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

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Abstract. We analyze an advection-diffusion-reaction problem with non-homogeneous boundary conditions that models the chromatography process, a vital stage in bioseparation. We prove stability and error estimates for both constant and affine adsorption, using the symplectic one-step implicit midpoint method for time discretization and finite elements for spatial discretization. In addition, we perform the stability analysis for the nonlinear, explicit adsorption in the continuous and semi-discrete cases. For the nonlinear, explicit adsorption, we also complete the error analysis for the semi-discrete case, and prove the existence of a solution for the fully discrete case. The numerical tests 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 biopharmaceuticals is expanding fast and 50% of top 100 drugs will most likely be derived from biotechnology [2,21]. The high demand for biopharmaceuticals is due to their effectiveness in treating various illnesses such as diabetes, anemia, cancer, etc. [38]. For example, monoclonal antibodies [41], general products from bioseparation are very useful medications in treating COVID-19 [1,3,4]. Other key factors driving the growth of the market are the rising investments in research and development of novel treatments, favorable government regulations, and theh increasing adoption of biopharmaceuticals by the global population [2]. To maximize the production capacity while minimizing costs, manufacturers are constantly developing new methods. Integrating new technologies into existing facilities is more economically viable than the alternative of constructing new biomanufacturing facilities, due to financial risks. 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 [19]. 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 [51]. The ideal media for the chromatography columns used for bioseparation are resin beds, monoliths, and membranes [50]. Membrane chromatography [11–13] 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 require additional processing stages, causing lower yield and higher production costs. The recent research in [12] is focused on multimodal membrane-based chromatography. The development of a modeling framework capable of characterizing the chromatography process under continuous flow circumstances is critical. Inhere we model this process for creating a simulation tool for transport in a porous medium by adopting the reactive transport (advection-diffusion-reaction) problem in [51].

Let Ω be a bounded domain in $\mathbf{R^d}$, where $d = 1,\ 2$, or 3, see Figure 1.1, with piecewise smooth boundary Γ. We partition the boundary into three non-overlapping parts $\Gamma = \Gamma_{\text{in}} \cup \Gamma_{\text{n}} \cup \Gamma_{\text{out}}$, where the inflow boundary is $\Gamma_{\text{in}} = \{x \in \Gamma : \overrightarrow{n} \cdot \mathbf{u}(x) < 0\}$, the outflow boundary is $\Gamma_{\text{out}} = \{x \in \Gamma : \overrightarrow{n} \cdot \mathbf{u}(x) > 0\}$, and the boundaries comprising no-flow hydraulic zone(s) are $\Gamma_{\text{n}} = \Gamma \backslash (\Gamma_{\text{in}} \cup \Gamma_{\text{out}})$. Let $\mathbf{u}$ denote the fluid velocity through the membrane, and $\overrightarrow{n}$ denote the unit outward normal to Ω. We assume that $\mathbf{u}$ is given, computed by the Darcy law [25], and satisfying the incompressibility condition $\boldsymbol{\nabla} \cdot \mathbf{u} = 0$, and $\mathbf{u} \cdot \overrightarrow{n}(x,t) = 0,\ \ x \in \Gamma_{\text{n}},\ t > 0$. 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 the 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 initial boundary value problem of finding the

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concentration $C(x,t)$:

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

For the inflow boundary, we keep the concentration fixed [10, 25].

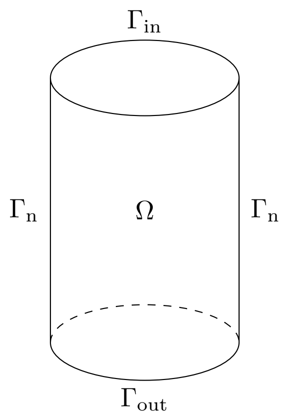

Fig. 1.1: Domain Ω

We consider three cases of isotherms: (i) constant isotherm, $q(C) = K$, (ii) affine isotherm, $q(C) = K_1 + K_2 C$ and (iii) nonlinear, explicit isotherm $q(C)$. A typical example of the nonlinear, explicit isotherm is Langmuir's isotherm [13, 48], $q(C) = \frac{q_{max}K_{eq}C}{1+K_{eq}C}$, where K_{eq} is Langmuir equilibrium constant and q_{max} is the maximum binding capacity of the porous medium. The main result of this paper is second-order accuracy by using the symplectic one-step implicit midpoint method for the time discretization, at the same computational cost as the Backward Euler method. The accuracy comes in two ways, such as the rate of convergence is higher and the mass is better conserved when the midpoint method is used. The fully discrete formulation of the problem (1.1) is given in Section 3. We perform stability analysis and error analysis for the nonlinear explicit $q(C)$ in Section 4. We also prove the existence of a fully discrete solution, and complete the stability analysis and error analysis for the constant and affine $q(C)$ in Section 4. The numerical tests validating these estimates are given in Section 5.

1.1. Previous work. The general advection-diffusion equation has been the subject of extensive mathematical study during the past decades [8, 14, 20, 33–35]. The analysis and the numerical computations are typically more difficult in the presence of reaction terms, especially nonlinear ones [43]. In [51], the author considered the constant linear and nonlinear adsorptions, and analyzed the problem using the first-order accurate backward Euler method for the time discretization, and the upwind Petrov-Galerkin (SUPG) finite element for spatial discretization, with numerical validation for each of the a priori estimates.

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 [5] norms are

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

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

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

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

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

with Ω a polyhedron, $X^h_{0,\Gamma_{\text{in}}} \subset H^1_{0,\Gamma_{\text{in}}}(\Omega)$. Let X^* be the dual space of $X^h_{0,\Gamma_{\text{in}}}$, with norm $\|f\|_* = \sup_{v \in X^h_{0,\Gamma_{\text{in}}}} \frac{(f,v)}{\|\nabla v\|}$. We denote $X^h_{\Gamma_{\text{in}}}$ as the restriction of functions in X^h to the boundary Γ_{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 $k \ge 1$ 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 $\le k$. 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 $X^h_{\Gamma_{\text{in}}}$ possesses the approximation property

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

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

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

Proof. This is the direct consequence of the Poincaré inequality that holds for $v \in H^1_{0,\Gamma_{\text{in}}}(\Omega)$ [27]. ∎

LEMMA 2.2. *(See [36, p.154]) Let $\mathcal{P}$ and $\mathcal{P}^1$ be the orthogonal projections with respect to the L^2 inner product (u,v) and H^1 inner product $(\nabla u, \nabla v)$, respectively. Then, for any $w \in X$,*

$$\nabla \mathcal{P}_{X^h} w = \mathcal{P}^1_{\nabla X^h} \nabla w.$$

LEMMA 2.3. *Given $g \in H^{r-1/2}(\Gamma_{in})$ for $r \ge 1$, 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 [29, Lemma 4],given here for the reader's convenience. Let $\Pi_h C$ denote X^h-interpolant of C and $\Pi_h g$ denote $X^h_{\Gamma_{\text{in}}}$- interpolant of g. Then, for $\hat{C}_h|_{\Gamma_{\text{in}}} = \Pi_h g$, we write the triangle inequality

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

From the interpolation theory [15] we get

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

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

2.1. Assumptions and preliminary results. We use the following subset of assumptions considered in [51]:

(F1) ω and ρ_s are constants in time and space [25].
(F2) $\mathbf{u}$ is nonzero and bounded in L^∞ norm [18, 44].
(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 [7, 18, 25, 44].
(F4) There exists a unique solution $C \in L^\infty(0, T, L^2(\Omega)) \cap L^2(0, T, H^1(\Omega))$ [44].
(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 $q'(C) \geq \kappa_1 > 0 \ \forall C \geq 0$ [9, 24, 25, 42–44].
(F6) The rate of increase in adsorption is Lipschitz continuous and bounded above so that $\frac{dq}{dC} = q'(C) \leq \kappa_2$ [25].
(F7) The second derivative of the adsorption, $q''(C)$, is Lipschitz continuous and bounded.

Remark 2.4. 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 [51]. Instead, we considered the non-homogeneous boundary condition at the inflow boundary.

In [9, 24, 25, 44, 51], 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 2.5. *Assuming no forcing term $f = 0$ and the positivity of the initial condition $0 < C_0(x)$, we have that*

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

Proof. From the incompressibility condition we have

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

If 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) becomes

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

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,

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

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

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 the Maximum Principle [40, pages 173-174], the maximum of $C(x,t)$ is on the boundary and $(D\boldsymbol{\nabla} C)\cdot \overrightarrow{n}(x,t) < 0$. This contradicts the boundary condition in (1.1), which concludes the argument. ∎

3. Variational Formulation. Let $\mathcal{P}$ be the orthogonal projection on $H^1(\Omega)$ with respect to the L^2 inner product (u,v). The standard Galerkin variational formulation for the transport problem (1.1) is: Find $C \in H^1(\Omega)$ such that $C\Big|_{\Gamma_{\text{in}}} = g$ and

$$(\frac{\partial}{\partial t}(\omega C + (1-\omega)\rho_s \mathcal{P}(q(C))), v) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, v) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} v) = (f,v),\ \forall\ v \in H^1_{0,\Gamma_{\text{in}}}(\Omega). \tag{3.1}$$

Next, we write a finite element approximation for (1.1).

3.1. Semi-Discrete in Space Approximation. Let $\mathcal{P}_h$ be the orthogonal projection on $X^h(\Omega)$ with respect to the L^2 inner product (u,v), and $g_h = \Pi_h g$ an interpolant of g. Then we obtain the following semi-discrete in-space formulation: Find $C_h \in X^h$ such that $C_h\Big|_{\Gamma_{\text{in}}} = g_h$ and $\forall\ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega)$,

$$(\frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s \mathcal{P}_h(q(C_h))), v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla} C_h, v_h) + (D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} v_h) = (f, v_h). \tag{3.2}$$

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 uniform time step size, $t_n = n\Delta t$, $t_{n+1/2} = \frac{t_n + t_{n+1}}{2}$, and $f^n(x) = f(x,t_n)$. We also denote by $C_h^n(x)$ the Finite Element approximation to $C(x,t_n)$.

For time discretization of (3.2) we use the refactorization of the midpoint method [17]: Given $C_h^n \in X^h$, find $C_h^{n+1} \in X^h$ such that $C_h^{n+1}\Big|_{\Gamma_{\text{in}}} = g_h$ satisfying

Step 1: Backward Euler method approximating the (3.2) on time interval $[t_n, t_{n+1/2}]$, $\forall\ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega)$,

$$\begin{aligned}((\omega + (1-\omega)\rho_s)\frac{q(C_h^{n+1/2}) - q(C_h^n)}{\Delta t/2}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h)\\ = (f^{n+1/2}, v_h).\end{aligned} \tag{3.3}$$

Step 2: Forward Euler method on time interval $[t_{n+1/2}, t_{n+1}]$, $\forall\ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega)$

$$\begin{aligned}((\omega + (1-\omega)\rho_s)\frac{q(C_h^{n+1}) - q(C_h^{n+1/2})}{\Delta t/2}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h)\\ = (f^{n+1/2}, v_h).\end{aligned} \tag{3.4}$$

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

3.3. Time-integrated finite element formulation. For the error analysis of the case of a nonlinear, explicit adsorption, we use a time-integrated version of the transport equation introduced in [39] and applied in different formulations [6, 44, 52]. To develop the time-integrated finite element discretization, we rewrite (1.1) by integrating in time to obtain

$$\omega C + (1-\omega)\rho_s q(C) + \int_0^t \mathbf{u}\cdot\boldsymbol{\nabla} C dt' - \boldsymbol{\nabla}\cdot\int_0^t D\boldsymbol{\nabla} C dt' = \int_0^t f dt' + \omega C_0 + (1-\omega)q(C_0). \tag{3.5}$$

