A SECOND-ORDER SYMPLECTIC METHOD FOR AN ADVECTION-DIFFUSION-REACTION PROBLEM IN BIOSEPARATION *

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Abstract. We consider an advection-diffusion-reaction problem with non-homogeneous boundary conditions modeling the chromatography process, a vital stage in bioseparation. We prove stability and error estimates for both constant and affine adsorption, using the midpoint method for time discretization and finite elements for spatial discretization. We also did the stability analysis for nonlinear, explicit adsorption in continuous case. We performed the numerical tests that validate our theoretical results.

Key words. Advection, Diffusion, Reaction, Chromatography, Adsorption, Bioseparation

AMS subject classifications. 65M12, 65M60, 76M10, 76S05

1. Introduction. The global market for biopharmeceuticals is expected to hit \$856.1 billion by 2030 and 50% of top 100 drugs will most likely be derived from biotechnology [1, 14]. The high demand for biopharmaceuticals is due to their effectiveness to treat various illness such as diabetes, anemia, cancer, etc. [25]. Other key factors driving the growth of the market are rising investments in the research and development of novel treatments, favorable government regulations, and increasing adoption of biopharmaceuticals by the global population [1]. To maximize the production capacity while minimizing its costs, manufacturers are constantly developing new methods. As an alternative to constructing new biomanufacturing facilities due to financial risk, integrating new technologies into existing facilities would be more economically viable. Upstream and downstream processes are typically part of a biomanufacturing facility. In the upstream process, cells cultured by genetically engineered methods release the desired product into a solution and in the downstream process, the product is purified from the solution [13]. The capacity of production is often limited by downstream purification, usually including chromatography. In the protein chromatography process, when the solution is pushed through the column, the materials in columns separate the proteins [34]. Ideal media for chromatography columns used for bioseparation are resin beds, monoliths, and membranes [33]. Membrane chromatography [6–8] addresses the low efficiency of resin chromatography, and uses a porous, absorptive membrane as the packing medium instead of the small resin beads The protein binding capacity is crucial in membrane chromatography as it determines the volume of membrane required for purification. Most absorption mechanisms, such as ion-exchange membranes, lose the protein binding capacity at relatively low conductivity and often requires additional processing stages, causing lower yield and higher production cost. Recent research in [7] has focused on multimodal membrane-based chromatography. The development of a modeling framework capable of characterizing the chromatography process under continuous flow circumstances is critical. To model this process for creating a simulation tool for transport in a porous medium, the reactive transport problem (advection-diffusion-reaction problem) considered in [34] is given below.

Let Ω be a bounded domain in $\mathbf{R^d}$, $d = 1,\ 2,\ or\ 3$ with piecewise smooth boundary Γ. We partition the boundary into three non-overlapping segments $\Gamma = \Gamma_{\text{in}} \cup \Gamma_n \cup \Gamma_{\text{out}}$ where inflow boundary, $\Gamma_{\text{in}} = \{x \in \Gamma : \overrightarrow{n} \cdot \mathbf{u}(x) < 0\}$, outflow boundary, $\Gamma_{\text{out}} = \{x \in \Gamma : \overrightarrow{n} \cdot \mathbf{u}(x) > 0\}$ and boundaries comprising no-flow hydraulic zone(s), $\Gamma_n = \Gamma \backslash (\Gamma_{\text{in}} \cup \Gamma_{\text{out}})$. Let $\mathbf{u}$ be a fluid velocity through the membrane and $\overrightarrow{n}$ denote the unit outward normal to Ω. We consider $\mathbf{u}$ is given, which is computed by Darcy [18] satisfying $\boldsymbol{\nabla} \cdot \mathbf{u} = 0$ and $\mathbf{u} \cdot \overrightarrow{n}(x,t) = 0, \quad x \in \Gamma_n,\ t > 0$. Let ω be the total porosity of the membrane ($0 \leq \omega \leq 1$), ρ_s be the density of the membrane, D be the diffusion tensor that represents diffusivity of fluid through the membrane, C and $q(C)$ be the concentration in the liquid and absorbed phases respectively. For a forcing function $f \in L^2(0,T;L^2(\Omega))$, given velocity $\mathbf{u}$ and initial concentration $C_0 \in L^2(\Omega)$, we consider the following

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initial boundary value problem of finding concentration $C(x,t)$:

$$
\begin{cases}
\omega\partial_t C + (1-\omega)\rho_s\partial_t q(C) + \boldsymbol{\nabla}\cdot(\mathbf{u}C) - \boldsymbol{\nabla}\cdot(D\boldsymbol{\nabla}C) = f,\ x\in\Omega,\ t>0,\\
C(x,t) = g,\ x\in\Gamma_{\text{in}},\ t>0,\\
(D\boldsymbol{\nabla}C)\cdot\overrightarrow{n}(x,t) = 0,\ x\in\Gamma_n\cup\Gamma_{\text{out}},\ t>0,\\
C(x,0) = C_0(x),\ x\in\Omega.
\end{cases}
\tag{1.1}
$$

For the inflow boundary, we keep the fixed concentration [5, 18]. The illustration of the domain is given in

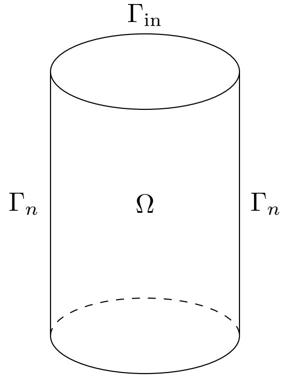

Fig. 1.1: Domain Ω

Figure 1.1.

In our paper, we consider three cases of isotherms. They are constant isotherm, $q(C) = K$, affine isotherm, $q(C) = K_1 + K_2C$ and nonlinear, explicit isotherm $q(C)$. A typical example for the nonlinear, explicit isotherm is Langmuir's isotherm [8, 31], $q(C) = \frac{q_{max}K_{eq}C}{1+K_{eq}C}$, where K_{eq} is Langmuir equilibrium constant, q_{max} is the maximum binding capacity of the porous medium. The main result of this paper is gaining improved accuracy by using the midpoint method for time discretization at the same computational cost as the Backward Euler method. The accuracy comes in two ways, such as rate of convergence is higher and the mass is better conserved when the midpoint method is used. The fully discrete formulation of the considered problem is given in Section 3. The stability analysis and error analysis for constant and affine $q(C)$ are given in Section 4. We also show the stability analysis for the nonlinear, explicit $q(C)$ in the same section. Numerical tests validating these estimates are given in Section 5.

2. Notation and Preliminaries.

We denote the $L^2(\Omega)$ norm and inner product by $\|\cdot\|$ and, $(\cdot,\cdot)$ respectively. We denote the usual Sobolev spaces $W^{m,p}(\Omega)$ with the associated norms $\|\cdot\|_{W^{m,p}(\Omega)}$ and in the case when $p=2$, we denote $W^{m,2}(\Omega) = H^m(\Omega) = \{v\in L^2(\Omega) : \frac{\partial^\alpha v}{\partial x^\alpha}\in L^2(\Omega),\ |\alpha|\le r\}$ where α is a multi-index, with norm $\|v\|_r = \left(\sum_{|\alpha|\le r}\int_\Omega\left|\frac{\partial^\alpha v}{\partial x^\alpha}\right|^2 d\Omega\right)^{1/2}$. The function space for the liquid phase concentration is defined as:

$$H^1_{0,\Gamma_{\text{in}}}(\Omega) := \{v : v\in H^1(\Omega)\text{ with } v=0 \text{ on } \Gamma_{\text{in}}\}.$$

We define the space $H^{1/2}(\Gamma_{\text{in}}) := \{g\in L^2(\Gamma_{\text{in}}) : \|g\|_{H^{1/2}(\Gamma_{\text{in}})} < \infty\}$ where

$$\|g\|_{H^{1/2}(\Gamma_{\text{in}})} = \inf_{\substack{G\in H^1(\Omega)\\ G\big|_{\Gamma_{\text{in}}=g}}}\|G\|_{H^1(\Omega)}.$$

The Bochner Space [2] norms are

$$\|C\|_{L^2(0,T;X)} = \left(\int_0^T\|C(\cdot,t)\|_X^2 dt\right)^{\frac{1}{2}},\ \|C\|_{L^\infty(0,T;X)} = \operatorname{ess}\sup_{0\le t\le T}\|C(\cdot,t)\|_X.$$

We also define discrete L^p-norms with $p = 2$ or ∞

$$\|C\|_{L^2(0,T,X)} = \big(\Delta t \sum_{n=0}^{N} \|C^n\|_X^2\big), \ \|C\|_{L^\infty(0,T,X)} = \max_{0\le n\le N} \|C^n\|_X.$$

For the Finite Element Approximation, we consider a regular triangulation of Ω, $\mathcal{T}_h = \{A\}$ with $\Omega = \bigcup_{A\in\mathcal{T}_h} A$. We choose a finite dimensional subspace $X_h \subset H^1(\Omega)$ and define

$$X^h_{0,\Gamma_{\rm in}} = \{v_h \in X_h : \ v_h = 0 \text{ on } \Gamma_{\rm in}\}$$

with Ω a polyhedron, $X^h_{0,\Gamma_{\rm in}} \subset H^1_{0,\Gamma_{\rm in}}(\Omega)$. We let $X^h_{\Gamma_{\rm in}}$ denote the restriction of functions in X_h to the boundary $\Gamma_{\rm in}$ and define $X^h_0 = \{v_h \in X_h : \ v_h = 0 \ on \ \partial\Omega\}$ with Ω a polyhedron, $X^h_0 \subset H^1_0(\Omega)$. Throughout, K will denote a constant taking different values in different instances. We assume that there exists a $k \geq 1$ such that X_h possesses the approximation property,

$$\inf_{C_h\in X_h} \|C - C_h\|_s \le K h^{r-s}\|C\|_r, \text{ for } \ s = 0, 1 \ \text{ and } \ 1 \le r \le k+1 \tag{2.1}$$

For example, (2.1) holds if X_h consists of piecewise polynomials of degree$\leq k$. We assume that a similar approximation holds on X^h_0. In particular, if $C \in H^r(\Omega) \cap H^1_0(\Omega)$, we will use

$$\inf_{C_h\in X^h_0} \|C - C_h\|_1 \le K h^{r-1}\|C\|_r. \tag{2.2}$$

We further assume that the space $X^h_{\Gamma_{\rm in}}$ possesses the approximation property

$$\inf_{C_h\in X^h_{\Gamma_{\rm in}}} \|C - C_h\|_{0,\Gamma_{\rm in}} \le K h^{r-1/2}\|C\|_{r-1/2,\Gamma_{\rm in}}. \tag{2.3}$$

LEMMA 2.1. *For all $v \in H^1_{0,\Gamma_{in}}(\Omega)$, there exists a constant $\tilde{K}_{PF}$ such that*

$$\|v\|_1 \le \tilde{K}_{PF}\|\boldsymbol{\nabla} v\|.$$

Proof. This is the direct consequence of the Poincaré inequality that holds for $v \in H^1_{0,\Gamma_{\rm in}}(\Omega)$ [20]. ∎

LEMMA 2.2. *Given $g \in H^{r-1/2}(\Gamma_{in})$ for $r \geq 1$, let $\Pi_h g$ denote the $X^h_{\Gamma_{in}}$-interpolant of g. Then, if X_h satisfies the approximation properties* (2.1)-(2.3)*,*

$$\inf_{\substack{\hat{C}_h\in X_h \\ \hat{C}_h|_{\Gamma_{in}}=\Pi_h g}} \|C - \hat{C}_h\|_1 \le K h^{r-1}\|C\|_r. \tag{2.4}$$

Proof. This proof follows the proof of [21, Lemma 4]. We give the proof for reader's convenience. Let $\Pi_h C$ denote X_h-interpolant of C and $\Pi_h g$ denote $X^h_{\Gamma_{\rm in}}$- interpolant of g. Then, for $\hat{C}_h|_{\Gamma_{\rm in}} = \Pi_h g$, we write the triangle inequality

$$\|C - \hat{C}_h\|_1 \le \|C - \Pi_h C\|_1 + \|\hat{C}_h - \Pi_h C\|_1. \tag{2.5}$$

From the interpolation theory [9], we get,

$$\|C - \Pi_h C\|_1 \le K h^{r-1}\|C\|_r. \tag{2.6}$$

We may choose $\hat{C}_h$ so that it has the same value at all interior nodes as does $\Pi_h C$. Since $\hat{C}_h|_{\Gamma_{\rm in}} = \Pi_h g$ and $(\Pi_h C)\Big|_{\Gamma_{\rm in}} = \Pi_h g$, we get $(\hat{C}_h - \Pi_h C) = 0$, which concludes the argument. ∎

2.1. Assumptions. We make the following assumptions [34]:

(F1) ω and ρ_s are constants in time and space [18].

(F2) $\mathbf{u}$ is nonzero and bounded in L^∞ norm [12,29].

(F3) $D(x) = [d_{ij}]_{i,j=1,2,\cdots,n}$ is symmetric positive definite and $\|D\|_\infty \leq \beta_1$, $|\frac{\partial}{\partial x_i} d_{ij}| \leq \beta_2$, for all i,j [3,12,18,29].

(F4) There exists a unique solution $C \in L^\infty(0,T,L^2(\Omega)) \cap L^2(0,T,H^1(\Omega))$ [29].

(F5) $q = q(C) \in C^1$ is an explicit, Lipschitz continuous function of C, $q(0) = 0$, $q(C) > 0$ for $C > 0$ and $q(C)$ is strictly increasing. Moreover, we assume that $q'(C) \geq \kappa_1 > 0\ \forall C \geq 0$ [4,17,18,27–29].

(F6) The rate of increase in adsorption is Lipschitz continuous and bounded above, so that $\frac{dq}{dC} = q'(C) \leq \kappa_2$ [18].

(F7) The second derivative of the adsorption, $q''(C)$, is Lipschitz continuous and bounded.

Remark 2.3. In our analysis, we drop the assumption "$C(x,t)$ is nondecreasing in time at every x and $C(x,t) = 0$ on Γ_{in}" stated in [34]. Instead, we considered the non-homogeneous boundary condition at the inflow boundary.

In [4,17,18,29,34], another assumption on the continuous and the discrete solution was imposed, namely that "C is non-negative". Using a maximum principle argument, we now prove that the continuous solution is positive and bounded above for all $(x,t) \in \Omega \times (0,T)$.

