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Comparison of the use of functional porous organic polymer (POP) and natural material zeolite for nitrogen removal and recovery from source-separated urine

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ABSTRACT

Recovering nitrogen from source-separated urine can offset fertilizer production, reduce the energy consumption associated with wastewater treatment, and help prevent certain pollutants from entering into wastewater treatment plants. This study evaluated the performance of a newly designed porous organic polymer (POP) for removing ammonium (NH_4^+) from synthetic hydrolyzed urine in comparison with natural clinoptilolite in terms of adsorption capacity (isotherm), adsorption rate (kinetics), regeneration rate, and adsorbent cost. NH_4^+ removal from hydrolyzed urine using the POP was rapid with a capacity of 74.96 mg/g, which is about five times higher than clinoptilolite (15.42 mg/g). In addition, the predicted capacity of both adsorbents decreased with the number of cycles using an integrated adsorption-regeneration model, but remained at about 83.4% and 21.6% of the pristine POP and clinoptilolite after 24 cycles, respectively. The POP had a higher adsorbent cost than clinoptilolite, however, it can be competitive to clinoptilolite with multiple uses if its production can be scaled up.

1. Introduction

With the growing world population, water demand and wastewater production have continuously increased. Wastewater contains various pollutants, with nitrogen as a main constituent. Excess nitrogen leads to eutrophication, algal blooms, and depletion of dissolved oxygen, all of which are harmful to aquatic ecosystem and human health [1]. On the other hand, nitrogen is a necessary macronutrient for organisms, and nitrogen fertilizer is used to increase crop production due to its favorable solubility and bioavailability [2]. In order to meet the food demand of the rising world population in an energy efficient way [3], nitrogen recovery from wastewater has gained increasing attention. For example, agricultural wastewater can be the most pressing problem related to nutrient management if it is not properly treated [4]. In the areas with highly concentrated livestock production [5], nutrient losses through runoff lead to eutrophication in receiving waters. Previous studies have investigated nutrient recovery technologies to produce fertilizer from agricultural wastewater to achieve sustainable agricultural production [6–8]. Various technologies have been used or developed for nitrogen removal and recovery, such as magnesium ammonium phosphate precipitation, electrochemical processes, ammonia stripping, membrane separation, and adsorption.

One major source of nitrogen in domestic wastewater is urine. It is noteworthy that human urine comprises about 1% of the domestic sewage by volume; however, it accounts for as high as 80% of total nitrogen [9] in domestic wastewater. High nitrogen concentration in undiluted urine has rendered great possibilities to recover nitrogen. Accordingly, urine source separation systems have been explored in Europe as alternatives to traditional wastewater collection since the end of the 20th century [10,11]. In such systems, feces and urine are collected separately, facilitating nutrient recycling with a small volume of wastewater. Compared with the end-of-pipe treatment, source separation systems have several distinct advantages, including improved nutrient removal performance of wastewater treatment plants and reduced energy consumption [12]. Additionally, source separation systems help prevent certain pollutants from entering into wastewater treatment systems, such as pharmaceuticals and hormones in urine [13]. Currently, more and more countries are engaging in urine separation. For instance, the "NoMix" toilet has been implemented in the Swiss Federal Institute of Aquatic Science and Technology (Eawag)

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institute [14], and University of Michigan in the U.S. has installed urine-diversion flush toilets in a building on the north campus [15]. In addition, urine separation and treatment has been critical for water recovery in space applications. Almost 82% of human wastewater in space comes from urine [16] that is captured and processed for water recycling, enabling long-duration space travel.

