A hybrid algal photosynthesis and ion-exchange (HAPIX) process for side stream wastewater treatment: experimental and modeling studies

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ABSTRACT

A hybrid ion-exchange and algal photosynthesis (HAPIX) process was used for treatment of side stream centrate from an anaerobic digester treating waste activated sludge. Although the high NH_4^+-N concentration of the centrate (~1180 mg/L) inhibited algal growth in unamended controls, addition of zeolite reduced the ammonia toxicity due to its ion exchange capacity. Na^+ was the major cation exchanged with NH_4^+. Growth of algae further reduced the NH_4^+-N concentrations. Different zeolite dosages (60, 150, and 250 g/L) resulted in different concentrations of NH_4^+-N in solution. Algae grown in lower zeolite dosage (60 g/L) had high protein contents. A mathematical model that combined ion-exchange and algal photosynthesis processes predicted the aqueous NH_4^+-N concentration well. The HAPIX process is feasible for treatment of high NH_4^+-N strength side stream wastewaters while regulating intracellular algal biomass contents by adjusting zeolite dosages.

KEYWORDS

Ion-exchange, algal photosynthesis, side stream, mathematical modeling, NH_4^+ removal.

INTRODUCTION

Algal-based wastewater treatment systems have the potential to reduce the energy cost of wastewater treatment processes by utilizing solar energy for biomass growth and nutrient removal. Some algal strains that show tolerance to various environmental stresses, such as *Chorella* spp and *Scenedesmus* spp, have been used in treating wastewater (Franchino et al., 2013; Rai et al., 1996)*;* however, NH_4^+-N concentrations as high as 200- 300 mg/L are known to inhibit algae growth (Lin et al., 2007; Park et al., 2010, Wang et al. 2015). Many research studies on algal treatment of anaerobic digestion side streams have been published recently. However, in most of these studies the centrate was diluted for the growth of algae due to the high NH_4^+-N concentrations, which are toxic to algae. Alternative solutions are necessary to treat high NH_4^+-N strength wastewater without addition of freshwater.

Zeolites are natural hydrated aluminosilicate minerals that have been used to reduce ammonium inhibition of microorganisms due to their high affinity for ammonium ions (Malovanyy *et al.*, 2013; Rožić *et al.*, 2000). It is possible to use the ion-exchange (IX) capacity of zeolites to reduce the toxicity of ammonia to algae. By varying the dosage of zeolite the liquid phase ammonium concentrations are affected. As a result, algae are exposed to various levels of N, which has the potential to induce different intercellular contents. Low levels of N can result in high levels of lipid accumulation, whereas high levels of N result in high algal cell protein contents. Harvested algae

with different intracellular contents can be used for different purposes. For example, algae with high protein content can be used as biofertilizer, while algae with high lipid content can be used for biofuel production. In this study, a novel hybrid algal photosynthesis and IX (HAPIX) process was developed to treat centrate from anaerobically digested sewage sludge. A mathematical model was also developed that can be used to facilitate the design and operation of full scale HAPIX processes. No prior mathematical models have been developed for the novel HAPIX system. The objectives of this research were to: 1) evaluate the impact of zeolite dosage on the nutrient removal efficiency of HAPIX and intercellular contents of algal biomass produced in HAPIX and 2) develop mathematical models to predict the performance of HAPIX process with varying doses of zeolite.

METHODOLOGY

Centrate used in this study was obtained from a pilot anaerobic digester treating waste activated sludge from a local enhanced phosphorus removal treatment facility. The anaerobic digester was operated under thermophilic conditions with a solids residence time of 21 days. Effluent from the digester was centrifuged at 4000 rpm for 15 mins and the supernatant was further filtered through a 1.5 μm filter. The filtrate was collected as centrate for this study. The characteristics of the centrate are summarized in Table 1.

Table 1. Characteristics of centrate from anaerobic digestion of sewage sludge

Parameters	Unit	Value
NH_4^+-N	mg L^{-1}	1,180
TP	mg L^{-1}	265±4.2
VFA	mg L^{-1}	822±4.9
COD	mg L^{-1}	2,340±0
Alkalinity	mg L^{-1} as CaCO$_3$	2,585±304
pH	-	8.0±0.1

Wild-type algae *Chlorella* originally harvested from a local wastewater treatment plant were enriched in diluted sludge centrate for this study. Algae were settled for 24 hours, and the settled algae were collected as the inoculum for HAPIX reactors. The chlorophyll *a* and dry weight of the algal inoculum was 81.1±2.5 mg L^{-1} and 5,412±159 mg L^{-1}, respectively. The algal inoculum was

washed with DI water three times to remove residuals from the diluted sludge centrate before seeding the HAPIX reactors.

