

Hybrid Ion Exchange and Biological Processes for Water and Wastewater Treatment: A Comprehensive Review of Process Applications and Mathematical Modeling

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Funding acquisition: Meng Wang;

Resources: Meng Wang;

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Abstract

Hybrid ion exchange (IX) and biological processes have been developed for various water and wastewater treatment applications. These hybrid systems integrate multiple physical, chemical, biological, hydrodynamics, and substrate transport processes to improve the treatment efficiencies and system stability. The mathematical description of the individual process has been well established previously; however, there is a lack of a holistic review and guidelines to develop hybrid models for different treatment systems. In this paper, we summarize the applications of hybrid IX and biological systems, critically review the representative individual process models, and propose the framework to integrate these models for the hybrid process. Additionally, we provide a comprehensive review of the equilibrium, kinetic, and thermodynamic models for the IX process and the key biological process models, along with their applied scenarios. Advanced data-driven modelling and its combination with mechanistic models are also discussed to overcome the drawbacks in conventional modeling approach. We highlight emerging techniques that would lead to higher fidelity models. This review provides a comprehensive guideline for the model development of hybrid systems and presents future research directions to build robust systems.

Keywords: water and wastewater treatment, ion exchange, biological processes, process applications, mathematical modeling

53 Nomenclature

Parameter	Definition
A	Interfacial area of the ion exchange (IX) resins
B	Constant in the Dubinin-Radushkevich (D-R) model
D_f	Diffusion coefficient within the biofilm phase
D_i	Diffusion coefficient in kinetic models within solid phase
D_{ij}	Surface diffusivity of the counter pair ions i - j
D_{is}	Surface diffusivity between i and the ionic groups s fixed within the solid phase
D_w	Substrate diffusion coefficient in the bulk liquid
F	Faraday constant
K	Equilibrium constant
$K_{B,j}^A$	Equilibrium constant for functional group j
K_F	Constant for an ion exchange equilibrium process in the Freundlich model
L_f	Thickness of the biofilm
L_w	Thickness of the hypothetical boundary layer
N_i	Flux of ion i
Q_{max}	Maximum IX capacity
Q_0	Monolayer adsorption capacity
R	Diameter of the IX resin
S_b	Concentration of substrate in the bulk liquid
S_f	Concentration of the substrate within the biofilm phase
S_s	Concentration of substrate at the interface of liquid and biofilm
T	Absolute temperature
V	Volume of the liquid
a_i	Ion activity of i
b	Constant which depends on the free energy of the IX
c_e	Equilibrium liquid phase concentration
c_i	Concentration of i in the liquid

n	Constant for specific IX process in the Freundlich model
k_1	Rate constant of the first order sorption
k_2	Rate constant of the second order sorption
k_f	Mass transfer coefficient in the liquid film
q_i	Concentration of i in the solid phase
q_e	Equilibrium solid phase concentration in the ion adsorption model
q_{max}	Ion-exchange capacity of the solid material in the D-R model
r	Radial position in the solid phase
r_f	Substrate utilization rate within the biofilm phase
r_s	Substrate utilization rate
t	Time
y_j	Mole fraction of ion j
y_s	Mole fraction of ionic fixed group s
ε	Polanyi potential
$\mathfrak{R}$	Ideal gas constant
Φ	Electric potential
$\nabla \bar{\mu}_i$	Surface chemical potential gradient of i

1. Introduction

In the United States, 46% of the total river and stream miles were classified as poor while 21% of the lakes are suffering from eutrophication resulted from nutrients overloading (USEPA 2017). Biological water and wastewater treatment systems are commonly used to remove nutrients, organic contaminants, and metals to protect ecosystems and public health (Rani et al. 2019). However, toxic compounds, irregular flow and transient loadings of the influent may impact the performance and the stability of biological processes (Jiang et al. 2019; Saidulu et al. 2021; Torres-Franco et al. 2021; Yenigün and Demirel 2013). Ion exchange (IX) is a reversible process where ions in insoluble solid materials are exchanged with other ions in an aqueous phase with a stoichiometrically equivalent amount (Saidulu et al. 2021). Hybrid IX with biological processes has the potential to abate the adverse impact of toxicities and inhibition on microorganisms and enhance system performance (Aponte-Morales et al. 2018; Beigbeder 2023; Lin et al. 2020; Waki et al. 2020; Wang et al. 2011).

IX materials such as zeolites and synthetic IX resins have been used in the hybrid IX and biological systems (Liu et al. 2020; Wang et al. 2018). In addition to abating the inhibition of high ammonia concentrations of high-strength wastewater, the hybrid process has been applied to the removal of heavy metals and natural organic matter (NOM). Examples of the applications include hybrid IX and algal systems (Wang et al. 2018), onsite wastewater treatment systems (Chen et al. 2019; Rodriguez-Gonzalez et al. 2016; Wang et al. 2011), and low impact development (LID) systems (Dietz 2007). Interactive IX and biological phenomena of the hybrid process induce complexity in understanding contaminant removal mechanisms. Elucidating these interactions is critical for system design and the enhanced efficacy of hybrid treatment systems. A recent review on the zeolite application in biological wastewater and solid waste treatment described the integration of zeolite ion-exchanger in anaerobic digestion, biological nutrient removal and composting for nutrient and heavy metal removals (Montalvo et al. 2020). Hybrid IX and biological processes can also be applied to stormwater and drinking water treatment. Additionally, there is a lack of review of the mathematical modeling of the hybrid system, which can decipher the interactions of the IX and biological processes and aid the system design.

Mathematical models are helpful tools to guide the design and optimization of water and

wastewater treatment systems and predict system performance (Hamed et al. 2021; Pell and Wörman 2009). Mathematical modeling of hybrid IX with biological processes, such as biological nutrient removal (BNR) and photosynthesis have been presented in prior studies (Aponte-Morales et al. 2018; van der Steen et al. 2015; Wang et al. 2018). These models incorporated mechanisms including IX equilibrium, mass transfer, and biological kinetics. However, there is a lack of best practices guiding the development of mathematical models for hybrid IX and biological systems, given the wide applications of these systems. Moreover, hybrid systems include reactions in different phases and mass transfer on each interface. The selection of models for each process is critical in developing hybrid IX and biological models. Thus, it is vital to assess the appropriate approach based on the system configuration and the objective of the applications by optimizing related variables with the assistance of mathematical model.

This review assesses the current state-of-the-art of hybrid IX and biological treatment processes, including their applications and mathematical models. The main advantages of hybrid systems are highlighted as the reduction of ammonia toxicity for wastewater treatment, the attenuation of transient influent system loading, and the extended life cycle of materials due to bioregeneration. Mathematical models are essential tools for improving hybrid system design and testing new hypotheses given the multiple (physical, chemical, and biological) mechanisms in these systems. Data-driven approaches are also illustrated as an advanced mathematical method to combine with mechanistic models to improve the understanding of the complicated IX and biological processes in hybrid systems. This review highlights properties and commonalities among modeling approaches and provides future guidance on research efforts to establish more robust hybrid systems.

2. Applications of hybrid ion exchange and biological processes

The hybrid IX-biological systems can be applied for the treatment of wastewater, stormwater runoff, and drinking water. Various applications and the system performance are summarized in Table 1. More details of the different applications are discussed in the following subsections.