Nitrogen contained in fresh urine is mainly in the form for urea ($OC(NH_2)_2$). During the long storage time, urea in fresh urine is hydrolyzed to ammonium (NH_4^+) and bicarbonate (HCO_3^-) [17]. Among various technologies for NH_4^+ removal and recovery, adsorption using adsorbents displays some advantages, including a high capacity and removal efficiency, fast reaction rate, and the ability to regenerate and reuse adsorbents [12]. There have been few studies on the use of adsorbents to remove and recover ammonium (NH_4^+) from human urine [18–21]. Most previous studies have focused on NH_4^+ removal using natural zeolites, which are relatively cheap and readily available in large quantities in many areas of the world. Tarpeh et al. [18] compared the performance of zeolites, biochars, and synthetic cation resins for nitrogen removal from source-separated urine. They found the cation resin (Dowex Mac 3 and Dowex 50) has higher removal efficiency, but also higher cost than clinoptilolite and biochar assuming 100% regeneration for all materials. In reality, adsorbents or resins are hard to achieve 100% regeneration after multiple uses, and they need to be replaced regularly to maintain good performance, especially for clinoptilolite and biochar.

Therefore, a comparison of different kinds of materials for NH_4^+ removal and recovery in single or multiple uses is necessary. In this study, a newly designed functional porous organic polymer (POP) based on a biphenyl monomer that is grafted with sulfonic acid was investigated for NH_4^+ removal. Functional POPs have recently been developed as a new type of adsorbent for water treatment and radionuclide sequestration [22–28]. For example, Aguila et al. [23] used simple free radical polymerization techniques to synthesize a POP for mercury capture. The POP synthesized is cost-effective and has the added benefits of recyclability, stability in a broad pH range, and selectivity for toxic metals and nutrients. Such performance is attributed to the material's physical properties including hierarchical porosity, a high density of chelating sites, tunable pore size, high surface area, and chemical stability [23]. The promising results of this work suggest that POPs can potentially be used as an economically viable material for nutrient recovery. To date, there is no study that has evaluated the application of POPs for NH_4^+ removal and recovery from source separated urine.

This study, therefore, aims to evaluate the feasibility of POPs for NH_4^+ removal and recovery from hydrolyzed urine by comparing its performance with zeolite (clinoptilolite). Clinoptilolite was chosen in this study because it is the most common and abundant high-siliceous zeolite and has been previously used to remove NH_4^+ from polluted water [29–31]. Specifically, four parameters will be examined to evaluate the feasibility: adsorption capacity, adsorption rate, regeneration rate, and material cost. To achieve the aim, the following four research objectives are formulated: (1) to compare NH_4^+ removal and recovery efficiency between clinoptilolite and POP in terms of adsorption capacity (isotherm), adsorption rate (kinetics), and regeneration rate; (2) to predict the performance of clinoptilolite and POP in terms of recovering nitrogen from urine over multiple adsorption-regeneration cycles; (3) to explore the mass transport mechanisms of the adsorption using clinoptilolite and POP; and (4) to estimate the material cost of single and multiple uses.

2. Materials and methods

2.1. Characterization of synthetic hydrolyzed urine

In this study, synthetic hydrolyzed urine was used and prepared based on the recipe from previous literature [32] by adding appropriate salts to deionized (DI) water with a pH around 9.1, similar to real hydrolyzed urine. The final composition is shown in Table 1. Synthetic hydrolyzed urine was prepared and stored in an amber bottle at 4 °C until it was used in experiments.

Table 1
The composition of synthetic hydrolyzed urine used in experiments assuming complete urea hydrolysis.

Chemical	Mole weight, g/mol	Synthetic hydrolyzed urine mol/L	g/L
NaCl	58.44	0.06	3.51
Na_2SO_4	142.04	0.015	2.13
KCl	74.55	0.045	3.35
NH_4OH	35.04	0.49	16.99
NaH_2PO_4	119.98	0.016	1.92
NH_4HCO_3	79.06	0.27	21.10
NH_4Cl	53.49	0.073	3.90
pH≈9.1			