Bowie Chabazite (a type of zeolite, product code: AZLB-Ca) from St. Cloud Mine (New Mexico) was sieved to obtain a particle size between 1.0-1.4 mm. Zeolite dosages evaluated were 60 (IA-60), 150 (IA-150) and 250 (IA-250) g/L, based on isotherm and kinetics studies. 500 mL of centrate was added to 1L Erlenmeyer flasks with the desired amount of zeolite. Reactors were set up in duplicate in a 21±2°C constant temperature room. A shaking table set at 100 ± 10 rpm provided mixing for the reactors. After 24 hours when the IX reaction reached equilibrium, 40 mL of pre-washed algae inoculum were added into each bottle, which was recorded as Day 0. DI water was added as needed to make up for water evaporation. The reactors were continuously illuminated at 121±6 μmol/m^2/s. Zeolite particles were always resident at the bottom of reactors due to their high density. The reactors were operated for three phases (Figure 1). Algae were harvested by centrifugation at 3,800 rpm for 10 mins when the algal biomass concentrations reached stationary state. The supernatant was replaced into original reactors for the continuous growth of algae. Recycling of supernatant were repeated twice. Reactors with only algal biomass were also set up as controls. Harvested algae were freeze-dried to measure the protein and starch contents.
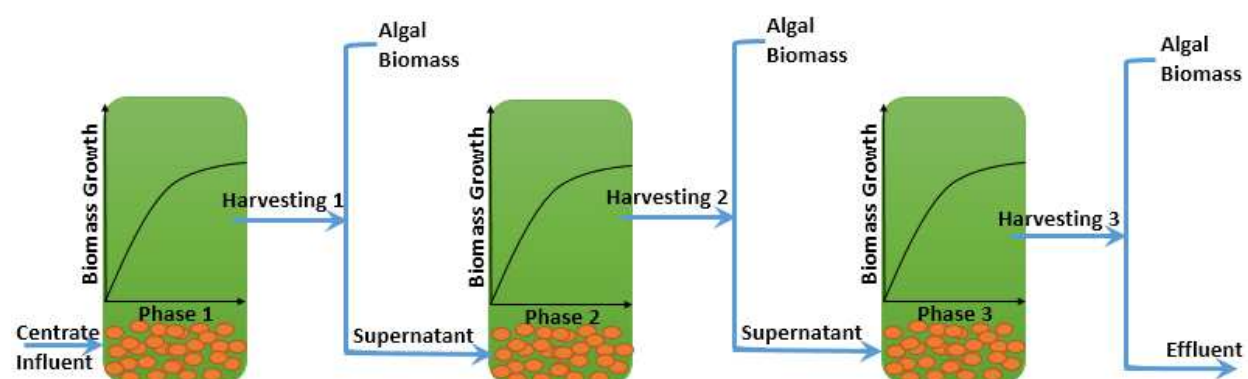

Figure 1. Overall operational strategy of HAPIX reactors

Analytical methods

Biomass dry weight (total suspended solids [TSS]), total volatile solids (VSS) and alkalinity were measured according to *Standard Methods* (APHA et al., 2012). COD was measured according to *Standard Methods* (5200B) using Orbeco-Hellige mid-range (0-1,500 mg/L) COD kits. Total P was measured using Hach TNT plus 845 test kits. Volatile fatty acid (VFA) concentrations were measured by the esterification method using Hach TNT plus 872 test kits. The results were reported as the equivalent concentration of acetic acid. Cations including NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} concentrations were measured using a Metrohm Peak 850 Professional AnCat ion chromatography (IC) system (Metrohm Inc., Switzerland).

The harvested algae were freeze-dried (Labconco, US) for starch and protein analysis. The total starch content of the algal biomass were measured using Megazyme total starch (AA/AMG) kits (catalog # K-TSTA), following Association of Official Agricultural Chemists (AOAC) Method 996.11. Protein content was analyzed by the bicinchionic acid colorimetric method (BAC) using Micro BC Assay Kits (Interchim, France).