Testing (3.5) by $v \in H^1_{0,\Gamma_{in}}(\Omega)$ we get,

$$(\omega C, v) + ((1-\omega)\rho_s q(C), v) + (\int_0^t \mathbf{u}\cdot\boldsymbol{\nabla} C dt', v) - (\boldsymbol{\nabla}\cdot\int_0^t D\boldsymbol{\nabla} C dt', v) \\ = (\int_0^t f dt', v) + (\omega C_0, v) + ((1-\omega)q(C_0), v). \tag{3.6}$$

Then the semi-discrete in space variational formulation is: Find $C_h \in X^h$ such that $C_h\big|_{\Gamma_{in}} = g_h$ and

$$(\omega C_h, v_h) + ((1-\omega)\rho_s q(C_h), v_h) + (\int_0^t \mathbf{u}\cdot\boldsymbol{\nabla} C_h dt', v_h) - (\boldsymbol{\nabla}\cdot\int_0^t D\boldsymbol{\nabla} C_h dt', v_h) \\ = (\int_0^t f dt', v_h) + (\omega C_0, v_h) + ((1-\omega)q(C_0), v_h), \quad \forall v_h \in X^h_{0,\Gamma_{in}}(\Omega). \tag{3.7}$$

Next, the fully discrete variational formulation using the midpoint time discretization can be written as: Given $C_h^n \in X^h$, find $C_h^{n+1} \in X^h$ such that $C_h^{n+1}\big|_{\Gamma_{in}} = g_h$ and

$$(\omega C_h^{N+1}, v_h) + ((1-\omega)\rho_s q(C_h^{N+1}), v_h) + (\sum_{n=0}^{N} \mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, v_h) - (\boldsymbol{\nabla}\cdot\sum_{n=0}^{N} D\boldsymbol{\nabla} C_h^{n+1/2}, v_h) \\ = (\sum_{n=0}^{N} f^{n+1/2}, v_h) + (\omega C_0, v_h) + ((1-\omega)q(C_0), v_h), \quad \forall v_h \in X^h_{0,\Gamma_{in}}(\Omega). \tag{3.8}$$

4. Time-Dependent Analysis.

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

4.1. Construction of $\hat{C}$.

Denote $\hat{C}$ as the solution of the following elliptic problem with nonhomogeneous mixed boundary conditions:

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

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 $x \in \Gamma_{in}\cap\Gamma_n$ such that*

$$\|\hat{C}\|^2 \le 4(K\beta_1)^2\|g\|^2_{L^2(\Gamma_{in})}, \qquad \|\boldsymbol{\nabla}\hat{C}\|^2 \le \frac{2(K\beta_1)^2}{\lambda}\|g\|^2_{L^2(\Gamma_{in})}. \tag{4.2}$$

Proof. The existence and uniqueness proof for the more general case can be found in [31, Theorem 2.4.2.7]. □

Lemma 4.2. *Let the domain Ω be a 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 $\|\hat{C^h}\|_{H^1(\Omega)} \le K\|g^h\|_{H^{1/2}(\Gamma-)}$.*

Proof. When Ω is two-dimensional, we use a similar technique to [32]. Under the compatibility condition $D\boldsymbol{\nabla} g^h\cdot\overrightarrow{n} = 0,$ when $x \in \Gamma_{\text{in}}\cap\Gamma_{\text{n}}$, let $\hat{C} \in H^1(\Omega)$ be the solution of

$$\begin{aligned} -\boldsymbol{\nabla}\cdot(D\boldsymbol{\nabla}\hat{C}) + \hat{C} &= 0, \; x \in \Omega, \\ \hat{C} &= g^h, \; \text{when } x \in \Gamma_{\text{in}}, \\ (D\boldsymbol{\nabla}\hat{C})\cdot\overrightarrow{n} &= 0, \; \text{if } x \in \Gamma_{\text{n}} \cup \Gamma_{\text{out}}. \end{aligned} \tag{4.3}$$

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_{in}, so that $g^h \in H^{1/2+\epsilon}(\Gamma_{\text{in}})$ for $0 < \epsilon \le \frac{1}{2}$. Thus, by elliptic regularity, we derive that $\hat{C} \in H^{1+\epsilon}(\Omega)$ and $\|\hat{C}\|_{1+\epsilon} \le K\|g^h\|_{1/2+\epsilon,\Gamma_{\text{in}}}$ for $0 < \epsilon \le \frac{1}{2}$. 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 $\|\hat{C} - \Pi_h \hat{C}\|_1 \le K h^\epsilon \|\hat{C}\|_{1+\epsilon}$ which can be proven as in, e.g., [26]. Thus, we get

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

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

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

Since the usual interpolant used in the two-dimensional case is not defined in three dimensions for $H^r(\Omega)$-functions, $r \le \frac{3}{2}$, we use the Scott-Zhang interpolant [23] when Ω is three-dimensional. The Scott-Zhang interpolant is well-defined for any function in $H^1(\Omega)$ [46]. ∎

Next, we start with the numerical analysis for the nonlinear, explicit isotherm.

4.2. Nonlinear, Explicit Isotherm. We consider the variational formulation (3.1), the semi-discrete in-space formulation (3.2), and the fully discrete formulation given in Subsection 3.2. First, we show a total mass balance balance relation for this nonlinear explicit isotherm. Unlike the [51], we dropped the assumption "$C(x,t)$ is nondecreasing in time at every x" and considered non-homogeneous boundary conditions at inflow boundary. We denote the antiderivative of the isotherm by $Q(\alpha) = \int_0^\alpha q(s)ds$, and

$$\begin{aligned}\mathcal{E}(t) = &\frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C - \frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C - \frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr \\ &+ \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C - \frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2\, dr \\ &+ \|\omega C(t) + (1-\omega)\rho_s q(C(t)) - 2(\omega\hat{C} + (1-\omega)\rho_s q(\hat{C}))\|^2,\end{aligned}$$

also

$$\begin{aligned}\mathcal{B}(t) = &\frac{3\omega}{4}\int_0^t \|\frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|\frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2\, dr \\ &+ \frac{3\omega}{4}\int_0^t \|\frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2\, dr + \|\omega C(0) + (1-\omega)\rho_s q(C(0)) - 2(\omega\hat{C} + (1-\omega)\rho_s q(\hat{C}))\|^2.\end{aligned}$$

THEOREM 4.3. *Assume that (F1)-(F6) are satisfied, $f \in L^2(0,T;L^2(\Omega))$, the variational problem (3.1) has a solution $C \in L^\infty(0,T,L^2(\Omega)) \cap L^2(0,T,H^1(\Omega))$, and let $\hat{C}$ be solution of (4.1). Then the following total mass balance relation holds:*

$$\begin{aligned}&\|\omega C(t) + (1-\omega)\rho_s q(C(t))\|^2 + \omega\int_0^t \|D^{1/2}\boldsymbol{\nabla} C(r)\|^2\, dr + 4(1-\omega)\rho_s\int_0^t\int_\Omega q'(C(r))(D^{1/2}\boldsymbol{\nabla} C(r))^2\, d\Omega\, dr \\ &\quad + 4(1-\omega)\rho_s\int_0^t \Big(\int_{\Gamma_{out}} Q(C(r))(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr + 2\omega\int_0^t\Big(\int_{\Gamma_{out}} C^2(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr + \mathcal{E}(t) \\ &= \|\omega C_0 + (1-\omega)\rho_s q(C_0)\|^2 + 4\int_0^t (f, \omega C + (1-\omega)\rho_s q(C) - (\omega\hat{C} + (1-\omega)\rho_s q(\hat{C})))\, dr \\ &\quad - 2\omega\int_0^t\Big(\int_{\Gamma_{in}} g^2(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr - 4(1-\omega)\rho_s\int_0^t\Big(\int_{\Gamma_{in}} Q(g)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr + \mathcal{B}(t).\end{aligned} \tag{4.4}$$

Proof. Let $\hat{C} \in H^1(\Omega)$ such that $\hat{C}\Big|_{\Gamma_{\text{in}}} = g$. We test (4.1) with $v = (\omega C + (1-\omega)\rho_s q(C)) - (\omega\hat{C} + (1-\omega)\rho_s q(\hat{C})) \in H^1_{0,\Gamma_{\text{in}}}(\Omega)$. By using the divergence theorem and the boundary conditions, we get

$$
\begin{aligned}
(\mathbf{u}\cdot\boldsymbol{\nabla}C, \omega C + (1-\omega)\rho_s q(C)) &= \frac{\omega}{2}\int_{\Gamma_{\text{in}}} g^2(\mathbf{u}\cdot\overrightarrow{n})ds + \frac{\omega}{2}\int_{\Gamma_{\text{out}}} C^2(\mathbf{u}\cdot\overrightarrow{n})ds \\
&\quad + (1-\omega)\rho_s\int_{\Gamma_{\text{in}}} Q(g)(\mathbf{u}\cdot\overrightarrow{n})ds + (1-\omega)\rho_s\int_{\Gamma_{\text{out}}} Q(C)(\mathbf{u}\cdot\overrightarrow{n})ds,
\end{aligned}
\tag{4.5}
$$

and

$$
\begin{aligned}
&\omega(D\boldsymbol{\nabla}C,\boldsymbol{\nabla}C) + (1-\omega)\rho_s(q'(C)D\boldsymbol{\nabla}C,\boldsymbol{\nabla}C) = \omega(D^{1/2}\boldsymbol{\nabla}C, D^{1/2}\boldsymbol{\nabla}C) + (1-\omega)\rho_s(q'(C)D^{1/2}\boldsymbol{\nabla}C, D^{1/2}\boldsymbol{\nabla}C) \\
&\quad = \omega\|D^{1/2}\boldsymbol{\nabla}C\|^2 + (1-\omega)\rho_s\int_\Omega q'(C)(D^{1/2}\boldsymbol{\nabla}C)^2\, d\Omega.
\end{aligned}
$$

Next, we move the terms involving $\hat{C}$ to the right-hand side terms, and express them as follows

$$
\begin{aligned}
(\mathbf{u}\cdot\boldsymbol{\nabla}C, \omega\hat{C}) &= \frac{3\omega}{8}(D^{1/2}\boldsymbol{\nabla}C, \frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}) \\
&= \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C\|^2 + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2,
\end{aligned}
$$

and

$$
\begin{aligned}
&(\mathbf{u}\cdot\boldsymbol{\nabla}C, (1-\omega)\rho_s q(\hat{C})) \\
&= \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C\|^2 + \frac{3\omega}{16}\|\frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2.
\end{aligned}
$$

Similarly,

$$
\omega(D\boldsymbol{\nabla}C, \boldsymbol{\nabla}\hat{C}) = \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C\|^2 + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2,
$$

and

$$
\begin{aligned}
&(D\boldsymbol{\nabla}C, (1-\omega)\rho_s q'(\hat{C})\boldsymbol{\nabla}\hat{C}) \\
&= \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C\|^2 + \frac{3\omega}{16}\|\frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2.
\end{aligned}
$$

Finally, we express the term involving the time derivative as

$$
\left(\frac{\partial}{\partial t}(\omega C + (1-\omega)\rho_s q(C)), \omega\hat{C} + (1-\omega)\rho_s q(\hat{C})\right) = \frac{\partial}{\partial t}(\omega C + (1-\omega)\rho_s q(C), \omega\hat{C} + (1-\omega)\rho_s q(\hat{C})).
\tag{4.6}
$$

Combining (4.5)-(4.6), we get

$$
\begin{aligned}
&\frac{1}{2}\frac{\partial}{\partial t}\|\omega C + (1-\omega)\rho_s q(C)\|^2 + \frac{\omega}{4}\|D^{1/2}\boldsymbol{\nabla}C\|^2 + \frac{\omega}{2}\int_{\Gamma_{\text{out}}} C^2(\mathbf{u}\cdot\overrightarrow{n})ds \\
&\quad + (1-\omega)\rho_s\int_{\Gamma_{\text{out}}} Q(C)(\mathbf{u}\cdot\overrightarrow{n})ds + (1-\omega)\rho_s\int_\Omega q'(C)(D^{1/2}\boldsymbol{\nabla}C)^2\, d\Omega + \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2 \\
&\quad + \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 + \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2 \\
&\quad + \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C - \frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2 \\
&= (f, \omega C + (1-\omega)\rho_s q(C) - (\omega\hat{C} + (1-\omega)\rho_s q(\hat{C}))) + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2
\end{aligned}
$$

$$
+ \frac{3\omega}{16}\|\frac{8\rho_s q(\hat{C})(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2 + \frac{3\omega}{16}\|\frac{8(1-\omega)\rho_s q'(\hat{C})}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}\|^2
$$
$$
- \frac{\omega}{2}\int_{\Gamma_{\text{in}}} g^2(\mathbf{u}\cdot\overrightarrow{n})ds - (1-\omega)\rho_s\int_{\Gamma_{\text{in}}} Q(g)(\mathbf{u}\cdot\overrightarrow{n})ds + \frac{\partial}{\partial t}(\omega C + (1-\omega)\rho_s q(C), \omega\hat{C} + (1-\omega)\rho_s q(\hat{C})).
$$

Integration on $[0,t]$ and the polarized identity yields (4.4). ◻

A direct consequence of Theorem 4.3 is the following stability bound.

