrease \( h \) and start the whole procedure over again from step I.

The interested reader is recommended to consult the references [53–56] for more details on the theory and application of the MADM.

4. Recurrence quantification analysis

4.1. Recurrence plot

A recurrence plot (RP) is a two-dimensional graphical representation that offers insight into the recurrent states
of a dynamical system in its \( m \)-dimensional phase space. It is possible to visually identify structure, i.e. determinism, in a time series by means of its RP.

Let \( X(i) \) be the \( i \)th point of a phase trajectory describing the dynamics of a nonlinear system in \( m \) dimensions. The recurrence matrix for such system is defined as

\[ R_{ij} = H(e - ||X(i) - X(j)||), \quad i, j = 1, \ldots, N, \quad (11) \]

where \( H(\bullet) \) denotes the Heaviside step function, \( || \bullet || \) represents the Euclidian norm and \( e \) is a predefined cutoff distance (threshold). The graphical depiction of a recurrence matrix, i.e. the RP, is an \( N \times N \) grid of points colored in black for unity and white for zero entries. Accordingly, the system returns to an \( e \)-neighborhood of any black point of the RP in phase space. Fig. 1 depicts the theoretical recurrence plots of system (1) for four different reactor residence times as developed using the MADM simulations.

### 4.2. RQA-based measures

In order to quantitatively analyze the structures of the RPs, Zbilut and Webber developed several measures, namely the recurrence rate (RR), the determinism (DET), the Shannon entropy of the line length distribution (ENT), the length of the longest line segment (MAXLINE), etc. [57]. We henceforth restrict our focus to the RR and DET in our study. The RR measures the density of the recurrence points throughout all the phase space trajectories and is defined as

\[ RR = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} R_{ij}. \quad (12) \]

Actually, the RR is related to the probability that a specific state recurs.

It is known that stochastic or chaotic behaviors form none or very short diagonal structures in the RPs whereas deterministic processes cause longer diagonals and less single, isolated recurrence points. Accordingly, the quantity DET measures the fraction of recurrent points forming diagonal line structures (of at least length \( l_{\text{min}} \)) and hence it assesses the determinism or predictability of the system [58]. This measure is defined as

\[ DET = \frac{\sum_{l=l_{\text{min}}}^{N} I \times P(l, e)}{\sum_{l=1}^{N} I \times P(l, e)}, \quad (13) \]

where the histogram of diagonal lines of length \( l \) is defined by

\[ P(\varepsilon, l) = \frac{1}{\varepsilon} \sum_{l=1}^{N} (1 - R_{i-l,j-1}(\varepsilon)) (1 - R_{i,j-l}(\varepsilon)) \prod_{k=0}^{l-1} R_{i+k,j+k}(\varepsilon). \quad (14) \]

When the experimental time series of a single state variable is available, it is possible to reconstruct the phase space by the method of delays as developed by Takens [59]. In other words, the mentioned method embeds a
scalar time series \(\{x_i\}, i = 1, 2, \ldots, \) into a space with \(d\) dimensions by

\[
x_i = (x_i, x_{i+1}, \ldots, x_{i+(d-1)\theta}), \quad x_i \in \mathbb{R}^d,
\]  

(15)

where \(\theta\) denotes the time delay and \(d\) is the embedding dimension. In theory, if the experimental time series \(\{x_i\}\) is infinite and noise-free, then the choice of the time delay \(\theta\) is arbitrary [60]. However, this condition is rarely encountered in practice and therefore a number of techniques to obtain the optimal time delay value have been suggested, e.g., by means of the auto-correlation function and the mutual information function [61,62]. Furthermore, an overestimation of the embedding dimension would cause an excessive computational burden for calculating properties from the reconstructed attractor. Hence, the minimum embedding dimension is chosen as the lowest value of an increasing sequence of integers starting from two, for which the invariant properties of the reconstructed attractor, e.g., the correlation dimension or entropy, are preserved [61].

As an unexpected, yet beneficial characteristic, March et al. have proved that the embedding dimension does not affect the RQA measures whatsoever [63]. Therefore, the quantification measures are calculated based on unembedded RPs, i.e. \(d = 1\), for computational convenience subsequently in this paper.

5. Chaos control strategy

According to definition (12), the dynamic behavior of system (1) shifts from chaotic to periodic as its RR increases. Thus, it is possible to minimize or eliminate chaos in the system by adjusting a control parameter like \(\tau\) so that the RR is maximized.