Table 1. Summary of recent research on hybrid IX-biological systems

Process	Type of water treated	System description	IX material	Dosage	Performance	Reference
IX-anaerobic digestion	Swine waste diluted with tap water	Batch	Zeolite	20 g/L	Methane production was improved by 210% compared with the one without zeolite.	Wang et al. 2011
IX-anaerobic digestion	Waste activated sludge	Batch	Natural zeolite	0.1 g/g VSS	Methane production was improved by 20% compared with the one without zeolite.	Tang et al. 2023
IX-denitrification	Nitrate-contaminated drinking water	Packed column with an empty bed contact time (EBCT) of 10 min; zeolite was regenerated in batch mode	Nitrate selective resin	1 g/L	The system can still achieve NO_3^- removal efficiencies of over 90% after 4 cycles of bioregeneration.	Ebrahimi and Roberts 2013
IX-nitrification	Centrate from anaerobic digestion of swine waste	Batch	Chabazite	150 g/L	The nitrification rate was increased from 0.16 to 0.36 mg-N (g-VSS) ⁻¹ h ⁻¹ .	Aponte-Morales et al. 2018
IX-nitrification-denitrification	Anaerobically digested swine wastewater	Constructed wetland with tidal flow of 50 L/d	Zeolite	340 g/L-reactor*	NH_4^+ -N and COD removal efficiencies were 61% and 86% under tidal operation respectively.	Han et al. 2019b
IX-nitrification-denitrification	Landfill leachate	Zeolite-biological aerated filter with hydraulic retention time (HRT) varying from 5.36 to 8.85 h	Natural zeolite	55.6% (v/v)	NH_4^+ -N, and total nitrogen (TN) removal efficiencies were about $93.5 \pm 2.4\%$ and $74.7 \pm 9.4\%$, respectively and stable FA was maintained to inhibit NOB to achieve nitrite production rate of 1.38 kg NO_2^- -N m ⁻³ day ⁻¹ .	Chen et al. 2019
IX-nitrification-denitrification	Urban domestic sewage	Sequence batch reactor (SBR) with an HRT of 12 h	Zeolite powder	0.9 g/L	The removal rates of TN and total phosphate (TP) were improved of by 4% and 2 %.	Lin et al. 2020
IX- nitrification-denitrification	Synthetic wastewater	Aerated zeolite trickling filter with an HRT of 24 h	Zeolite	-	Total nitrogen removal efficiency was enhanced to 80%.	Liu et al. 2021

IX-partial nitrification-Anammox	Iron oxide red wastewater	Two-stage zeolite-biological aerated filter with HRT between 5.8 h and 11.6 h	Natural zeolite	87.5% (v/v)	TN removal efficiency was above 70% in the steady stage, among which 52% was removed in the 1 st filter by zeolite and 48% was removed in the 2 nd filter by biological process.	Feng et al. 2019
IX-sulfur oxidizing denitrification	Slaughterhouse wastewater	Up-flow packed bed reactor with an EBCT of 8 h	Zeolite	826 g/L-reactor*	NH ₄ ⁺ -N and NO ₃ ⁻ -N removal efficiencies were almost 100%, with 56% increase compared with traditional sulfur oxidizing denitrification.	Tong et al. 2022
IX-algal photosynthesis	Centrate from anaerobic digester	Batch, with algae harvested twice	Chabazite	60, 150, and 250 g/L	NH ₄ ⁺ -N concentrations were reduced from over 1000 mg/L to around 10 mg/L, with the removal efficiency over 90%.	Wang et al. 2018
IX-algal photosynthesis	Secondary urban wastewater (UWW)	Pretreated UWW with zeolite, and then switched to sequential-batch cultivation mode	Commercial natural zeolite	25, 50, 75% and 100% (v/v)	The average biomass yield with 50% zeolite medium was about 70% higher than the one without zeolite.	López-Rosales et al. 2022
IX-algal photosynthesis	Centrate from anaerobic digester	Batch	Clinoptilolite	100 g/L	NH ₄ ⁺ -N removal efficiency was 99%, which was increased by 209% in comparison with the one without clinoptilolite.	Beigbeder 2023
IX-algae-yeast consortia	Swine wastewater	Batch	Synthetic zeolite	75, 100, 125, and 150 g/L	The highest removal efficiencies of TN, NH ₄ ⁺ -N, and TP were 94%, 99%, and 84%, respectively.	Lu et al. 2023
IX-biodegradation	Untreated drinking water	Drinking water treatment pilot plant with an EBCT of 10.8 min	Anion exchange resin-Purolite® A860	-	DOC removal efficiency was 81%, improved by over 22% compared with that of granular activated carbon (GAC) or biological activated carbon (BAC).	Liu et al. 2020

110 *Calculated based on literature and the unit is g zeolite/L reactor

2.1 Mitigation of ammonia toxicity in biological wastewater treatment processes

High ammonia concentrations in centrate from anaerobic digesters, agricultural wastewater and industrial wastewater are toxic to microorganisms by inhibiting the activity of cytosolic enzymes or affecting the pH and concentrations of other cations inside microbial cells (Kadam and Boone, 1996; Liu et al. 2019). In BNR processes, free ammonia (FA) concentrations ranging from 10-150 mg/L have been shown to inhibit ammonia oxidizing bacteria (AOB) activity, while 0.1-1 mg/L inhibit nitrite oxidizing bacteria (NOB) (Anthonisen et al. 1976; Jiang et al. 2019). In addition, long-term inhibition by FA changes the cell density and morphology of AOB, reducing system recoverability (Jiang et al. 2019). High concentrations of FA can also inhibit other biological processes, such as the anaerobic digestion process (Chen et al. 2008; Jiang et al. 2019; Li et al. 2023) and algal photosynthesis (Lu et al. 2019).

IX resin amended systems have been used to abate ammonia toxicity. Among the IX resins, zeolites are commonly used in wastewater treatment (Han et al. 2021; Metcalf et al. 2003). Zeolites have porous structures consisting of three-dimensional frameworks of SiO_4^{4-} and AlO_4^{5-} tetrahedra linked through shared oxygen atoms, and occupied by alkali (e.g., Li^+ , Na^+ , K^+) and alkaline earth cations (e.g., Be^{2+} , Ca^{2+} , Mg^{2+}), which lead to high cation exchange abilities. The selectivity sequence for some cations is $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. The system can also be used for heavy metal removal and the selectivity sequence for heavy metals are affected by pH (Colella 1996; Inglezakis et al. 2003). Natural zeolites have a high affinity for NH_4^+ and can be integrated with biological processes to reduce ammonia toxicity and improve the system performance (Fig. 1). Na^+ is the major counter ion with NH_4^+ when using zeolite as the IX resin. After IX process, biological consumption of NH_4^+ in the liquid phase creates the concentration gradient that promotes the desorption of NH_4^+ from solid phase of the zeolite, thus the bioregeneration of the zeolite. Bio-regenerated zeolite can support the continuous operation of the wastewater treatment system (Hong et al. 2019; Rožić et al. 2000; Zamzow et al. 1990; Zhou and Boyd 2014). Zeolite can also serve as the biofilm carrier and provide niches with favorable environmental conditions for microorganisms. For example, zeolite amended BNR provided aerobic/anaerobic conditions for nitrifiers and denitrifiers with counter diffusion of substrate and oxygen to enhance the system performance (Han et al. 2019a, Tang et al. 2023). The formation of biofilm will also boost the resilience of functional microorganisms in response to environmental

stressors. Additionally, K^+ and Mg^{2+} released during the IX process can promote biomass growth (López-Rosales et al. 2022, Tang et al. 2023). In those systems, factors such as pH, size of zeolites, contact time, zeolite dosage, and other cations in the wastewater will impact the IX behavior (Huang et al. 2010). Heavy metals in the wastewater such as Pb(II), Cd(II), and Cr(VI) can be removed by IX in the system, reducing the toxicity for biomass (Silva et al. 2023). Zeolite can also be applied for dye wastewater treatment due to the adsorption of dye on the surface of zeolite and biomass (Gneedy et al. 2022, Senila et al. 2022).