Theorem 4.4. *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)*. Let the antiderivative be $A(C) = \int_0^C sq'(s)ds$. Then we get the following bound:*

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

Proof. See [47, Theorem 18]. ◻

Remark 4.5. We note that in the case of Langmuir's isotherm, the antiderivative is

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

Next, we turn to the stability of the semidiscrete in space approximations in (3.2), and denote:

$$
Q_h(\alpha) = \int_0^\alpha \mathcal{P}(q(s))ds,
$$
$$
\mathcal{E}_h(t) = \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla}C_h - \frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla}C_h - \frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr
$$
$$
+ \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla}C_h - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr
$$
$$
+ \frac{3\omega}{4}\int_0^t \|D^{1/2}\boldsymbol{\nabla}C_h - \frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr
$$
$$
+ \|\omega C_h(t) + (1-\omega)\rho_s\mathcal{P}(q(C_h(t))) - 2(\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2,
$$

and

$$
\mathcal{B}_h(t) = \frac{3\omega}{4}\int_0^t \|\frac{8}{3}D^{-1/2}\hat{C}\mathbf{u}\|^2\, dr + \frac{3\omega}{4}\int_0^t \|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr
$$
$$
+ \frac{3\omega}{4}\int_0^t \|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr + \frac{3\omega}{4}\int_0^t \|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr
$$
$$
+ \|\omega C(0) + (1-\omega)\rho_s\mathcal{P}(q(C(0))) - 2(\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2.
$$

Theorem 4.6. *Assume that (F1)-(F6) are satisfied, C_h solves the semi-discrete in space Finite Element formulation with nonlinear adsorption* (3.2)*, $f \in L^2(0,T;L^2(\Omega))$, $\hat{C}$ is the solution of (4.1), $Q_h(\alpha) \geq 0$, and $\mathcal{P}^1(q'(C_h)) \geq 0$. The following total mass balance relation holds:*

$$
\|\omega C_h(t) + (1-\omega)\rho_s\mathcal{P}(q(C_h(t)))\|^2 + \omega\int_0^t \|D^{1/2}\boldsymbol{\nabla}C_h(r)\|^2\, dr
$$

$$+ 4(1-\omega)\rho_s \int_0^t \left(\int_\Omega \mathcal{P}^1(q'(C_h(r)))(D^{1/2}\boldsymbol{\nabla} C_h(r))^2 \, d\Omega \right) dr$$
$$+ 4(1-\omega)\rho_s \int_0^t \Big(\int_{\Gamma_{out}} Q(C_h(r))(\mathbf{u}\cdot \overrightarrow{n}) ds \Big) dr + 2\omega \int_0^t \Big(\int_{\Gamma_{out}} C_h^2(\mathbf{u}\cdot \overrightarrow{n}) ds \Big) dr + \mathcal{E}_h(t)$$
$$= \|\omega C(0) + (1-\omega)\rho_s \mathcal{P}(q(C_h(0)))\|^2 + 4\int_0^t (f, \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h)) - (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))) \, dr$$
$$+ \mathcal{B}_h(t) - 2\omega \int_0^t \Big(\int_{\Gamma_{in}} g_h^2(\mathbf{u}\cdot \overrightarrow{n}) ds \Big) dr - 4(1-\omega)\rho_s \int_0^t \Big(\int_{\Gamma_{in}} Q(g_h)(\mathbf{u}\cdot \overrightarrow{n}) ds \Big) dr.$$

Proof. Let $\hat{C}_h \in X^h(\Omega)$ such that $\hat{C}_h\Big|_{\Gamma_{\text{in}}} = g_h$ be the interpolant given in Lemma 4.2, and $\mathcal{P}$, $\mathcal{P}^1$ be the orthogonal projections with respect to the L^2 and H^1 inner products , respectively. Then we test (3.2) with $v_h = (\omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))) - (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \in X^h_{0,\Gamma_{\text{in}}}(\Omega)$ to obtain

$$\begin{aligned}
&\Big(\frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s q(C_h)), \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))\Big) \\
&\quad + \big(\mathbf{u}\cdot\boldsymbol{\nabla} C_h, \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))\big) + \omega(D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} C_h) + (1-\omega)\rho_s(D\boldsymbol{\nabla} C_h, \mathcal{P}^1(q'(C_h)\boldsymbol{\nabla} C_h)) \\
&= (f, \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h)) - (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))) \\
&\quad + \Big(\frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s q(C_h)), (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\Big) \\
&\quad + \big(\mathbf{u}\cdot\boldsymbol{\nabla} C, (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\big) + \omega(D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla}\hat{C}_h) + (1-\omega)\rho_s(D\boldsymbol{\nabla} C_h, \mathcal{P}^1(q'(\hat{C}_h)\boldsymbol{\nabla}\hat{C}_h)).
\end{aligned} \tag{4.7}$$

We rewrite the first term in the left hand side as

$$\Big(\frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s q(C_h)), \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))\Big) = \frac{1}{2}\frac{\partial}{\partial t}\|\omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))\|^2. \tag{4.8}$$

Following the technique used in Theorem 4.3 we get

$$\begin{aligned}
&(\mathbf{u}\cdot\boldsymbol{\nabla} C_h, \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h))) \\
&= \frac{\omega}{2}\int_{\Gamma_{\text{in}}} g_h^2(\mathbf{u}\cdot\overrightarrow{n}) ds + \frac{\omega}{2}\int_{\Gamma_{\text{out}}} C_h^2(\mathbf{u}\cdot\overrightarrow{n}) ds \\
&\quad + (1-\omega)\rho_s\int_{\Gamma_{\text{in}}} Q_h(g_h)(\mathbf{u}\cdot\overrightarrow{n}) ds + (1-\omega)\rho_s\int_{\Gamma_{\text{out}}} Q_h(C_h)(\mathbf{u}\cdot\overrightarrow{n}) ds,
\end{aligned} \tag{4.9}$$

and

$$\begin{aligned}
&\omega(D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} C_h) + (1-\omega)\rho_s\mathcal{P}^1(q'(C_h)D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} C_h) \\
&= \omega\|D^{1/2}\boldsymbol{\nabla} C_h\|^2 + (1-\omega)\rho_s\int_\Omega \mathcal{P}^1(q'(C_h))(D^{1/2}\boldsymbol{\nabla} C_h)^2 \, d\Omega.
\end{aligned} \tag{4.10}$$

Also, the terms on the right-hand side write as

$$(\mathbf{u}\cdot\boldsymbol{\nabla} C_h, \omega\hat{C}_h) = \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h\|^2 + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h - \frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2, \tag{4.11}$$

and

$$\begin{aligned}
&(\mathbf{u}\cdot\boldsymbol{\nabla} C_h, (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&= \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h\|^2 + \frac{3\omega}{16}\|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h - \frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2.
\end{aligned}$$

Moreover,

$$\omega(D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla}\hat{C}_h) \tag{4.12}$$

$$= \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h\|^2 + \frac{3\omega}{16}\|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2,$$

$$\begin{aligned}(D\boldsymbol{\nabla} C_h, (1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))\boldsymbol{\nabla}\hat{C}_h) \\ = \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h\|^2 + \frac{3\omega}{16}\|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\ - \frac{3\omega}{16}\|D^{1/2}\boldsymbol{\nabla} C_h - \frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2,\end{aligned} \tag{4.13}$$

and

$$\begin{aligned}\Big(\frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s q(C_h)), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))\Big) \\ = \frac{\partial}{\partial t}(\omega C_h + (1-\omega)\rho_s q(C_h), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))).\end{aligned} \tag{4.14}$$

Combining (4.8)-(4.14) and integrating both sides from 0 to t, we obtain

$$\begin{aligned}&\frac{1}{2}\|\omega C_h(t) + (1-\omega)\rho_s\mathcal{P}(q(C(t)))\|^2 + \frac{\omega}{4}\int_0^t \|\boldsymbol{\nabla} C_h(r)\|^2\, dr + \frac{\omega}{2}\int_0^t \Big(\int_{\Gamma_{\text{out}}} C_h^2(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr \\
&+ (1-\omega)\rho_s\int_0^t\int_{\Gamma_{\text{out}}} Q_h(C_h(r))(\mathbf{u}\cdot\overrightarrow{n})ds\, dr + (1-\omega)\rho_s\int_0^t\int_\Omega \mathcal{P}^1(q'(C_h(r)))(D^{1/2}\boldsymbol{\nabla} C_h(r))^2\, d\Omega\, dr \\
&+ \frac{3\omega}{16}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C_h(r) - \frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2\, dr + \frac{3\omega}{16}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C_h(r) - \frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr \\
&+ \frac{3\omega}{16}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C_h(r) - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr \\
&+ \frac{3\omega}{16}\int_0^t \|D^{1/2}\boldsymbol{\nabla} C_h(r) - \frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr \\
=& \int_0^t (f, \omega C_h + (1-\omega)\rho_s\mathcal{P}(q(C_h)) - (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))))\, dr + \frac{3\omega}{16}\int_0^t \|\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2\, dr \\
&+ \frac{3\omega}{16}\int_0^t \|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\, dr + \frac{3\omega}{16}\int_0^t \|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr \\
&+ \frac{3\omega}{16}\int_0^t \|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\, dr + \frac{1}{2}\|\omega C_h(0) + (1-\omega)\rho_s\mathcal{P}(q(C_h(0)))\|^2 \\
&- \frac{\omega}{2}\int_0^t \Big(\int_{\Gamma_{\text{in}}} g_h^2(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr - (1-\omega)\rho_s\int_0^t \Big(\int_{\Gamma_{\text{in}}} Q_h(g_h)(\mathbf{u}\cdot\overrightarrow{n})ds\Big)\, dr \\
&+ (\omega C_h(t) + (1-\omega)\rho_s q(C_h(t)), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&- (\omega C_h(0) + (1-\omega)\rho_s q(C_h(0)), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))).\end{aligned}$$

Writing the last two terms as

$$\begin{aligned}&(\omega C_h(t) + (1-\omega)\rho_s q(C_h(t)), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&= \frac{1}{4}\|(\omega C_h(t) + (1-\omega)\rho_s q(C_h(t))\|^2 + \frac{1}{4}\|2(\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2 \\
&\quad - \frac{1}{4}\|\omega C_h(t) + (1-\omega)\rho_s q(C_h(t)) - 2(\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2,\end{aligned}$$

and

$$\begin{aligned}&- (\omega C_h(0) + (1-\omega)\rho_s q(C_h 0)), \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&= -\frac{1}{4}\|(\omega C_h(0) + (1-\omega)\rho_s q(C_h(0))\|^2 - \frac{1}{4}\|2(\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2\end{aligned}$$

$$+\frac{1}{4}\|\omega C_h(0)+(1-\omega)\rho_s q(C_h(0))-2(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2,$$

yields the claimed result. ∎

4.3. Semi-discrete in space error estimate. The following result gives an a priori error estimate of the semi-discrete in space approximation (3.7) for the case of nonlinear adsorption.