PROPOSITION 2.4. *Assuming no forcing term $f = 0$ and positivity of the initial condition $0 < C_0(x)$, then we have*

$$0 < C(x,t) \leq \max_{x\in\Omega}\{C(x,0), g(x)\} \qquad \text{for all } (x,t) \in \Omega \times [0,T)$$

of (1.1) *is positive and bounded by the initial condition and the boundary condition g.*

Proof. Since $\mathbf{u}$ is incompressible, we rewrite the convective term as

$$\boldsymbol{\nabla} \cdot (uC) = (\boldsymbol{\nabla} \cdot u)C + \mathbf{u} \cdot \boldsymbol{\nabla} C = u \cdot \boldsymbol{\nabla} C.$$

Next, we rewrite the adsorption term as

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} = q'(C)\frac{\partial C}{\partial t}.$$

Then the equation (1.1) writes

$$(\omega + (1-\omega)\rho_s q'(C))\partial_t C + \mathbf{u} \cdot \boldsymbol{\nabla} C - \boldsymbol{\nabla} \cdot (D\boldsymbol{\nabla} C) = f,\ x \in \Omega,\ t > 0. \tag{2.7}$$

Since $q'(C) > 0$ by assumption (F5), we can divide (2.7) by $(\omega + (1-\omega)\rho_s q'(C))$. Hence, assuming $f = 0$, (2.7) writes,

$$-\partial_t C + \sum_{i,j=1}^{n} ((\omega + (1-\omega)\rho_s q'(C))^{-1} D_{ij})\frac{\partial^2 C}{\partial x_i \partial x_j} + \sum_{i,j=1}^{n} \Big((\omega + (1-\omega)\rho_s q'(C))^{-1}\big(\frac{\partial D_{ij}}{\partial x_i} - u_j\big)\Big)\frac{\partial C}{\partial x_j} = 0.$$

We assume that $C_0(x) > 0$. Suppose the claim in the proposition is false. Then there is a $y \in \bar{\Omega}$ and $T > 0$ such that $C(y,T) = 0$ and $C(x,t) > 0$ for $(x,t) \in \bar{\Omega} \times [0,T)$. Therefore, by Maximum Principle [26, pages 173-174], $C(x,t)$ is on the boundary and $(D\boldsymbol{\nabla} C) \cdot \overrightarrow{n}(x,t) < 0$. This contradicts the boundary condition we have in (1.1). Hence, we prove the claim. ∎

3. Variational Formulation. The standard Galerkin variational formulation for (1.1) is: Find $C \in H^1(\Omega)$ such that $C\Big|_{\Gamma_{\text{in}}} = g$ and

$$((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, v) + (u \cdot \boldsymbol{\nabla} C, v) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} v) = (f, v),\ \text{for all } v \in H^1_{0,\Gamma_{\text{in}}}(\Omega), \tag{3.1}$$

where we used the Green's Theorem to the diffusive term, the boundary condition $(D\nabla C)\cdot n(x,t)=0,\ x\in\Gamma_n\cup\Gamma_{\text{out}}$ and the fact that $v\in H^1_{0,\Gamma_{\text{in}}}$ to get

$$-(\nabla\cdot(D\nabla C),v)=-\int_\Gamma(D\nabla C)\cdot\vec{n}v\ ds+(D\nabla C,\nabla v)=(D\nabla C,\nabla v).$$

Next, we write a finite element approximation of the variational formulation of the transport problem. We state both semi-discrete in space and fully discrete approximations.

3.1. Semi-Discrete in Space Approximation. We denote g_h as interpolant of g. Then we obtain the following semi-discrete in space formulation: Find $C_h\in X_h$ such that $C_h\Big|_{\Gamma_{\text{in}}}=g_h\in X^h_{\Gamma_{\text{in}}}$ and

$$((\omega+(1-\omega)\rho_s q'(C_h))\frac{\partial C_h}{\partial t},v_h)+(u\cdot\nabla C_h,v_h)+(D\nabla C_h,\nabla v_h)=(f,v_h),\ \text{for all } v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega). \tag{3.2}$$

3.2. Fully-discrete approximation. We partition the time interval as $t_0=0<t_1<t_2<\cdots<t_N=T$. Let $\Delta t=t_{n+1}-t_n$ be the time step size, $t_n=n\Delta t$ and $f^n(x)=f(x,t_n)$. Let $C_h^n(x)$ denote the Finite Element approximation to $C(x,t_n)$. We define $t_{n+1/2}=\frac{t_n+t_{n+1}}{2}$. First, we recall the first order Backward Euler time discretization scheme for Finite Element Approximation (3.2): Given $C_h^n\in X^h$, find $C_h^{n+1}\in X^h$ satisfying

$$((\omega+(1-\omega)\rho_s q'(C_h^{n+1}))\frac{C_h^{n+1}-C_h^n}{\Delta t},v_h)+(u\cdot\nabla C_h^{n+1},v_h)+(D\nabla C_h^{n+1},\nabla v_h)=(f^{n+1},v_h), \tag{3.3}$$

for all $v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega)$.
Next, we propose the midpoint method for time discretization in Finite Element Approximation (3.2): Given $C_h^n\in X^h$, find $C_h^{n+1}\in X^h$ satisfying

$$((\omega+(1-\omega)\rho_s q'(C_h^{n+1/2}))\frac{C_h^{n+1}-C_h^n}{\Delta t},v_h)+(u\cdot\nabla C_h^{n+1/2},v_h)+(D\nabla C_h^{n+1/2},\nabla v_h)=(f^{n+1/2},v_h), \tag{3.4}$$

for all $v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega)$ where $C_h^{n+\frac{1}{2}}$ denotes $\frac{C_h^n+C_h^{n+1}}{2}$.
In order to simplify computation, we use the refactorization of the midpoint method [11] for time discretization. Hence, we get the following full discretization: Given $C_h^n\in X^h$, find $C_h^{n+1}\in X^h$ satisfying
Step 1: Backward Euler step at the half-integer time step $t_{n+1/2}$

(3.5)
$$((\omega+(1-\omega)\rho_s q'(C_h^{n+1/2}))\frac{C_h^{n+1/2}-C_h^n}{\Delta t/2},v_h)+(u\cdot\nabla C_h^{n+1/2},v_h)+(D\nabla C_h^{n+1/2},\nabla v_h)=(f^{n+1/2},v_h),$$

for all $v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega)$.
Step 2: Forward Euler step at t_{n+1}

(3.6)
$$((\omega+(1-\omega)\rho_s q'(C_h^{n+1/2}))\frac{C_h^{n+1}-C_h^{n+1/2}}{\Delta t/2},v_h)+(u\cdot\nabla C_h^{n+1/2},v_h)+(D\nabla C_h^{n+1/2},\nabla v_h)=(f^{n+1/2},v_h),$$

for all $v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega)$.

Remark 3.1. Step 2 is equivalent to a linear extrapolation $C_{n+1}=2C_{n+1/2}-C_n$.

Remark 3.2. In [35], the Streamline-Upwinded Petrov-Galerkin (SUPG) was analyzed for the highly advective flows, instead of Finite Element Approximation (FEM). When $\delta=0$ in [35, Equation (11)], SUPG and FEM are equivalent. Hence, [35, Theorem 2.1] is applicable to prove the solvability of (3.4) for C_h^{n+1}.

4. Time-Dependent Analysis. In this section, before we perform the stability and error analysis for the time dependent problem, first we construct a continuous extension of the Dirichlet data g inside the domain Ω, $\hat{C}$ to deal with the non-homogeneous boundary condition.

4.1. Construction of $\hat{C}$. Denote $\hat{C}$ as solution of the following elliptic problem with non-homogeneous mixed boundary conditions:

$$
\begin{aligned}
-\boldsymbol{\nabla}\cdot(D\boldsymbol{\nabla}\hat{C})+\hat{C}&=0,\ x\in\Omega,\\
\hat{C}&=g,\ \text{if } x\in\Gamma_{\text{in}},\\
(D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n}&=0,\ \text{if } x\in\Gamma_n\cup\Gamma_{\text{out}}.
\end{aligned}
\tag{4.1}
$$

Lemma 4.1. *For every $f\in L^2(\Omega)$ and every $g\in H^{1/2}(\Gamma_{in})$, there exists a unique solution $\hat{C}\in H^2(\Omega)$ of (4.1) under the compatibility condition $D\boldsymbol{\nabla}g\cdot\overrightarrow{n}=0$ if $x\in\Gamma_-\cap\Gamma_n$. The energy estimates for $\hat{C}$ and $\boldsymbol{\nabla}\hat{C}$ are as follows,*

$$
\|\hat{C}\|^2\le 4(K\beta_1)^2\|g\|^2_{L^2(\Gamma_{in})},
\tag{4.2}
$$

$$
\|\boldsymbol{\nabla}\hat{C}\|^2\le\frac{2(K\beta_1)^2}{\lambda}\|g\|^2_{L^2(\Gamma_{in})}.
\tag{4.3}
$$

Remark 4.2. The energy bound given in [22, Theorem 2.3.3.6] is

$$
\|\hat{C}\|_{H^2(\Omega)}\le K\|g\|_{H^{1/2}(\Gamma_{\text{in}})}
$$

for all $\hat{C}\in H^2(\Omega)$ and some constant K.

Proof. The existence and uniqueness proof for the more general case can be found in [22, Theorem 2.4.2.7]. For energy bounds, we take the dot product with $\hat{C}$, then apply Green's Theorem to the diffusive term to obtain

$$
-(\boldsymbol{\nabla}\cdot(D\boldsymbol{\nabla}\hat{C}),\hat{C})=-\int_\Gamma(D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n}\hat{C}\ ds+(D\boldsymbol{\nabla}\hat{C},\boldsymbol{\nabla}\hat{C})=-\int_{\Gamma_{\text{in}}}(D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n}g\ ds+(D\boldsymbol{\nabla}\hat{C},\boldsymbol{\nabla}\hat{C})
$$

where we used the boundary condition $(D\boldsymbol{\nabla}\hat{C})\cdot n=0$, $x\in\Gamma_n\cup\Gamma_{\text{out}}$ and $\hat{C}(x)=g(x)$, $x\in\Gamma_{\text{in}}$. Hence, we get the following variational formulation,

$$
\|\hat{C}\|^2+(D\boldsymbol{\nabla}\hat{C},\boldsymbol{\nabla}\hat{C})=\int_{\Gamma_{\text{in}}}(D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n}g\ ds.
$$

Let λ be the minimum eigenvalue of D.

$$
(D\boldsymbol{\nabla}\hat{C},\boldsymbol{\nabla}\hat{C})\ =\ (D^{1/2}\boldsymbol{\nabla}\hat{C},D^{1/2}\boldsymbol{\nabla}\hat{C})\ =\ \|D^{1/2}\boldsymbol{\nabla}\hat{C}\|^2\ge\lambda\|\boldsymbol{\nabla}\hat{C}\|^2.
$$

Hence, we get,

$$
\begin{aligned}
\|\hat{C}\|^2+\lambda\|\boldsymbol{\nabla}\hat{C}\|^2&\le\int_{\Gamma_{\text{in}}}(D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n}g\ ds,\\
&\le\|D\boldsymbol{\nabla}\hat{C}\cdot\overrightarrow{n}\|_{L^2(\Gamma_{\text{in}})}\|g\|_{L^2(\Gamma_{\text{in}})},\\
&\le\beta_1\|\boldsymbol{\nabla}\hat{C}\cdot\overrightarrow{n}\|_{L^2(\Gamma_{\text{in}})}\|g\|_{L^2(\Gamma_{\text{in}})}.
\end{aligned}
$$

By using the trace theorem [10, p. 316], we get

$$
\|\hat{C}\|^2+\lambda\|\boldsymbol{\nabla}\hat{C}\|^2\le K\beta_1\|\hat{C}\|_{H^2(\Omega)}\|g\|_{L^2(\Gamma_{\text{in}})}.
\tag{4.4}
$$

We use the following equivalence of norms [10, p. 271],

$$
\|\hat{C}\|_{H^2(\Omega)}\le K(\|\hat{C}\|+\|\boldsymbol{\nabla}\cdot\Big(D\boldsymbol{\nabla}\hat{C}\Big)\|).
$$

By using Young and Cauchy-Schwarz inequalities (4.4) becomes,

$$
\frac{1}{2}\|\hat{C}\|^2+\lambda\|\boldsymbol{\nabla}\hat{C}\|^2\le 2(K\beta_1)^2\|g\|^2_{L^2(\Gamma_{\text{in}})}.
$$

Hence we get the bounds (4.2) and (4.3). ∎

LEMMA 4.3. *Let the domain Ω be convex polyhedral. Given $g^h \in X^h_{\Gamma_{in}}$, there exists a $\hat{C^h} \in X^h$ such that $\hat{C^h}|_{\Gamma-} = g^h$ and $\|\hat{C^h}\|_{H^1(\Omega)} \leq K\|g^h\|_{H^{1/2}(\Gamma-)}$.*

Proof. In the case when Ω is two-dimensional, we follow the similar technique in [23] to prove it. Under the compatibility condition $D\nabla g^h \cdot \overrightarrow{n} = 0,$ when $x \in \Gamma_{\text{in}} \cap \Gamma_n$, let $\hat{C} \in H^1(\Omega)$ be the solution of

$$
\begin{aligned}
-\nabla \cdot (D\nabla\hat{C}) + \hat{C} &= 0,\ x \in \Omega,\\
\hat{C} &= g^h,\ \text{when } x \in \Gamma_{\text{in}},\\
(D\nabla\hat{C}) \cdot \overrightarrow{n} &= 0,\ \text{if } x \in \Gamma_n \cup \Gamma_{\text{out}}.
\end{aligned}
\tag{4.5}
$$

Since X^h is assumed to be a continuous finite element subspace, we see that g^h is continuous and piecewise smooth along the boundary Γ_-, so that $g^h \in H^{1/2+\epsilon}(\Gamma_{\text{in}})$ for $0 < \epsilon \leq \frac{1}{2}$. Thus, by elliptic regularity, we derive that $\hat{C} \in H^{1+\epsilon}(\Omega)$ and $\|\hat{C}\|_{1+\epsilon} \leq K\|g^h\|_{1/2+\epsilon,\Gamma_{\text{in}}}$ for $0 < \epsilon \leq \frac{1}{2}$. Let $\hat{C^h} := \Pi_h\hat{C}$ be the X^h-interpolant of $\hat{C}$ so that $\hat{C^h}|_{\Gamma_{\text{in}}} = g^h$. Then, we have the estimates $\|\hat{C} - \Pi_h\hat{C}\|_1 \leq Kh^\epsilon\|\hat{C}\|_{1+\epsilon}$ which can be proven as in, e.g., [19]. Thus, we get the desired result

$$
\begin{aligned}
\|\hat{C^h}\|_1 = \|\Pi_h\hat{C}\|_1 &\leq \|\hat{C} - \Pi_h\hat{C}\|_1 + \|\hat{C}\|_1,\\
&\leq K(h^\epsilon\|\hat{C}\|_{1+\varepsilon} + \|\hat{C}\|_1),\\
&\leq K(h^\epsilon\|g^h\|_{1/2+\epsilon,\Gamma_{\text{in}}} + \|g^h\|_{1/2,\Gamma_{\text{in}}}),\\
&\leq K\|g^h\|_{1/2,\Gamma_{\text{in}}}.
\end{aligned}
$$

where in the last step we used an inverse assumption on $X^h_{\Gamma_{\text{in}}}$: there exists a constant K, independent of h, p^h such that

$$\|p^h\|_{s,\Gamma-} \leq Kh^{t-s}\|p^h\|_{t,\Gamma_{\text{in}}},\ \forall p^h \in X^h_{\Gamma_{\text{in}}},\ 0 \leq t \leq s \leq 1.$$

Since the usual interpolant such as the one used in two-dimensional case, is not defined in three dimensions for $H^r(\Omega)$-functions, $r \leq \frac{3}{2}$, we use Scott-Zhang interpolant [16] when Ω is three-dimensional. Scott-Zhang interpolant is well-defined for any function in $H^1(\Omega)$ [30]. ∎

Next, to have a full insight of the analysis, we start with the simplest case of constant adsorption. Unlike previous work, in [34] we dropped the assumption "$C(x,t)$ is nondecreasing in time at every x" and considered non-homogeneous boundary condition at inflow boundary.

