Application of delay differential equations in the adsorption of pollutants by nanoparticles: numerical modelling and optimization with specialised software

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I. Abstract

This study explores the use of delay differential equations to model the adsorption of contaminants in decontamination processes using nanoparticles, providing a detailed description of the dynamics of adsorption and desorption in aqueous systems. A simplified model has been developed that incorporates delays in two differential equations. This model accurately captures the reaction and transport times in the interaction between nanoparticles and contaminants, such as heavy metals and organic compounds.

The approach presented allows the simulation of adsorption kinetics, evaluating the influence of parameters such as adsorption rate, desorption and time delay on the concentration of the pollutant and the amount adsorbed. The versatility in the choice of these parameters allows the model to be applicable in both industrial and environmental contexts, facilitating the optimisation of water decontamination processes. Practical examples of heavy metal adsorption by iron oxide nanoparticles are illustrated. These examples emphasize the need to adjust parameters based on specific system characteristics, enhancing process efficiency.

Overall, the proposed model emerges as a useful tool for the simulation and understanding of adsorption processes in complex systems, providing a robust theoretical basis for future research on the use of nanoparticles in the removal of aquatic pollutants.

II. Context of Decontamination with Nanoparticles

Nanoparticles have been widely used for pollutant removal due to their high surface area and unique nanoscale properties. Common pollutants that can be removed by nanoparticles include heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), inorganic contaminants (e.g., nitrates and phosphates) and organic pollutants such as dyes, pharmaceuticals and pesticides.

Several studies have applied delay differential equations to model adsorption processes involving nanoparticles in decontamination. These models capture important dynamics in adsorption and desorption processes, especially when memory or transport time effects affect the efficiency of contaminant removal.

Advanced modeling approaches, including time-delayed differential equations, have proven effective in capturing the dynamic interactions between nanoparticles and contaminants in processes such as adsorption and advanced oxidation. For instance, time delays allow for better representation of the non-instantaneous diffusion and interaction of pollutants with nanoparticles, as evidenced in advanced Fenton processes and mathematical models by (Sahai et al., 2021) and (Chawla et al., 2024a). These studies demonstrate the utility of such models in real-world applications like the adsorption of heavy metals (e.g., Pb or Hg), where understanding the interplay of adsorption and desorption dynamics is critical. The incorporation of dual time delays enhances the predictive power and realism of these models, making them valuable for optimizing the design and efficiency of decontamination systems. The delay in the equation captures the time it takes for the pollutant to diffuse and reach the surface of the nanoparticle, which is essential for optimising industrial and environmental decontamination processes. The authors of this software recommend reviewing articles on modelling with delay differential equations and their application in the removal of pollutants using nanoparticles (Mathematics | Special Issue: The Delay Differential Equations and Their Applications, n.d.) (Chawla et al., 2024b).

In these processes, nanoparticles act as adsorbents, being able to interact with contaminants through adsorption mechanisms, where the contaminants adhere to the surface of the nanoparticles. These can be made of various materials, such as metal oxides (iron oxide or titanium dioxide), carbon (carbon nanotubes or graphene) or functionalised polymers. On the other hand, adsorbates correspond to the contaminants to be removed, such as heavy metal ions (e.g., Pb^{2+} or Cd^{2+}) or organic compounds (e.g., dye molecules or pharmaceuticals). These contaminants, usually present in liquid media, are reduced in concentration in the liquid phase by the adsorption process.

III. Delay Differential Equations

The process of adsorption, governed by the interaction between the adsorbate and the adsorbent, can be described using delay differential equations. These equations take into account not only the instantaneous changes in the system but also the delay effects that arise due to diffusion and surface interactions. Below, we present the foundational equations that model the dynamics of adsorption and desorption in systems involving nanoparticles.

Equation for Adsorbate Concentration, $C(t)$:

$$\frac{dC(t)}{dt} = -k_1 C(t) + k_2 Q(t-\tau)$$

This equation represents the rate of change in the concentration of the adsorbate within the liquid phase. The rate of change of adsorbate concentration decreases due to adsorption $-k_1 C(t)$ and increases due to delay desorption $k_2 Q(t-\tau)$.