THEOREM 4.7. *Assume that (F1)-(F7) are satisfied, the variational formulation* (3.6) *with nonlinear adsorption 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* (3.7)*. Then for all* $1\le r\le k+1$ *and each* $T>0$ *we have*

$$\omega\int_0^T\|(C-C_h)\|^2dt+\|\int_0^T D^{1/2}\boldsymbol{\nabla}(C-C_h)dt'\|^2\le h^{2r-2}\int_0^T\|C\|_r^2dt \\ \times\exp\Big(T+\frac{3T\|u\|_\infty^2\|D^{-1/2}\|_\infty^2}{\omega}\Big)\Big(4\|D^{1/2}\|_\infty^2+3\omega+4\|u\|_\infty^2\|D^{-1/2}\|_\infty^2+\frac{3(1-\omega)^2\rho_s^2\kappa_2^2}{\omega}\Big)K^2. \tag{4.15}$$

Proof. First we let $v=v_h\in X^h_{0,\Gamma_{\rm in}}\subset H^1_{0,\Gamma_{\rm in}}(\Omega)$ in (3.6), and then subtract (3.7) from (3.6) to obtain

$$0=(\omega(C-C_h),v_h)+((1-\omega)\rho_s(q(C)-q(C_h)),v_h)+(\int_0^t u\cdot\boldsymbol{\nabla}(C-C_h)dt',v_h) \\ -(\boldsymbol{\nabla}\cdot\int_0^t D\boldsymbol{\nabla}(C-C_h)dt',v_h),\quad\forall v_h\in X^h_{0,\Gamma_{in}}(\Omega). \tag{4.16}$$

Choosing $v_h=C_h-\hat{C}_h=C_h-C+C-\hat{C}_h\in X^h_{0,\Gamma_{\rm in}}$ gives

$$\begin{aligned}&(\omega(C-C_h),C-C_h)+((1-\omega)\rho_s(q(C)-q(C_h)),C-C_h)\\&\quad+(\int_0^t u\cdot\boldsymbol{\nabla}(C-C_h)dt',C-C_h)+(\int_0^t D\boldsymbol{\nabla}(C-C_h)dt',\boldsymbol{\nabla}(C-C_h))\\&=(\omega(C-C_h),C-\hat{C}_h)+((1-\omega)\rho_s(q(C)-q(C_h)),C-\hat{C}_h)\\&\quad+(\int_0^t u\cdot\boldsymbol{\nabla}(C-C_h)dt',C-\hat{C}_h)+(\int_0^t D\boldsymbol{\nabla}(C-C_h)dt',\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big)).\end{aligned}$$

The Cauchy-Schwarz inequality and integration on $[0,T]$ yields

$$\begin{aligned}&\omega\int_0^T\|C-C_h\|^2dt+2(1-\omega)\rho_s\int_0^T\int_\Omega\big(\int_0^1(q'(\theta C+(1-\theta)C_h))d\theta\big)(C-C_h)^2d\Omega\,dt\\&\quad+\|\int_0^T D^{1/2}\boldsymbol{\nabla}(C-C_h)dt'\|^2\\&\le\big(1+\frac{3\|u\|_\infty^2\|D^{-1/2}\|_\infty^2}{\omega}\big)\int_0^T\|\int_0^t D^{1/2}\boldsymbol{\nabla}(C-C_h)dt'\|^2dt+4\|D^{1/2}\|_\infty^2\int_0^T\|\boldsymbol{\nabla}\Big(C-\hat{C}_h\Big)\|^2dt\\&\quad+\big(3\omega+4\|u\|_\infty^2\|D^{-1/2}\|_\infty^2+\frac{3(1-\omega)^2\rho_s^2\kappa_2^2}{\omega}\big)\int_0^T\|C-\hat{C}_h\|^2dt.\end{aligned}$$

Discarding the second term in the left hand side and using the Gronwall's inequality gives

$$\begin{aligned}&\omega\int_0^T\|(C-C_h)\|^2dt+\|\int_0^T D^{1/2}\boldsymbol{\nabla}(C-C_h)dt'\|^2\\&\le\exp\Big(T+\frac{3T\|u\|_\infty^2\|D^{-1/2}\|_\infty^2}{\omega}\Big)\\&\quad\times\Big(4\|D^{1/2}\|_\infty^2++3\omega+4\|u\|_\infty^2\|D^{-1/2}\|_\infty^2+\frac{3(1-\omega)^2\rho_s^2\kappa_2^2}{\omega}\Big)\int_0^T\inf_{\substack{\hat{C_h}\in X^h\\ \hat{C_h}|_{\Gamma_{\rm in}}=g_h}}\|C-\hat{C}_h\|_1^2dt.\end{aligned}$$

Let boundary term g_h be the interpolant of g in $X^h_{\Gamma_{\rm in}}$. Then Lemma 2.3 finally implies (4.15). ∎

In the following two sections we prove the solvability and the stability of the fully discrete system (3.3)-(3.4), approximating (1.1) for the nonlinear explicit isotherm.

4.3.1. Existence of the solution to the fully discrete system. By adding and subtracting $\hat{C}_h$, we can rewrite the fully discretized (3.3)-(3.4) as follows:
Given $C_h^n - \hat{C}_h \in X^h_{0,\Gamma_{\rm in}}$, find $C_h^{n+1} - \hat{C}_h \in X^h_{0,\Gamma_{\rm in}}$ such that
(4.17)

$$(D\nabla(C_h^{n+1} - \hat{C}_h), \nabla v_h) = -2\Big(\big(\omega + (1-\omega)\rho_s q'(\frac{C_h^{n+1} - \hat{C}_h + C_h^n + \hat{C}_h}{2})\big)\frac{(C_h^{n+1} - \hat{C}_h) - (C_h^n - \hat{C}_h)}{\Delta t}, v_h\Big)$$
$$+ 2(f^{n+1/2}, v_h) - (\mathbf{u}\cdot\nabla(C_h^{n+1} - \hat{C}_h + C_h^n + \hat{C}_h), v_h) + (\nabla\cdot(D\nabla(C_h^n + \hat{C}_h)), v_h),\ \forall v_h \in X^h_{0,\Gamma_{\rm in}}.$$

To simplify the presentation, we drop the subscript h throughout this section. By the Lax-Milgram theorem [16, corollary 5.8], we have that

$$\forall\ l \in X^*,\ \text{there exists an unique solution } \Psi \in X_{0,\Gamma_{\rm in}} \text{ of } (D\boldsymbol{\nabla}\Psi, \boldsymbol{\nabla} v) = (l, v),\ \forall v \in X_{0,\Gamma_{\rm in}}.$$

Then, the operator $T : X^* \to X_{0,\Gamma_{\rm in}}$ defined by $T(l) = \Psi$ is a well-defined linear and continuous operator:

$$\|T\| = \sup_{l\in X^*}\frac{\|T(l)\|_{X_{0,\Gamma_{\rm in}}}}{\|l\|_*} = \sup_{l\in X^*}\frac{\|\boldsymbol{\nabla}\Psi\|}{\|l\|_*} \le \frac{1}{\lambda},\ \text{since } \|\boldsymbol{\nabla}\Psi\| \le \frac{1}{\lambda}\|l\|_*.$$

Next, we define the nonlinear operator $N : X_{0,\Gamma_{\rm in}} \to X^*$ by

$$N(\psi) = 2f^{n+\frac{1}{2}} - 2\big(\omega + (1-\omega)\rho_s q'(\frac{\psi + C^n + \hat{C}}{2})\big)\frac{\psi - (C^n - \hat{C})}{\Delta t} - \mathbf{u}\cdot\nabla(\psi + C^n + \hat{C}) + \boldsymbol{\nabla}\cdot(D\nabla(C^n + \hat{C})),$$

and the operator $\mathcal{F} : X_{0,\Gamma_{\rm in}} \to X_{0,\Gamma_{\rm in}}$ by $\mathcal{F} = T(N(\psi))$.

LEMMA 4.8. *$N : X_{0,\Gamma_{in}} \to X^*$ is a bounded operator*

$$\|N(\psi)\|_* \le \|\mathbf{u}\|_\infty\|\boldsymbol{\nabla}\psi\| + \frac{2\omega + 2(1-\omega)\kappa_2}{\Delta t}\|\psi\| + \frac{2\omega + 2(1-\omega)\kappa_2}{\Delta t}\|C^n - \hat{C}\| + \|2f^{n+\frac{1}{2}}\|_*$$
$$+ \|\boldsymbol{\nabla}\cdot(D\nabla(C^n + \hat{C}))\|_* + \|\mathbf{u}\|_\infty\|\nabla(C^n + \hat{C})\|.$$

Proof. The proof follows from (F6), the triangle and Cauchy-Schwarz inequalities.

LEMMA 4.9. *$N : X_{0,\Gamma_{in}} \to X^*$ is a continuous operator.*

Proof. It suffices to show that $\|N(\psi_1) - N(\psi_2)\|_* \to 0$ if $\|\boldsymbol{\nabla}(\psi_1 - \psi_2)\| \to 0$. Here,

$$\|N(\psi_1) - N(\psi_2)\|_* \le \frac{2\omega}{\Delta t}\|\psi_2 - \psi_1\|_* + \|\mathbf{u}\cdot\boldsymbol{\nabla}(\psi_2 - \psi_1)\|_*$$
$$+ \frac{2(1-\omega)\rho_s}{\Delta t}\|q'(\frac{\psi_2 + C^n + \hat{C}}{2})(\psi_2 - (C^n - \hat{C})) - q'(\frac{\psi_1 + C^n + \hat{C}}{2})(\psi_1 - (C^n - \hat{C}))\|_*.$$

Using the Cauchy-Schwarz and Poincaré-Friedrichs inequalities, the Lipschitz continuity of q' and (F6)-(F7) we get

$$\|N(\psi_1) - N(\psi_2)\|_*$$
$$\le \Big(\frac{2\omega K_{\rm PF}}{\Delta t} + \frac{2(1-\omega)\rho_s\kappa_2 K_{\rm PF}}{\Delta t} + \frac{2(1-\omega)\rho_s K K_{\rm PF}}{\Delta t}\|\psi_1 - (C^n - \hat{C})\|\Big)\|\psi_2 - \psi_1\| + \|\mathbf{u}\|_\infty\|\boldsymbol{\nabla}(\psi_2 - \psi_1)\|$$
$$= \frac{2K_{\rm PF}}{\Delta t}\Big(\omega + (1-\omega)\rho_s\kappa_2 + (1-\omega)\rho_s K\|\psi_1 - (C^n - \hat{C})\|\Big)\|\psi_2 - \psi_1\| + K_{\rm PF}\|\mathbf{u}\|_\infty\|\boldsymbol{\nabla}(\psi_2 - \psi_1)\|,$$

which concludes the argument. ∎

LEMMA 4.10. *$\mathcal{F} : X_{0,\Gamma_{in}} \to X_{0,\Gamma_{in}}$ is a compact map.*

Proof. Since $T : X^* \to X_{0,\Gamma_{\text{in}}}$ is a bounded linear operator, we only need to show that $N : X_{0,\Gamma_{\text{in}}} \to X^*$ is a compact map. By Lemmas 4.8-4.9 we have that $N : X_{0,\Gamma_{\text{in}}} \to X^*$ is a bounded and continuous operator respectively, and the Rellich-Kondrachov theorem [28, page 272] provides the compact embedding $X_{0,\Gamma_{\text{in}}} \hookrightarrow L^2$. Therefore $N : X_{0,\Gamma_{\text{in}}} \to L^2 \hookrightarrow X^*$ is compact.

$$\begin{array}{ccccc} \psi \in X_{0,\Gamma_{in}} & \hookrightarrow & L^2(\Omega) & \longrightarrow & N(\psi) \in X^* \\ & \searrow^{\mathcal{F}} & & & \downarrow T \\ & & & & X_{0,\Gamma_{in}} \end{array}$$

∎

To prove the solvability of the problem (4.17), it suffices to show that $\mathcal{F}$ has a fixed point, i.e., there exists $\psi = \mathcal{F}(\psi) \in X_{0,\Gamma_{\text{in}}}$.