4.2. Constant Isotherm. In this subsection, we state and prove a *priori* stability and a *priori* error estimates for the case of constant adsorption. In this case of adsorption, $q(C) = K$ with $K \geq 0$. Since $q(C)$ is constant, it implies $\frac{\partial q}{\partial t} = 0$ and hence the variational formulation given in (3.1) simplifies to the following: Find $C \in H^1(\Omega)$ such that $C\Big|_{\Gamma_{\text{in}}} = g$ and :

$$(\omega\frac{\partial C}{\partial t}, v) + (\mathbf{u} \cdot \nabla C, v) + (D\nabla C, \nabla v) = (f, v),\ \text{for all}\ \ v \in H^1_{0,\Gamma_{\text{in}}}(\Omega). \tag{4.6}$$

The semi-discrete in space Finite Element formulation with constant adsorption is as follows: Find $C_h \in X_h$ such that $C_h\Big|_{\Gamma_{\text{in}}} = g_h$ and :

$$(\omega\frac{\partial C_h}{\partial t}, v_h) + (\mathbf{u} \cdot \nabla C_h, v_h) + (D\nabla C_h, \nabla v_h) = (f, v_h),\ \text{for all}\ \ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega). \tag{4.7}$$

By using Midpoint time discretization, we get fully discrete approximation: Given $C^n_h \in X^h$, find $C^{n+1}_h \in X^h$ satisfying

$$(\omega\frac{C^{n+1}_h - C^n_h}{\Delta t}, v_h) + (u \cdot \nabla C^{n+1/2}_h, v_h) + (D\nabla C^{n+1/2}_h, \nabla v_h) = (f^{n+1/2}, v_h),\ \text{for all}\ \ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega). \tag{4.8}$$

For the analysis, we recall the refactorization of midpoint method [11] for time discretization to get the following full discretization: Given $C_h^n \in X^h$, find $C_h^{n+1} \in X^h$ satisfying
Step 1: Backward Euler step at the half-integer time step $t_{n+1/2}$
(4.9)
$$(\omega \frac{C_h^{n+1/2} - C_h^n}{\Delta t/2}, v_h) + (u \cdot \boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega).$$

Step 2: Forward Euler step at t_{n+1}
(4.10)
$$(\omega \frac{C_h^{n+1} - C_h^{n+1/2}}{\Delta t/2}, v_h) + (u \cdot \boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega).$$

Next theorem gives a stability bound in a sense that the solution is bounded in space.

THEOREM 4.4. *Assume that (F1)-(F6) are satisfied and the variational formulation with constant adsorption given by (4.6) has a solution $C \in L^\infty(0, T, L^2(\Omega)) \cap L^2(0, T, H^1(\Omega))$ with $f \in L^2(0, T; L^2(\Omega))$. Let $\hat{C}$ be the continuous extension of the Dirichlet data g inside the domain Ω and satisfies (4.1). The bounds on $\|\hat{C}\|^2$ and $\|\boldsymbol{\nabla}\hat{C}\|^2$ are given in (4.2) and (4.3) respectively. Then we get the following stability bound:*

$$\|C(t)\|^2 + \frac{\lambda}{\omega}\int_0^t \|\boldsymbol{\nabla} C(r)\|^2 \, dr + \frac{2}{\omega}\int_0^t \int_{\Gamma_{out}} ((C)^2)(\mathbf{u}\cdot \vec{n}) ds dr \le \frac{4}{\omega}\int_0^t \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2 \, dr + 8\|\hat{C}\|^2$$
$$+ \Big(\frac{\lambda}{\omega} + \frac{4\beta_1^2}{\lambda\omega}\Big)\int_0^t \|\boldsymbol{\nabla}\hat{C}\|^2 \, dr - \frac{2}{\omega}\int_0^t \int_{\Gamma_{in}} ((g)^2)(\mathbf{u}\cdot\vec{n}) ds dr + 3\|C_0\|^2 + \frac{8K_{PF}^2}{\lambda\omega}\int_0^t \|f\|^2 \, dr.$$

Proof. Let $\hat{C}(x) \in H^1(\Omega)$ such that $\hat{C}\Big|_{\Gamma_{\text{in}}} = g$. Take $v = C - \hat{C} \in H^1_{0,\Gamma_{\text{in}}}(\Omega)$. Then (4.7) yields to

$$(\omega\frac{\partial C}{\partial t}, C - \hat{C}) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, C - \hat{C}) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\Big(C - \hat{C}\Big)) = (f, C - \hat{C}).$$

Thus, we get,

$$(\omega\frac{\partial C}{\partial t}, C) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, C) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) = (\omega\frac{\partial C}{\partial t}, \hat{C}) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\hat{C}) + (f, C - \hat{C}). \tag{4.11}$$

We rewrite the first term in (4.11),

$$(\omega\frac{\partial C}{\partial t}, C) = \omega(\frac{\partial C}{\partial t}, C) = \frac{\omega}{2}\frac{\partial}{\partial t}\|C\|^2. \tag{4.12}$$

By using divergence theorem and boundary conditions, we get

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C, C) = \frac{1}{2}\Big(\int_{\Gamma_{\text{in}}} ((g)^2)(\mathbf{u}\cdot\vec{n}) ds\Big) + \frac{1}{2}\Big(\int_{\Gamma_{\text{out}}} ((C)^2)(\mathbf{u}\cdot\vec{n}) ds\Big). \tag{4.13}$$

Let λ be the minimum eigenvalue of D. Then we get,

$$(D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) \;=\; (D^{1/2}\boldsymbol{\nabla} C, D^{1/2}\boldsymbol{\nabla} C) \;=\; \|D^{1/2}\boldsymbol{\nabla} C\|^2 \ge \lambda\|\boldsymbol{\nabla} C\|^2. \tag{4.14}$$

In the right-hand side terms, we get following estimates,

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) \le \|\mathbf{u}\cdot\boldsymbol{\nabla} C\|\|\hat{C}\| \le \frac{\lambda}{4\|\mathbf{u}\|_\infty^2}\|\mathbf{u}\cdot\boldsymbol{\nabla} C\|^2 + \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2.$$

Then by using boundedness of $\mathbf{u}$, we get

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) \le \frac{\lambda}{4}\|\boldsymbol{\nabla} C\|^2 + \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2. \tag{4.15}$$

Next,

$$(D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\hat{C}) \ \leq \|D\|_\infty \|\boldsymbol{\nabla} C\| \|\boldsymbol{\nabla}\hat{C}\| \leq \beta_1 \|\boldsymbol{\nabla} C\| \|\boldsymbol{\nabla}\hat{C}\| \leq \frac{\lambda}{4}\|\boldsymbol{\nabla} C\|^2 + \frac{\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}\|^2. \tag{4.16}$$

$$(f, C-\hat{C}) \leq \|f\| \|C-\hat{C}\| \leq \frac{2K_{PF}^2}{\lambda}\|f\|^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla} C\|^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla}\hat{C}\|^2. \tag{4.17}$$

Next,

$$(\omega \frac{\partial C}{\partial t}, \hat{C}) = \omega \frac{\partial}{\partial t}(C, \hat{C}) - \omega (C, \frac{\partial \hat{C}}{\partial t}) = \omega \frac{\partial}{\partial t}(C, \hat{C}). \tag{4.18}$$

Combining (4.12)-(4.18), we get

$$\begin{aligned}
&\frac{\partial}{\partial t}\Big(\frac{\omega}{2}\|C\|^2\Big) + \frac{\lambda}{4}\|\boldsymbol{\nabla} C\|^2 + \frac{1}{2}\int_{\Gamma_{\text{out}}} ((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds \leq \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2 \\
&+ \Big(\frac{\lambda}{4} + \frac{\beta_1^2}{\lambda}\Big)\|\boldsymbol{\nabla}\hat{C}\|^2 - \frac{1}{2}\Big(\int_{\Gamma_{\text{in}}} ((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{2K_{PF}^2}{\lambda}\|f\|^2 + \omega\frac{\partial}{\partial t}(C, \hat{C}).
\end{aligned}$$

Next, integrating both sides from 0 to t, we obtain

$$\begin{aligned}
&\frac{\omega}{2}\|C(t)\|^2 + \frac{\lambda}{4}\int_0^t \|\boldsymbol{\nabla} C(r)\|^2 \ dr + \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{out}}} ((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) \ dr \\
&\leq \int_0^t \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2 \ dr + \Big(\frac{\lambda}{4} + \frac{\beta_1^2}{\lambda}\Big)\int_0^t \|\boldsymbol{\nabla}\hat{C}\|^2 \ dr + \frac{\omega}{2}\|C(0)\|^2 \\
&- \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{in}}} ((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) \ dr - \omega(C(0), \hat{C}) + \frac{2K_{PF}^2}{\lambda}\int_0^t \|f\|^2 \ dr + \omega(C(t), \hat{C}).
\end{aligned} \tag{4.19}$$

Here,

$$\begin{aligned}
&\omega(C(t), \hat{C}) \leq \omega\|C(t)\|\|\hat{C}\| \leq \frac{\omega}{4}\|C(t)\|^2 + \omega\|\hat{C}\|^2. \\
&-\omega(C(0), \hat{C}) \leq \omega|(C(0), \hat{C})| \leq \omega\|C(0)\|\|\hat{C}\| \leq \frac{\omega}{4}\|C(0)\|^2 + \omega\|\hat{C}\|^2
\end{aligned}$$

Hence (4.19) becomes

$$\begin{aligned}
&\frac{\omega}{2}\|C(t)\|^2 + \frac{\lambda}{4}\int_0^t \|\boldsymbol{\nabla} C(r)\|^2 \ dr + \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{out}}} ((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) \ dr \\
&\leq \int_0^t \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2 \ dr + \Big(\frac{\lambda}{4} + \frac{\beta_1^2}{\lambda}\Big)\int_0^t \|\boldsymbol{\nabla}\hat{C}\|^2 \ dr - \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{in}}} ((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) \ dr + \frac{\omega}{4}\|C(0)\|^2 + \omega\|\hat{C}\|^2 \\
&+ \frac{2K_{PF}^2}{\lambda}\int_0^t \|f\|^2 \ dr + \frac{\omega}{4}\|C(t)\|^2 + \omega\|\hat{C}\|^2 + \frac{\omega}{2}\|C(0)\|^2.
\end{aligned}$$

Simplifying the above inequality and using $C(0) = C_0$, we get the claimed result. ∎

Remark 4.5. Putting (4.12), (4.13) and (4.18) into (4.11), we get,

$$\begin{aligned}
&\frac{\omega}{2}\frac{\partial}{\partial t}\|C\|^2 + \Big(\int_{\Gamma_{\text{out}}} (C^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) = -\Big(\int_{\Gamma_{\text{in}}} (g^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + (f, C-\hat{C}) \\
&\omega\frac{\partial}{\partial t}(C, \hat{C}) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\hat{C}).
\end{aligned} \tag{4.20}$$

If $f = 0$ and $\hat{C} = 0$ in (4.20), we get the balance of mass as follows

$$\frac{\omega}{2}\frac{\partial}{\partial t}\|C\|^2 + \Big(\int_{\Gamma_{\text{out}}} (C^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) = -\Big(\int_{\Gamma_{\text{in}}} (g^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big). \tag{4.21}$$

Recall that $\mathbf{u}\cdot\overrightarrow{n} > 0$ on Γ_{out} and $\mathbf{u}\cdot\overrightarrow{n} < 0$ on Γ_{in}.

Next theorem gives a *priori* error estimate for the case of constant adsorption and semi discrete in space where we will use the notation

$$K^2 = \max\Big\{\Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big)K_1^2, \frac{8K_{PF}^2\omega^2}{\lambda^2}K_1^2, \frac{4\omega}{\lambda}\Big\}.$$

THEOREM 4.6. *Assume that (F1)-(F6) are satisfied and the variational formulation with constant adsorption given by (4.6) has an exact solution $C \in H^1(0,T,H^{k+1}(\Omega))$ and C_h solves the semi-discrete in space Finite Element formulation with constant adsorption given by (4.7). Then for $1 \le r \le k+1$ there exists a positive constant K independent of h such that:*

$$\|C - C_h\|_{L^2(0,T;H^1(\Omega))} \le K\Big(h^{r-1}\|C\|_{L^2(0,T;H^r(\Omega))} + h^{r-1}\Big\|\frac{\partial C}{\partial t}\Big\|_{L^2(0,T;H^r(\Omega))} + \|(C_h - \hat{C}_h)(0)\|\Big).$$

Proof. The weak formulation of continuous and discrete problems are given by (4.6) and (4.7), respectively, where $C\Big|_{\Gamma_{\text{in}}} = g$ and $C_h\Big|_{\Gamma_{\text{in}}} = g_h$ are required.
First we let $v = v_h \in X_{0,\Gamma_{\text{in}}}^h \subset H_{0,\Gamma_{\text{in}}}^1(\Omega)$ in (4.6) and then subtract (4.7) from (4.6) to get

$$(\omega\frac{\partial(C-C_h)}{\partial t}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}(C-C_h), v_h) + (D\boldsymbol{\nabla}(C-C_h), \boldsymbol{\nabla}v_h) = 0, \text{ for all } v_h \in X_{0,\Gamma_{\text{in}}}^h. \tag{4.22}$$

Then for any $\hat{C}_h(x) \in X_h$ such that $\hat{C}_h\Big|_{\Gamma_{\text{in}}} = g_h$, we have that

$$\begin{aligned}(\omega\frac{\partial(C_h-\hat{C}_h)}{\partial t}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big), v_h) + (D\boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big), \boldsymbol{\nabla}v_h)\\ = (\omega\frac{\partial(C-\hat{C}_h)}{\partial t}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big), v_h) + (D\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big), \boldsymbol{\nabla}v_h),\ \forall v_h \in X_{0,\Gamma_{\text{in}}}^h.\end{aligned} \tag{4.23}$$

We choose $v_h = C_h - \hat{C}_h \in X_{0,\Gamma_{\text{in}}}^h$. Then, we get

$$\begin{aligned}(\omega\frac{\partial(C_h-\hat{C}_h)}{\partial t}, C_h-\hat{C}_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big), C_h-\hat{C}_h) + (D\boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big), \boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big))\\ = (\omega\frac{\partial(C-\hat{C}_h)}{\partial t}, C_h-\hat{C}_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big), C_h-\hat{C}_h) + (D\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big), \boldsymbol{\nabla}\Big(C_h-\hat{C}_h\Big)).\end{aligned} \tag{4.24}$$