Equation for Amount Adsorbed, $Q(t)$:

$$\frac{dQ(t)}{dt} = k_1 C(t-\tau) - k_2 Q(t)$$

This equation describes the rate of change in the amount of adsorbate bound to the nanoparticle surface. The rate of change of the adsorbed amount increases due to delay adsorption $k_1 C(t-\tau)$ and decreases due to desorption $-k_2 Q(t)$.

To solve this system of differential equations with delay, we require initial conditions defined in the interval $t \in [-\tau, 0]$:

Initial Concentration: $C(t) = C_0$ for $t \in [-\tau, 0]$

Initial adsorbed quantity: $Q(t) = Q_0$ for $t \in [-\tau, 0]$

Symbol	Description	Unit
$\boldsymbol{C(t)}$	Adsorbate concentration	mg/L
$\boldsymbol{Q(t)}$	Amount adsorbed	mg/g
$\boldsymbol{t}$	Time	min/h

$\boldsymbol{k_1}$	Adsorption rate constant	1/min
$\boldsymbol{k_2}$	Desorption rate constant	1/min
$\boldsymbol{\tau}$	Delay time	min
$\boldsymbol{C_0}$	Initial adsorbed quantity	mg/L
$\boldsymbol{Q_0}$	Initial amount of adsorbate adsorbed per unit mass of adsorbent.	mg/g

The delay (τ) can represent the time required for the adsorbate to reach the active site on the adsorbent or the transport time within the system. The inclusion of delays can complicate the analytical solution of the equations, often needing numerical methods suited for those equations. This model is a simplification and can be adjusted or extended according to the specific characteristics of the adsorption process under study, including factors such as multiple adsorption stages, variations in temperature, pH, among others.

The numerical parameter values and initial conditions established for this delay adsorption model simulation are presented:

$$k_1 = 0.05 \text{ min}^{-1}, k_2 = 0.02 \text{ min}^{-1}, \tau = 3\text{min}, C_0 = 10 \text{ mg/L} \text{ and } Q_0 = 0 \text{ mg/g}.$$

With the values established, it is feasible to proceed to the numerical resolution of the delay differential equations applied to the proposed adsorption model. These values, although representative and valid as a starting point, can be adapted to precisely fit the specific properties of the adsorbent and adsorbate, as well as the experimental conditions of the analysed system. Such tuning not only allows a better fit of the model, but also facilitates obtaining results that are more in line with the actual operating conditions and parameters inherent to different adsorption contexts, thus providing a flexible framework for application in various investigations.

IV. Physical Interpretation of Parameters in Nanoparticle Adsorption Processes

The adsorption process with nanoparticles can be modelled by means of delay differential equations, such as those shown above:

1. Adsorption and Desorption Rates (k_1 and k_2):

The adsorption rate constant (k_1) depends on the affinity of the pollutant for the nanoparticle surface. For example, iron oxide nanoparticles may have a high affinity for lead ions, and the value of k_1 will be high. The desorption rate constant (k_2) reflects the tendency of the contaminant to be released from the surface of the nanoparticle. A low value of k_2 will indicate a strong retention of the contaminant on the nanoparticle.

2. Process Delay (τ):

The delay (τ) can represent the time it takes for the contaminant to reach the surface of the nanoparticle, or the time it takes to fully settle or adhere to the surface. In the case of nanoparticles dispersed in a liquid medium, this delay may be related to the diffusion of the contaminant through the medium until it encounters the active adsorption surfaces. This phenomenon is particularly important in nanoparticle systems, as their small size allows particles to disperse over a large volume before the contaminants start to be adsorbed effectively.

V. Case Example: Adsorption of Heavy Metals with Iron Oxide Nanoparticles

Suppose we are trying to remove lead ions Pb^{2+} from a contaminated water source using iron oxide nanoparticles (Fe_3O_4). In this case, the iron oxide nanoparticles serve as the adsorbent, and the Pb^{2+} ions represent the adsorbate. Initially, the concentration of lead in the water C_0 is 10 mg/L, and no lead is adsorbed on the nanoparticles, so the initial amount adsorbed is Q_0= 0.

For this system the adsorption rate constant is $k_1 = 0.05\ \mathrm{min}^{-1}$, indicating a good adsorption rate due to the high affinity of Pb^{2+} for the iron oxide surface. The desorption rate constant is $k_2 = 0.02\ \mathrm{min}^{-1}$, suggesting that although some desorption may occur, most of the lead will remain attached to the nanoparticles. The delay time is $\tau = 3\mathrm{min}$, reflecting the time required for the lead ions to diffuse through the aqueous medium and reach the active surfaces of the nanoparticles.