THEOREM 4.11. *For any $v \in X_{0,\Gamma_{in}}$ and $f \in X^*$, there exists $\psi = C^{n+1} - \hat{C} \in X_{0,\Gamma_{in}}$ solution to (4.17).*

Proof. Consider $\psi_\alpha = \alpha\mathcal{F}(\psi_\alpha)$ in $X_{0,\Gamma_{\text{in}}}$, $0 \le \alpha \le 1$ defined by

$$\begin{aligned}\psi_\alpha = T\Big(& 2\alpha f^{n+\frac{1}{2}} - 2\alpha\big(\omega + (1-\omega)\rho_s q'(\frac{\psi + C^n + \hat{C}}{2})\big)\frac{\psi - (C^n - \hat{C})}{\Delta t} \\ & - \alpha\mathbf{u}\cdot\nabla(\psi + C^n + \hat{C}) + \alpha\boldsymbol{\nabla}\cdot(D\nabla(C^n + \hat{C}))\Big),\end{aligned}$$

which holds if and only if $\psi_\alpha \in X_{0,\Gamma_{\text{in}}}$ satisfies

$$\begin{aligned}(D\boldsymbol{\nabla}\psi_\alpha, \boldsymbol{\nabla}v) = & -2\alpha\Big(\big(\omega + (1-\omega)\rho_s q'(\frac{\psi_\alpha + C^n + \hat{C}}{2})\big)\frac{\psi_\alpha - (C^n - \hat{C})}{\Delta t}, v\Big) \\ & + 2(\alpha f^{n+1/2}, v) - (\alpha\mathbf{u}\cdot\boldsymbol{\nabla}\Big(\psi_\alpha + C^n + \hat{C}\Big), v) - (\alpha D\boldsymbol{\nabla}\Big(C^n + \hat{C}\Big), \boldsymbol{\nabla}v),\ \forall v \in X_{0,\Gamma_{\text{in}}}.\end{aligned}$$

Then by the Leray-Schauder fixed-point theorem [30,45], we only need to prove an a priori bound on $\|\boldsymbol{\nabla}\psi_\alpha\|$, independent of α. This follows by setting $v = \psi_\alpha$ and using the Cauchy-Schwarz and Poincaré-Friedrichs inequalities

$$\|\boldsymbol{\nabla}\psi_\alpha\| \le \frac{2K_{\text{PF}}}{\lambda}\|f^{n+1/2}\| + \frac{K_{\text{PF}}}{\lambda}\|\mathbf{u}\cdot\nabla(C^n + \hat{C})\| + \frac{\beta_1}{\lambda}\|\nabla(C^n + \hat{C})\| + \frac{2K_{\text{PF}}(\omega + (1-\omega)\rho_s\kappa_2)}{\lambda\Delta t}\|C^n - \hat{C}\|,$$

for $0 \le \alpha \le 1$. ∎

4.3.2. Stability of the solution to the fully discrete system. Inhere we derive an energy-like bound for (3.3)-(3.4), the fully discrete version of the adsorption equation (1.1) for a nonlinear, explicit isotherm, using the midpoint method for the time discretization. We recall that at the continuous level, we proved that the solution $C > 0$ is positive, and it is bounded by the initial and boundary conditions. Nevertheless, positivity and at the discrete level, and a discrete the Maximum Principle are hard to obtain, and usually hold under a CFL condition, i.e., the timestep has to be $\mathcal{O}(h^2)$ [49]. We use the following notations: $Q_h(\alpha) = \int_0^\alpha \mathcal{P}(q(s))ds$,

$$\begin{aligned}\mathcal{E}_h^n = & \frac{3\Delta t\omega}{4}\sum_{n=0}^{N}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2} - \frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2 \\ & + \frac{3\Delta t\omega}{4}\sum_{n=0}^{N}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2} - \frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 \\ & + \frac{3\Delta t\omega}{4}\sum_{n=0}^{N}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2} - \frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2\end{aligned}$$

$$+\frac{3\Delta t\omega}{4}\sum_{n=0}^{N}\|D^{1/2}\nabla C_h^{n+1/2}-\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\nabla\hat{C}_h\|^2$$
$$+\|\omega C_h^{N+1}+(1-\omega)\rho_s q(C_h^{N+1})-2(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2,$$

and

$$\begin{aligned}\mathcal{B}_h^n=&\frac{3N\Delta t\omega}{4}\|\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2+\frac{3N\Delta t\omega}{4}\|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2\\&+\frac{3N\Delta t\omega}{4}\|\frac{8}{3}D^{-1/2}\nabla\hat{C}_h\|^2+\frac{3N\Delta t\omega}{4}\|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\nabla\hat{C}_h\|^2\\&+\|\omega C_h^0+(1-\omega)\rho_s q(C_h^0)-2(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\|^2.\end{aligned}$$

THEOREM 4.12. *Suppose the assumptions (F1)-(F7) are satisfied so that the fully discrete formulation has a smooth solution* $\{C_h^n\}_{n=0}^N\in L^2(0,T;H^1(\Omega))$*. Then for all* $N>0$*,*

$$\begin{aligned}&\|\omega C_h^{N+1}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{N+1}))\|^2+\Delta t\omega\sum_{n=0}^{N}\|\nabla C_h^{n+1/2}\|^2+2\Delta t\omega\sum_{n=0}^{N}\int_{\Gamma_{out}}(C_h^{n+1/2})^2(\mathbf{u}\cdot\overrightarrow{n})ds\\&+4(1-\omega)\Delta t\rho_s\sum_{n=0}^{N}\int_{\Gamma_{out}}Q_h(C_h^{n+1/2})(\mathbf{u}\cdot\overrightarrow{n})ds\\&+4(1-\omega)\Delta t\rho_s\sum_{n=0}^{N}\int_{\Omega}\mathcal{P}^1(q'(C_h^{n+1/2}))(D^{1/2}\nabla C_h^{n+1/2})^2\ d\Omega+\frac{1}{4}\mathcal{E}_h^n\\&=\|\omega C_h^0+(1-\omega)\rho_s\mathcal{P}(q(C_h^0)\|^2+\mathcal{B}_h^n\\&+4\Delta t\sum_{n=0}^{N}(f,\omega C_h^{n+1/2}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{n+1/2}))-(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))))\\&-2N\Delta t\omega\int_{\Gamma_{in}}g_h^2(\mathbf{u}\cdot\overrightarrow{n})ds-4(1-\omega)N\Delta t\rho_s\int_{\Gamma_{in}}Q_h(g_h)(\mathbf{u}\cdot\overrightarrow{n})ds.\end{aligned}$$

Proof. Let $\hat{C}_h\in X^h$ such that $\hat{C}_h\Big|_{\Gamma_{\rm in}}=g_h$. Take

$$v_h=\omega C_h^{n+1/2}+(1-\omega)\mathcal{P}(q(C_h^{n+1/2}))-(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))\in X_{0,\Gamma_{\rm in}}^h(\Omega).$$

Then (3.3) yields to

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

Using polarization identity in the first term, we get,

$$
\begin{aligned}
&\frac{1}{2}(\|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1/2}))\|^2 + \|\omega C_h^n + (1-\omega)\rho_s \mathcal{P}(q(C_h^n))\|^2 \\
&- \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^n + (1-\omega)\rho_s \mathcal{P}(q(C_h^n)))\|^2) \\
&+ \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))) \\
&+ \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big(\omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))\Big)) \\
&= \frac{\Delta t}{2}(f^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))) \\
&+ (\omega C_h^{n+1/2} + (1-\omega)\rho_s q(C_h^{n+1/2}) - \omega C_h^n - (1-\omega)\rho_s q(C_h^n), (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&+ \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&+ \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big((\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)\Big))).
\end{aligned}
\tag{4.18}
$$

Next, (3.4) yields to

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

Using polarization identity first term, we get

$$
\begin{aligned}
&\frac{1}{2}(\|\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1}))\|^2 - \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1/2}))\|^2 \\
&- \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1})))\|^2) \\
&+ \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))) \\
&+ \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big(\omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))\Big)) \\
&= \frac{\Delta t}{2}(f^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))) \\
&+ (\omega C_h^{n+1} + (1-\omega)\rho_s q(C_h^{n+1}) - \omega C_h^{n+1/2} - (1-\omega)\rho_s q(C_h^{n+1/2}), \omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&+ \frac{\Delta t}{2}(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&+ \frac{\Delta t}{2}(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big((\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)\Big)))
\end{aligned}
\tag{4.19}
$$

Adding (4.18) and (4.19), we get

$$
\begin{aligned}
&\frac{1}{2}(\|\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1}))\|^2 - \|\omega C_h^{n} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n}))\|^2 \\
&- \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1})))\|^2 \\
&+ \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^{n} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n})))\|^2) \\
&+ \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))) \\
&+ \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big(\omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))\Big)) \\
&= \Delta t(f^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))) \\
&+ (\omega C_h^{n+1} + (1-\omega)\rho_s q(C_h^{n+1}) - \omega C_h^{n} - (1-\omega)\rho_s q(C_h^{n}), (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&+ \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&+ \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big((\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)\Big))).
\end{aligned}
\tag{4.20}
$$

Using (3.3) and (3.4), we get,

$$
\begin{aligned}
&- \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1})))\|^2 \\
&+ \|\omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}((C_h^{n+1/2})) - (\omega C_h^{n} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n})))\|^2 = 0
\end{aligned}
$$

Consequently, we have,

$$
\begin{aligned}
&\frac{1}{2}(\|\omega C_h^{n+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1}))\|^2 - \|\omega C_h^{n} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n}))\|^2) \\
&+ \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))) \\
&+ \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big(\omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2}))\Big)) \\
&= \Delta t(f^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))) \\
&+ (\omega C_h^{n+1} + (1-\omega)\rho_s q(C_h^{n+1}) - \omega C_h^{n} - (1-\omega)\rho_s q(C_h^{n}), (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&+ \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, (\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&+ \Delta t(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla}\Big((\omega\hat{C}_h + (1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)\Big))).
\end{aligned}
\tag{4.21}
$$

Doing a similar analysis as in the semidiscrete case, we get,

$$
\begin{aligned}
&\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla} C_h^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\rho_s\mathcal{P}(q(C_h^{n+1/2}))) \\
&= \frac{\Delta t\omega}{2}\int_{\Gamma_{\text{in}}} g_h^2(\mathbf{u}\cdot\overrightarrow{n})ds + \frac{\Delta t\omega}{2}\int_{\Gamma_{\text{out}}}(C_h^{n+1/2})^2(\mathbf{u}\cdot\overrightarrow{n})ds \\
&+ \Delta t(1-\omega)\rho_s\int_{\Gamma_{\text{in}}} Q_h(g_h)(\mathbf{u}\cdot\overrightarrow{n})ds + \Delta t(1-\omega)\rho_s\int_{\Gamma_{\text{out}}} Q_h(C_h^{n+1/2})(\mathbf{u}\cdot\overrightarrow{n})ds.
\end{aligned}
\tag{4.22}
$$