MATHEMATICAL MODEL DEVELOPMENT

The mathematical model developed accounts for IX kinetics between co-ionic species NH_4^+ and Na^+ by surface diffusion (Auerbach et al., 2003) and algal growth under multiplicative limitation (Lee and Zhang, 2016). A conceptual model of the process is shown in Figure 2.
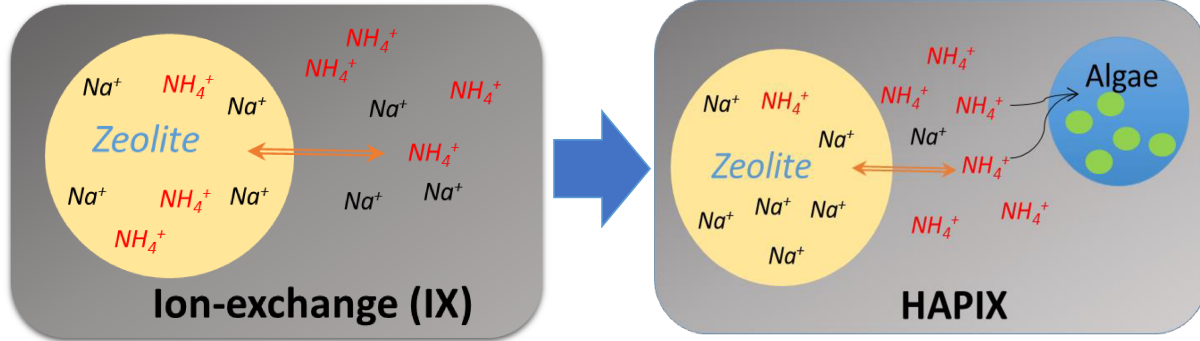

Figure 2: Schematic of the HAPIX process showing the combination of IX and algal photosynthesis.

In the HAPIX system the *main modeling assumptions* are given as follows:

1. The chabazite particles are spherical and homogenous, and the limiting diffusion process is an intraparticle surface diffusion process.
2. The IX process is such that the exchange of co-ions in the bulk liquid and solid phase is between NH_4^+ and Na^+, and there is no competition for IX sites by other cations.
3. Ion-ion and ion-solid interactions within the chabazite are ignored and Fickian diffusion is the driving mechanism for ionic migration.
4. There is dual limitation to algal growth due to light intensity and the nutrient NH_4^+.

In the aqueous phase, the NH_4^+ concentration is influenced by IX and utilization by algae, which leads to the following equation for the mass balance of the batch system:

$$\frac{dC_{NH_4^+}}{dt} = \frac{J_{NH_4^+} A}{V} - r_{NH_4^+} \tag{1}$$

where A is the chabazite particle interfacial area, V is the volume of liquid in the reactor, $C_{NH_4^+}$ is the NH_4^+ concentration in the aqueous phase, $J_{NH_4^+}$ is the mass flux of NH_4^+ ions between the bulk liquid and solid phase, and $r_{NH_4^+}$ is the rate of substrate utilization.

Several approaches have been adopted to model surface diffusion in zeolitic materials, including semi-empirical, Fickian-based, Nernst-Planck ,and Maxwell-Stefan models (Lito et al., 2012). The homogeneous surface diffusion model (HSDM) is a Fickian-based model that has been used successfully in previous studies to model ion exchange kinetics in microporous materials. The

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main model assumptions are that the material is homogeneous, isotropic, spherical, and that the surface diffusive flux is controlled by Fick's first law of diffusion leading to:

$$J_{NH_4^+} = -D_s \left. \frac{\partial q_{NH_4^+}}{\partial r} \right|_{r=R} \tag{2}$$

where D_S is the surface diffusivity coefficient, r is the radial coordinate in the chabazite particle, $q_{NH_4^+}$ is the NH$_4^+$ concentration in the solid phase, and R is the radius of chabazite particles. The mass balance for the chabazite phase based on the HSDM is:

$$\frac{\partial q_{NH_4^+}}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q_{NH_4^+}}{\partial r} \right) \tag{3}$$