Initially, the liquid phase contains a high concentration of lead $C_0 =$ 10 mg/L, with no adsorption on the nanoparticles. As time progresses, the adsorption process begins, reducing the lead concentration in the liquid phase due to the interaction with the nanoparticles. The time delay τ = 3 min indicates that the adsorption process is not instantaneous; the lead ions require time to diffuse and reach the nanoparticles. While adsorption is dominant, some desorption occurs at a low rate $k_2 = 0.02\ \mathrm{min}^{-1}$, allowing a fraction of the lead ions to return to the liquid phase. Consequently, the system evolves towards an equilibrium in which a significant fraction of Pb^{2+} ions is adsorbed on the nanoparticles, substantially reducing the pollutant concentration in the water.

The proposed model accurately describes adsorption kinetics in decontamination processes using nanoparticles, capturing the pollutant's dynamic behaviour during its adhesion process to the adsorbent surface with a time delay. This feature is particularly relevant in applications where nanoparticles are used for the removal of pollutants from wastewater or drinking water sources, as it provides a detailed representation of the variation of concentrations over time and facilitates the optimisation of the design of removal processes. With appropriate parameters, the model is presented as an effective tool for simulations to predict the behaviour of various adsorption systems in both industrial and environmental contexts. In addition, a simplified adsorption model incorporating delays is introduced using two delay differential equations, providing a useful basis for describing systems where reaction or transport times directly impact the dynamics of the adsorption process.

VI. Oscillatory Behavior with Dual Delay Times: A More Realistic Approach

In systems where nanoparticles are used to adsorb contaminants such as nitrates, it is often observed that the adsorption and desorption processes do not occur instantaneously, nor do they share identical delay times. The time required for the contaminant to diffuse through the solution to the nanoparticle surface differs from the duration needed for the adsorbed contaminant to desorb back into the solution. Distinctions in delay times may result in oscillatory behavior, reflecting the dynamic interplay between adsorption and desorption.

To account for this more realistic scenario, the model can be extended to incorporate two distinct delay times:

Equation for Adsorbate Concentration, $C(t)$:

$$\frac{dC(t)}{dt} = -k_1 C(t) + k_2 Q(t - \tau_2)$$

In this equation, the term $k_2 Q(t - \tau)$ includes a delay τ_2, which represents the desorption time for the contaminant to release from the nanoparticle surface back into the liquid phase.

Equation for the Amount Adsorbed, $Q(t)$:

$$\frac{dQ(t)}{dt} = k_1 C(t - \tau_1) - k_2 Q(t)$$

Here, $k_1 C(t - \tau_1)$ includes a delay τ_1, capturing the time required for the contaminant to diffuse and reach the nanoparticle surface before being adsorbed.

To simulate oscillatory behavior with this dual-delay model, the following parameter values are suggested:

$$k_1 = 10\ \mathrm{min}^{-1},\ k_2 = 2\ \mathrm{min}^{-1}, \tau_1 = 0.1\ \mathrm{min}\ , \tau_2 = 5\ \mathrm{min}, C_0 = 20\ \mathrm{mg/L} \text{ and } Q_0 = 0\ \mathrm{mg/g}$$

These values are based on experimental observations in similar nanoparticle systems and provide a more realistic representation of the dynamic nature of adsorption processes involving contaminants like nitrates. The differentiated delay times τ_1 and τ_2 reflect the distinct diffusion and desorption times associated with contaminant interactions with nanoparticle surfaces.

Given that the adsorption and desorption times in nanoparticle systems are often distinct, does the dual delay model provide a more accurate representation of the real adsorption and desorption processes? This model, with separate delay times for diffusion to the surface and release from the surface, might better capture the complex dynamics observed in real-world contaminant adsorption processes involving nanoparticles. This example provides a comparison between the simplified model with a single delay time and the more realistic approach with two delay times ($\tau_1$and τ_2). The dual model is a more realistic approach when modelling adsorption processes with nanoparticles where diffusion and desorption occur at different times.