Next,

$$
\begin{aligned}
&\Delta t\omega(D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) + \Delta t(1-\omega)\rho_s\mathcal{P}^1(q'(C_h^{n+1/2}))D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} C_h^{n+1/2}) \\
&= \Delta t\omega(D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2}, D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2}) \\
&+ \Delta t(1-\omega)\rho_s(\mathcal{P}^1(q'(C_h^{n+1/2}))D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2}, D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2}) \\
&= \Delta t\omega\|D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2}\|^2 + \Delta t(1-\omega)\rho_s\int_\Omega \mathcal{P}^1(q'(C_h^{n+1/2}))(D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2})^2\ d\Omega.
\end{aligned}
$$

Next, in the right-hand side terms, we get the following equalities,

$$\begin{aligned}
(4.23)\qquad & \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\omega\hat{C}_h) \\
&= \frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{3\Delta t\omega}{16}\|\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2-\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2,
\end{aligned}$$

$$\begin{aligned}
(4.24)\qquad & \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))) \\
&= \frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{3\Delta t\omega}{16}\|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 \\
&\quad -\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2,
\end{aligned}$$

$$\begin{aligned}
(4.25)\qquad & \Delta t\omega(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h) \\
&= \frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{3\Delta t\omega}{16}\|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2-\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2,
\end{aligned}$$

$$\begin{aligned}
(4.26)\qquad & \Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))\boldsymbol{\nabla}\hat{C}_h) \\
&= \frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{3\Delta t\omega}{16}\|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&\quad -\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2.
\end{aligned}$$

Combining (4.22)-(**??**), we get

$$\begin{aligned}
&\frac{1}{2}(\|\omega C_h^{n+1}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{n+1}))\|^2-\|\omega C_h^{n}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{n}))\|^2)+\frac{\omega\Delta t}{4}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2 \\
&\quad +(1-\omega)\Delta t\rho_s\int_{\Gamma_{\text{out}}}Q_h(C_h^{n+1/2})(\mathbf{u}\cdot\overrightarrow{n})ds+\Delta t(1-\omega)\rho_s\int_\Omega\mathcal{P}^1(q'(C_h^{n+1/2}))(D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2})^2\,d\Omega \\
&\quad +\frac{\Delta t\omega}{2}\int_{\Gamma_{\text{out}}}(C_h^{n+1/2})^2(\mathbf{u}\cdot\overrightarrow{n})ds+\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2 \\
&\quad +\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2 \\
&\quad +\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&\quad +\frac{3\Delta t\omega}{16}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}-\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&= \Delta t(f^{n+1/2},\omega C_h^{n+1/2}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{n+1/2}))-(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h)))) \\
&\quad -\frac{\Delta t\omega}{2}\int_{\Gamma_{\text{in}}}g_h^2(\mathbf{u}\cdot\overrightarrow{n})ds+\frac{3\Delta t\omega}{16}\|\frac{8}{3}D^{-1/2}\hat{C}_h\mathbf{u}\|^2 \\
&\quad +\frac{3\Delta t\omega}{16}\|\frac{8\rho_s\mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega}D^{-1/2}\mathbf{u}\|^2+\frac{3\Delta t\omega}{16}\|\frac{8}{3}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&\quad +\frac{3\Delta t\omega}{16}\|\frac{8(1-\omega)\rho_s\mathcal{P}^1(q'(\hat{C}_h))}{3\omega}D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2-(1-\omega)\rho_s\Delta t\int_{\Gamma_{\text{in}}}Q_h(g_h)(\mathbf{u}\cdot\overrightarrow{n})ds \\
&\quad +(\omega C_h^{n+1}+(1-\omega)\rho_s q(C_h^{n+1})-\omega C_h^{n}-(1-\omega)\rho_s q(C_h^{n}),(\omega\hat{C}_h+(1-\omega)\rho_s\mathcal{P}(q(\hat{C}_h))).
\end{aligned}$$

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

$$\begin{aligned}
(4.27)\qquad & \frac{1}{2}\|\omega C_h^{N+1}+(1-\omega)\rho_s\mathcal{P}(q(C_h^{N+1}))\|^2+\frac{\omega\Delta t}{4}\sum_{n=0}^{N}\|D^{1/2}\boldsymbol{\nabla}C_h^{n+1/2}\|^2 \\
&+\frac{\Delta t\omega}{2}\sum_{n=0}^{N}\Big(\int_{\Gamma_{\text{out}}}(C_h^{n+1/2})^2(\mathbf{u}\cdot\overrightarrow{n})ds\Big)+\Delta t(1-\omega)\rho_s\sum_{n=0}^{N}\Big(\int_{\Gamma_{\text{out}}}Q_h(C_h^{n+1/2}(\mathbf{u}\cdot\overrightarrow{n})ds\Big)
\end{aligned}$$

$$
\begin{aligned}
&+ \Delta t(1-\omega)\rho_s \sum_{n=0}^{N} \left(\int_\Omega \mathcal{P}^1(q'(C_h^{n+1/2})(D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2})^2 \; d\Omega \right) \\
&+ \frac{3\Delta t\omega}{16} \sum_{n=0}^{N} \|D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2} - \frac{8}{3} D^{-1/2}\hat{C}_h \mathbf{u}\|^2 \\
&+ \frac{3\Delta t\omega}{16} \sum_{n=0}^{N} \|D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2} - \frac{8\rho_s \mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega} D^{-1/2}\mathbf{u}\|^2 \\
&+ \frac{3\Delta t\omega}{16} \sum_{n=0}^{N} \|D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2} - \frac{8}{3} D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&+ \frac{3\Delta t\omega}{16} \sum_{n=0}^{N} \|D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2} - \frac{8(1-\omega)\rho_s \mathcal{P}^1(q'(\hat{C}_h))}{3\omega} D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 \\
&= \Delta t \sum_{n=0}^{N} (f^{n+1/2}, \omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))) \\
&+ \frac{3N\Delta t\omega}{16} \|\frac{8}{3} D^{-1/2}\hat{C}_h \mathbf{u}\|^2 + \frac{3N\Delta t\omega}{16} \|\frac{8\rho_s \mathcal{P}(q(\hat{C}_h))(1-\omega)}{3\omega} D^{-1/2}\mathbf{u}\|^2 \\
&+ \frac{3N\Delta t\omega}{16} \|\frac{8(1-\omega)\rho_s \mathcal{P}^1(q'(\hat{C}_h))}{3\omega} D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2 + \frac{1}{2}\|\omega C_h^0 + (1-\omega)\rho_s \mathcal{P}(q(C_h^0)\|^2 \\
&- \frac{N\Delta t\omega}{2} \int_{\Gamma_{\text{in}}} g_h^2 (\mathbf{u}\cdot \overrightarrow{n}) ds - (1-\omega)N\Delta t \rho_s \int_{\Gamma_{\text{in}}} Q(g_h)(\mathbf{u}\cdot\overrightarrow{n}) ds \\
&+ (\omega C_h^{N+1} + (1-\omega)\rho_s q(C_h^{N+1}, \omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&- (\omega C_h^0 + (1-\omega)\rho_s q(C_h^0, \omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) + \frac{3N\Delta t\omega}{16} \|\frac{8}{3} D^{-1/2}\boldsymbol{\nabla}\hat{C}_h\|^2.
\end{aligned} \tag{4.28}
$$

Here,

$$
\begin{aligned}
&(\omega C_h^{N+1} + (1-\omega)\rho_s q(C_h^{N+1}), \omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&= \frac{1}{2}(\omega C_h^{N+1} + (1-\omega)\rho_s q(C_h^{N+1}), 2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))) \\
&= \frac{1}{4}\|(\omega C_h^{N+1} + (1-\omega)\rho_s q(C_h^{N+1})\|^2 + \frac{1}{4}\|2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))\|^2 \\
&- \frac{1}{4}\|\omega C_h^{N+1} + (1-\omega)\rho_s q(C_h^{N+1}) - 2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))\|^2,
\end{aligned}
$$

and

$$
\begin{aligned}
&- (\omega C_h^0 + (1-\omega)\rho_s q(C_h^0)), \omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))) \\
&= -\frac{1}{2}(\omega C_h^0 + (1-\omega)\rho_s q(C_h^0, 2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))) \\
&= -\frac{1}{4}\|(\omega C_h^0 + (1-\omega)\rho_s q(C_h^0)\|^2 - \frac{1}{4}\|2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))\|^2 \\
&+ \frac{1}{4}\|\omega C_h^0 + (1-\omega)\rho_s q(C_h^0) - 2(\omega\hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h)))\|^2.
\end{aligned}
$$

Hence (4.27) becomes

$$
\begin{aligned}
&\frac{1}{4}\|\omega C_h^{N+1} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{N+1})\|^2 + \frac{\Delta t\omega}{4} \sum_{n=0}^{N} \|\boldsymbol{\nabla} C_h^{n+1/2}\|^2 \\
&+ \frac{\Delta t\omega}{2} \sum_{n=0}^{N} \int_{\Gamma_{\text{out}}} (C_h^{n+1/2})^2 (\mathbf{u}\cdot\overrightarrow{n}) ds + \frac{1}{4}\mathcal{E}_h^n + (1-\omega)\Delta t\rho_s \sum_{n=0}^{N} \int_{\Gamma_{\text{out}}} Q(C_h^{n+1/2})(\mathbf{u}\cdot\overrightarrow{n}) ds
\end{aligned}
$$

$$+ (1-\omega)\Delta t \rho_s \sum_{n=0}^{N} \int_{\Omega} \mathcal{P}^1(q'(C_h^{n+1/2}))(D^{1/2}\boldsymbol{\nabla} C_h^{n+1/2})^2 \, d\Omega$$
$$= \frac{1}{4}\|\omega C_h^0 + (1-\omega)\rho_s \mathcal{P}(q(C_h^0)\|^2 + \frac{1}{4}\mathcal{B}_h^n$$
$$+ \Delta t \sum_{n=0}^{N} (f, \omega C_h^{n+1/2} + (1-\omega)\rho_s \mathcal{P}(q(C_h^{n+1/2})) - (\omega \hat{C}_h + (1-\omega)\rho_s \mathcal{P}(q(\hat{C}_h))))$$
$$- \frac{N\Delta t \omega}{2} \int_{\Gamma_{\text{in}}} g_h^2(\mathbf{u}\cdot\overrightarrow{n})ds - (1-\omega)N\Delta t \rho_s \int_{\Gamma_{\text{in}}} Q(g_h)(\mathbf{u}\cdot\overrightarrow{n})ds$$

Simplifying the above inequality, we get the claimed result. ∎

Next, for the constant isotherm, we omit the proofs of Theorem 4.13 and Theorem 4.14 since they could be retrieved from the nonlinear case by plugging in $q(C) = K$ with $K \geq 0$ and dropping the other assumptions except (F1)-(F6).

4.4. 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 (**??**) simplifies to the following: Find $C \in H^1(\Omega)$ such that $C\Big|_{\Gamma_{\text{in}}} = g$ and :

$$(\bar{\omega}\frac{\partial C}{\partial t}, v) + (\mathbf{u}\cdot\boldsymbol{\nabla} C, v) + (D\boldsymbol{\nabla} C, \boldsymbol{\nabla} v) = (f, v), \text{ for all } \ v \in H^1_{0,\Gamma_{\text{in}}}(\Omega). \tag{4.29}$$

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

$$(\bar{\omega}\frac{\partial C_h}{\partial t}, v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla} C_h, v_h) + (D\boldsymbol{\nabla} C_h, \boldsymbol{\nabla} v_h) = (f, v_h), \text{ for all } \ v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega). \tag{4.30}$$

For the analysis, we recall the refactorization of midpoint method [17] for time discretization, and we get the following full discretization: Given $C_h^n \in X^h$, find $C_h^{n+1} \in X^h$ such that $C_h^{n+1}\Big|_{\Gamma_{\text{in}}} = g_h$ satisfying
Step 1: Backward Euler step at the half-integer time step $t_{n+1/2}$
(4.31)
$$(\bar{\omega}\frac{C_h^{n+1/2} - C_h^n}{\Delta t/2}, v_h) + (u\cdot\boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega).$$

Step 2: Forward Euler step at t_{n+1}
(4.32)
$$(\bar{\omega}\frac{C_h^{n+1} - C_h^{n+1/2}}{\Delta t/2}, v_h) + (u\cdot\boldsymbol{\nabla} C_h^{n+1/2}, v_h) + (D\boldsymbol{\nabla} C_h^{n+1/2}, \boldsymbol{\nabla} v_h) = (f^{n+1/2}, v_h), \text{ for all } v_h \in X^h_{0,\Gamma_{\text{in}}}(\Omega).$$

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

THEOREM 4.13. *Assume that (F1)-(F6) are satisfied and the variational formulation with affine adsorption given by* (4.29) *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). *Then we get the following bound:*

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

Proof. This follows the same proof as we did in the nonlinear case. ∎

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

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

THEOREM 4.14. *Assume that (F1)-(F6) are satisfied and the variational formulation with affine adsorption given by* (4.29) *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 affine adsorption given by* (4.30). *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. This follows the same proof as we did in the nonlinear case. ∎

Next, we find the energy bound for the discrete version of the adsorption equation (1.1) for affine 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, the timestep has to be $\mathcal{O}(h^2)$ [49].