The initial and boundary conditions were assigned to reflect the experimental conditions. During the adsorption phase of the experiment (24 hours), no NH$_4^+$ was assumed to be in the zeolite and strictly IX occurred. In the second phase, both IX and NH$_4^+$ utilization by algae were present. The end of the adsorption phase provided the starting point for the simulation of the HAPIX phase. The following equations are the initial and boundary conditions used:

$$\begin{cases} q_{NH_4^+}(0 \leq t \leq 24hr, r) = 0 \\ q_{NH_4^+}(t > 24hr, r) = q_{hpx} \\ \dfrac{\partial q_{NH_4^+}}{\partial r} = 0, r = 0, t > 0 \\ q^{eq} = \dfrac{QKC_{NH_4^+}}{C_{Na^+} + KC_{NH_4^+}} \end{cases} \tag{4}$$

where C_{Na^+} is the aqueous phase concentration of Na$^+$, q_{hpx} is solid phase concentration during the HAPIX phase, and Q and K are constants in the IX isotherm related to maximum adsorption capacity and affinity for the exchanger, respectively. The first equation is the initial condition, which states that initially there are no NH$_4^+$ ions present in the zeolite. The second equation imposes a Neumann boundary condition at the center of the chabazite particles, and the third is an IX isotherm which provides the equilibrium relationship between the NH$_4^+$ concentration at the zeolite surface, and the NH$_4^+$ concentration in the bulk liquid.

Algae have been shown to be inhibited by high NH$_3$-N concentrations as high as 150 mg/L. Light is one of the limiting factors to algal growth due to light attenuation in the reactor, caused by self-shading by algal biomass. We follow an approach whereby a multiplicative model is used to describe microbial kinetics when algae are exposed to an inhibitory substrate and limited light intensity conditions (Lee and Zhang, 2016). The multiplicative theory in this research assumes the algal growth rate is a function of the nutrient and light intensity, given by the Andrew's equation combined with the Chalker model:

$$\left\{ \begin{array}{l} r_{NH_4^+} = \dfrac{\mu_{max,NH_4^+} C_{NH_4^+} X_A}{Y_A \left(\dfrac{C_{NH_4^+}^2}{K_{I,NH_4^+}} + K_{S,NH_4^+} + C_{NH_4^+} \right)} * \theta^{(T-20)} \tanh(I_{av}/I_k) \\[4em] I_{av} = \dfrac{I_0}{kdX_A} 1 - \exp(-kdX_A) \end{array} \right\} \qquad (5)$$

where μ_{max,NH_4^+} (T^{-1}) is the maximum specific growth rate, X_A (M L^{-1}) is the phototrophic biomass concentration, Y_A (dimensionless) is the yield coefficient, K_{S,NH_4^+} (M L^{-1}) is the half saturation constant, $K_{I,AOB}$ is the inhibition coefficient (M L^{-1}), θ is the Arrhenius growth coefficient (dimensionless), I_{av} $(\text{M L}^{-2}\,\text{T}^{-1})$ is the average light intensity, I_k is the light half saturation coefficient (M), k $(\text{L}^2\,\text{M}^{-1})$ is the light attenuation rate, d is the reactor diameter, and T is temperature (T). Substitution of the rate expression (Eq. 5) into the mass balance (Eq. 1) yields the following equations for the NH_4^+-N concentration and phototrophic biomass growth rate:

$$\left\{ \begin{array}{l} \dfrac{dC_{NH_4^+}}{dt} = -\dfrac{3M}{RV} D_s \left. \dfrac{\partial q_{NH_4^+}}{\partial r} \right|_{r=R} - \dfrac{\mu_{max,NH_4^+} C_{NH_4^+} X_A}{Y_A \left(\dfrac{C_{NH_4^+}^2}{K_{I,NH_4^+}} + K_{S,NH_4^+} + C_{NH_4^+} \right)} * \theta^{(T-20)} \tanh(I_{av}/I_k) \\[4em] \dfrac{dX_A}{dt} = \dfrac{\mu_{max,NH_4^+} C_{NH_4^+} X_A}{Y_A \left(\dfrac{C_{NH_4^+}^2}{K_{I,NH_4^+}} + K_{S,NH_4^+} + C_{NH_4^+} \right)} * \theta^{(T-20)} \tanh(I_{av}/I_k) Y_A \end{array} \right\} \qquad (6)$$