Let $\phi_h = C_h - \hat{C}_h$ and $\eta = C - \hat{C}_h$. Notice that both C_h and $\hat{C}_h$ are equal to g_h on Γ_{in}. Hence $\phi_h\Big|_{\Gamma_{\text{in}}} = 0$. Hence, (4.24) becomes

$$(\omega\frac{\partial\phi_h}{\partial t}, \phi_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h, \phi_h) + (D\boldsymbol{\nabla}\phi_h, \boldsymbol{\nabla}\phi_h) = (\omega\frac{\partial\eta}{\partial t}, \phi_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}\eta, \phi_h) + (D\boldsymbol{\nabla}\eta, \boldsymbol{\nabla}\phi_h). \tag{4.25}$$

We obtain lower bounds for the terms on the left and upper bounds for the term in the right of (4.25) by using the assumptions and Young's and Cauchy-Schwarz inequalities. We rewrite the first term in (4.25),

$$(\omega\frac{\partial\phi_h}{\partial t}, \phi_h) = \omega(\frac{\partial\phi_h}{\partial t}, \phi_h) = \frac{\omega}{2}\frac{\partial}{\partial t}\|\phi_h\|^2. \tag{4.26}$$

Next,

$$\begin{aligned}(\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h, \phi_h) &= \frac{1}{2}\Big(\int_{\Gamma}((\phi_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big),\\ &= \frac{1}{2}\Big(\int_{\Gamma_{\text{in}}}((\phi_h)^2)(\mathbf{u}\cdot\vec{n})ds + \int_{\Gamma_{\text{out}}}((\phi_h)^2)(\mathbf{u}\cdot\vec{n})ds + \int_{\Gamma_n}((\phi_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big).\end{aligned}$$

We know that $\phi_h\Big|_{\Gamma_{\text{in}}} = 0$, on $\Gamma_{\text{out}},\ \mathbf{u}\cdot\overrightarrow{n} > 0$ and on $\Gamma_n,\ \mathbf{u}\cdot\overrightarrow{n} = 0$.
Hence, we get,

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h, \phi_h) = \frac{1}{2}\Big(\int_{\Gamma_{\text{out}}}((\phi_h)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) \geq 0. \tag{4.27}$$

Following the same steps in Theorem 4.4, we get the following bounds

$$(D\boldsymbol{\nabla}\phi_h, \boldsymbol{\nabla}\phi_h) \geq \lambda\|\boldsymbol{\nabla}\phi_h\|^2. \tag{4.28}$$

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\eta, \phi_h) \leq \frac{K_{PF}^2}{\lambda}\|\mathbf{u}\|_\infty^2\|\eta\|_1^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla}\phi_h\|^2. \tag{4.29}$$

$$(D\boldsymbol{\nabla}\eta, \boldsymbol{\nabla}\phi_h)\ \leq \frac{\beta_1^2}{\lambda}\|\eta\|_1^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla}\phi_h\|^2. \tag{4.30}$$

Next,

$$(\omega\frac{\partial\eta}{\partial t}, \phi_h) \leq \omega\Big\|\frac{\partial\eta}{\partial t}\Big\|\|\phi_h\| \leq \frac{K_{PF}^2\omega^2}{\lambda}\Big\|\frac{\partial\eta}{\partial t}\Big\|^2 + \frac{\lambda}{4K_{PF}^2}\|\phi_h\|^2 \leq \frac{K_{PF}^2\omega^2}{\lambda}\Big\|\frac{\partial\eta}{\partial t}\Big\|^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla}\phi_h\|^2. \tag{4.31}$$

Combining (4.26)-(4.31) and integrating from 0 to T, we get

$$\|\phi_h(T)\|^2 + \frac{\lambda}{2\omega}\int_0^T \|\boldsymbol{\nabla}\phi_h\|^2\ dt \leq \Big(\frac{2K_{PF}^2\|\mathbf{u}\|_\infty^2 + 2\beta_1^2}{\omega\lambda}\Big)\int_0^T \|\eta\|_1^2\ dt + \frac{2K_{PF}^2\omega}{\lambda}\int_0^T \Big\|\frac{\partial\eta}{\partial t}\Big\|^2\ dt + \|\phi_h(0)\|^2. \tag{4.32}$$

Hence, (4.32) implies

$$\int_0^T \|\boldsymbol{\nabla}\phi_h\|^2\ dt \leq \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\lambda^2}\Big)\int_0^T \|\eta\|_1^2\ dt + \frac{4K_{PF}^2\omega^2}{\lambda^2}\int_0^T \Big\|\frac{\partial\eta}{\partial t}\Big\|^2\ dt + \frac{2\omega}{\lambda}\|\phi_h(0)\|^2. \tag{4.33}$$

By using the Lemma 2.1, we get

$$\int_0^T \|\phi_h\|_1^2\ dt \leq \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\lambda^2}\Big)\int_0^T \|\eta\|_1^2\ dt + \frac{4K_{PF}^2\omega^2}{\lambda^2}\int_0^T \Big\|\frac{\partial\eta}{\partial t}\Big\|^2\ dt + \frac{2\omega}{\lambda}\|\phi_h(0)\|^2. \tag{4.34}$$

Triangle inequality gives

$$\|C - C_h\|_1 \leq \|\eta\|_1 + \|\phi_h\|_1.$$

Thus, we get

$$\int_0^T \|C - C_h\|_1^2\ dt \leq 2\int_0^T \|\eta\|_1^2\ dt + 2\int_0^T \|\phi_h\|_1^2\ dt. \tag{4.35}$$

Now using inequality (4.34) in (4.35) yields

$$\int_0^T \|C - C_h\|_1^2\ dt \leq \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big)\int_0^T \|\eta\|_1^2\ dt + \frac{8K_{PF}^2\omega^2}{\lambda^2}\int_0^T \Big\|\frac{\partial\eta}{\partial t}\Big\|^2\ dt + \frac{4\omega}{\lambda}\|\phi_h(0)\|^2.$$

Since $\hat{C}_h$ is arbitrary, we have the following inequality

$$\int_0^T \|C - C_h\|_1^2\ dt \leq \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big)\int_0^T \inf_{\substack{\hat{C}_h\in X_h\\ \hat{C}_h|_{\Gamma_{\text{in}}}=g_h}} \|C - \hat{C}_h\|_1^2\ dt$$
$$+ \frac{8K_{PF}^2\omega^2}{\lambda^2}\int_0^T \inf_{\substack{\hat{C}_h\in X_h\\ \hat{C}_h|_{\Gamma_{\text{in}}}=g_h}} \Big\|\frac{\partial(C - \hat{C}_h)}{\partial t}\Big\|^2\ dt + \frac{4\omega}{\lambda}\|\phi_h(0)\|^2.$$

Let g_h be the interpolant of g in $X^h_{\Gamma_{\rm in}}$. Then by using Lemma 2.2, for $1 \le r \le k+1$ we get,

$$
\begin{aligned}
\int_0^T \|C - C_h\|_1^2 \, dt \le \Big(2 + \frac{8K_{PF}^2 \|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) K_1^2 h^{2r-2} \int_0^T \|C\|_r^2 \, dt \\
+ \frac{8K_{PF}^2 \omega^2 K_1^2 h^{2r-2}}{\lambda^2} \int_0^T \Big\| \frac{\partial C}{\partial t} \Big\|_r^2 \, dt + \frac{4\omega}{\lambda} \|\phi_h(0)\|^2.
\end{aligned} \tag{4.36}
$$

Let

$$
K^2 = \max\Big\{ \Big(2 + \frac{8K_{PF}^2 \|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) K_1^2, \frac{8K_{PF}^2 \omega^2}{\lambda^2} K_1^2, \frac{4\omega}{\lambda} \Big\}.
$$

Thus (4.36) implies

$$
\|C - C_h\|^2_{L^2(0,T;H^1(\Omega))} \le K^2 \Big(h^{2r-2} \|C\|^2_{L^2(0,T;H^r(\Omega))} + h^{2r-2} \Big\| \frac{\partial C}{\partial t} \Big\|^2_{L^2(0,T;H^r(\Omega))} + \|\phi_h(0)\|^2 \Big).
$$

Consequently, we prove the claim. ∎

Next, we find the energy bound for the discrete version of adsorption equation (1.1) for constant isotherm using the midpoint method for the time discretization. At a continuous level, we proved $C > 0$ and bounded by initial and boundary conditions. But at a discrete level, the Maximum Principle is very hard to implement, usually timestep has to be $\mathcal{O}(h^2)$ [32].

Theorem 4.7. *Suppose the assumptions (F1)-F(7) are satisfied so that the fully discrete formulation given by (4.8) has a smooth solution $\{C_h^n\}_{n=0}^N \in L^2(0,T;H^1(\Omega))$. Then for all $N > 0$,*

$$
\begin{aligned}
&\|C_h^{N+1}\|^2 + \frac{2}{\omega} \Delta t \sum_{n=0}^N \Big(\int_{\Gamma_{out}} ((C_h^{n+1/2})^2)(\mathbf{u} \cdot \overrightarrow{n}) ds \Big) + \frac{\lambda}{\omega} \Delta t \sum_{n=0}^N \|\boldsymbol{\nabla} C_h^{n+1/2}\|^2 \\
&\le \frac{4N\Delta t \|\mathbf{u}\|_\infty^2 + 8\lambda\omega}{\omega\lambda} \|\hat{C}_h\|^2 + \frac{2N\Delta t}{\omega} \Big(\int_{\Gamma_{in}} ((g_h)^2)(-\mathbf{u} \cdot \overrightarrow{n}) ds \Big) + \frac{4N\Delta t \beta_1^2 + N\Delta t \lambda^2}{\omega\lambda} \|\boldsymbol{\nabla} \hat{C}_h\|^2 \\
&+ \frac{8K_{PF}^2}{\omega\lambda} \Delta t \sum_{n=0}^N \|f^{n+1/2}\|^2 + 3\|C_h^0\|^2.
\end{aligned}
$$

Proof. Let $\hat{C}_h(x) \in X^h$ such that $\hat{C}_h\Big|_{\Gamma_{\rm in}} = g_h$. Take $v_h = C_h^{n+1/2} - \hat{C}_h \in X^h_{0,\Gamma_{\rm in}}(\Omega)$. Then (4.9) yields to

$$
\begin{aligned}
&(\omega(C_h^{n+1/2} - C_h^n), C_h^{n+1/2}) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) \\
=&\frac{\Delta t}{2} (f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1/2} - C_h^n), \hat{C}_h) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} \hat{C}_h).
\end{aligned}
$$

Using polarization identity in first term, we get,

$$
\begin{aligned}
&(\frac{\omega}{2} \|C_h^{n+1/2}\|^2 - \frac{\omega}{2} \|C_h^n\|^2 + \frac{\omega}{2} \|C_h^{n+1/2} - C_h^n\|^2) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) \\
&= \frac{\Delta t}{2} (f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1/2} - C_h^n), \hat{C}_h) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} \hat{C}_h).
\end{aligned} \tag{4.37}
$$

Next, (4.10) yields to

$$
\begin{aligned}
&(\omega(C_h^{n+1} - C_h^{n+1/2}), C_h^{n+1/2}) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) \\
=&\frac{\Delta t}{2} (f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1} - C_h^{n+1/2}), \hat{C}_h) + \frac{\Delta t}{2} (\mathbf{u} \cdot \boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \frac{\Delta t}{2} (D \boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} \hat{C}_h).
\end{aligned}
$$

Using polarization identity first term, we get

$$\frac{\omega}{2}(\|C_h^{n+1}\|^2 - \|C_h^{n+1/2}\|^2 - \|C_h^{n+1} - C_h^{n+1/2}\|^2) + \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) + \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2})$$
$$= \frac{\Delta t}{2}(f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1} - C_h^{n+1/2}), \hat{C}_h) + \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\hat{C}_h). \tag{4.38}$$

Adding (4.37) and (4.38), we get

$$\begin{aligned}
&\frac{\omega}{2}(\|C_h^{n+1}\|^2 - \|C_h^{n}\|^2 + \|C_h^{n+1/2} - C_h^{n}\|^2 - \|C_h^{n+1} - C_h^{n+1/2}\|^2) + \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2})\\
&+ \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) = \Delta t(f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1} - C_h^{n}), \hat{C}_h)\\
&+ \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\hat{C}_h).
\end{aligned} \tag{4.39}$$

Using (4.9) and (4.10), we get,

$$\frac{1}{2}\|C_h^{n+1/2} - C_h^{n}\|^2 - \frac{1}{2}\|C_h^{n+1} - C_h^{n+1/2}\|^2 = 0.$$

Consequently we have,

$$\frac{\omega}{2}(\|C_h^{n+1}\|^2 - \|C_h^{n}\|^2) + \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) + \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2})$$
$$= \Delta t(f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) + (\omega(C_h^{n+1} - C_h^{n}), \hat{C}_h) + \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) + \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\hat{C}_h). \tag{4.40}$$

Doing the similar analysis as in continuous case, we get,

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, C_h^{n+1/2}) = \frac{1}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{1}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big). \tag{4.41}$$

Next,

$$(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) \geq \lambda\|\boldsymbol{\nabla} C_h^{n+1/2}\|^2. \tag{4.42}$$

The bounded term on the right side using similar techniques as in continuous case is shown below:

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \hat{C}_h) \leq \frac{\lambda}{4}\|\boldsymbol{\nabla} C_h^{n+1/2}\|^2 + \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}_h\|^2. \tag{4.43}$$

$$(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\hat{C}_h) \leq \frac{\lambda}{4}\|\boldsymbol{\nabla} C_h^{n+1/2}\|^2 + \frac{\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2. \tag{4.44}$$

$$(f^{n+1/2}, C_h^{n+1/2} - \hat{C}_h) \leq \frac{2K_{PF}^2}{\lambda}\|f^{n+1/2}\|^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla} C_h^{n+1/2}\|^2 + \frac{\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2. \tag{4.45}$$

Putting (4.41)-(4.45) into (4.40), we get,

$$\begin{aligned}
&\frac{\omega}{2}\|C_h^{n+1}\|^2 - \frac{\omega}{2}\|C_h^{n}\|^2 + \frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{\Delta t\lambda}{4}\|\boldsymbol{\nabla} C_h^{n+1/2}\|^2\\
&\leq \frac{\|\mathbf{u}\|_\infty^2\Delta t}{\lambda}\|\hat{C}_h\|^2 - \frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{\Delta t\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2\\
&+ \frac{2K_{PF}^2\Delta t}{\lambda}\|f^{n+1/2}\|^2 + \frac{\Delta t\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2 + (\omega(C_h^{n+1} - C_h^{n}), \hat{C}_h).
\end{aligned} \tag{4.46}$$

Next, we sum over $n=0$ to $n=N$ to get

$$\begin{aligned}
&\frac{\omega}{2}\|C_h^{N+1}\|^2-\frac{\omega}{2}\|C_h^0\|^2+\frac{\Delta t}{2}\sum_{n=0}^{N}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\frac{\Delta t\lambda}{4}\sum_{n=0}^{N}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2\\
&\leq\frac{N\|\mathbf{u}\|_\infty^2\Delta t}{\lambda}\|\hat{C}_h\|^2-\frac{N\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\frac{N\Delta t\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2\\
&+\frac{2K_{PF}^2\Delta t}{\lambda}\sum_{n=0}^{N}\|f^{n+1/2}\|^2+\frac{N\Delta t\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2+(\omega(C_h^{N+1}-C_h^0),\hat{C}_h).
\end{aligned}\tag{4.47}$$

Here,

$$(\omega(C_h^{N+1}-C_h^0),\hat{C}_h)\leq\frac{\omega}{4}\|C_h^{N+1}\|^2+\frac{\omega}{4}\|C_h^0\|^2+2\omega\|\hat{C}_h\|^2.$$

After simplification, we get the desired result. ∎

Remark 4.8. Putting (4.41) into (4.40), we get,

$$\begin{aligned}
&\frac{\omega}{2}\|C_h^{n+1}\|^2-\frac{\omega}{2}\|C_h^n\|^2+\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\\
&=-\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\Delta t(f^{n+1/2},C_h^{n+1/2}-\hat{C}_h)\\
&+(\omega(C_h^{n+1}-C_h^n),\hat{C}_h)+\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\hat{C}_h)+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h).
\end{aligned}\tag{4.48}$$

If $f=0$ and $\hat{C}_h=0$ in (4.48), we get the balance of mass as follows

$$\begin{aligned}
&\frac{\omega}{2}(\|C_h^{n+1}\|^2-\|C_h^n\|^2)+\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\\
&=\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(-\mathbf{u}\cdot\overrightarrow{n})ds\Big).
\end{aligned}\tag{4.49}$$

Recall that $\mathbf{u}\cdot\overrightarrow{n}>0$ on Γ_{out} and $\mathbf{u}\cdot\overrightarrow{n}<0$ on Γ_{in}.