The simulations described in this example of dual delays will be implemented and detailed in the guide available at the end of the document. This guide provides a step-by-step explanation on how to use the program, from introducing the equations and parameters to configuring and executing the simulations. Currently, scientific literature on the modelling of pollutant adsorption processes on nanoparticles by means of differential equations with two-time delays is limited. However, there are studies that address adsorption with models that incorporate time delays or analyse adsorption-desorption dynamics in systems with nanoparticles (Mayoral et al., 2011).

VII. Conclusion

The model, based on differential equations with two different delays, provides an accurate and dynamic description of adsorption and desorption processes in systems containing nanoparticles, such as Fe_3O_4@Ag, for pollutant removal. By adding two delay times, it is possible to represent more realistically the phenomena related to the diffusion of the pollutant towards the adsorbent surface and its subsequent dispersion, reflecting the oscillatory behaviours observed in the simulations. These oscillations highlight the dynamic interplay between adsorption and desorption, demonstrating how delays affect the time evolution of the concentrations. The numerical simulations corroborate the effectiveness of the model to improve fundamental parameters and to develop more efficient decontamination systems, highlighting it as a useful tool for industrial and environmental uses.

VIII. References

Chawla, R., Kumar, D., & Baleanu, D. (2024a). Numerical investigation of two fractional operators for time fractional delay differential equation. *Journal of Mathematical Chemistry*, *62*(8), 1912–1934. https://doi.org/10.1007/S10910-024-01637-1/FIGURES/4

Chawla, R., Kumar, D., & Baleanu, D. (2024b). Numerical investigation of two fractional operators for time fractional delay differential equation. *Journal of Mathematical Chemistry*, *62*(8), 1912–1934. https://doi.org/10.1007/S10910-024-01637-1/FIGURES/4

Mayoral, E., De, E., Cruz, L. A., Longoria, L. C., & Nahmad-Achar, E. (2011). Estudio del proceso de adsorción-desorción de contaminantes en medios confinados mediante simulaciones computacionales. *Revista Internacional de Contaminación Ambiental*, *27*(3), 253–261. http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S0188-49992011000300010&lng=es&nrm=iso&tlng=es

Sahai, N., Gogoi, M., & Ahmad, N. (2021). Mathematical Modeling and Simulations for Developing Nanoparticle-Based Cancer Drug Delivery Systems: A Review. *Current Pathobiology Reports*, *9*(1), 1–8. https://doi.org/10.1007/S40139-020-00219-5/TABLES/2

USER GUIDE FOR DELAY DIFFERENTIAL EQUATIONS (DDEs)

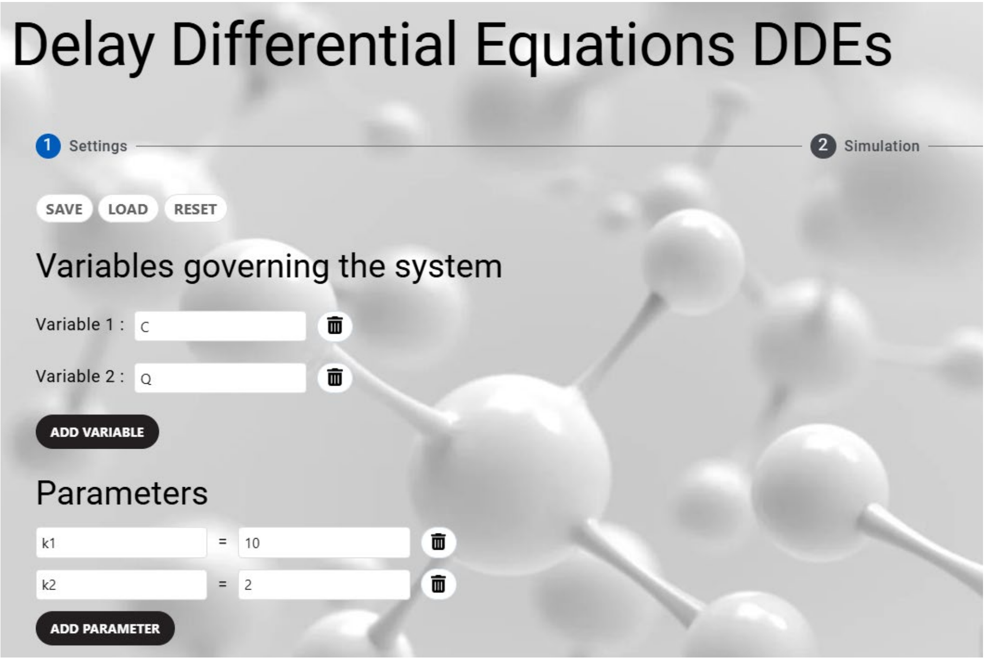
Step 1: Initial Setup

1. **Open the Program**: Start the "Delay Differential Equations (DDEs)" program on your computer.
2. **Settings Section**: At the top, you will see "Delay Differential Equations DDEs" with a Settings section where you can save or load previous configurations.