RESULTS

HAPIX reactors performance

Over 95% of IX activity between NH_4^+ and Na^+ occurred within 24 hours after the addition of chabazite. The decrease in NH_4^+ concentrations eliminated the ammonia toxicity to algae at all dosages. NH_4^+-N concentrations of IA-60, IA-150 and IA-250 were reduced from 84 meq/L (1,180 mg/L) to 13 meq/L (184 mg/L), 7.7 meq/L (107 mg/L), and 3.8 meq/L (53mg/L), respectively, after IX (Figure 3). The growth of algae in IA-60, IA-150 and IA-250 reactors during Phase 1 further reduced the aqueous NH_4^+-N concentrations to 37.6 mg/L, 10.5 mg/L, and 5.5 mg/L, respectively. Harvesting algae and recycling the supernatant for Phase 2 cultivation resulted in an overall decrease in cation concentrations. The increase in pH from 7.5 to 9.5-10.1 on day 9 likely induced the precipitation of Ca^{2+} and Mg^{2+}, which contributed to this decrease. The increase in pH was mainly attributed to the algae growth. The ion-exchange process (IX-control without algae)

also increased pH but not as high as in the HAPIX reactors. All the HAPIX reactors with three chabazite dosages showed the similar trends. The overall cation concentrations decreased during Phase 2. Note that there were also slight decreases of Na^+ during Phase 2, probably due to the lack of K^+ in the liquid phase and algae biomass started to uptake Na^+ from surrounding solutions (Barber and Shieh, 1973). Algae showed a favorable uptake of K^+ over Na^+, and algae can also accumulate high Na^+ in the biomass (Schaedle and Jacobson, 1965; 1967). Further research on the cations transport and uptake by algae are needed to identify the driving force for the different metabolic pathways.
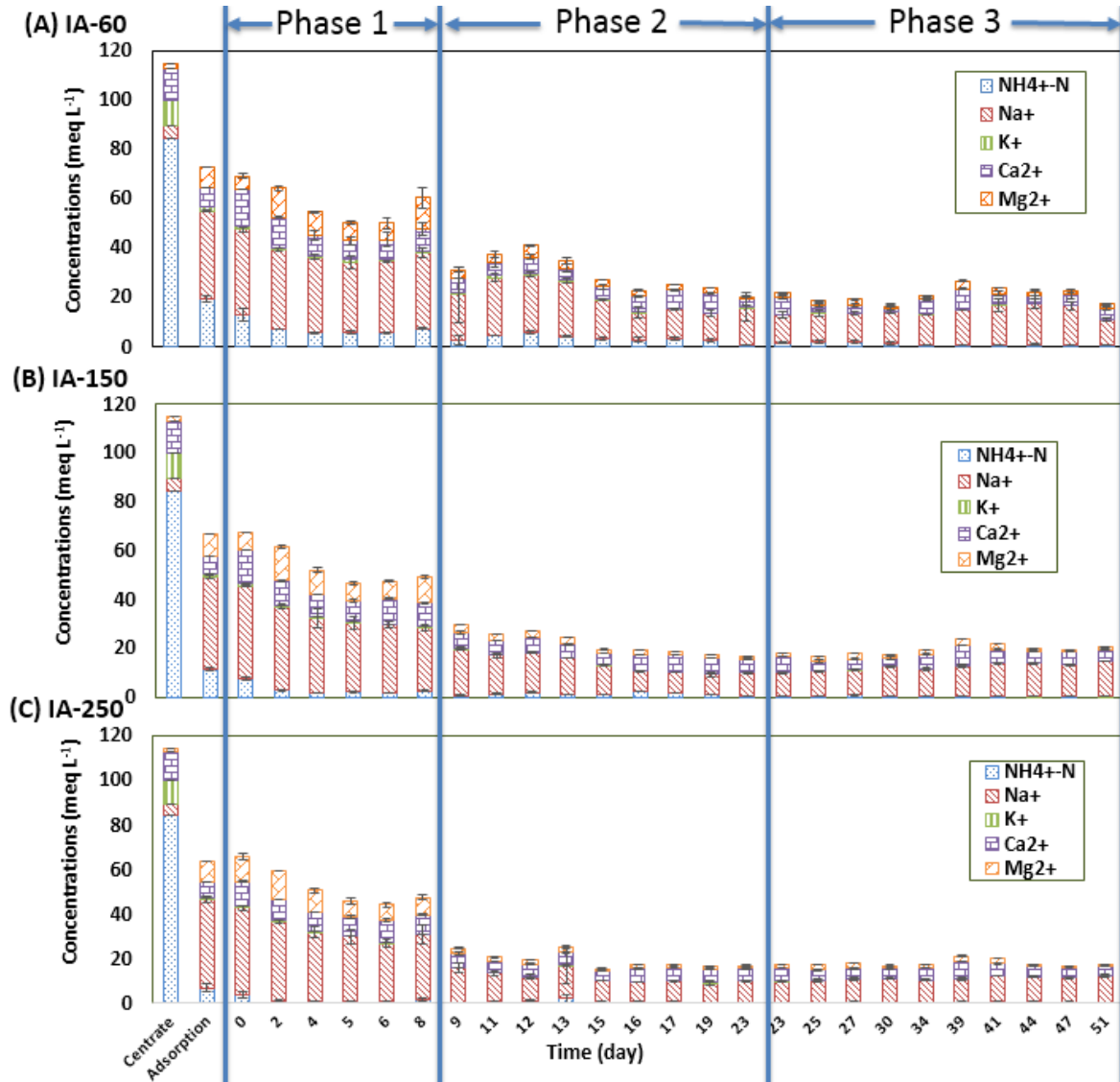