Next theorem gives a *priori* error estimate for the case of constant adsorption in fully discrete case where we will use the notation

$$K^2=\max\Big\{\Big(2+\frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2+8\beta_1^2}{\lambda^2}\Big)K_2^2,\frac{8K_{PF}^2\omega^2}{\lambda^2}K_2^2,\frac{8K_1TK_{PF}^2}{\lambda^2},\frac{2\omega}{\lambda}\Big\}.$$

THEOREM 4.9. *Suppose the assumptions (F1)-F(7) are satisfied so that the fully discrete formulation given by (4.8) has a smooth solution $\{C_h^n\}_{n=0}^N\in L^2(0,T;H^1(\Omega))$ and the variational formulation with constant adsorption given by* (4.6) *has an exact solution $C\in H^1(0,T,H^{k+1}(\Omega))$. Let $\phi_h^n=\hat{C}_h-C_h^n$. Then for $1\leq r\leq k+1$ and $N>0$ there exists a positive constant K such that:*

$$\begin{aligned}
&\Delta t\sum_{n=0}^{N+1}\|C(t_{n+1/2})-C_h(t_{n+1/2})\|_1^2\leq K^2\Big(h^{2r-2}\Delta t\sum_{n=0}^{N+1}\|C(t_{n+1/2})\|_r^2+h^{2r-2}\Big\|\frac{\partial C}{\partial t}\Big\|^2_{L^2(0,T;H^r(\Omega))}\\
&+(\Delta t)^4\|C_{ttt}\|^2_{L^\infty(0,T;L^\infty)}+\|\phi_h^0\|^2\Big).
\end{aligned}$$

Proof. Let the approximate solution at time $t^{n+1/2}$ be $C_h^{n+1/2}$. Then by using midpoint method, we get, the fully discrete variational formulation is as follows:
Given $C_h^n\in X^h$, find $C_h^{n+1}\in X^h$ such that $C_h^{n+1}\Big|_{\Gamma_{\text{in}}}=g_h$ and satisfying,

$$(\omega\frac{C_h^{n+1}-C_h^n}{\Delta t},v_h)+(u\cdot\boldsymbol{\nabla}C_h^{n+1/2},v_h)+(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}v_h)=(f^{n+1/2},v_h),\ \text{for all}\ \ v_h\in X^h_{0,\Gamma_{\text{in}}}(\Omega).\tag{4.50}$$

Let C_t represent $\frac{\partial C}{\partial t}$. We write the following variational formulation for the exact solution C.
(4.51)
$$(\omega\frac{C(t_{n+1})-C(t_n)}{\Delta t},v)+(\mathbf{u}\cdot\boldsymbol{\nabla}C(t_{n+1/2}),v)+(D\boldsymbol{\nabla}C(t_{n+1/2}),\boldsymbol{\nabla}v)=(f^{n+1/2},v)+(r^n,v),\ \forall\ v\in H^1_{0,\Gamma_{\rm in}}(\Omega).$$

where time discretization error, $r^n=\frac{C(t_{n+1})-C(t_n)}{\Delta t}-\frac{C_t(t_{n+1})+C_t(t_n)}{2}$.
Let $e^n=C(t_n)-C_h^n$ and $v=v_h\in X^h_{0,\Gamma_{\rm in}}\subset H^1_{0,\Gamma_{\rm in}}(\Omega)$ in (4.51) and then subtract (4.50) from (4.51) to get

$$(\omega\frac{e^{n+1}-e^n}{\Delta t},v_h)+(\mathbf{u}\cdot\boldsymbol{\nabla}e^{n+1/2},v_h)+(D\boldsymbol{\nabla}e^{n+1/2},\boldsymbol{\nabla}v_h)=(r^n,v_h),\ \text{for all}\ \ v_h\in X^h_{0,\Gamma_{\rm in}}(\Omega). \tag{4.52}$$

Then for any $\hat{C}_h(x)\in X_h$ such that $\hat{C}_h\Big|_{\Gamma_{\rm in}}=g_h$, we write that $e^n=C(t_n)-C_h^n=C(t_n)-\hat{C}_h+\hat{C}_h-C_h^n$. Let $\phi_h^n=\hat{C}_h-C_h^n$ and $\eta^n=\hat{C}_h-C(t_n)$. Notice that both C_h^n and $\hat{C}_h^n$ are equal to g_h on $\Gamma_{\rm in}$. Hence $\phi_h^n\Big|_{\Gamma_{\rm in}}=0$. We choose $v_h=\phi_h^{n+1/2}\in X^h_{0,\Gamma_{\rm in}}$. Then (4.52) becomes

$$\begin{aligned}&(\omega\frac{\phi_h^{n+1}-\phi_h^n}{\Delta t},\phi_h^{n+1/2})+(\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h^{n+1/2},\phi_h^{n+1/2})+(D\boldsymbol{\nabla}\phi_h^{n+1/2},\boldsymbol{\nabla}\phi_h^{n+1/2})\\&=(\omega\frac{\eta^{n+1}-\eta^n}{\Delta t},\phi_h^{n+1/2})+(\mathbf{u}\cdot\boldsymbol{\nabla}\eta^{n+1/2},\phi_h^{n+1/2})+(D\boldsymbol{\nabla}\eta^{n+1/2},\boldsymbol{\nabla}\phi_h^{n+1/2})+(r^n,\phi_h^{n+1/2}).\end{aligned}$$

We obtain lower bounds for the terms on the left and upper bounds for the term in the right of (4.53) by using the assumptions and Young's and Cauchy-Schwarz inequalities. We rewrite the first term in (4.53),

$$(\omega\frac{\phi_h^{n+1}-\phi_h^n}{\Delta t},\phi_h^{n+1/2})=\frac{\omega}{2\Delta t}(\|\phi_h^{n+1}\|^2-\|\phi_h^n\|^2). \tag{4.53}$$

Following the same steps in Theorem 4.6, we get the following bounds

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h^{n+1/2},\phi_h^{n+1/2})\geq 0. \tag{4.54}$$

$$(D\boldsymbol{\nabla}\phi_h^{n+1/2},\boldsymbol{\nabla}\phi_h^{n+1/2})\geq\lambda\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.55}$$

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\eta^{n+1/2},\phi_h^{n+1/2})\leq\frac{2K_{PF}^2\|\mathbf{u}\|_\infty^2}{\lambda}\|\eta^{n+1/2}\|_1^2+\frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.56}$$

$$(D\boldsymbol{\nabla}\eta^{n+1/2},\boldsymbol{\nabla}\phi_h^{n+1/2})\ \leq\frac{2\beta_1^2}{\lambda}\|\eta^{n+1/2}\|_1^2+\frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.57}$$

Next,

$$\begin{aligned}(\omega\frac{\eta^{n+1}-\eta^n}{\Delta t},\phi_h^{n+1/2})&=\big(\frac{\omega}{\Delta t}\int_{t_n}^{t_{n+1}}\eta_t d\tau,\phi_h^{n+1/2}\big),\\&\leq\frac{2K_{PF}^2\omega^2}{\lambda\Delta t^2}\big(\int_{t_n}^{t_{n+1}}\|\eta_t\|d\tau\big)^2+\frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2.\end{aligned}$$

Hence, after applying Cauchy-Schwarz inequality we get,

$$(\omega\frac{\eta^{n+1}-\eta^n}{\Delta t},\phi_h^{n+1/2})\leq\frac{2K_{PF}^2\omega^2}{\lambda\Delta t^2}\big(\int_{t_n}^{t_{n+1}}\|\eta_t\|^2d\tau\big)+\frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.58}$$

Next,

$$(r^n,\phi_h^{n+1/2})\leq\frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2+\frac{2K_{PF}^2}{\lambda}\|r^n\|^2. \tag{4.59}$$

Combining (4.53)-(4.59), we get

$$\begin{aligned}
&\frac{\omega}{2\Delta t}(\|\phi_h^{n+1}\|^2 - \|\phi_h^n\|^2) + \frac{\lambda}{2}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 \\
&\le \frac{2K_{PF}^2\|\mathbf{u}\|_\infty^2\|\eta^{n+1/2}\|_1^2}{\lambda} + \frac{2\beta_1^2\|\eta^{n+1/2}\|_1^2}{\lambda} + \frac{2K_{PF}^2\omega^2}{\lambda\Delta t}\Big(\int_{t_n}^{t_{n+1}}\|\eta_t\|^2 d\tau\Big) + \frac{2K_{PF}^2}{\lambda}\|r^n\|^2.
\end{aligned} \tag{4.60}$$

Multiplying (4.60) by $\frac{2\Delta t}{\omega}$ and summing over $n=0$ to $n=N$, we get

$$\begin{aligned}
&\|\phi_h^{N+1}\|^2 + \frac{\lambda}{\omega}\sum_{n=0}^{N+1}\Delta t\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 \ \le \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\omega\lambda}\Big)\sum_{n=0}^{N+1}\Delta t\|\eta^{n+1/2}\|_1^2 \\
&+ \frac{4K_{PF}^2}{\lambda\omega}\int_0^T\|\eta_t\|^2 dt + \frac{4K_{PF}^2}{\omega\lambda}\sum_{n=0}^{N+1}\Delta t\|r^n\|^2 + \|\phi_h^0\|^2.
\end{aligned} \tag{4.61}$$

To bound r^n, we use Taylor expansion about $t^{n+1/2}$. Hence,

$$\begin{aligned}
\sum_{n=0}^{N+1}\Delta t\|r^n\|^2 &\le K_1\sum_{n=0}^{N+1}\Delta t(\Delta t^2\|C_{ttt}\|_{L^\infty}(0,T;L^\infty))^2, \\
&\le K_1 N\Delta t(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2, \\
&\le K_1 T(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2.
\end{aligned}$$

Therefore, (4.61) implies

$$\begin{aligned}
&\|\phi_h^{N+1}\|^2 + \frac{\lambda}{\omega}\sum_{n=0}^{N+1}\Delta t\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 \le \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\omega\lambda}\Big)\sum_{n=0}^{N+1}\Delta t\|\eta^{n+1/2}\|_1^2 \\
&+ \frac{4K_{PF}^2\omega}{\lambda}\int_0^T\|\eta_t\|^2 dt + \frac{4K_1TK_{PF}^2}{\omega\lambda}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \|\phi_h^0\|^2.
\end{aligned}$$

Hence, we can write,

$$\begin{aligned}
&\sum_{n=0}^{N+1}\Delta t\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 \le \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\lambda^2}\Big)\sum_{n=0}^{N+1}\Delta t\|\eta^{n+1/2}\|^2 \\
&+ \frac{4K_{PF}^2\omega^2}{\lambda^2}\int_0^T\|\eta_t\|_1^2 dt + \frac{4K_1TK_{PF}^2}{\lambda^2}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{\omega}{\lambda}\|\phi_h^0\|^2.
\end{aligned}$$

By using the Lemma 2.1, we get

$$\begin{aligned}
&\sum_{n=0}^{N+1}\Delta t\|\phi_h^{n+1/2}\|_1^2 \le \Big(\frac{4K_{PF}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\lambda^2}\Big)\sum_{n=0}^{N+1}\Delta t\|\eta^{n+1/2}\|_1^2 \\
&+ \frac{4K_{PF}^2\omega^2}{\lambda^2}\int_0^T\|\eta_t\|^2 dt + \frac{4K_1TK_{PF}^2}{\lambda^2}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{\omega}{\lambda}\|\phi_h^0\|^2.
\end{aligned}$$

Triangle inequality gives

$$\sum_{n=0}^{N+1}\Delta t\|e^{n+1/2}\|_1^2 \le \sum_{n=0}^{N+1}2\Delta t\big(\|\phi_h^{n+1/2}\|_1^2 + \|\eta^{n+1/2}\|_1^2\big).$$

Thus, we get

$$\begin{aligned}
&\sum_{n=0}^{N+1}\Delta t\|e^{n+1/2}\|_1^2 \le \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big)\sum_{n=0}^{N+1}\Delta t\|\eta^{n+1/2}\|_1^2 \\
&+ \frac{8K_{PF}^2\omega^2}{\lambda^2}\int_0^T\|\eta_t\|^2 dt + \frac{8K_1TK_{PF}^2}{\lambda^2}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{2\omega}{\lambda}\|\phi_h^0\|^2.
\end{aligned}$$

Since $\hat{C}_h$ is arbitrary, we have the following inequality

$$\sum_{n=0}^{N+1} \Delta t \|e^{n+1/2}\|_1^2 \leq \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) \sum_{n=0}^{N+1} \Delta t \inf_{\substack{\hat{C}_h \in X_h \\ \hat{C}_h|_{\Gamma_{\text{in}}} = g_h}} \|C^{n+1/2} - \hat{C}_h\|_1^2$$
$$+ \frac{8K_{PF}^2\omega^2}{\lambda^2} \int_0^T \inf_{\substack{\hat{C}_h \in X_h \\ \hat{C}_h|_{\Gamma_{\text{in}}} = g_h}} \Big\| \frac{\partial (C - \hat{C}_h)}{\partial t} \Big\|^2 dt + \frac{8K_1 T K_{PF}^2}{\lambda^2} (\Delta t^2 \|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{2\omega}{\lambda} \|\phi_h^0\|^2.$$