Step 2: Entering the System Equations

Add Equations:

- Locate the section titled **Equations governing the system.**
- **Equation 1** and **Equation 2** are already set up for editing.
- Enter your equations in the provided text fields. In this example, the variables are $\boldsymbol{C}$ and $\boldsymbol{Q}$.
- If you need additional equations, click **ADD EQUATION**.



Delay Differential Equations DDEs

Variables governing the system

Variable 1 : C

Variable 2 : Q

Parameters

k1 = 10

k2 = 2

Step 3: Defining Parameters

Enter Parameters:

- Go to the **Parameters** section.
- You will find fields labeled $\boldsymbol{k_1}, \boldsymbol{k_2}, \boldsymbol{k_3}$, etc., where you can enter the values of your parameters.
- To add more parameters, click **ADD PARAMETER**.
- In this example, parameters $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$ are already included with specific values ($\boldsymbol{k_1} = \mathbf{10\ min^{-1}}$ and $\boldsymbol{k_2} = \mathbf{2\ min^{-1}}$).

Step 4: Defining Delays

Enter Delays:

- Move to the **Delays** section.
- Enter the desired delay value. In the example, $\boldsymbol{\tau_1}$ has a value of $\mathbf{0.1\ min}$ and $\boldsymbol{\tau_2}$ $\mathbf{5\ min.}$
- If you need additional delays, select **ADD DELAY**.

Step 5: Entering the Terms of the Equations

Set Up the Terms:

- In the Terms of the equations section, enter the terms for each equation.

For **Equation 1**, the form of the equation is:

$$\frac{dC(t)}{dt} = -k_1 C(t) + k_2 Q(t - \tau_2)$$

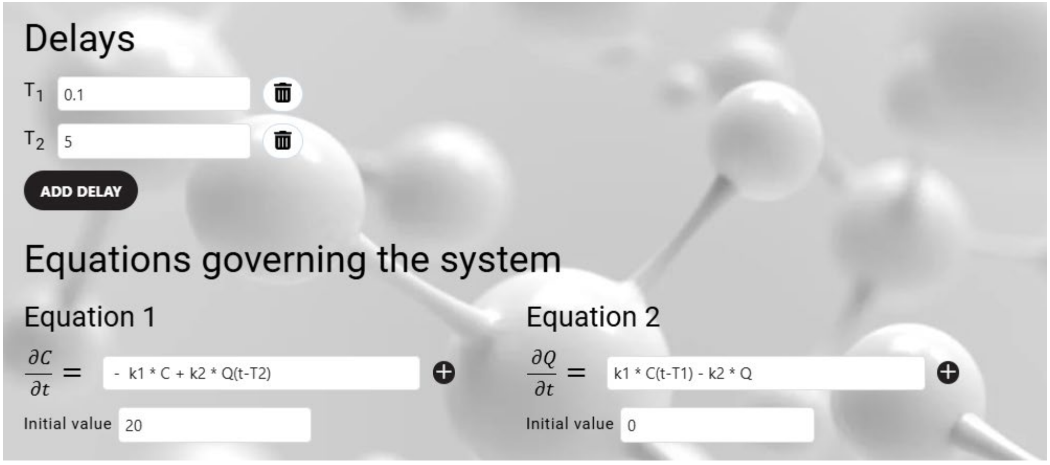
with an **Initial value** of $20\ \mathrm{mg/L}$.

For **Equation 2**, the equation is:

$$\frac{dQ(t)}{dt} = k_1 C(t - \tau_1) - k_2 Q(t)$$

with an **Initial value** of **Initial concentration of adsorbate** $0\ \mathrm{mg/g}$

- Adjust the equations as needed.