The combination of IX and nitrification process has been applied to landfill leachate treatment, swine waste treatment, and textile wastewater treatment (Aponte-Morales et al. 2018; Chang et al. 2009; Martins et al. 2017). Natural or modified zeolite has shown the potential to create a micro-environment that favors the growth of *Nitrosobacteria* to aid the partial nitrification-anammox (PN/A) process because adsorbing NH_4^+ onto zeolite benefitted the process by maintaining a suitable NO_2^-/NH_4^+ ratio (Chen et al. 2019; Waki et al. 2020). In addition, combining a membrane aeration module in a packed bed reactor for IX-nitrification-denitrification would improve the hydrodynamic conditions and the system performance (Almutairi and Weatherley 2015).

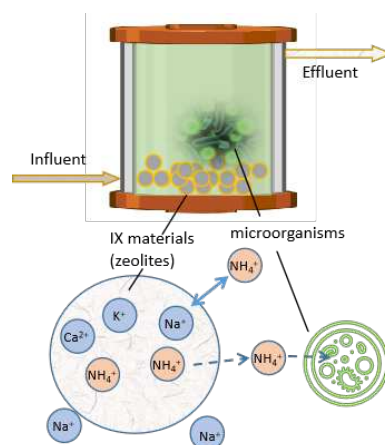


Fig. 1 The hybrid ion exchange (IX) and biological system showing the integration of natural zeolites and microorganism for NH_4^+ removal.

IX can also be combined with algae photosynthesis to reduce the ammonia toxicity when treating high ammonia wastewater and promote the biomass production (Lu et al., 2019). The systems have been applied to treat centrate from an anaerobic digester and secondary urban wastewater with low ammonia-tolerant marine microalgae (López-Rosales et al. 2022; Zalivina 2019). Moreover, IX

amended bioprocess can modulate bioproducts, such as lipids and protein, from algae biomass for different applications (Wang et al. 2018).

In the anaerobic digestion process, bioreactor with zeolite will reduce the ammonia toxicity and improve the methane production, when treating swine waste, livestock waste, and waste activated sludge (Tang et al. 2023; Zheng et al. 2015; Wang et al. 2011). The zeolite-biofilm retained functional microorganisms promoting hydrolysis and acidification, thus more substrates are available for methanogenesis for methane production (Tang et al. 2023).

2.2 Treatment of stormwater runoff

Excess nutrient discharge to surface water and groundwater systems can deteriorate water quality and ecosystems and pose significant public health issues (Akhtar et al. 2021; Bowen et al. 2007; Ouyang 2005). Among the various forms of nutrients, NH_4^+ has the highest concentration in the first flush, which is the initial portion of a runoff event (Hathaway et al. 2012). LID infrastructure, such as bioretention systems, is an effective solution since it can reduce peak flow rates, increase groundwater recharge, and remove heavy metals and nutrients (Dietz 2007).

In the conventional bioretention systems, nutrient removal efficiency is limited because there is only a single soil layer providing an aerobic environment for nitrification to occur, and the lack of anoxic area limited the denitrification process or extra NH_4^+ removal pathways (Erickson et al. 2014). Modifications have been made to enhance nitrogen removal by incorporating zeolites in the aerobic layer of bioretention systems (Fig. 2). An approach that amended soil media with zeolites found that the NH_4^+ removal efficiency could reach almost 70% in laboratory bioretention column studies (Jiang et al. 2018). Moreover, bioretention columns with zeolites demonstrated higher adsorption capacities for NH_4^+ removal than columns without zeolites (Jiang et al. 2019). However, one caveat is that the salinity of the effluent from the system increases due to the exchange of NH_4^+ with Na^+ . Another laboratory study using simulated stormwater showed that the hybrid IX and biological process was effective by allowing the IX material, clinoptilolite, to accumulate NH_4^+ from stormwater, which would be nitrified by nitrifiers later (Khorsha et al. 2021). Additionally, it was found that nitrification regenerated exchange sites on the clinoptilolite, allowing for continuous effective NH_4^+ removal.

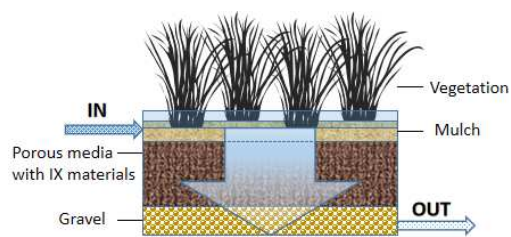


Fig. 2 Modified bioretention systems with ion exchange (IX) materials for improved nitrogen (N) removal

Constructed wetlands are also widely used for non-point source pollution control. Similar to bioretention systems, zeolites can serve as adsorbents in wetland systems, where NH_4^+ was adsorbed during cold seasons and subsequently desorbed during warm seasons for nitrification (Wen et al. 2012). In this way, nitrification was enhanced, abating seasonal nitrogen removal fluctuations. The removal efficiency of nitrogen was improved by 50%, compared with the system without zeolites (Wen et al. 2012). The NH_4^+ removal efficiency can reach over 60% even at a low temperature of 10 °C (Han et al. 2019b). Moreover, nitrous oxide (N_2O) emissions from wetlands can also be reduced by adding zeolite as a soil amendment (Zaman et al. 2008).

2.3 IX and biological process for organic matters and nitrate removal in drinking water

The presence of NOM in drinking water can impact odor, color, taste, and cause the formation of disinfection byproducts. The combination of IX and biological process can be applied to remove NOM from drinking water (Liu et al. 2020). Anion exchange resins can assist the removal of NOM through IX between NOM and its counter ion, such as chloride (Levchuk et al. 2018; Rahmani 2017). Biofilm formed on the IX resins can uptake the NOM from the exchange sites, leading to the regeneration of the IX resins (Fig. 3). IX resins for wastewater treatment can be divided into strong-acid cation resins, weak-acid cation resins, strong-base anion resins, weak-base anion resins, and Metal-selective chelating resins. For NOM removal, the most common rinses are strongly basic-anion exchange rinses, where the chemical matrix consists of styrene, divinylbenzene (DVB) and sulfonic acid functional groups (Levchuk et al. 2018). It has been confirmed in a laboratory-scale study that in a biofiltration system, 81% of the total dissolved organic carbon (DOC) removal can be achieved, which was much higher than around 65% DOC removal efficiency with biological activated carbon (Liu et al. 2020). When serving as a pre-treatment process for membrane filtration, the combination of IX and the biological process can reduce biofouling effectively by removing NOM (Schulz et al. 2017). The IX

and biological systems prevent the production of high concentrations of brine and NOM wastewater due to the bioregeneration of the system. While the conventional regeneration of IX resins by highly concentrated salt solution will produce high saline wastewater that is harmful to the aquatic environment.

Nitrate (NO_3^-) is another issue in drinking water, which can be solved by hybrid IX and biological method. NO_3^- can be removed by anion exchange resin, which can be regenerated by NaCl solution later, and the removal efficiency reached over 98%. The functional groups of resins for NO_3^- removal are tertiary or quaternary ammonium (Edgar and Boyer 2022). The NO_3^- saturated IX resin can also be recovered by liquid containing other inorganic ions and organic compounds. The regeneration spent brine was then purified by biological denitrification process before drained (Edgar and Boyer 2022; Tabassum 2019). The IX and bioregeneration nitrate removal process has been confirmed as a sustainable method, where the NO_3^- selective resin can be bioregenerated for six cycles with less than 6% resin capacity lost (Ebrahimi and Roberts 2013).