Let g_h be the interpolant of g in $X_{\Gamma_{\text{in}}}^h$. Then by using Lemma 2.2, for $1 \leq r \leq k+1$ we get,

$$\begin{aligned} \sum_{n=0}^{N+1} \Delta t \|e^{n+1/2}\|_1^2 &\leq \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) K_2^2 h^{2r-2} \sum_{n=0}^{N+1} \Delta t \|C^{n+1/2}\|_r^2 \\ &+ \frac{8K_{PF}^2\omega^2}{\lambda^2} K_2^2 h^{2r-2} \int_0^T \Big\| \frac{\partial C}{\partial t} \Big\|_r^2 dt + \frac{8K_1 T K_{PF}^2}{\lambda^2} (\Delta t^2 \|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{2\omega}{\lambda} \|\phi_h^0\|^2. \end{aligned} \tag{4.62}$$

Let

$$K^2 = \max\Big\{ \Big(2 + \frac{8K_{PF}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) K_2^2, \frac{8K_{PF}^2\omega^2}{\lambda^2} K_2^2, \frac{8K_1 T K_{PF}^2}{\lambda^2}, \frac{2\omega}{\lambda} \Big\}.$$

Thus (4.62) implies the claim. ∎

4.3. Affine Isotherm. In the case of affine adsorption, $q(C) = K_1 + K_2 C$ with $K_1,\ K_2 \geq 0$. It implies $\frac{\partial q}{\partial t} = K_2 \frac{\partial C}{\partial t}$. Let $\bar{\omega} = (\omega + (1-\omega)\rho_s K_2)$. Hence, the variational formulation given in (3.1) simplifies to the following: Find $C \in H^1(\Omega)$ such that $C\Big|_{\Gamma_{\text{in}}} = g$ and :

$$(\bar{\omega}\frac{\partial C}{\partial t}, v) + (\mathbf{u} \cdot \boldsymbol{\nabla} C, v) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} v) = (f, v), \text{ for all } v \in H_{0,\Gamma_{\text{in}}}^1(\Omega). \tag{4.63}$$

The semi-discrete in space Finite Element formulation with affine adsorption is as follows: Find $C_h \in X_h$ such that $C_h\Big|_{\Gamma_{\text{in}}} = g_h$ and

$$(\bar{\omega}\frac{\partial C_h}{\partial t}, v_h) + (\mathbf{u} \cdot \boldsymbol{\nabla} C_h, v_h) + (D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} v_h) = (f, v_h), \text{ for all } v_h \in X_{0,\Gamma_{\text{in}}}^h(\Omega). \tag{4.64}$$

For the analysis, we recall the refactorization of midpoint method [11] for time discretization, we get the following full discretization: Given $C_h^n \in X^h$, find $C_h^{n+1} \in X^h$ satisfying
Step 1: Backward Euler step at the half-integer time step $t_{n+1/2}$
(4.65)

$$(\bar{\omega}\frac{C_h^{n+1/2} - C_h^n}{\Delta t/2}, v_h) + (u \cdot \boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X_{0,\Gamma_{\text{in}}}^h(\Omega).$$

Step 2: Forward Euler step at t_{n+1}
(4.66)

$$(\bar{\omega}\frac{C_h^{n+1} - C_h^{n+1/2}}{\Delta t/2}, v_h) + (u \cdot \boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X_{0,\Gamma_{\text{in}}}^h(\Omega).$$

Remark 4.10. All the theorems proved for the constant adsorption is true for the affine adsorption where ω is replaced by $\bar{\omega}$.

4.4. Nonlinear, Explicit Isotherm. We consider the nonlinear isotherm with an explicit representation, for example, Langmuir's isotherm [8,31] is as follows:

$$q(C) = \frac{q_{max} K_{eq} C}{1 + K_{eq} C},$$

where K_{eq} is Langmuir equilibrium constant, q_{max} is the maximum binding capacity of the porous medium. Recall that for the case of nonlinear isotherm with explicit representation,

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} = q'(C)\frac{\partial C}{\partial t}.$$

We consider the variational formulation given in (3.1). The semi-discrete in space formulation is given in (3.2) and the fully discrete formulation is given in the subsection 3.2. Next, we show the stability bound for this isotherm. Unlike previous work, in [34] we dropped the assumption "$C(x,t)$ is nondecreasing in time at every x" and considered non-homogeneous boundary condition at inflow boundary.

THEOREM 4.11. *Assume that (F1)-(F6) are satisfied and the variational formulation given by (3.1) has a solution $C \in L^\infty(0,T,L^2(\Omega)) \cap L^2(0,T,H^1(\Omega))$ with $f \in L^2(0,T;L^2(\Omega))$. Let $\hat{C}$ be the continuous extension of the Dirichlet data g inside the domain Ω and satisfies (4.1). The bounds on $\|\hat{C}\|^2$ and $\|\boldsymbol{\nabla}\hat{C}\|^2$ are given in (4.2) and (4.3) respectively. Let the antiderivative be $A(C) = \int_0^C sq'(s)ds$. Then we get the following stability bound:*

$$\begin{aligned}
&\|C(t)\|^2 + \frac{4}{\omega}\int_\Omega (1-\omega)\rho_s A(C(t))d\Omega + \frac{\lambda}{\omega}\int_0^t \|\boldsymbol{\nabla} C(r)\|^2\,dr + \frac{2}{\omega}\int_0^t \Big(\int_{\Gamma_{out}} ((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\,dr \\
&\le \frac{4}{\omega}\int_0^t \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2\,dr + \Big(\frac{\lambda}{\omega} + \frac{4\beta_1^2}{\lambda\omega}\Big)\int_0^t \|\boldsymbol{\nabla}\hat{C}\|^2\,dr - \frac{2}{\omega}\int_0^t \Big(\int_{\Gamma_{in}} ((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\,dr \\
&+ 3\|C(0)\|^2 + \frac{8K_{PF}^2}{\lambda\omega}\int_0^t \|f\|^2\,dr + \frac{16(\omega^2 + (1-\omega)^2\rho_s^2 K^2)}{\omega^2}\|\hat{C}\|^2 + \frac{4}{\omega}\int_\Omega (1-\omega)\rho_s A(C(0))d\Omega.
\end{aligned}$$

Proof. Let $\hat{C}(x) \in H^1(\Omega)$ such that $\hat{C}\Big|_{\Gamma_{\rm in}} = g$. Take $v = C - \hat{C} \in H^1_{0,\Gamma_{\rm in}}(\Omega)$. Then (3.1) yields to

$$((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, C - \hat{C}) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, C - \hat{C}) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\Big(C - \hat{C}\Big)) = (f, C - \hat{C}).$$

Thus, we get,

$$\begin{aligned}
&((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, C) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, C) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) \\
&= ((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, \hat{C}) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla}\hat{C}) + (f, C - \hat{C}).
\end{aligned} \tag{4.67}$$

Let the antiderivative be

$$A(C(t)) = \int_0^C a(s)ds = \int_0^C sq'(s)ds.$$

We rewrite the first term in (4.67),

$$((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, C) = \int_\Omega (\omega + (1-\omega)\rho_s q'(C))C\frac{\partial C}{\partial t}d\Omega = \frac{\partial}{\partial t}\int_\Omega \Big(\frac{\omega}{2}|C|^2 + (1-\omega)\rho_s A(C(t))\Big)d\Omega. \tag{4.68}$$

Next using the same steps in Theorem (4.4), we get the following bounds:

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C, C) = \frac{1}{2}\Big(\int_{\Gamma_{\rm in}} ((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{1}{2}\Big(\int_{\Gamma_{\rm out}} ((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big). \tag{4.69}$$

$$(D\boldsymbol{\nabla} C, \boldsymbol{\nabla} C) \ge \lambda\|\boldsymbol{\nabla} C\|^2. \tag{4.70}$$

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C, \hat{C}) \le \frac{\lambda}{4}\|\boldsymbol{\nabla} C\|^2 + \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2. \tag{4.71}$$

$$(D\nabla C, \nabla \hat{C}) \leq \frac{\lambda}{4}\|\nabla C\|^2 + \frac{\beta_1^2}{\lambda}\|\nabla \hat{C}\|^2. \tag{4.72}$$

$$(f, C - \hat{C}) \leq \frac{2K_{PF}^2}{\lambda}\|f\|^2 + \frac{\lambda}{4}\|\nabla C\|^2 + \frac{\lambda}{4}\|\nabla \hat{C}\|^2. \tag{4.73}$$

Next,

$$((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, \hat{C}) = \omega\frac{\partial}{\partial t}(C, \hat{C}) + (1-\omega)\rho_s\frac{\partial}{\partial t}(q(C), \hat{C}). \tag{4.74}$$

Combining (4.68)-(4.74), we get

$$\frac{\partial}{\partial t}\int_\Omega \left(\frac{\omega}{2}|C|^2 + (1-\omega)\rho_s A(C(t))\right)d\Omega + \frac{\lambda}{4}\|\nabla C\|^2 + \frac{1}{2}\int_{\Gamma_{\text{out}}}((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds \leq \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2$$
$$+ \Big(\frac{\lambda}{4} + \frac{\beta_1^2}{\lambda}\Big)\|\nabla \hat{C}\|^2 - \frac{1}{2}\Big(\int_{\Gamma_{\text{in}}}((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + \frac{2K_{PF}^2}{\lambda}\|f\|^2 + \omega\frac{\partial}{\partial t}(C, \hat{C}) + (1-\omega)\rho_s\frac{\partial}{\partial t}(q(C), \hat{C}).$$

Let $C(0) = C_0$ and $A(C_0) = A_0$. Integrating both sides from 0 to t, we obtain

(4.75)
$$\int_\Omega \left(\frac{\omega}{2}|C(t)|^2 + (1-\omega)\rho_s A(C(t))\right)d\Omega + \frac{\lambda}{4}\int_0^t \|\nabla C(r)\|^2 dr + \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{out}}}((C)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr$$
$$\leq \int_0^t \frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}\|^2 dr + \Big(\frac{\lambda}{4} + \frac{\beta_1^2}{\lambda}\Big)\int_0^t \|\nabla \hat{C}\|^2 dr - \frac{1}{2}\int_0^t \Big(\int_{\Gamma_{\text{in}}}((g)^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr + \frac{2K_{PF}^2}{\lambda}\int_0^t \|f\|^2 dr$$
$$+ \omega(C(t) - C_0, \hat{C}) + (1-\omega)\rho_s(q(C(t)) - q(C_0), \hat{C}) + \int_\Omega \left(\frac{\omega}{2}|C_0|^2 + (1-\omega)\rho_s A_0\right)d\Omega.$$

Next,

$$\omega(C(t), \hat{C}) \leq \omega\|C(t)\|\|\hat{C}\| \leq \frac{\omega}{8}\|C(t)\|^2 + 2\omega\|\hat{C}\|^2.$$
$$-\omega(C_0, \hat{C}) \leq \omega|(C_0, \hat{C})| \leq \omega\|C_0\|\|\hat{C}\| \leq \frac{\omega}{8}\|C_0\|^2 + 2\omega\|\hat{C}\|^2.$$

By using Cauchy-Schwarz and Young's inequalities, we get,

$$(1-\omega)\rho_s(q(C(t)) - q(C_0), \hat{C}) \leq \frac{4(1-\omega)^2\rho_s^2 K^2}{\omega}\|\hat{C}\|^2 + \frac{\omega}{8}(\|C(t)\|^2 + \|C_0\|^2).$$

Hence after simplification, we prove the claim. □

Remark 4.12. For the case of Langmuir's isotherm,

$$A(C(t)) = ln(1 + C) + \frac{1}{1+C} + constant.$$

Remark 4.13. Putting (4.68) and (4.69) into (4.67), we get,

(4.76)
$$\frac{\partial}{\partial t}\int_\Omega \left(\frac{\omega}{2}\|C\|^2 + (1-\omega)\rho_s A(C(t))\right)d\Omega + \Big(\int_{\Gamma_{\text{out}}}(C^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + (D\nabla C, \nabla C) = -\Big(\int_{\Gamma_{\text{in}}}(g^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)$$
$$+ (f, C - \hat{C})((\omega + (1-\omega)\rho_s q'(C))\frac{\partial C}{\partial t}, \hat{C}) + +(\mathbf{u}\cdot\nabla C, \hat{C}) + (D\nabla C, \nabla \hat{C})$$

If $f = 0$ and $\hat{C} = 0$ in (4.76), we get the balance of mass as follows

(4.77)
$$\frac{\partial}{\partial t}\int_\Omega \left(\frac{\omega}{2}\|C\|^2 + (1-\omega)\rho_s A(C(t))\right)d\Omega + \Big(\int_{\Gamma_{\text{out}}}(C^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big) + (D\nabla C, \nabla C) = -\Big(\int_{\Gamma_{\text{in}}}(g^2)(\mathbf{u}\cdot\overrightarrow{n})ds\Big).$$

Recall that $\mathbf{u}\cdot\overrightarrow{n} > 0$ on Γ_{out} and $\mathbf{u}\cdot\overrightarrow{n} < 0$ on Γ_{in}.

5. Numerical Test. In this section, we perform some numerical tests to show that the midpoint method described in Subsection 3.2 gives second order convergence rate for the considered PDE model for the constant, affine and nonlinear, explicit adsorptions. For checking the order of convergence, we assume the following: $\mathbf{u} = (1,1)$, $D = I$, $\Omega = [0,1] \times [0,1]$, $\omega = 0.5$, X^h = the space of continuous piecewise affine functions, exact solution is $C(x,y,t) = t^2(x^3 - \frac{3}{2}x^2 + 1)\cos(\frac{\pi}{4}y)$. The body force f, initial condition C_0, and boundary conditions are determined by the true solution. The norms used in the table are defined as follows,

$$\|C\|_{\infty,0} := \text{ess} \sup_{0<t<T} \|C(\cdot,t)\|_{L^2(\Omega)} \text{ and } \|C\|_{0,0} := \left(\int_0^T \|C(\cdot,t)\|^2_{L^2(\Omega)}\, dt \right)^{1/2}.$$

Next, for the plot of concentration profile in each case, we consider the following: $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$, $\Omega = [0,2] \times [0,10]$, $\omega = 0.5$, X^h = the space of continuous piecewise affine functions.

5.1. Tests for the case of constant isotherm. In this subsection, we first check the convergence rate for the case of constant isotherm in the first test and in the second test we plot the concentration profile. We also show the comparison of total mass after each test.