THEOREM 4.15. *Suppose the assumptions (F1)-(F7) are satisfied so that the fully discrete formulation has a smooth solution* $\{C_h^n\}_{n=0}^N \in L^2(0,T;H^1(\Omega))$. *Then for all* $N > 0$,

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

Proof. Let $\hat{C}_h \in X^h$ 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 (4.31) yields to

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

Using polarization identity in the first term, we get,

(4.33)

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

Next, (4.32) yields to

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

Using polarization identity first term, we get

(4.34)

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

Adding (4.33) and (4.34), we get

$$\begin{aligned}(4.35)\quad &\frac{\bar{\omega}}{2}(\|C_h^{n+1}\|^2-\|C_h^n\|^2+\|C_h^{n+1/2}-C_h^n\|^2-\|C_h^{n+1}-C_h^{n+1/2}\|^2)+\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},C_h^{n+1/2})\\ &+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})=\Delta t(f^{n+1/2},C_h^{n+1/2}-\hat{C}_h)+(\bar{\omega}(C_h^{n+1}-C_h^n),\hat{C}_h)\\ &+\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\hat{C}_h)+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h).\end{aligned}$$

Using (4.31) and (4.32), 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,

$$\begin{aligned}(4.36)\quad &\frac{\bar{\omega}}{2}(\|C_h^{n+1}\|^2-\|C_h^n\|^2)+\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},C_h^{n+1/2})+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\\ &=\Delta t(f^{n+1/2},C_h^{n+1/2}-\hat{C}_h)+(\bar{\omega}(C_h^{n+1}-C_h^n),\hat{C}_h)+\Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\hat{C}_h)+\Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h).\end{aligned}$$

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

$$(4.37)\quad (\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},C_h^{n+1/2})=\frac{1}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big)+\frac{1}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\vec{n})ds\Big).$$

Next,

$$(4.38)\quad (D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\geq\lambda\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2.$$

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

$$(4.39)\quad (\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\hat{C}_h)\leq\frac{\lambda}{4}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{\|\mathbf{u}\|_\infty^2}{\lambda}\|\hat{C}_h\|^2.$$

$$(4.40)\quad (D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h)\leq\frac{\lambda}{4}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2.$$

$$(4.41)\quad (f^{n+1/2},C_h^{n+1/2}-\hat{C}_h)\leq\frac{2K_{\text{PF}}^2}{\lambda}\|f^{n+1/2}\|^2+\frac{\lambda}{4}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2+\frac{\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2.$$

Putting (4.37)-(4.41) into (4.36), we get,

$$\begin{aligned}(4.42)\quad &\frac{\bar{\omega}}{2}\|C_h^{n+1}\|^2-\frac{\bar{\omega}}{2}\|C_h^n\|^2+\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\vec{n})ds\Big)+\frac{\Delta t\lambda}{4}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2\\ &\leq\frac{\|\mathbf{u}\|_\infty^2\Delta t}{\lambda}\|\hat{C}_h\|^2-\frac{\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big)+\frac{\Delta t\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2\\ &+\frac{2K_{\text{PF}}^2\Delta t}{\lambda}\|f^{n+1/2}\|^2+\frac{\Delta t\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2+(\bar{\omega}(C_h^{n+1}-C_h^n),\hat{C}_h).\end{aligned}$$

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

$$\begin{aligned}(4.43)\quad &\frac{\bar{\omega}}{2}\|C_h^{N+1}\|^2-\frac{\bar{\omega}}{2}\|C_h^0\|^2+\frac{\Delta t}{2}\sum_{n=0}^{N}\Big(\int_{\Gamma_{\text{out}}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\vec{n})ds\Big)+\frac{\Delta t\lambda}{4}\sum_{n=0}^{N}\|\boldsymbol{\nabla}C_h^{n+1/2}\|^2\\ &\leq\frac{N\|\mathbf{u}\|_\infty^2\Delta t}{\lambda}\|\hat{C}_h\|^2-\frac{N\Delta t}{2}\Big(\int_{\Gamma_{\text{in}}}((g_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big)+\frac{N\Delta t\beta_1^2}{\lambda}\|\boldsymbol{\nabla}\hat{C}_h\|^2\\ &+\frac{2K_{\text{PF}}^2\Delta t}{\lambda}\sum_{n=0}^{N}\|f^{n+1/2}\|^2+\frac{N\Delta t\lambda}{4}\|\boldsymbol{\nabla}\hat{C}_h\|^2+(\bar{\omega}(C_h^{N+1}-C_h^0),\hat{C}_h).\end{aligned}$$

Here,

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

After simplification, we get the desired result. ∎

Remark 4.16. Putting (4.37) into (4.36), we get,

$$\begin{aligned}
&\frac{\bar{\omega}}{2}\|C_h^{n+1}\|^2 - \frac{\bar{\omega}}{2}\|C_h^n\|^2 + \frac{\Delta t}{2}\Big(\int_{\Gamma_{\rm out}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\vec{n})ds\Big) + \Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\\
&= -\frac{\Delta t}{2}\Big(\int_{\Gamma_{\rm in}}((g_h)^2)(\mathbf{u}\cdot\vec{n})ds\Big) + \Delta t(f^{n+1/2},C_h^{n+1/2}-\hat{C}_h)\\
&+ (\bar{\omega}(C_h^{n+1}-C_h^n),\hat{C}_h) + \Delta t(\mathbf{u}\cdot\boldsymbol{\nabla}C_h^{n+1/2},\hat{C}_h) + \Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}\hat{C}_h).
\end{aligned} \tag{4.44}$$

If $f=0$ and $\hat{C}_h=0$ in (4.44), we get the balance of mass as follows

$$\begin{aligned}
&\frac{\bar{\omega}}{2}(\|C_h^{n+1}\|^2 - \|C_h^n\|^2) + \frac{\Delta t}{2}\Big(\int_{\Gamma_{\rm out}}((C_h^{n+1/2})^2)(\mathbf{u}\cdot\vec{n})ds\Big) + \Delta t(D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}C_h^{n+1/2})\\
&= \frac{\Delta t}{2}\Big(\int_{\Gamma_{\rm in}}((g_h)^2)(-\mathbf{u}\cdot\vec{n})ds\Big).
\end{aligned} \tag{4.45}$$

Recall that $\mathbf{u}\cdot\vec{n} > 0$ on $\Gamma_{\rm out}$ and $\mathbf{u}\cdot\vec{n} < 0$ on $\Gamma_{\rm in}$.

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

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

THEOREM 4.17. *Suppose the assumptions (F1)-(F7) are satisfied so that the fully discrete formulation has a smooth solution* $\{C_h^n\}_{n=0}^N \in L^2(0,T;H^1(\Omega))$ *and the variational formulation with affine adsorption given by* (4.29) *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* $1\le r\le k+1$ *and* $N>0$ *there exists a positive constant* K *such that:*

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

Proof. Let the approximate solution at time $t^{n+1/2}$ be $C_h^{n+1/2}$. Then by using the midpoint method, we get, the fully discrete variational formulation as follows:

Given $C_h^n\in X^h$, find $C_h^{n+1}\in X^h$ such that $C_h^{n+1}\Big|_{\Gamma_{\rm in}} = g_h$ and satisfying,

$$(\bar{\omega}\frac{C_h^{n+1}-C_h^n}{\Delta t},v_h) + (u\cdot\boldsymbol{\nabla}C_h^{n+1/2},v_h) + (D\boldsymbol{\nabla}C_h^{n+1/2},\boldsymbol{\nabla}v_h) = (f^{n+1/2},v_h),\ \text{for all}\ \ v_h\in X^h_{0,\Gamma_{\rm in}}(\Omega). \tag{4.46}$$

Let C_t represent $\frac{\partial C}{\partial t}$. We write the following variational formulation for the exact solution C.

$$(\bar{\omega}\frac{C(t_{n+1})-C(t_n)}{\Delta t},v) + (\mathbf{u}\cdot\boldsymbol{\nabla}C(t_{n+1/2}),v) + (D\boldsymbol{\nabla}C(t_{n+1/2}),\boldsymbol{\nabla}v) = (f^{n+1/2},v) + (r^n,v),\ \forall\ v\in H^1_{0,\Gamma_{\rm in}}(\Omega). \tag{4.47}$$

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 (4.47) and then subtract (4.46) from (4.47) to get

$$(\bar{\omega}\frac{e^{n+1}-e^n}{\Delta t},v_h) + (\mathbf{u}\cdot\boldsymbol{\nabla}e^{n+1/2},v_h) + (D\boldsymbol{\nabla}e^{n+1/2},\boldsymbol{\nabla}v_h) = (r^n,v_h),\ \text{for all}\ \ v_h\in X^h_{0,\Gamma_{\rm in}}(\Omega). \tag{4.48}$$

Then for any $\hat{C}_h \in X^h$ such that $\hat{C}_h\Big|_{\Gamma_{\text{in}}} = g_h$, 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 Γ_{in}. Hence $\phi_h^n\Big|_{\Gamma_{\text{in}}} = 0$. We choose $v_h = \phi_h^{n+1/2} \in X^h_{0,\Gamma_{\text{in}}}$. Then (4.48) becomes

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

We obtain lower bounds for the terms on the left and upper bounds for the term on the right of (4.49) by using the assumptions and Young's and Cauchy-Schwarz inequalities. We rewrite the first term in (4.49),

$$(\bar{\omega}\frac{\phi_h^{n+1} - \phi_h^n}{\Delta t}, \phi_h^{n+1/2}) = \frac{\bar{\omega}}{2\Delta t}(\|\phi_h^{n+1}\|^2 - \|\phi_h^n\|^2). \tag{4.49}$$

Following the same steps in Theorem 4.14, we get the following bounds

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\phi_h^{n+1/2}, \phi_h^{n+1/2}) \geq 0. \tag{4.50}$$

$$(D\boldsymbol{\nabla}\phi_h^{n+1/2}, \boldsymbol{\nabla}\phi_h^{n+1/2}) \geq \lambda\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.51}$$

$$(\mathbf{u}\cdot\boldsymbol{\nabla}\eta^{n+1/2}, \phi_h^{n+1/2}) \leq \frac{2K_{\text{PF}}^2\|\mathbf{u}\|_\infty^2}{\lambda}\|\eta^{n+1/2}\|_1^2 + \frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.52}$$

$$(D\boldsymbol{\nabla}\eta^{n+1/2}, \boldsymbol{\nabla}\phi_h^{n+1/2}) \ \leq \frac{2\beta_1^2}{\lambda}\|\eta^{n+1/2}\|_1^2 + \frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.53}$$

Next,

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

Hence, after applying Cauchy-Schwarz inequality we get,

$$(\bar{\omega}\frac{\eta^{n+1} - \eta^n}{\Delta t}, \phi_h^{n+1/2}) \leq \frac{2K_{\text{PF}}^2\bar{\omega}^2}{\lambda\Delta t^2}\big(\int_{t_n}^{t_{n+1}} \|\eta_t\|^2 d\tau\big) + \frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2. \tag{4.54}$$