2.2. Characterization of adsorbents

Two adsorbents, clinoptilolite and POP, were used in the experiments. The physical properties of the adsorbents are shown in Table 2. Clinoptilolite was obtained from the St. Cloud Zeolite Company (Winston, New Mexico), and it was sieved to get a particle size ranging from 0.5 to 1 mm. Furthermore, the clinoptilolite was washed with DI water and dried at 108 °C for 24 h before experiments began. The POP used in this study was synthesized from a biphenyl monomer which was then grafted with sulfonic acid at the University of South Florida. The synthesized POP is designed to include functional groups that specifically target the N and P nutrients and hold these nutrients using molecular interactions-forces found in nature (the synthesized process is presented in Figure S1). This design is novel in its attempts to capture nutrients, such as urea, phosphate, and others, by using a natural receptor grafted into the porous materials. The materials synthesized are stable in high and low pH environments and highly porous with accessible surface areas above 340 m^2/g allowing for the nutrients to easily reach the abundant binding sites. The POP was produced at lab-scale, therefore only a limited amount of POP can be used in this study.

2.3. Quantification of adsorption rate

All kinetic and isotherm experiments were conducted at the bench-scale in batch and performed on an Innova 2000 Platform Shaker at 200 rpm. Experiments were conducted in triplicate trials in ambient laboratory temperature of 23 °C, which was considered as the average temperature of the stored source-separated urine ranging from 5 ℃ to 35 ℃ [33]. Control samples of synthetic hydrolyzed urine without adsorbent were measured at each sample time for all batch studies. Batch kinetic tests were performed using the synthetic hydrolyzed urine with the same adsorbent dose to evaluate the time required to reach equilibrium. Adsorbents were added into the synthetic hydrolyzed urine, shaking for 5 min, 30 min, 1 h, 2 h, 6 h, 1 day, and 2 days. 25 g of

Table 2
Physical properties of clinoptilolite and POP.

	Clinoptilolite	POP
Pore Structure	Macroporous	Hierarchical porous (1)
pH Stability	3-10	3-10
Thermal Stability	Up to 650 ℃	Up to 200 ℃
Functional Group	Hydrous sodium aluminosilicate	Sulfonic acid
BET Surface Area	40 m^2/g	340 m^2/g
Pore volume	0.058 cm^3/g	0.17 cm^3/g

(1) i.e. existence of micropores (≤ 2 nm) and mesopores (between 2 and 50 nm).

clinoptilolite was added to 50 mL synthetic hydrolyzed urine; 0.05 g of POP was added to 5 mL synthetic hydrolyzed urine due to the limited amount of POP.

The adsorption kinetics reflect the relationship between the rate of retention or release of a solute from an aqueous environment to an adsorbent phase at a given condition. In batch adsorption, several models describing the diffusion of solutes at the surface and in the pores of the adsorbent. Among them, pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been widely used to describe the rate of adsorption in liquid-solid interactions given in Eqs. 1 and 2 [34,35]. In the PFO model, the rate of adsorption process is proportional to the difference between the adsorbent phase concentration at equilbrium, q_e, and the adsorbent phase concentration at a defined time [36]. The PSO kinetics model, however, assumes the sharing or exchanging of electrons between adsorbent and adsorbate is the rate-limiting step and the adsorption process is governed by chemisorption [37].

$$q_t = q_e \bullet (1 - e^{-k_1 t}) \tag{1}$$

$$q_t = \frac{q_e^2 \bullet k_2 \bullet t}{1 + q_e \bullet k_2 \bullet t} \tag{2}$$

where q_e is the adsorbent phase concentration of NH_4^+ at equilibrium, mg /g; q_t is the adsorbent phase concentration of NH_4^+ at time t, mg/g; k_1 is the pseudo-first-order rate constant, 1/min; k_2 is the pseudo-second-order rate constant, g/mg·min; t is the time, min. The parameters of q_e and k_1 or q_e and k_2 were obtained by fitting to the experiment data using nonlinear least squares regression (Origin 8.5). The adsorbent phase concentration of NH_4^+ at time t, q_t (mg/g), was calculated by Eq. 3:

$$q_t = \frac{(c_0 - c_t) \bullet V}{m} \tag{3}$$

where c_0 is the initial NH_4^+ concentration in synthetic hydrolyzed urine, mg NH_4^+/L; c_t is the NH_4^+ concentration in synthetic hydrolyzed urine at time t, mg NH_4^+/L; V is the volume of synthetic hydrolyzed urine, L; m is the amount of adsorbent, g.