$(h, \Delta t) \rightarrow$	$(\frac{1}{128}, \frac{1}{2})$	$(\frac{1}{128}, \frac{1}{4})$	$(\frac{1}{128}, \frac{1}{8})$	$(\frac{1}{128}, \frac{1}{16})$	$(\frac{1}{128}, \frac{1}{32})$
$\|C - C_h\|_{\infty,0}$	0.0871011	0.0462486	0.0238288	0.0120901	0.00608901
Rate	-	0.91328	0.9567	0.97888	0.98955
$\|C - C_h\|_{0,0}$	0.0622419	0.0340122	0.0179402	0.00923882	0.00469204
Rate	-	0.87183	0.92286	0.95742	0.97749
$\|\nabla C - \nabla C_h\|_{0,0}$	0.100308	0.0548173	0.0289367	0.0149649	0.00773043
Rate	-	0.87173	0.92173	0.95132	0.95296
$\|C - C_h\|_{0,1}$	0.11805	0.0645117	0.0340468	0.017587	0.00904294
Rate	-	0.87177	0.92204	0.95301	0.95965

Table 5.1: Temporal convergence rates for the BE approximation with a constant adsorption model to the non steady-state problem.

$(h, \Delta t) \rightarrow$	$(\frac{1}{128}, \frac{1}{2})$	$(\frac{1}{128}, \frac{1}{4})$	$(\frac{1}{128}, \frac{1}{8})$	$(\frac{1}{128}, \frac{1}{16})$	$(\frac{1}{128}, \frac{1}{32})$
$\|C - C_h\|_{\infty,0}$	0.0465279	0.011173	0.00269747	0.000664032	0.000164628
Rate	-	2.0581	2.0503	2.0223	2.012
$\|C - C_h\|_{0,0}$	0.0385999	0.00906892	0.00219412	0.000539591	0.000133763
Rate	-	2.0896	2.0473	2.0237	2.0122
$\|\nabla C - \nabla C_h\|_{0,0}$	0.714751	0.178008	0.0442268	0.0110284	0.00312606
Rate	-	2.0055	2.0089	2.0037	1.8188
$\|C - C_h\|_{0,1}$	0.715792	0.178239	0.0442812	0.0110416	0.00312892
Rate	-	2.0057	2.009	2.0037	1.8192

Table 5.2: Temporal convergence rates for the midpoint approximation with a constant adsorption model to the non steady-state problem.

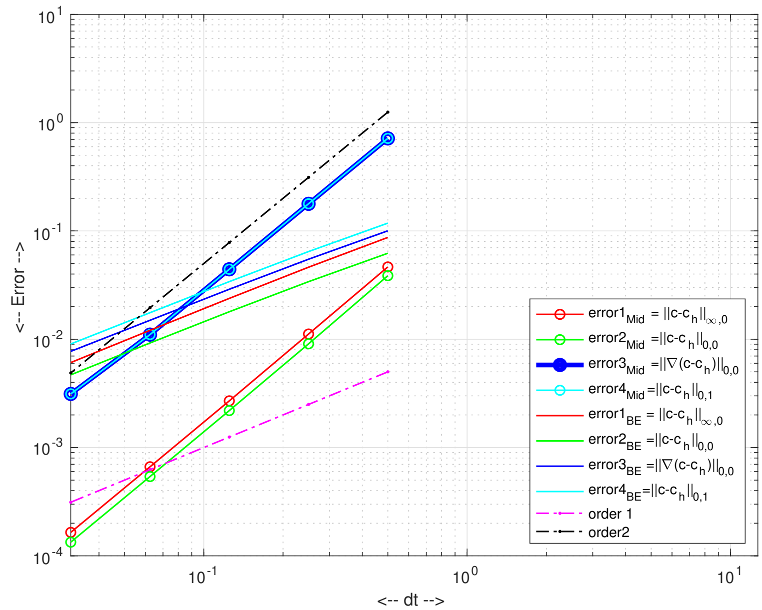

Fig. 5.1: Constant Isotherm: Temporal rate of convergence of BE and Midpoint, T=1.0, h=1/128. Notice that Midpoint is giving order 2 whereas BE is giving order 1.

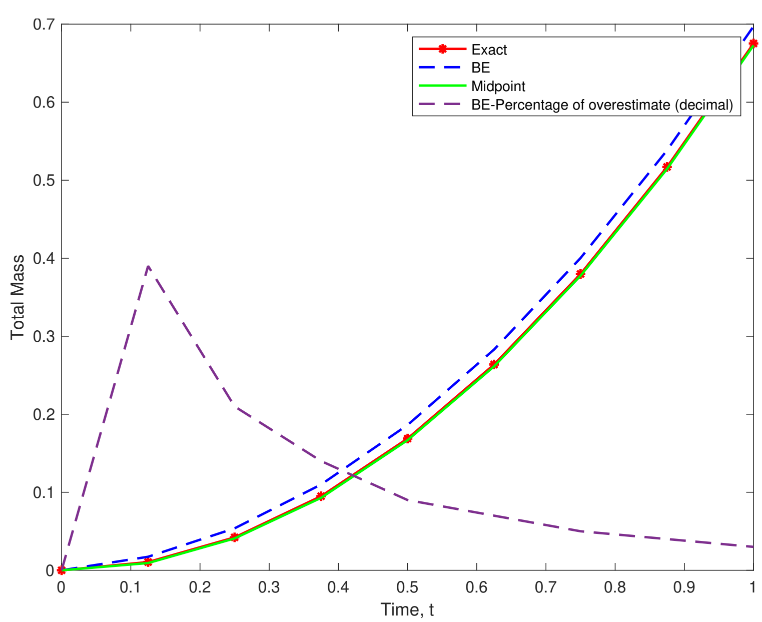

Fig. 5.2: Constant Isotherm: Comparison of total mass for exact solution, BE, Midpoint, $T = 1.0$, $h = 1/128$, $dt = 1/8$. Notice that BE overestimates total mass rather than underestimates.

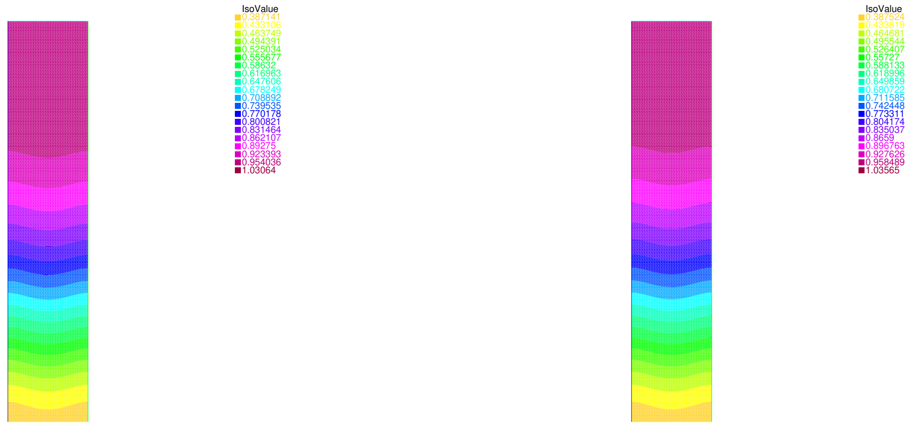

Fig. 5.3: Constant isotherm: Plot of concentration while using BE (Left) & Midpoint (Right), $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

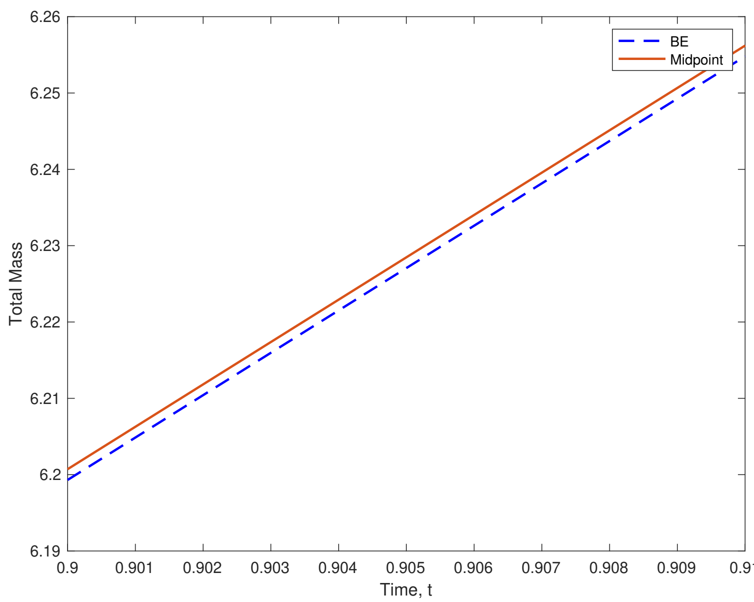

Fig. 5.4: Constant isotherm: Comparison of total mass, $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

5.2. Tests for the case of affine isotherm. In this subsection, we first check the convergence rate for the case of affine isotherm in the first test and in the second test we plot the concentration profile. We also show the comparison of total mass after each test.

$(h,\Delta t)\ \rightarrow$	$(\frac{1}{128},\frac{1}{2})$	$(\frac{1}{128},\frac{1}{4})$	$(\frac{1}{128},\frac{1}{8})$	$(\frac{1}{128},\frac{1}{16})$	$(\frac{1}{128},\frac{1}{32})$
$\Vert C-C_h\Vert_{\infty,0}$	0.141342	0.075632	0.039242	0.0200057	0.0101035
Rate	-	0.90212	0.9466	0.97199	0.98556
$\Vert C-C_h\Vert_{0,0}$	0.0954833	0.0510779	0.0266862	0.0136784	0.00693
Rate	-	0.90255	0.93661	0.96419	0.98097
$\Vert\nabla C-\nabla C_h\Vert_{0,0}$	0.154705	0.0827994	0.0432733	0.0222213	0.0113464
Rate	-	0.90183	0.93614	0.96153	0.96971
$\Vert C-C_h\Vert_{0,1}$	0.181798	0.0972866	0.0508403	0.0260938	0.0132953
Rate	-	0.90202	0.93627	0.96227	0.97279

Table 5.3: Temporal convergence rates for the BE approximation with an affine adsorption model to the non steady-state problem.

$(h,\Delta t)\ \rightarrow$	$(\frac{1}{128},\frac{1}{2})$	$(\frac{1}{128},\frac{1}{4})$	$(\frac{1}{128},\frac{1}{8})$	$(\frac{1}{128},\frac{1}{16})$	$(\frac{1}{128},\frac{1}{32})$
$\Vert C-C_h\Vert_{\infty,0}$	0.0362764	0.00901857	0.00224664	0.000561211	0.000140536
Rate	-	2.0081	2.0051	2.0012	1.9976
$\Vert C-C_h\Vert_{0,0}$	0.0306995	0.00722705	0.00174822	0.000429612	0.000106604
Rate	-	2.0867	2.0475	2.0248	2.0108
$\Vert\nabla C-\nabla C_h\Vert_{0,0}$	0.712515	0.177229	0.0439172	0.0108973	0.00307773
Rate	-	2.0073	2.0128	2.0108	1.824
$\Vert C-C_h\Vert_{0,1}$	0.713176	0.177376	0.043952	0.0109057	0.00307958
Rate	-	2.0074	2.0128	2.0108	1.8243

Table 5.4: Temporal convergence rates for the midpoint approximation with an affine adsorption model to the non steady-state problem.

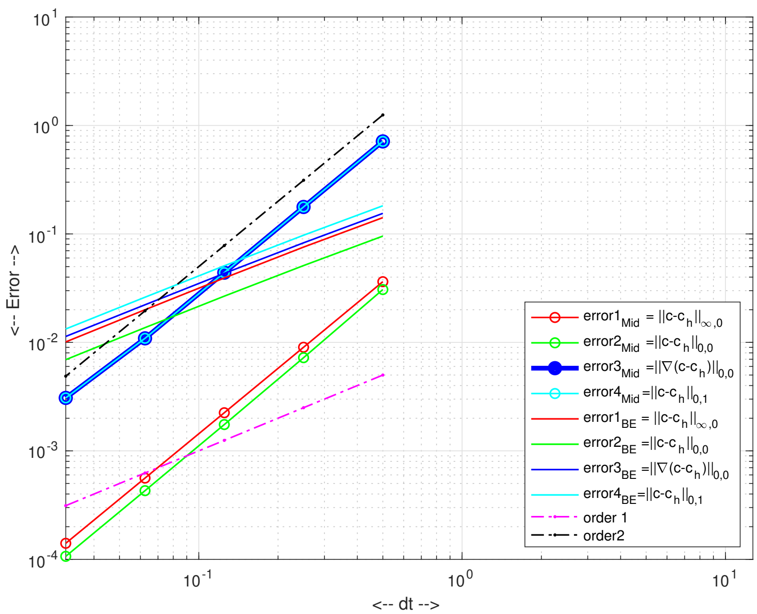

Fig. 5.5: Affine Isotherm: Temporal rate of convergence of BE and Midpoint, $T = 1.0$, $h = 1/128$. Notice that Midpoint is giving order 2 whereas BE is giving order 1.

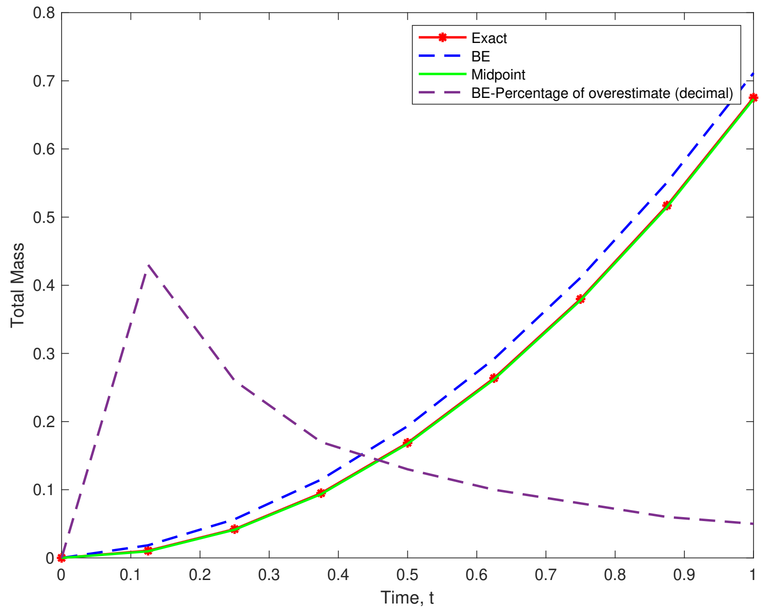

Fig. 5.6: Affine Isotherm: Comparison of total mass for exact solution, BE, Midpoint, $T = 1.0$, $h = 1/128$, $dt = 1/8$. Notice that BE overestimates total mass rather than underestimates.