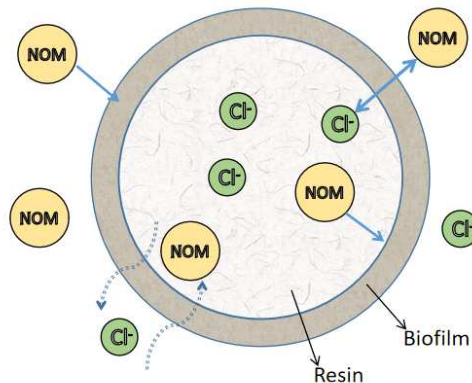


Fig. 3 Natural organic matter (NOM) removal process by hybrid ion exchange (IX) and biological process

3. Mathematical modeling of hybrid IX and biological processes

While experimental studies and new technologies are increasingly being developed for the hybrid processes, the lack of models that assist in elucidating mechanisms and facilitating reactor design limit enhanced efficacy of technologies. Mathematical models are powerful tools to understand the interactive mechanisms and predict the performance. The proper application of models would prove indispensable in IX material selection and determine optimal reactor configuration and operation conditions that lead to reduced cost and improved removal and recovery efficiencies. Previous models established for each individual process will be illustrated in the following sections. Hybrid ion exchange and biological process modeling can be developed through the integration of individual processes with the consideration of transport process among multiple phases and their interfaces (Fig. 4). The framework starts with a process description to conceptualize the mechanisms considered. Subsequently, experimental data should be collected to assist the calibration and verification of the individual components of the model for designing an integrated model for the hybrid system.

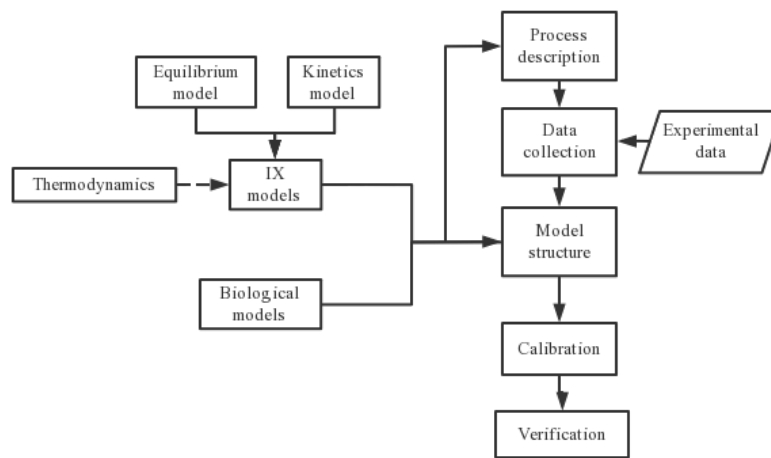


Fig. 4 Proposed approach for modeling the hybrid ion exchange (IX) and biological systems

Hybrid IX and biological processes are multiphase systems including bulk liquid, biomass, and solid (IX material) phases. Mass balance expressions for each phase of the system are required for the process description. Fig. 5 depicts the conceptual phases and interfaces of the hybrid IX and biological system including the substrate concentration gradient from the bulk liquid to the solid phase (Alonso et al. 2021; Shen et al. 2012). In this system, it is assumed that the substrates will be transported from the bulk liquid to the interface between the liquid and the biofilm phases, mainly by

diffusion, and the thickness of biofilm layer is constant (Gaebler and Eberl 2018; Grady Jr et al. 2011). Reactor configurations and operational conditions of the hybrid system largely dictate which phases should be included during model conceptualization.

In well-mixed batch hybrid systems which contain suspended microorganisms, solid IX materials, and liquid, the boundary layer and biofilm phases shown in Fig. 5 can be ignored when the biofilm is thin and does not inhibit the diffusion process (Aponte-Morales et al. 2018). Independent IX and biological process experiments can be conducted to aid the selection of appropriate IX model and biological model, respectively. This approach has successfully simulated data in hybrid algal photosynthesis and IX wastewater treatment system (Wang et al. 2018).

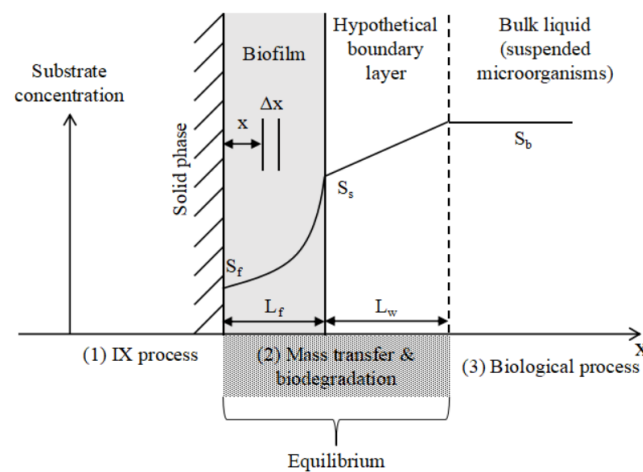


Fig. 5 The hypothetical mass transfer in hybrid ion exchange (IX) and biological system. 1) IX process within the solid phase; 2) Mass transfer and biodegradation processes within biofilm and boundary layer, including biofilm and hypothetical boundary layer which can be ignored in some conditions; 3) biological process in the bulk liquid phase.

In the following subsections, we critically review the individual IX and biological process modeling and interfacial phase (boundary between each phase) modeling that affects the hybrid modeling for batch and continuous operations.

3.1 Ion exchange model

Ion exchange is the key dynamic process that affects hybrid system performance. IX equilibrium and kinetic models are required to describe the physico-chemical process between the liquid and the solid phases.

3.1.1 Ion exchange equilibrium and kinetic modeling for hybrid systems

The models used to describe IX equilibrium can be divided into three groups: ion adsorption (semi-empirical model), homogeneous mass action, and heterogeneous mass action (Luqman, 2012; Mareev et al. 2022). Table 2 summarizes the underlying assumptions behind the various equilibrium models and the application scenarios.

The Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherms are semi-empirical adsorption models that describe single component adsorption. They have been widely used to describe IX equilibrium (Bezzina et al. 2020; Moghimi et al. 2020). In the mathematical description of hybrid systems, the main advantage of using these models is the relatively simple implementation for fitting equilibrium data.

The homogeneous mass action model assumes the IX sites are homogeneously distributed across the resin. This model contains the equilibrium among counter ions and is more theoretically sound. IX among multiple ions can be described using the homogeneous mass action model. However, it is more challenging to implement than semi-empirical models because more ions and parameters are involved leading to more complicated calculation.

The third group includes the heterogeneous mass action model which consider heterogeneous IX sites with different IX capacities (Koopal et al. 2020; Lito et al. 2012). For example, if IX resin comprises two-functional groups including sulfonate ($-\text{SO}_3^-$) and phosphate acid ($-\text{PO}_3^-$), where each group has a different IX capacity (Lito et al. 2012), heterogeneous mass action model should be used in this case. The heterogeneous model requires more parameters (e.g., the values of the equilibrium constant K for the different functional groups and ions) than the homogeneous model, which means more data are needed for fitting heterogeneous mass action models.

Four main kinetic models have been commonly applied to describe IX phenomena (Table 3). Among these models, semi-empirical models are based on the sorption capacity of the IX resin. They depend on the relative amounts (no matter if counted by volume or mass) of solid and liquid, i.e., if the amount of solid or liquid is changed, the rate constants (k_1 and k_2) in the models will be changed. Thus, the two semi-empirical equations can only be used in batch systems but not any other continuous systems with inlet or outlet flows during the experiments (Jiang et al. 2020; Luqman 2012; Rengaraj et al. 2007).