Delays

T_1 0.1

T_2 5

Equations governing the system

Equation 1

$\frac{\partial C}{\partial t} =$ - k1 * C + k2 * Q(t-T2)

Initial value 20

Equation 2

$\frac{\partial Q}{\partial t} =$ k1 * C(t-T1) - k2 * Q

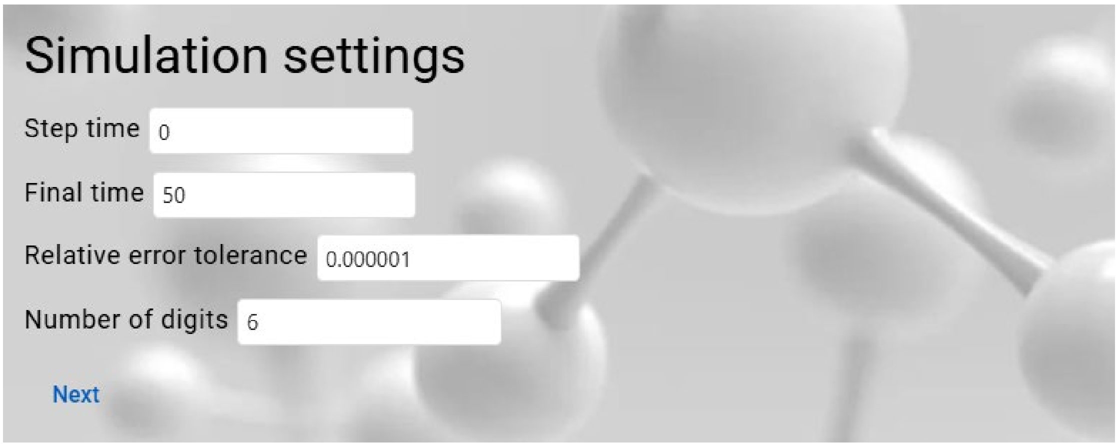
Initial value 0

Step 6: Setting Up the Simulation

Define Simulation Values:

In the Simulation settings section:

- **Step time**: Enter the time step for the simulation.
- **Final time**: Define the final time for the simulation.
- **Relative error tolerance**: Set the relative error tolerance, e.g., 0.0001.
- **Number of digits**: Define the number of digits for the results.



Simulation settings

Step time: 0

Final time: 50

Relative error tolerance: 0.000001

Number of digits: 6

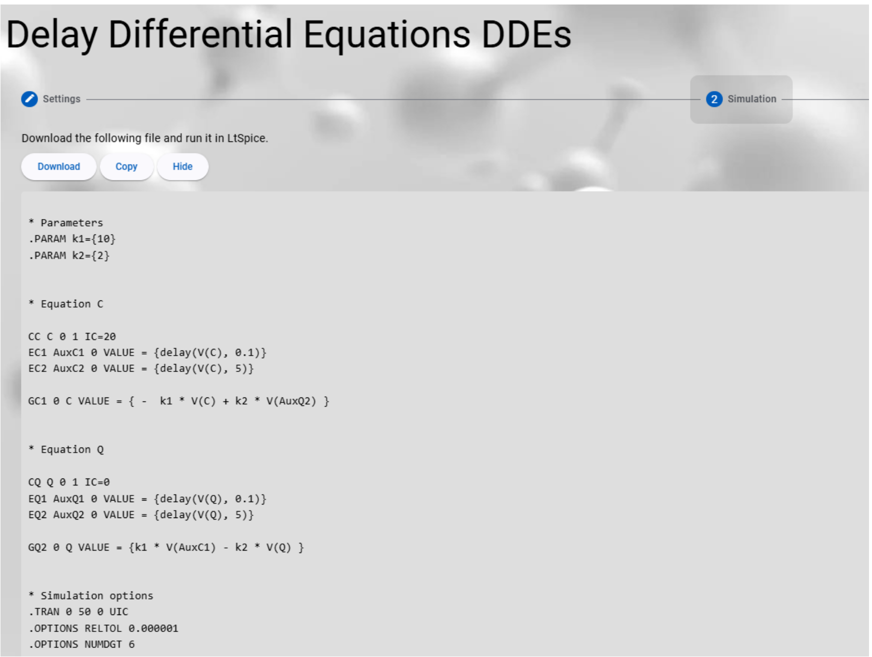
Step 7: Start the Simulation

Run the Simulation:

- Once you have configured all parameters, equations, and delays, click **Next** or the corresponding button to start the simulation.
- The program will calculate the results based on the delay differential equations you entered.