Figure 3. Cation concentrations over time (a) chabazite dosage of 60 g/L; (b) chabazite dosage of 150 g/L; and (c) chabazite dosage of 250 g/L. Centrate: cations of the centrate; Adsorption: cations after adsorption for 24 hours; Day 0 indicated the time when algae were added; Phase 1: initial algae growth phase; Phase2 and Phase 3; algae grown in recycled supernatant.

The addition of chabazite decreased the ammonia toxicity to algae. Algae biomass in all the HAPIX reactors increased from 500 mg/L to over 1500 mg/L after 8 days (Figure 4). However, the control reactor without the addition of chabazite showed an inhibition of algae growth due to the high concentrations of NH_4^+ in the influent. The algae showed immediate growth during Phase I due to the relative high NH_4^+-N concentrations in the liquid phase 184 mg/L, 107 mg/L and 53 mg/L for IA-60, IA-150 and IA-250, respectively. However, during Phase 2 and Phase 3, longer lag period for the algae growth was required. The total biomass harvested from IA-60, IA-150 and IA-250 were 1587 mg, 1248 mg and 1187 mg, respectively. More biomass was harvested from the reactor with lower chabazite dosage. Supernatant was recycled in the reactors during Phases 2 and 3, thus there were less cations available for IX with NH_4^+ in the solid phase. Introducing new influent with selective cations and creating a concentration gradient between the liquid and solid phase may increase the selective reversal NH_4^+ desorption to the liquid phase.
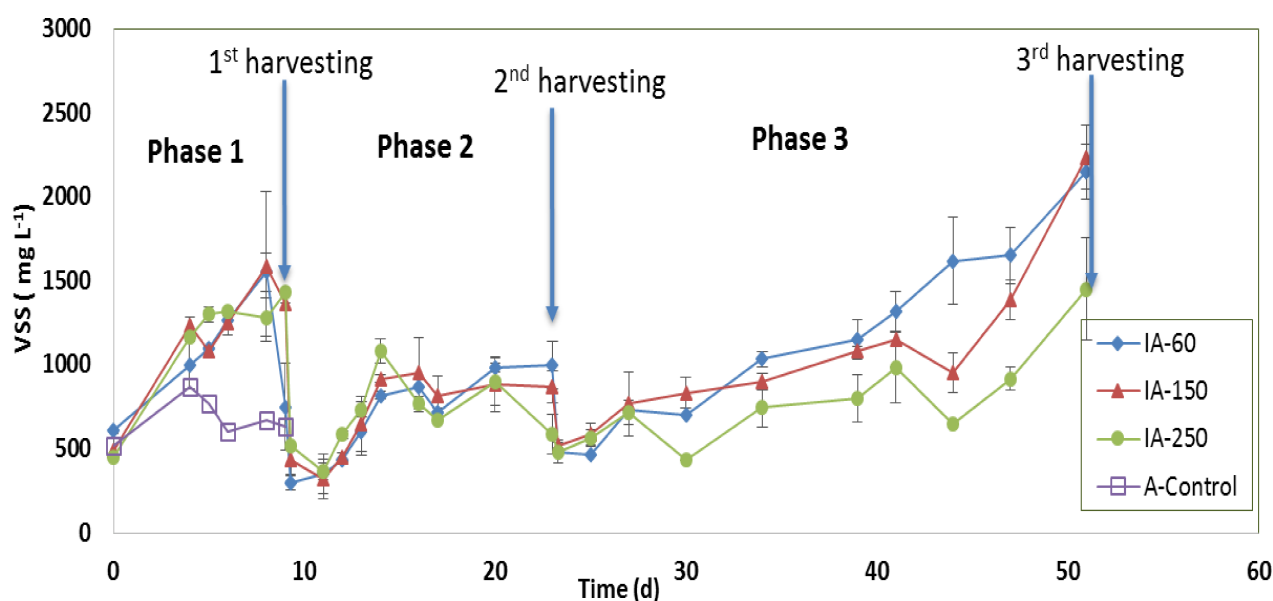