In Fick's law-based models, ionic diffusion is considered as the rate-limiting step in the IX process. Table 3 shows Fick's law-based equation assuming the IX particles are spherical. To complete the mathematical description, initial and boundary conditions are required. Equations 1-3 show the general specification of these conditions (Inglezakis et al. 2019):

$$q_i = q_{i,0}, c_i = c_{i,0} \text{ at } t = 0 \quad (1)$$

$$\frac{\partial q_i}{\partial t} = 0 \text{ at } r = 0, t > 0 \quad (2)$$

$$q_i = f(c_i) \text{ at } r = R \text{ for all } t \quad (3)$$

where c_i and q_i are the concentrations of component i in the liquid and solid phase, respectively, $c_{i,0}$ and $q_{i,0}$ are the initial concentrations in those phases, r is the radial coordinate, R is the IX resin particle radius, t is time, and $f(c_i)$ is one of the IX equilibrium models in Table 2.

It should be noted that the boundary condition in Equation 3 is specified at the IX resin surface and adds the most complexity to the numerical solution of the equations due to the non-linearity of IX equilibrium models. This requires numerical techniques such as predictor-corrector methods to be used in the numerical solution (Press et al. 2007).

The Nernst-Planck equation considers the electric field, which could affect the behavior of ions in an electrolyte solution. The model has been validated with IX resins for H^+ , Na^+ and bromate (BrO_3^-) removal (Mestri et al. 2023; Turner et al. 1966). Both ion-ion and ion-solid interactions are considered in the model. The diffusivity coefficient is not heavily dependent on the composition within IX materials but the properties of each counter ion. Additionally, in a binary system with dilute ionic solutions, both Nernst-Planck equation and Maxwell-Stefan equation can describe the process well (Lito and Silva 2008; Luo et al. 2018). It has been recognized that a chemical potential gradient is the driving force for ionic migration rather than concentration gradients. Nernst-Planck or Maxwell-Stefan formulations that represent more rigorous descriptions of the migration of a charged chemical species could be used in the future models (Cardoso et al. 2016; Figueiredo et al. 2018; Lito et al. 2015).

With the combination of appropriate equilibrium and kinetic models, the dynamic behavior of exchanged ions can be described and predicted. For instance, if the IX process is fast enough, equilibrium models can serve as one of the boundary conditions for Fick's law-based models on the surface of the solid phase (Aponte-Morales et al. 2018).

Table 2. Equilibrium models used to model IX equilibrium processes

Groups of the equilibrium model	Formula*	Assumptions	Applied IX resin and counter ions	References
Ion Adsorption and Related models	Langmuir model $q_e = \frac{Q_0 b c_e}{1 + b c_e}$	The homogeneous surface of the absorbent material; monolayer coverage.	Magnetite-natural zeolite and nickel ion (Ni^{2+}); zeolite and NH_4^+ ; activated teff straw and heavy metals (Cr, Cd, Pb, Ni, and Cu); metal organic frameworks and Pb(II).	Baseri and Tizro 2017; Bashir et al. 2019; Desta 2013; Goyal et al. 2021; Malekian et al. 2011; Masel 1996
	Freundlich model $q_e = K_F c_e^{1/n}$	Energetically heterogeneous surface.	Na-based zeolite and zinc ion (Zn^{2+}); ion exchange resin and NO_3^- ; hydrotalcite and chromium Cr (VI); synthetic zeolite and Co(II).	Chabani et al. 2006; Nasseh et al. 2021; Ostroski et al. 2009; Proctor and Toro-Vazquez 1996; Terry 2004; Wang and Guo 2020
	D-R model $q_e = q_{\max} e^{-B \epsilon^2}$	Heterogeneous surface or porous solid material.	Zeolites and several cations (Cs^+ , Sr^{2+} , Ca^{2+} and Mg^{2+}).	El-Rahman et al. 2006; Wang and Guo 2020
Homogeneous Mass Action Models	$K = \frac{q_{A^{z_A}}^{z_B} [B^{z_B}]^{z_A}}{(Q_{\max} - q_{A^{z_A}})^{z_A} [A^{z_A}]^{z_B}}$	No difference in IX capacity among sites.	Chabazite and NH_4^+ .	Koopal et al. 2020; Payne 2018
Heterogeneous Mass Action Models	$K_{B,j}^A = \frac{\bar{a}_{j,A}^{z_B} \alpha_B^{z_A}}{\bar{a}_{j,B}^{z_A} \alpha_A^{z_B}} (j = 1, 2)$	The solid phase is comprised of two or more functional groups with different IX capacities.	$\text{K}^+/\text{Na}^+/\text{Cl}^-/\text{clinoptilolite}$	Koopal et al. 2020; Luqman 2012

*In the Langmuir model, q_e is the equilibrium solid phase concentration (mg/g), Q_0 is the monolayer adsorption capacity (mg/g), c_e is the equilibrium liquid phase concentration (mg/L), and b is a constant which depends on the free energy of the IX process; in the Freundlich model, K_F (mg/g) and n are constants for the specific IX process; in the D-R model, $q_{\max}$ is the ion-exchange capacity of the solid material (mol/g), q_e is the equilibrium solid phase concentration (mol/g), B is a constant (mol^2/kJ^2), and ϵ is the Polanyi potential (kJ/mol), and it can be calculated as $\epsilon = \mathcal{R}T \ln(1 + 1/c_e)$; in the homogeneous mass action models, K is the equilibrium constant, A^{z_A} and B^{z_B} are counter ions with valences z_A and z_B , $q_{A^{z_A}}$ is the concentration of A^{z_A} in the solid phase, and $Q_{\max}$ is the maximum IX capacity; in the heterogeneous mass action models, $K_{B,j}^A$ is the equilibrium constant for each functional group j , a_i is the activity for i .

3.1.2 impact of temperature and competing ions

Temperature also plays a key in the IX process and therefore, thermodynamic considerations are important. The diffusion rate of related ions across an external boundary layer and internal sorption sites within the pores increases with an increase in temperature. In addition, equilibrium is influenced by temperature as shown in Eq. 5-7. The thermodynamic parameters, Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) can be calculated by the following equations:

$$\Delta G^0 = -\Re T \ln K_1 \quad (4)$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T \quad (6)$$

where K_1 and K_2 are the equilibrium constants at the temperatures at T_1 and T_2 respectively, and $\Re$ is the gas constant. A negative ΔG value means the IX process can happen spontaneously, a positive value of ΔH means the IX process is endothermic, and the values of ΔS in equation 6 reflects the affinity of the IX materials for the ions (El-Rahman et al. 2006). In a study using anion exchange resins, results showed that enthalpy and $1/T$ had a linear relationship (Singare et al. 2008; Sutirman et al. 2021), which was consistent with equation 5. Thus, after confirmed at several temperature points by experiment, the relationship of K and enthalpy can be determined, and the value of K can be calculated and used into IX models at different temperatures.

Hybrid system performance can also be significantly affected by multiple chemical species, so that IX equilibrium and kinetic models that account for more than one component are important. For the IX equilibrium model, a comprehensive study using a synthetic resin (Amberlite IR-120), considering ten binary systems and five ternary systems, found that the homogeneous mass action model provided better results than the heterogeneous mass action model (Valverde et al. 1999). However, another study using the natural zeolite, clinoptilolite, for a system with $K^+/Na^+/Cl^-$ /clinoptilolite showed that the heterogeneous mass action model provided a more accurate fit to experimental data (Lito et al. 2012). For kinetic models in multicomponent systems, which contain multiple counter ions, the Maxwell-Stefan equation can describe the IX process better than the other three models mentioned above (Luo et al. 2018; Silva and Lito 2007; Wesselingh et al. 1995). More experimental data and characterization of the IX resin is needed to identify the appropriate model that is theoretically sound.