Step 8: Download and Run the File in LTSpice

1. **Download the File:**
   - In the Settings section, you will see options to Download, Copy, or Show the necessary file.
   - Click Download to save the file to your computer.
2. **Run the File in LTSpice:**
   - Open LTSpice on your computer.
   - Load the downloaded file by opening it in LTSpice.



Download the following file and run it in LtSpice.

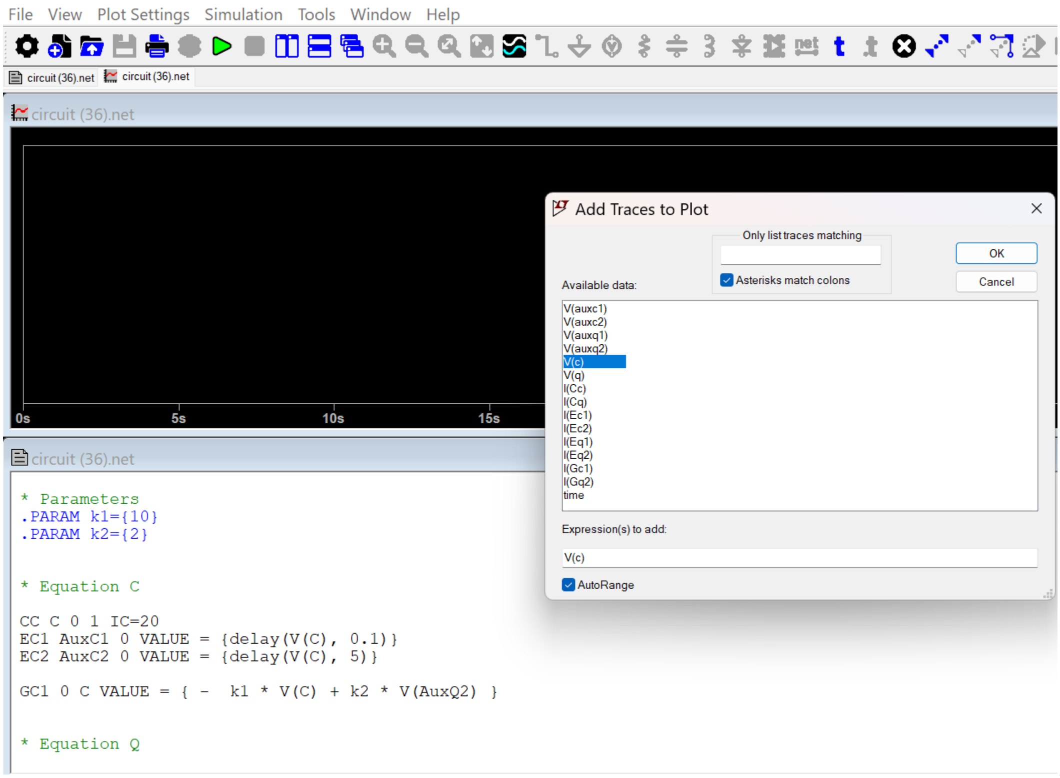
```
* Parameters
.PARAM k1={10}
.PARAM k2={2}


* Equation C

CC C 0 1 IC=20
EC1 AuxC1 0 VALUE = {delay(V(C), 0.1)}
EC2 AuxC2 0 VALUE = {delay(V(C), 5)}

GC1 0 C VALUE = { -  k1 * V(C) + k2 * V(AuxQ2) }


* Equation Q

CQ Q 0 1 IC=0
EQ1 AuxQ1 0 VALUE = {delay(V(Q), 0.1)}
EQ2 AuxQ2 0 VALUE = {delay(V(Q), 5)}

GQ2 0 Q VALUE = {k1 * V(AuxC1) - k2 * V(Q) }


* Simulation options
.TRAN 0 50 0 UIC
.OPTIONS RELTOL 0.000001
.OPTIONS NUMDGT 6
```

Step 9: Simulate and Export Results

1. Run the Simulation:

- In LTSpice, run the simulation to generate results based on the loaded file.
- During the simulation, monitor the variables of interest.