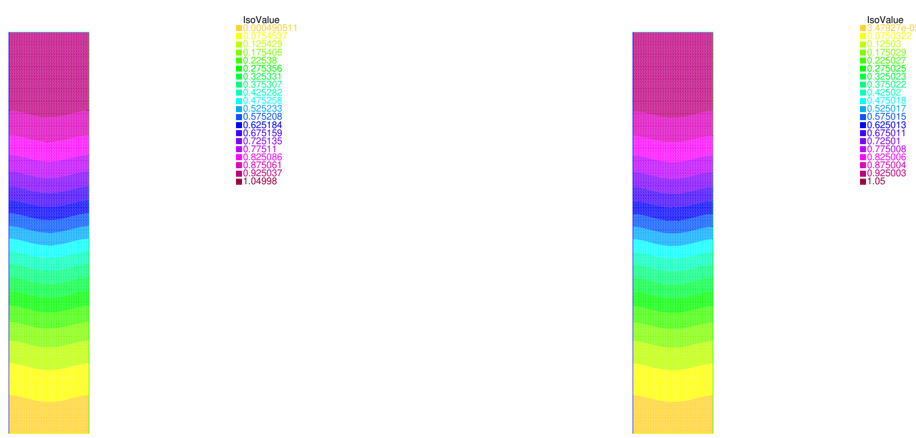

Fig. 5.7: Affine isotherm: Plot of concentration while using BE (Left) & Midpoint (Right), $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

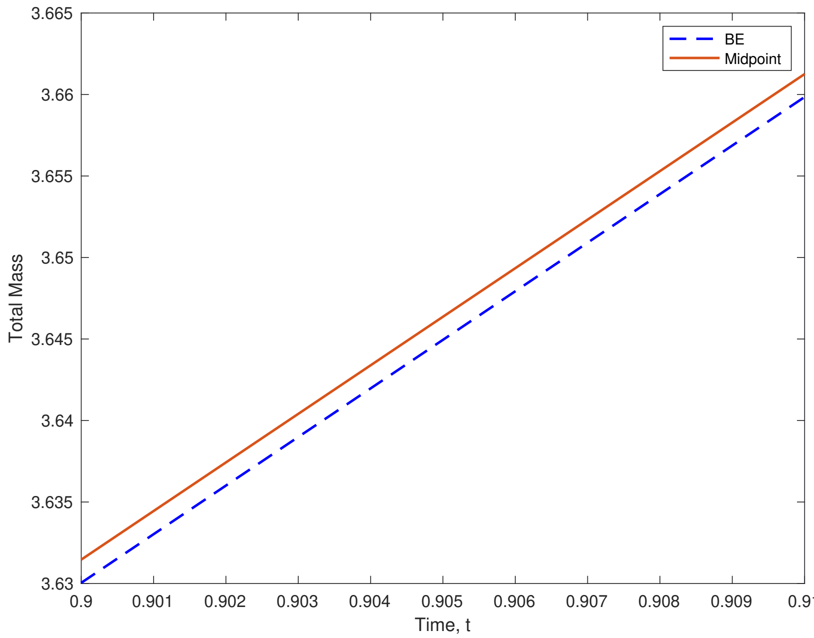

Fig. 5.8: Affine isotherm: Comparison of total mass, $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

5.3. Tests for the case of nonlinear, explicit isotherm. In this subsection, we first check the convergence rate for the case of nonlinear, explicit isotherm in the first test and in the second test we plot the concentration profile. We also show the comparison of total mass after each test. In this test problems, we use Langmuir's isotherm with $q_{max} = K_{eq} = 1$ where $q(C) = \frac{q_{max}K_{eq}C}{1+K_{eq}C} = \frac{C}{1+C}$. We simplify the problem formulation to a single (nonlinear) transport equation in one unknown C using

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} = \frac{1}{(1+C)^2}\frac{\partial C}{\partial t}.$$

While using Backward Euler discretization, we compute solutions by lagging the nonlinearity $q'(C_h^{n+1})$ as [15]

$$q'(C_h^{n+1})\frac{C_h^{n+1} - C_h^n}{\Delta t} \approx q'(C_h^n)\frac{C_h^{n+1} - C_h^n}{\Delta t}.$$

For the midpoint method, we use the standard (second order) linear extrapolation [24] of $C_h^{n+1/2}$ while computing $q'(C_h^{n+1/2})$ as

$$q'(C_h^{n+1/2})\frac{C_h^{n+1} - C_h^n}{\Delta t} \approx q'(\frac{3C_h^n - C_h^{n-1}}{2})\frac{C_h^{n+1} - C_h^n}{\Delta t}.$$

$(h, \Delta t) \rightarrow$	$(\frac{1}{128}, \frac{1}{2})$	$(\frac{1}{128}, \frac{1}{4})$	$(\frac{1}{128}, \frac{1}{8})$	$(\frac{1}{128}, \frac{1}{16})$	$(\frac{1}{128}, \frac{1}{32})$
$\|C - C_h\|_{\infty,0}$	0.0636074	0.0374917	0.0206665	0.0108985	0.00558454
Rate	-	0.76262	0.85928	0.92316	0.96462
$\|C - C_h\|_{0,0}$	0.0522838	0.0310798	0.0169125	0.00883222	0.00451535
Rate	-	0.75039	0.87789	0.93724	0.96794
$\|\boldsymbol{\nabla} C - \boldsymbol{\nabla} C_h\|_{0,0}$	0.0847469	0.0502647	0.0273473	0.0143409	0.00746467
Rate	-	0.75362	0.87815	0.93126	0.94199
$\|C - C_h\|_{0,1}$	0.0995773	0.0590973	0.0321544	0.0168424	0.00872408
Rate	-	0.75272	0.87808	0.93292	0.94902

Table 5.5: Temporal convergence rates for the BE approximation with a Langmuir adsorption model to the non steady-state problem.

$(h, \Delta t) \rightarrow$	$(\frac{1}{128}, \frac{1}{2})$	$(\frac{1}{128}, \frac{1}{4})$	$(\frac{1}{128}, \frac{1}{8})$	$(\frac{1}{128}, \frac{1}{16})$	$(\frac{1}{128}, \frac{1}{32})$
$\|C - C_h\|_{\infty,0}$	0.0357416	0.00951864	0.00242801	0.000611192	0.000153313
Rate	-	1.9088	1.971	1.9901	1.9951
$\|C - C_h\|_{0,0}$	0.0307399	0.00741601	0.00181065	0.00044712	0.000111214
Rate	-	2.0514	2.0341	2.0178	2.0073
$\|\boldsymbol{\nabla} C - \boldsymbol{\nabla} C_h\|_{0,0}$	0.744766	0.191186	0.0475431	0.0117471	0.00323681
Rate	-	1.9618	2.0077	2.0169	1.8597
$\|C - C_h\|_{0,1}$	0.7454	0.19133	0.0475776	0.0117556	0.00323872
Rate	-	1.962	2.0077	2.0169	1.8599

Table 5.6: Temporal convergence rates for the midpoint approximation with a Langmuir adsorption model to the non steady-state problem.

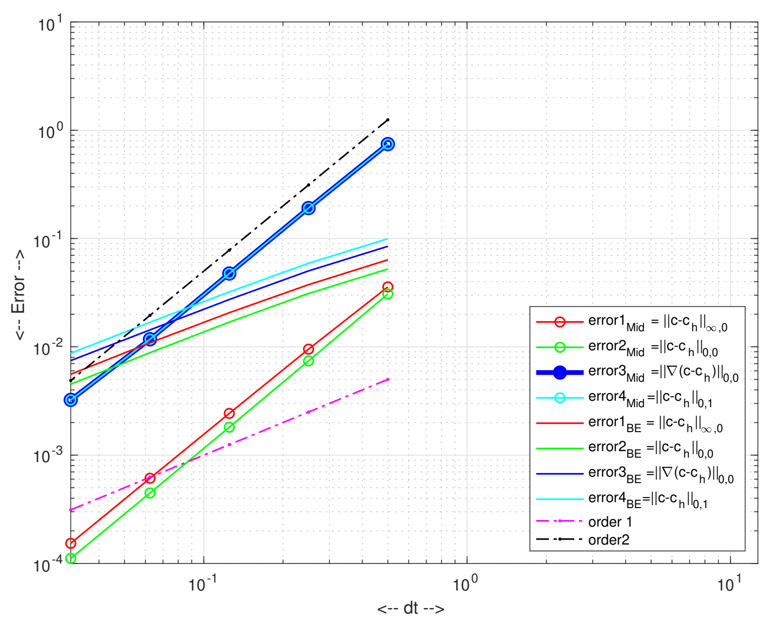

Fig. 5.9: Langmuir Isotherm: Temporal rate of convergence of BE and Midpoint, $T = 1.0$, $h = 1/128$. Notice that Midpoint is giving order 2 whereas BE is giving order 1.

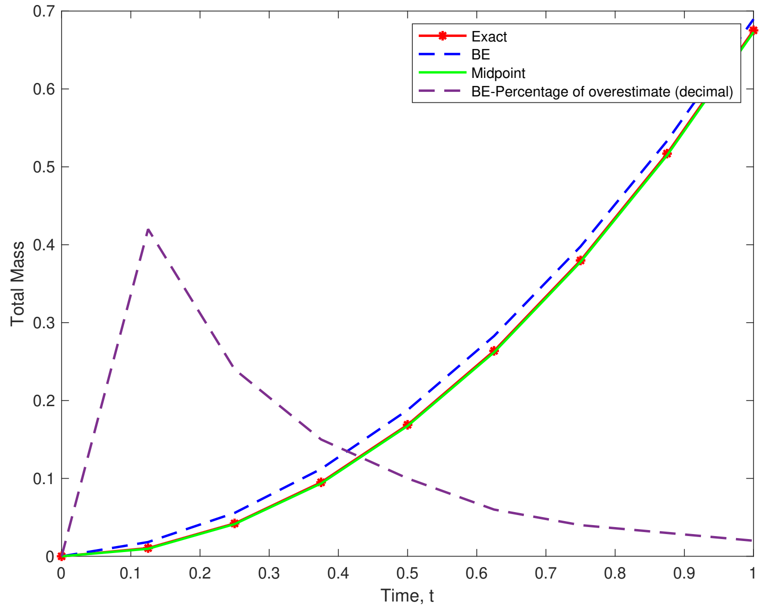

Fig. 5.10: Langmuir Isotherm: Comparison of total mass for exact solution, BE, Midpoint, $T = 1.0$, $h = 1/128$, $dt = 1/8$. Notice that BE overestimates total mass rather than underestimates.

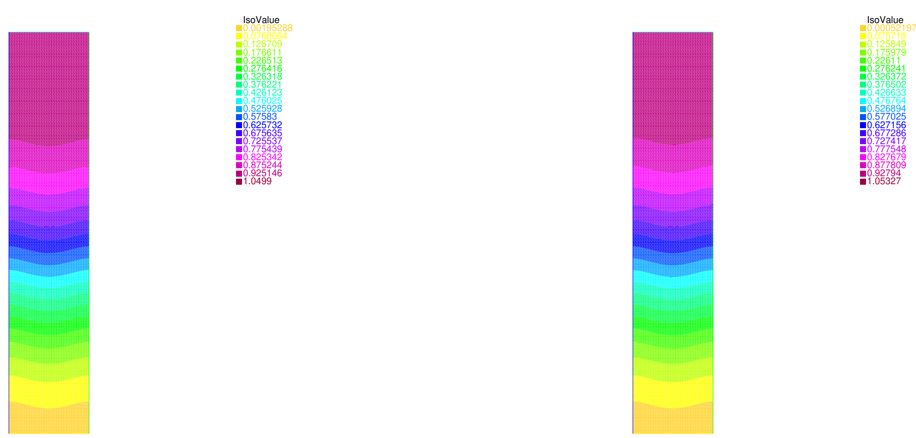

Fig. 5.11: Langmuir isotherm: Plot of concentration while using BE (Left) & Midpoint (Right), $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

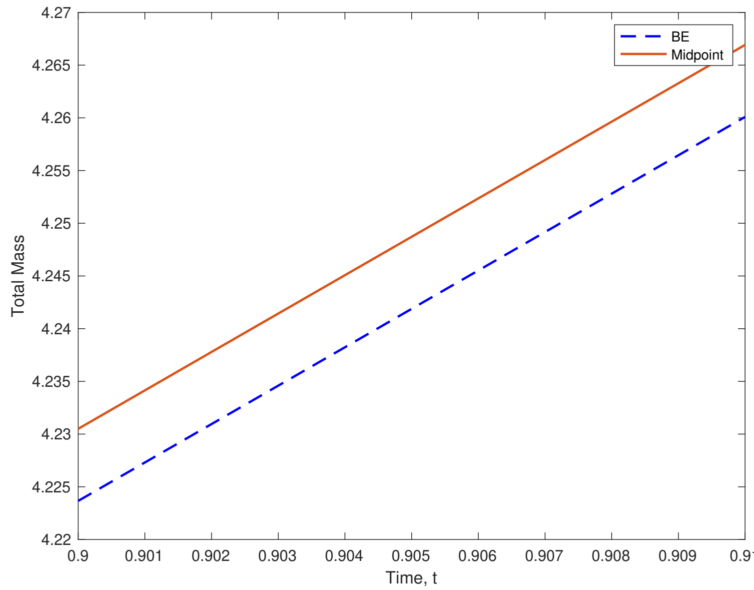

Fig. 5.12: Langmuir isotherm: Comparison of total mass, $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

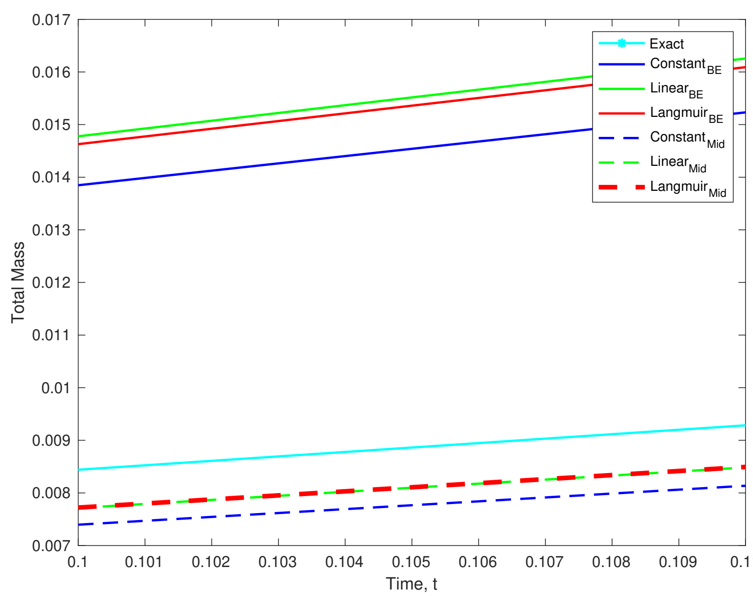

Fig. 5.13: Comparison of total mass for exact solution, Constant adsorption, affine adsorption, Langmuir adsorption, $T = 1.0$, $h = 1/128$, $dt = 1/8$, $\mathbf{u} = (1, 1)$.

In the Figure 5.3, Figure 5.7 and Figure 5.11, the concentration front gradually advances through the height of the membrane over time as it evolves in accordance with the contour of the velocity profile.

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6. Conclusion. We provided a complete stability and error analysis of a simulation tool for modeling adsorption process for the constant and affine adsorption cases. For the nonlinear, explicit adsorption, we proved stability analysis for the continuous case. The error analysis for this case is more involved and is work in progress. But numerically, we showed that midpoint method gives second order convergence for all adsorption cases. The next most important step in developing this tool is coupling this reactive transport problem with porous media flow where velocity is approximated.

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