361 Table 3. Kinetic models of IX process (Luqman 2012)

Kinetic model	Formula*	Description
Semi-empirical models	The pseudo first order rate equation: $\frac{d\bar{q}_i}{dt} = k_1 (\bar{q}_{i,e} - \bar{q}_i)$	The first-order equation is widely utilized to describe the IX mechanism.
	The pseudo second order rate equation: $\frac{d\bar{q}_i}{dt} = k_2 (\bar{q}_{i,e} - \bar{q}_i)^2$	Both equations are used in batch systems.
Fick's law-based model	$\frac{\partial q_i}{\partial t} = D_i \left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right)$	Assumes that IX resins are spherical, and the diffusion-driven model is based on Fick's law.
Nernst-Planck model	$N_i = -D_i \left(\frac{\partial q_i}{\partial r} \right) - D_i z_i q_i \frac{F}{\Re T} \left(\frac{\partial \phi}{\partial r} \right)$	Considers the impact of the electric field.
Maxwell-Stefan model	$-\nabla \bar{\mu}_i - F z_i \nabla \phi = \sum_{\substack{j=1 \\ j \neq i}}^{n_c} \frac{y_j \Re T (u_i - u_j)}{D_{ij}} + \frac{y_s \Re T u_i}{D_{is}}$	Assumes that surface diffusion is the only transport mechanism.

* k_1 is the rate constant of the first order sorption; $\bar{q}_{i,e}$ is the sorbed solute concentration at equilibrium; $\bar{q}_i$ is the concentration of ion i in the solid phase; k_2 is the rate constant of the second order sorption; D_i in Nernst-Planck model is the diffusion coefficient, and r is the radial position in the IX resin; q_i is the concentration of ion i at the selected position in the solid phase; N_i is the flux of ion i ; D_i in Maxwell-Stefan model is the self-diffusion coefficients of chemical species i ; F is the Faraday constant; R is the ideal gas constant; T is the absolute temperature (K); ϕ is the electric potential; $\nabla \bar{\mu}_i$ is the surface chemical potential gradient of i ; D_{ij} is the surface diffusivity of the pair i - j ; D_{is} is the surface diffusivity between i and the ionic groups s fixed within the solid phase; y_j is the mole fraction of ion j ; and y_s is the mole fraction of ionic fixed group, s .

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3.2 Mathematical modeling of biological processes

The commonly used biological models to describe the biological kinetics in hybrid systems include Activated Sludge Model (ASM), Anaerobic Digestion Model (ADM), River Water Quality Model (RWQM) and their variants (Table 4).

Based on the involved biological processes and the data collected, an appropriate model structure can be selected or modified, and then it can be calibrated by adjusting the parameters. After verification, the model can be applied to a specific system, of which some of the characteristics have been known, such as the initial biomass distribution and the initial substrates concentrations (Hulsbeek et al. 2002). These models have been serving as a valuable tool to design, operate, and predict the performance of various biological processes. In these models, except RWQM1, algal process is not involved. To simulate the algal-bacterial consortia, kinetic models should be modified by adding algal kinetic equations. Besides substrates, light intensity also plays a vital role in algae growth. Various kinetic models describing the algal process (Lee et al. 2015; Singh and Mishra 2019), can be integrated into the biological process models.

3.3 Impact of biofilm and its mathematical model development

When a biofilm layer is included in the hybrid modeling, diffusion and bioreaction within the biofilm layer should be considered (Deena et al. 2022; Verma et al. 2022). Table 5 lists the equations related to the processes involved. Assuming a spherical biofilm layer coating resin particle, Equation 8 describes the substrates' concentration in the biofilm layer (Cunningham and Mendoza-Sanchez 2006). On the interface of solid IX material and the biofilm, the substrate concentration can be calculated by the equilibrium equations described in the equilibrium modeling section.

The diffusion of the substrates from the bulk liquid to the interface between the liquid and the biofilm phases can be described by Equation 7 (Grady Jr et al. 2011). Fick's first law (Equation 10) can describe the flux exiting the boundary layer towards the biofilm.

When the mass transfer between biofilm and hypothetical boundary layer reaches equilibrium, Equation 11 is finally applied to describe the boundary condition at the liquid/biofilm interface, where the substrate is transferred from the liquid phase to the outer face of the biofilm (Rittmann and McCarty 2012). Various research on biofilm-covered granular systems and biofilm-membrane systems has confirmed this model (Chen et al. 2021; Rittmann and McCarty 2012; Shafahi and Vafai 2011;

Shen et al. 2012). However, there is a lack of research on the model of the biofilm attached to ion exchange resin because diffusion in the boundary layer is not a dominant step of the system (Shen et al. 2012; Walker and Weatherley 1997). One of the significant challenges in hybrid modeling is determining the dynamics of the biofilm thickness, L_f . Advances in soft matter research based on emerging phase-field methods are theoretically sound for tracking the biofilm/bulk liquid interface (Zhang et al. 2008).

In well-mixed batch systems, physico-chemical and biological models mentioned above are combined to describe the IX, mass transfer, and biological kinetics processes. In this case, the mass balance expression can be written as:

$$\frac{dc_i}{dt} = \frac{N_i A}{V} - r_s \quad (12)$$

where A is the interfacial area of the ion exchange resin particles, V is the volume of the liquid, c_i is the concentration of the i^{th} chemical species in the aqueous phase, N_i is the flux of ions between the bulk liquid and solid phase, r_s is the substrate utilization rate in the bulk liquid, and t is time.

In Equation 12, c_i equals S_b ; N_i can be substituted by N_s (Equation 8); A is the interfacial area of the liquid phase and the equilibrium layer, which means that the radius calculating for A is the sum of R , L_w , and L_f . Therefore, the overall model can be developed by combining Equation 7-12.

In terms of continuum-scale biofilm modeling, an approach such as phase-field modeling would represent a more state-of-the-art description (Li et al. 2020; Tierra et al. 2015). The Cahn-Hillard equation, which was initially applied in the material science community, has found applications in complex fluids and soft matter systems (Kim et al. 2016). The strength of phase-field modeling is that it would account for one of the biggest challenges in biofilm modeling related to the evolution of the free boundary at the interface between the bulk liquid and biofilm surface. Biofilms can be regarded as soft matter systems and are amenable to phase-field approaches. However, these models are yet to be applied widely within the environmental engineering discipline. Combining chemical potential driven ionic fluxes to describe IX and phase-field modeling for biological processes would represent a significant step forward in advancing hybrid IX and biological process modeling.

418 Table 4. Description and application of the models for biological process

Model	Processes included in the model	Application	Examples of application in different reactors and treatment systems
ASM1	Growth of biomass, decay of biomass, ammonification of organic nitrogen, hydrolysis of particulate organics	Modeling biological removal of organic carbon, NH_4^+ , and TN	Aerobic membrane bioreactor (MBR) treating dilute municipal wastewater; Cyclic activated sludge system (CASS) treating wastewater with different COD:N ratios. (Baek et al. 2009; Gao et al. 2018; Henze et al. 2000; Kang et al. 2014;)
ASM2 / ASM2d	Hydrolysis, processes of facultative heterotrophic organisms, processes of phosphorus-accumulating organisms, nitrification, chemical precipitation	Modeling biological removal of organic carbon, N, and P	ASM2: Bench-scale sequencing batch reactor (SBR) for phosphorus removal, with EPS concentration involved; ASM2d: Pilot plant was operated under a UCT configuration treating municipal wastewater. (García-Usach et al. 2010; Henze et al. 2000; Yang et al. 2017)
ASM3	Compared with ASM1: no decay of biomass but endogenous respiration	Modeling biological removal of organic carbon, NH_4^+ , and TN	CSTR system, where ASM3 was modified with nitrification/denitrification process; Shortcut nitrogen removal within an algal–bacterial consortium; Drinking water treatment by MBR for soluble microbial products (SMPs) (Arashiro et al. 2017; Henze et al. 2000; Iacopozzi et al. 2007; Shayan et al. 2022).
ADM1	Acidogenesis, acetogenesis, acetoclastic methanogenesis, hydrogenotrophic methanogenesis, physicochemical reactions	Simulating full-scale anaerobic sludge digestion, modeling biogas production	Pilot-scale two-stage aerobic digestion; Aerobic digestion treating agricultural waste (Blumensaat and Keller 2005; Galí et al. 2009).
RWQM1	Compared with ASM series: especially involved algae processes (growth, endogenous respiration, and death), and physicochemical reactions	Modeling for rivers, stormwater pollution, and water treatment plants	Oxygen and nitrogen conversion processes in the river; Algae-based activated sludge wastewater treatment process; High-Rate Algal Ponds (HRAPs). (Pierong et al. 2016; Reichert et al. 2001; Solimeno et al. 2017)