Figure 4. Algal biomass growth over time. Arrow indicated the algae harvesting.

The particulate N was calculated by subtracting the soluble N from total N of the mixed liquor. Algae grown in IA-60 (lower chabazite dosage) had a significantly higher N content in the biomass (Figure 5). Similar trends were also observed in the protein content of the biomass (Figure 6). Higher NH_4^+ concentrations tended to produce biomass with a high N and protein content. The protein contents were much higher than starch for the algae grown in all the HAPIX reactors. The intercellular contents of algae are regulated by the NH_4^+ concentrations can be controlled by the chabazite dosages in HAPIX reactors.
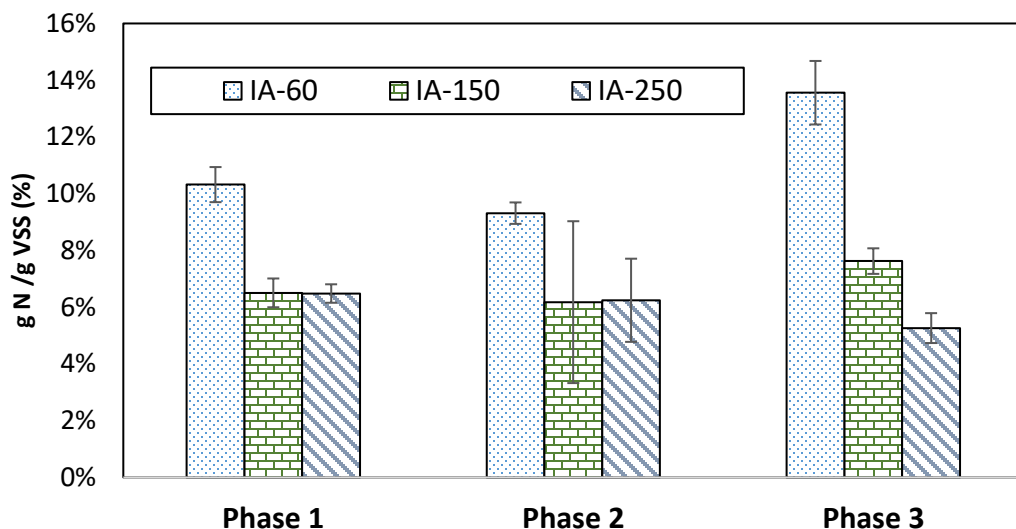
Figure 5. Percentage of N in algae harvested from different dosages of chabazite (IA-60: chabazite dosage of 60 g/L; IA-150 chabazite dosage of 150 g/L; A-control: without chabazite addition).
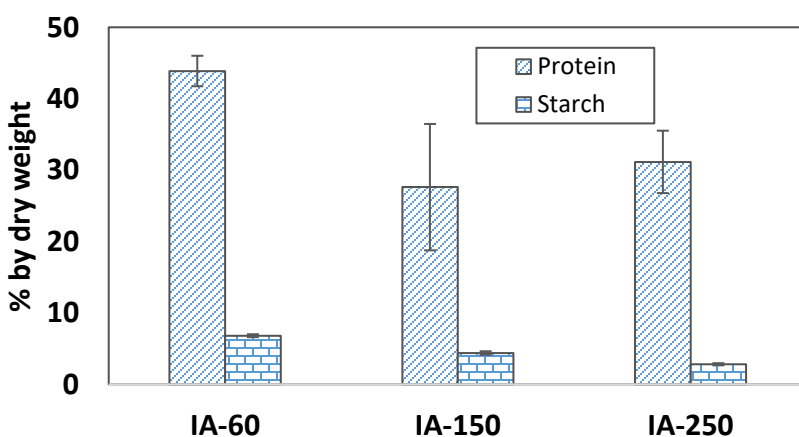

Figure 6. Starch and protein contents of algae grown in different dosages of chabazite (IA-60: chabazite dosage of 60 g/L; IA-150 chabazite dosage of 150 g/L; A-control: without chabazite addition).