2. Save the Desired Variables:



☑ Asterisks match colons

Available data:

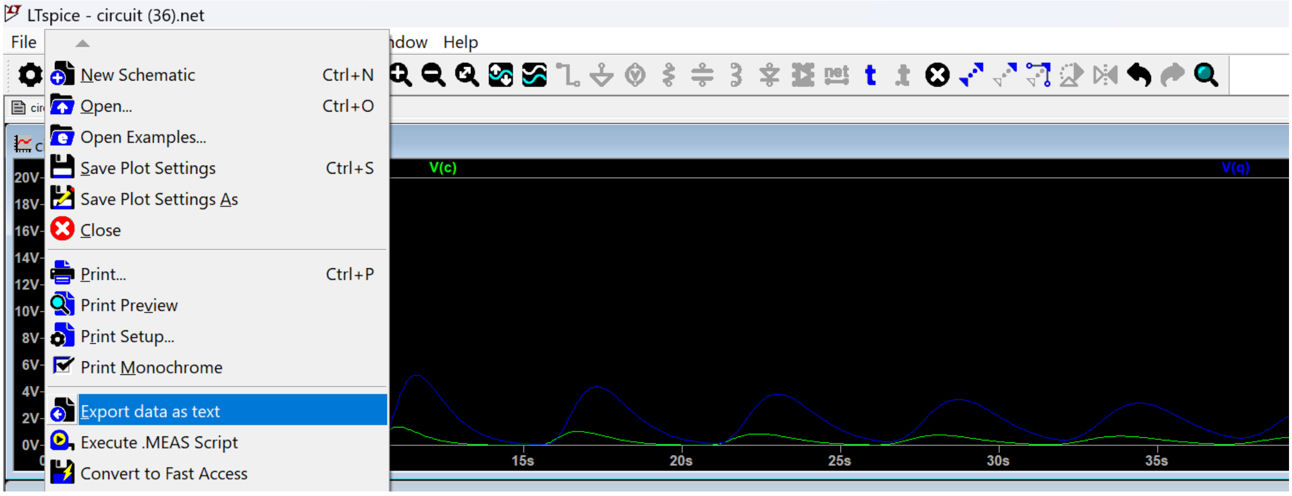
```
V(auxc1)
V(auxc2)
V(auxq1)
V(auxq2)
V(c)
V(q)
I(Cc)
I(Cq)
I(Ec1)
I(Ec2)
I(Eq1)
I(Eq2)
I(Gc1)
I(Gq2)
time
```

Expression(s) to add: V(c)

☑ AutoRange

```
* Parameters
.PARAM k1={10}
.PARAM k2={2}


* Equation C

CC C 0 1 IC=20
EC1 AuxC1 0 VALUE = {delay(V(C), 0.1)}
EC2 AuxC2 0 VALUE = {delay(V(C), 5)}

GC1 0 C VALUE = { -  k1 * V(C) + k2 * V(AuxQ2) }


* Equation Q
```

After the simulation is complete, select the variables you wish to save for analysis.

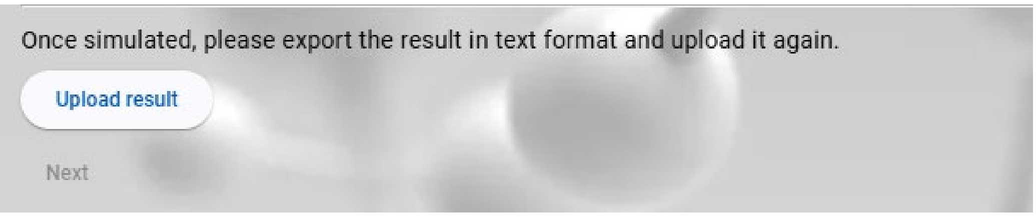


Export the results in **text format (TXT)** by saving them in LTSpice. This exported file will contain the values of the variables over time or other relevant data.

Step 10: Upload Results Back into the DDEs Program

1. **Upload the Results:**

- Return to the Delay Differential Equations (DDEs) program interface.



Once simulated, please export the result in text format and upload it again.

Click **Upload result** and select the TXT file you saved from LTSpice.

2. **Generate Graphs:**

- Once uploaded, the DDEs program will automatically recognize the data from LTSpice.
- The program can then plot the data, allowing you to visualize the results with clear, accurate graphs.