420 Table 5. Equations describing substrates' concentrations for each layer.

Equations	
$\frac{\partial S_f}{\partial t} = D_f \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial S_f}{\partial r} \right) - r_f, R < r < R + L_f$	(7)
$N_s = k_f (S_b - S_s)$	(8)
$k_f = D_w / L_w$	(9)
$N_s = D_f \left. \frac{\partial S_f}{\partial x} \right _{x=L_f}$	(10)
$k_f (S_b - S_s) = D_f \left. \frac{\partial S_f}{\partial x} \right _{x=L_f}$	(11)

* In Equation 7, S_f is the concentration of the substrate within the biofilm phase, D_f is the diffusion coefficient, r is a radial coordinate, and r_f is the substrate utilization rate in the biofilm layer; in Equation 8, N_s is the flux; S_b is the concentration of substrate in the bulk liquid, S_s is the concentration of substrate at the interface of liquid and biofilm; and k_f is the mass transfer coefficient of the liquid film; in Equation 9, D_w is the substrate diffusion coefficient in the bulk liquid; L_w is the thickness of the hypothetical boundary layer; in Equation 10, D_f is the effective diffusivity within the biofilm phase, $\frac{\partial S_f}{\partial x}$ is the concentration gradient, and L_f is the thickness of the biofilm.

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422 3.4 Modeling of continuous flow reactor

423 Models accounting for hydraulic processes should be developed for applications of hybrid
 424 modeling in full-scale water and wastewater treatment systems. (Benjamin and Lawler 2013; Polat
 425 Bulut and Aslan 2021). Irrespective of the system being dealt with, the mass balance theory remains the
 426 same. The mathematical description then involves advection-diffusion-reaction (ADR) processes
 427 (Clement et al. 1997). The addition of advection term in the ADR model involves more parameters,
 428 increasing the complexity in comparison to adsorption-biological models described in section 3.1-3.3.
 429 There is rich literature focused on IX or adsorption modeling work in column-like packed-bed reactors
 430 (da Costa et al. 2020; Ma et al. 2019). The modeling framework developed for the adsorption-
 431 biological column processes for biological active granular activated carbon (bGAC) system can be
 432 adapted to the hybrid IX-biological process (Lin and Ho 2022; Suksomboon et al. 2019). In their work,

the model for DOC removal was based on a similar mass transfer system as described in Fig. 5, taking adsorption equilibrium, kinetics, and ASM framework into consideration. The advection along the column depth was included as the key differentiating factor with the batch systems (Alonso et al. 2021). The term was based on mass balance equation in the column reactor including parameters like column depth and flow velocity.

There are also models for microbial growth and transport in porous media. Biofilm growth, attachment, and detachment process was also included in another model of a porous column (Gaebler and Eberl 2018). It simplified the porous column by dividing the whole column into small parallel, non-communicating flow channels. Groundwater flow system including advection-dispersion-reaction process, which is similar to the porous media column system, can also be modified to fit the continuous column system by including the IX term in the governing equation (Crop 2016; Gupta et al. 2021).

In addition to groundwater system, another example in the literature that models the ADR process is wettability alteration of carbonate rocks (Magzymov et al. 2021). Langmuir-based kinetics is used for modeling the key reaction of desorbing non-wetting components attached to the rock and removed through the chemically-altered water injection process during representative secondary and tertiary recovery stages. Transport of components through the system is modeled using advection and diffusion terms. Experimental data on oil recovery was used to calibrate the different model parameters and results show predictability under varied conditions of high/low flow rates or fast or slow reaction kinetics (Magzymov et al. 2021).

Since the continuous column systems mentioned above share similar processes with IX-biological continuous column systems, including solid phase adsorption, biological process, and transport process, modification of the models of IX continuous column, GAC system, continuous column with porous media, and the ADR process is an effective method to develop the continuous IX-biological model. What should be done is to adjust the model for each individual process based on the integrated frame model work.

4. Challenges in modeling of the hybrid IX-biological systems

One of the main challenges in hybrid system modeling is the limited availability of data. Sufficient experimental data is required to calibrate the hybrid model. For example, it is difficult to measure dissolved oxygen (DO) along the depth in the column systems packed with solid material,

which will affect the biological kinetics. When biofilm and porous IX materials are involved, it makes it more difficult to get the characterization and chemical dynamic data inside the biofilm or the porous media.

Another challenge is to determine the rate-limiting step in the hybrid system and select the appropriate mathematical descriptions. Early attempts at understanding the interplay between processes utilized empirical approaches to determine rate-limiting processes (Lahav and Green 2000). Their study investigated the effects of biofilm on IX capacity and kinetics. The empirical model showed that pore diffusion within the zeolite was the rate-limiting step. However, the limiting step shifted from pore diffusion to film diffusion in a system with biofilm-covered chabazite. The authors indicated the counter-intuitive nature of this result, given that film diffusion is 3 to 4 orders of magnitude greater than the typical pore diffusion coefficient in zeolites (Lahav and Green 2000). In addition, it is important to consider the mathematical description of the process to be included in the model. For example, the N metabolism pathways such as nitrification, denitrification, anaerobic ammonia oxidation (anammox), may vary from reactor to reactor. The biological model to describe the involved process should be modified accordingly to reflect the metabolic pathways. This illustrates the importance of models with a more robust theoretical basis to test various hypotheses related to the dynamics of whether biological or chemical processes exhibit more influence.

5. Outlook of hybrid ion exchange and biological modeling

5.1 Applications of data-driven approaches in biological-IX systems

The multiple physical-chemical-biological processes involved in the hybrid IX and biological process increased the complicity of the mechanistic modeling of the system. The rapidly advanced machine learning (ML) and artificial intelligence (AI) technologies provided a potential alternative to model the hybrid IX and biological systems. The ML/AI technologies have less dependence on the clarity of the process mechanism. If a data set with adequate quantity and quality is available, the ML/AI technologies can train a “black box” model that may accurately predict the characteristics of biofilm, chemical concentrations, and other variables in the hybrid IX and biological systems which could be challenges for traditional kinetics-based models as mentioned in the last section.

Numerous ML/AI studies have been conducted on biological wastewater treatment including activated sludge systems (Sin and Al 2021), anaerobic digestion (Cruz et al. 2022), and algal systems

(Sundui et al. 2021). Note that Sin and Al (2021), Cruz et al (2022), and Sundui et al (2021) are review papers that well summarized the state of art of ML/AI application in the corresponding specific biological wastewater treatment systems. Most of past ML/AL studies on biological wastewater treatment were focused on system fault detection, prediction of water quality or operation condition, and optimization of process control, as pointed out by the above review papers as well as several other review papers on data-driven approaches in wastewater treatment (Malviya and Jaspal 2021; Newhart et al. 2019; Singh et al. 2022).