Next,

$$(r^n, \phi_h^{n+1/2}) \leq \frac{\lambda}{8}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 + \frac{2K_{\text{PF}}^2}{\lambda}\|r^n\|^2. \tag{4.55}$$

Combining (4.49)-(4.55), we get

$$\begin{aligned}
&\frac{\bar{\omega}}{2\Delta t}(\|\phi_h^{n+1}\|^2 - \|\phi_h^n\|^2) + \frac{\lambda}{2}\|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2\\
&\leq \frac{2K_{\text{PF}}^2\|\mathbf{u}\|_\infty^2\|\eta^{n+1/2}\|_1^2}{\lambda} + \frac{2\beta_1^2\|\eta^{n+1/2}\|_1^2}{\lambda} + \frac{2K_{\text{PF}}^2\bar{\omega}^2}{\lambda\Delta t}\big(\int_{t_n}^{t_{n+1}} \|\eta_t\|^2 d\tau\big) + \frac{2K_{\text{PF}}^2}{\lambda}\|r^n\|^2.
\end{aligned} \tag{4.56}$$

Multiplying (4.56) by $\frac{2\Delta t}{\bar{\omega}}$ and summing over $n = 0$ to $n = N$, we get

$$
\begin{aligned}
\|\phi_h^{N+1}\|^2 + \frac{\lambda}{\bar{\omega}} \sum_{n=0}^{N+1} \Delta t \|\boldsymbol{\nabla}\phi_h^{n+1/2}\|^2 \ &\le \Big(\frac{4K_{\mathrm{PF}}^2\|\mathbf{u}\|_\infty^2 + 4\beta_1^2}{\bar{\omega}\lambda}\Big) \sum_{n=0}^{N+1} \Delta t \|\eta^{n+1/2}\|_1^2 \\
+ \frac{4K_{\mathrm{PF}}^2}{\lambda\bar{\omega}} \int_0^T \|\eta_t\|^2 dt + \frac{4K_{\mathrm{PF}}^2}{\bar{\omega}\lambda} \sum_{n=0}^{N+1} \Delta t \|r^n\|^2 + \|\phi_h^0\|^2. &
\end{aligned} \tag{4.57}
$$

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, (4.57) implies

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

Hence, we can write,

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

By using the Lemma 2.1, we get

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

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

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

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

$$
\sum_{n=0}^{N+1} \Delta t \|e^{n+1/2}\|_1^2 \le \Big(2 + \frac{8K_{\mathrm{PF}}^2\|\mathbf{u}\|_\infty^2 + 8\beta_1^2}{\lambda^2}\Big) \sum_{n=0}^{N+1} \Delta t \inf_{\substack{\hat{C_h} \in X^h \\ \hat{C_h}|_{\Gamma_{\mathrm{in}}} = g_h}} \|C^{n+1/2} - \hat{C}_h\|_1^2
$$

$$+\frac{8K_{\rm PF}^2\bar{\omega}^2}{\lambda^2}\int_0^T \inf_{\substack{\hat{C_h}\in X^h\\ \hat{C_h}|_{\Gamma_{\rm in}}=g_h}} \Big\|\frac{\partial(C-\hat{C_h})}{\partial t}\Big\|^2 dt + \frac{8K_1TK_{\rm PF}^2}{\lambda^2}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2 + \frac{2\bar{\omega}}{\lambda}\|\phi_h^0\|^2.$$

Let g_h be the interpolant of g in $X^h_{\Gamma_{\rm in}}$. Then by using Lemma 2.3, for $1 \le r \le k+1$ we get,

$$\begin{aligned}\sum_{n=0}^{N+1}\Delta t\|e^{n+1/2}\|_1^2 &\le \Big(2+\frac{8K_{\rm PF}^2\|\mathbf{u}\|_\infty^2+8\beta_1^2}{\lambda^2}\Big)K_2^2h^{2r-2}\sum_{n=0}^{N+1}\Delta t\|C^{n+1/2}\|_r^2\\ &+\frac{8K_{\rm PF}^2\bar{\omega}^2}{\lambda^2}K_2^2h^{2r-2}\int_0^T\Big\|\frac{\partial C}{\partial t}\Big\|_r^2dt+\frac{8K_1TK_{\rm PF}^2}{\lambda^2}(\Delta t^2\|C_{ttt}\|_{L^\infty(0,T;L^\infty)})^2+\frac{2\bar{\omega}}{\lambda}\|\phi_h^0\|^2.\end{aligned} \tag{4.58}$$

Let

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

Thus (4.58) implies the claim. ∎

5. Numerical Test. In this section, we perform numerical tests to show that the midpoint method described in Subsection 3.2 gives a second-order convergence rate for the considered PDE model for the constant, affine, and nonlinear, explicit adsorptions. Since the results are similar, we only show the nonlinear, explicit adsorption case. 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, the exact solution is $C(x,y,t) = t^2(x^3 - \frac{3}{2}x^2 + 1)\cos(\frac{\pi}{4}y)$. The true solution determines the body force f, initial condition C_0, and boundary conditions. The norms used in the table are defined as follows,

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

Next, for the plot of the 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 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 problem, 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 [22]

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

For the midpoint method, we use the standard (second order) linear extrapolation [37] 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 5.1: 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 5.2: Temporal convergence rates for the midpoint approximation with a Langmuir adsorption model to the non-steady-state problem.

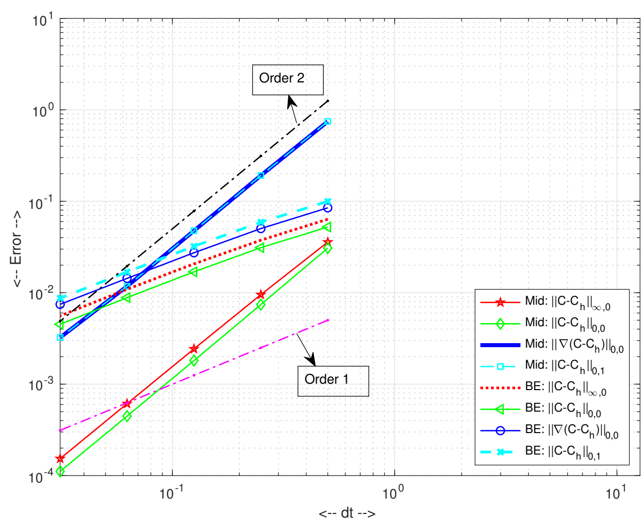

Fig. 5.1: Langmuir Isotherm: Temporal rate of convergence of BE and Midpoint, $T = 1.0$, $h = 1/128$. Notice that Midpoint is giving order 2 whereas BE is giving order 1.

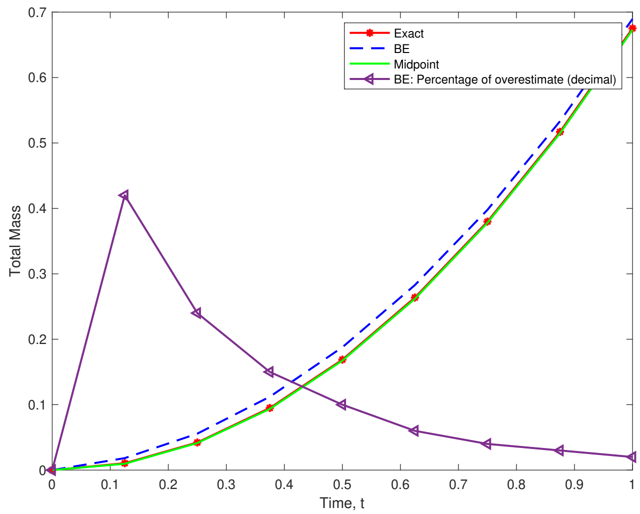

Fig. 5.2: Langmuir Isotherm: Comparison of total mass for exact solution, BE, Midpoint, $T = 1.0$, $h = 1/128$, $dt = 1/8$. Notice that BE overestimates total mass rather than underestimates.

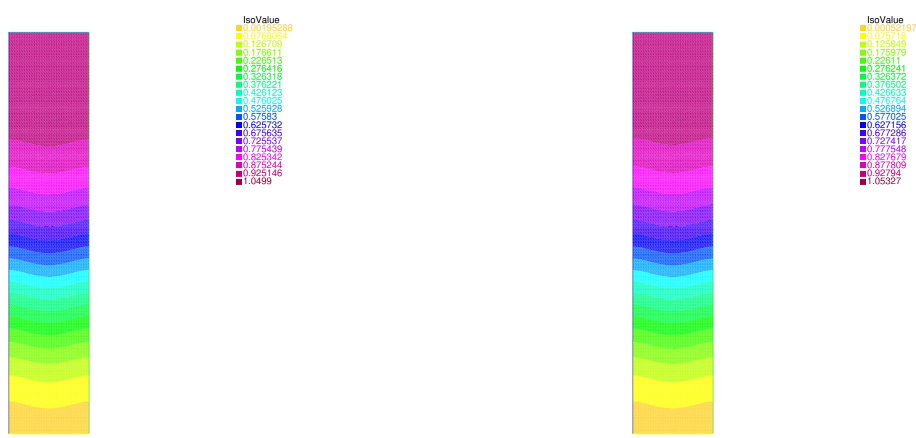

Fig. 5.3: Langmuir isotherm: Plot of concentration while using BE (Left) & Midpoint (Right), $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

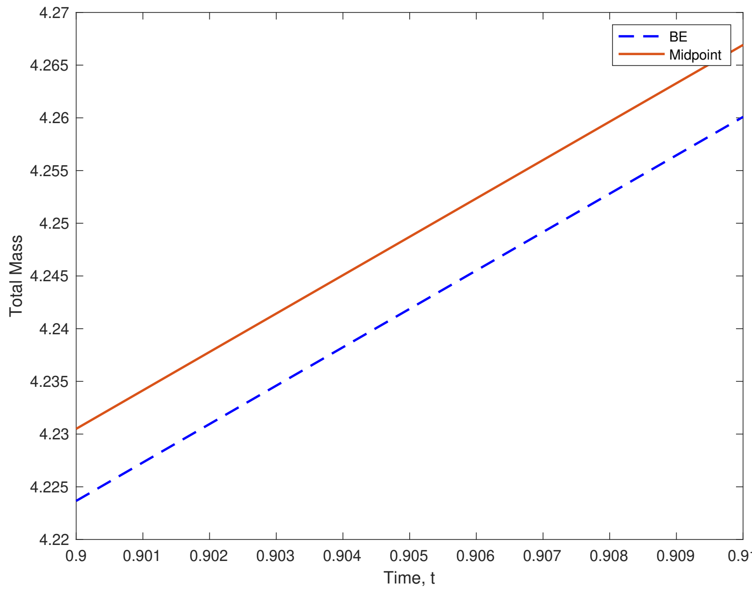

Fig. 5.4: Langmuir isotherm: Comparison of total mass, $f = 0$, $g = 1$, $T = 3.0$, $h = 1/128$, $dt = 1/128$, $\mathbf{u} = (0, 2x(x-2))$, $D = I$.

In the Figure 5.3, the concentration front gradually advances through the height of the membrane over time as it evolves following the contour of the velocity profile. Although we cannot visibly see the difference among two plots for BE and midpoint in Figure 5.3, we can see the significant difference in total mass evolution in Figure 5.4.

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6. Conclusion. We provided a detailed stability and error analysis of a simulation tool for modeling the adsorption process for the constant and affine adsorption cases. For the nonlinear, explicit adsorption, we proved stability analysis for the continuous case and semi-discrete case and the existence of a solution for the fully discrete case. The error analysis for this case is more involved and under some assumptions, we were able to show an error estimate for the semi-discrete case. But numerically, we showed that the 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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