This maximization can be carried out by many optimization techniques such as the gradient ascent algorithm (GAA) which consists of the following steps for finding a local maximum of the multivariable function \(f(x)\):

1. Choose an initial \(x_0\) randomly.
2. Update \(x_{n+1} \leftarrow x_n + \gamma \nabla f(x_n)\), where \(\gamma\) is a suitably small, positive scalar and \(\nabla(\bullet)\) denotes gradient operator. The choice of \(\gamma\) shall guarantee that \(f(x_{n+1}) \geq f(x_n) \geq \cdots \geq f(x_1) \geq f(x_0)\).
3. Repeat step 2 until the sequence \(\{x_0, x_1, \ldots, x_n\}\) converges.

Fig. 2 theoretically demonstrates that the proposed control scheme can successfully covert a chaotic state of system (1), e.g., occurring at \(k_f = 5.90 \times 10^{-4}\), to a totally periodic state, which corresponds to \(k_f = 5.49 \times 10^{-4}\), as developed using the MADM simulations.

Fig. 3 depicts the time series of the ceric ions concentration at these two states as obtained from the four-variable Montanator model. The origin is shifted to the reaction induction time, i.e. the period required for the initiation of oxidation and appearance of the very change in concentrations, in order to avoid presenting trivial data.

One salient advantage of choosing the RR as an RQA-based measure in our control design over other chaotic measures lies in the fact that only a short time series is adequate for a robust RQA [15,64]. This new approach allows for the realization of an enhanced real-time control system. As Fig. 4 illustrates, the proposed control algorithm can theoretically eliminate chaos in the reactor by maximization of the system determinism through adjusting the inlet flow rate intermittently.

6. Experimental design and results

As we briefly noted previously, it is possible to apply the proposed control strategy in a model-free context through phase space reconstruction by embedding an experimental time-series. This shall be regarded as a significant benefit as we know mathematical models of complex systems, if
available in the first place, are usually inaccurate or not reliable enough due to inevitable, and sometimes crude, simplifications. In what follows in this section, we provide an account of our experimental attempt made to control the BZ-CSTR chaos based on the previously discussed RQA-based control strategy.

The BZ reaction was carried out in a rectangular cuboid CSTR (4 cm³ internal volume) made of quartz. Two silicon tubes (2 mm ID) were mounted to the top of the reactor; one for inlet flow and the other for outlet flow. The CSTR was placed inside a UV–vis spectrophotometer (Shimadzu UV-1700) in order to record the dynamic concentration variations of cerium (IV) ions ($\lambda_{\text{max}} = 318$ nm) throughout the experiment. Malonic acid, ceric sulfate ($\text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$), sodium bromate, all of analytical grade, and sulfuric acid ($\text{H}_2\text{SO}_4$, 98%) were supplied by Merck (Germany) and used without further purification. The temperature in the CSTR was controlled at $23.0 \pm 0.1 \, ^{\circ}\text{C}$ by means of an air fan, embedded in the spectrophotometer, while monitoring the effluent stream temperature. A complete mixing inside the reactor was assured by a small magnet bar (5 mm length) vibrating under the influence...
of an alternating magnetic field, i.e. a rectangular coil connected to a variable-frequency AC power supply. A custom computer program was prepared (coded in Visual Basic 6) to perform the following tasks repeatedly in certain time intervals: (1) perform data acquisition from the spectrophotometer at the rate of 2 Hz continuously and calculate DET values, (2) calculate the next flow rate in the trend to maximize the DET by the GAA and (3) change the flow rate of the syringe pump to the value calculated in the previous stage through the LPT port of the PC and an electronic interface circuit. Fig. 5 illustrates the experimental flow chart.

Starting from two arbitrary total flow rates, namely 13.17 and 13.06 cm$^3$/h, the implemented control strategy led us to a maximum DET of about 93%, i.e. almost deterministic behavior, as the blue line and circles in Fig. 6 show.

It can be also seen from the recurrence plots depicted in Fig. 7 that the employed feedback control was able to suppress chaos and enforce a deterministic order.

Fig. 8 shows the time series for the uncontrolled state (chaotic) and the controlled state (deterministic) of our experimental setup.

7. Conclusion

We investigated the theoretical and experimental chaos control in the bromate–cerium–malonic acid Belousov–Zhabotinsky reactive flow system. The control strategy was based on maximizing the target function of the recurrence rate and determinism, as two reliable measures of recurrence quantification analysis, through a feedback loop. For the mathematical analysis of the proposed control structure, the multistage Adomian decomposition method was concluded superior in treatment of the four-variable Montanator model. As the results have well demonstrated, the BZ-CSTR chaos was successfully controlled to almost periodic behavior in a robust fashion, both in theory and experiment.

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