ML/AI application in IX technology was relatively limited. Most of the existing reports focused on removal of heavy metals such as lead (Zeng et al. 2022), cadmium (Fawzy et al. 2018; Nasr et al. 2017), zinc (Ullah et al. 2020), nickel (Fawzy et al. 2016b), chromium (Fawzy et al. 2016a), and copper (Bhagat et al. 2021; Bleotu et al. 2018). Similar to biological wastewater systems, most of the past ML/AI applications in IX focused on variable prediction and operation condition optimization.

Although the application of ML/AI to an integrated IX-biological system is rare, the great success of ML/AI in biological systems and IX technologies indicates a bright future of overcoming the challenges in integrated biological-IX systems, like determination of the biofilm characteristics and the chemical concentrations within biofilm and estimating biofilm growth in porous formations, using ML/AI. In addition, response surface methodology (RSM) has been used for system optimization (Almasi et al. 2019), which can be combined with data-driven method such as artificial neural network (ANN) to optimize and predict the performance of the treatment process (Wang et al. 2022).

However, recall the challenge of limited data availability mentioned in the last section. It is a common challenge in many biological and chemical engineering systems. To address the low data availability issue, ML/AI models could be combined with a kinetic or mechanistic model, which may be developed based on prior known physical laws, to reduce the model dependence on data. One typical type of such a modeling framework is known as physics-informed neural networks (PINN). PINN has been demonstrated to be effective in modeling many engineering systems including fluids systems, chemical reaction systems, and water distribution systems (Falas et al. 2020; Raissi et al. 2019). Attempts of PINN have been extended to biological systems (Mei et al. 2019) and IX systems (Santana et al. 2022) in recent years. Sin and Al (2021) also proposed an integrated modeling framework consisting of mechanistic models and data-driven models as shown in Figure 6. However,

how to blend ML/AI models with mechanistic models to get the most powerful modeling framework is still in exploration. In the future, advancements on both sides (i.e., ML/AI models and mechanistic or kinetic models) would create unlimited possibilities in forming a new modeling framework to help improve the knowledge of biological systems.

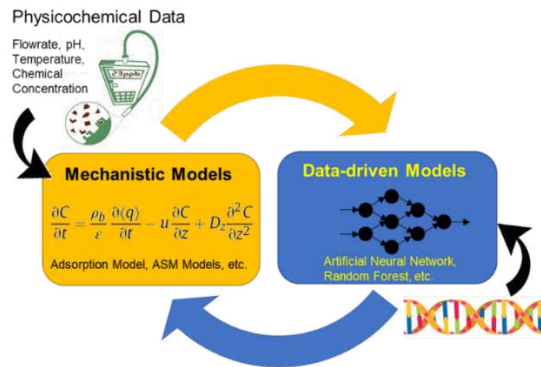


Fig. 6 A Proposed Integrated Modeling Framework of Mechanistic Model and Data-driven Models (Adapted from Sin and Al 2021).

5.2 Utilization of modern laboratory technologies to enhance hybrid IX modeling

Many of the modeling studies to date primarily use concentrations of ionic species and biomass in the bulk liquid in the case of batch systems, and effluent concentrations for fixed-bed hybrid systems for model calibration and validation. Advances in imaging technologies such as confocal microscopy and microprobes that enable determining chemical species concentrations within biofilms would provide an additional source of data for validating higher fidelity models (Beyenal and Babauta 2013; Wang et al. 2020).

The electric cell-substrate impedance sensing (ECIS) technique has been applied to monitor the activities of animal cells, determine cell properties, and test the toxicity of drinking water in real-time without invasion and damage to the cells (Wegener et al. 2000; Widder et al. 2015). Research on wastewater biofilm formation confirmed that a real-time cell analysis (RTCA) technology based on ECIS could be successfully used to quantitatively and continuously monitor the initial biofilm attachment process by obtaining the time-biomass images (Wang et al. 2020).

Since the concentrations of substrates and the extracellular environment such as DO and pH within the biofilm are challenging to be measured directly, microsensor technologies have been developed. The needle-type microsensor can be inserted into the biofilm to conduct the measurement

without damaging the biofilm and its structure. The results are reliable because the tip of the sensor is made of inert materials, which would not affect biofilm activities. At present, the technology has been applied in environmental biofilms, medical biofilms, and biofilms for energy and bioproducts, involving the processes of mass balances, reaction kinetics, and metabolic pathways (Babauta et al. 2012; James et al. 2008; Okabe et al. 2002). Profiles for both concentration gradients with depth and concentration over time can be obtained. The generated data can support the development of the mathematical models that describe these processes (Beyenal and Babauta 2013; Subramanian et al. 2020).

Advanced techniques like x-ray computed tomography can be implemented for capturing the growth of biofilm in porous formations. The advantage of such a technique is that it provides rich three-dimensional digital data of the growth of biofilm over the course of the experiment enabling the mapping of biofilm growth spatially and temporally (Davit et al. 2011, Iltis et al. 2011). Such data can be used to corroborate other observations of biofilm growth such as hydraulic conductivity changes. Such valuable experimental data at the pore- and column-scale can enable the development of suitable models at a scale relevant for wastewater remediation purposes (Peszynska et al. 2016).

There remain two major challenges with the application of x-ray computed tomography for imaging biofilm growth. The first is that the longer exposure of x-ray (or the dose of x-ray) can potentially stunt the growth of biofilm locally in the region where the biofilm growth is imaged. Such destruction can be minimized by acquiring faster x-ray scans to limit exposure and secondly by allowing enough time in between x-ray scans for biological processes to restabilize the local environment. The second challenge with x-ray imaging is being able to resolve the growth of biofilm in the wastewater domain. This is because both wastewater and biofilm phases present similar contrast when exposed to x-ray due to similar phase densities (Shastry et al. 2020). One way to circumvent this is by using contrast agents that selectively interact with the biofilm, for example, the application of Barium compounds like Barium sulfate particle suspensions that adhere to biofilm that provide a bright contrast with x-ray imaging (Davit et al. 2011; Ostvar et al. 2018). Other contrast agents suggested in the literature include ferrous sulfate where it is suggested that the oxidized state of ion allows for its adherence to the biofilm showing a brighter contrast during imaging (Carrel et al. 2017).

As the development of imaging and microsensor technologies evolves, biofilm characteristics

and processes will become accessible at finer spatiotemporal resolutions offering valuable information for calibrating biofilm models. In turn, the development of sophisticated biofilm growth models will help explain mechanisms of biofilm activities in hybrid systems.

6. Concluding Remarks

This review summarizes the application of hybrid ion exchange (IX) and biological processes to a wide range of environmental issues. We highlight the current state of modeling approaches and suggest a path toward advancing the current state-of-the-art. The models of individual processes in the hybrid systems already have comprehensive development theoretically and practically. However, there is a lack of applicable comprehensive mathematical model for the hybrid IX and biological systems. Models of similar systems can be modified to fit the purpose. Advanced data-driven model methods and emerging technologies can assist with the model development process. Emerging imaging and microsensor technologies can provide insight into the dynamics of the hybrid system and provide valuable information useful for model development. In addition, soft matter models can be adapted into environmental engineering applications as an alternative biofilm modeling approach. This review highlights hybrid IX and biological systems as an active area of research and elucidates the requirement for further efforts along various complementary avenues that would ultimately lead to the development of new technologies to address many pressing environmental problems.

Acknowledgment

This material is based upon work supported by the US National Science Foundation under Grant No.2000761 and the E. Willard & Ruby S. Miller Faculty Fellowship in the College of Earth and Mineral Sciences at The Pennsylvania State University. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the sponsors.

Statements and Declarations

- **Competing Interests**

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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