HAPIX modeling

Figure 7 shows the temporal variation of modeled and experimental NH_4^+ concentrations in the reactors. As the chabazite dose increased from 60 g to 150 g, the rate at which the concentration changed was faster since there are more IX sites available for uptake. The results show that most of the uptake onto the chabazite occurs within the first 4 hours of the experiment. For the reactor with 60 g of chabazite, the model overestimated the removal rate of NH_4^+ when compared to the experimental data. This could be due to the presence of competing cations in solution which the IX component of the model is unable to capture. Another plausible explanation for the discrepancy between the model NH_4^+ concentration profile and the experimental data is that the reactor for 60 g of chabazite showed more algal growth which could have resulted in a thicker algal biofilm retarding the rate of ion flux to the IX media.
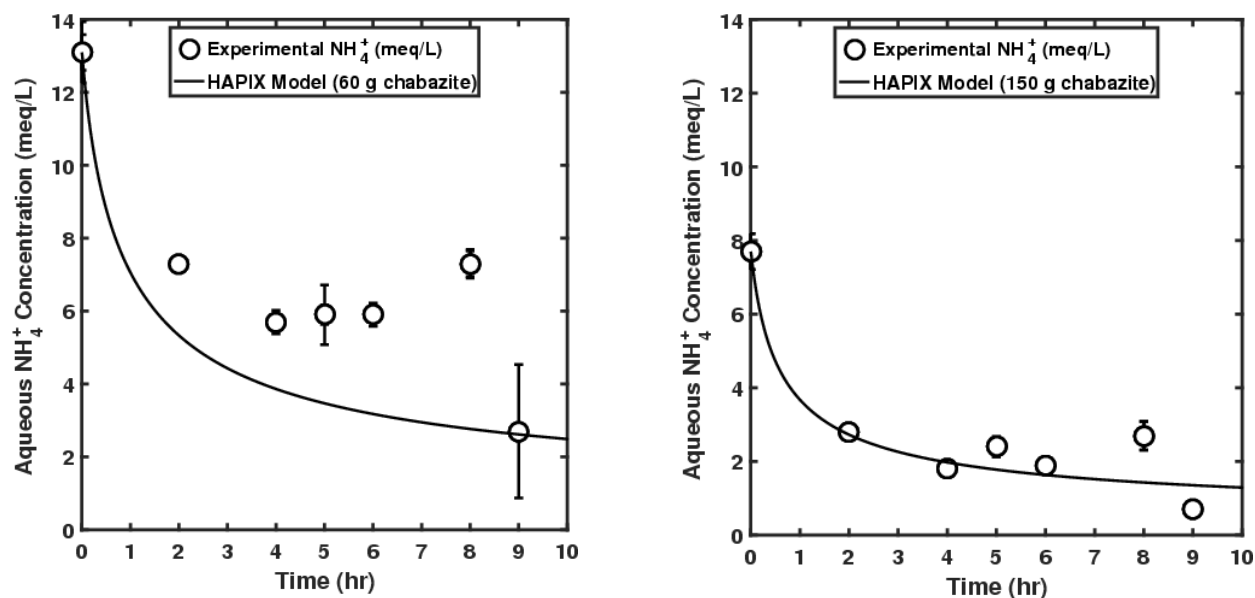
Figure 7. Aqueous NH_4^+-N versus time for chabazite dosages of 60 g/L (left) and 150 g/L (right), respectively.

CONCLUSIONS

This research presents the feasibility of a HAPIX process for high NH_4^+-N side stream treatment. A mathematical model describing the HAPIX process has been developed that accurately predicts the fate of NH_4^+-N and algal biomass growth over time. The HAPIX process effectively removed NH_4^+-N to below 10 mg/L. Different dosages of zeolite induced different NH_4^+-N concentrations in the liquid phase, which resulted in different N and protein contents in the algal biomass. The HAPIX process serves a two-fold purpose for removal of high strength NH_4^+-N wastewater and the potential for biofuel and commercial biopolymer production.

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