Results of the batch kinetic experiments were used to determine the intra-particle diffusivity, which were used in the integrated adsorption and regeneration model developed by Zhang et al. [38]. The intra-particle diffusion coefficient (D_s) was determined using the empirical correlation developed by Crank [39], which includes both surface diffusion and pore diffusion:

$$\frac{M_t}{M_\infty} = 1 - \sum\nolimits_{n=0}^{\infty} \frac{6\alpha(\alpha + 1)e^{\frac{-D_S q_n^2 t}{r^2}}}{9 + 9\alpha + q_n^2\alpha^2} \tag{4}$$

where M_t is the amount of NH_4^+ adsorbed at time t, = $V(c_0 - c_t)$, mg; M_∞ is the amount of NH_4^+ adsorbed at equilibrium, = $V(c_0 - c_e)$, mg; r is the radius of the adsorbent particle, m, and q_n are the non-zero roots of $\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$; α is the ratio of the amount of NH_4^+ in solution to the amount of NH_4^+ adsorbed at equilibrium, $\alpha = \frac{Vc_e}{M_\infty}$.

2.4. Quantification of adsorption capacity and regeneration potential

Batch isotherm experiments were conducted with the doses of adsorbents varying to achieve approximately 10%–90% NH_4^+ removal. For the clinoptilolite isotherm test, six glass bottles were filled with 50 mL hydrolyzed urine and 5 g, 10 g, 15 g, 20 g, 25 g, and 30 g clinoptilolite were added separately. For the POP isotherm test, six glass screw thread vials were filled with 5 mL hydrolyzed urine and 0.05 g, 0.1 g, 0.15 g, 0.2 g, 0.25 g, and 0.3 g POP were added separately. Samples were mixed on a shaker table at 200 rpm for 6 h and 2 h (clinoptilolite and POP, respectively) to ensure the equilibrium is reached (based on the kinetic experiment).

Clinoptilolite (25 g) and POP (0.05 g) that were saturated with NH_4^+ were regenerated in triplicate during batch isotherm studies, with 50 mL and 5 mL of NaCl solution (1 mol/L), respectively. Adsorbents and regeneration solution were mixed on a shaker table at 200 rpm for 6 h and 2 h (clinoptilolite and POP, respectively). The NH_4^+ concentration in the regeneration solution was measured to determine the amount of NH_4^+ desorbed from adsorbents and the isotherm parameters for desorption.

Freundlich and Langmuir models are commonly used isotherms, as expressed in Eqs. 5 and 6 [40,41]. Freundlich isotherm is an empirical model that can be applied to multilayer adsorption, with nonuniform distribution of adsorption heat and affinities over a heterogeneous surface [41]. The Langmuir isotherm model assumes a completely homogeneous surface, where the adsorption can only occur at a finite number of definite localized sites [40].

$$q_e = k_F \bullet c_e^{1/n} \tag{5}$$

$$q_e = \frac{q_m \bullet k_L \bullet c_e}{1 + k_L \bullet c_e} \tag{6}$$

where k_F is a Freundlich constant (an indicator of adsorption capacity), $(mg/g)(L/mg)^{1/n}$; $1/n$ is the adsorption intensity; q_e is the adsorbent phase concentration at equilibrium, mg/g; c_e is the equilibrium concentration in solution, mg/L; k_L is a Langmuir constant related to the binding energy of adsorption, L/mg; q_m is the saturated maximum monolayer adsorption capacity, mg/g. The isotherm parameters, k_F and n, and q_m and k_L, were obtained by fitting to the c_e and q_e data using nonlinear least squares regression (Origin 8.5).

2.5. Column test of adsorption and regeneration

The continuous flow (up-flow) adsorption experiments were conducted in a glass column (5.68 cm diameter, 24 cm length) (see Figure S2 for setup and Table S1 for design parameters), filled with 210 g clinoptilolite. DI water was pumped at a speed of 10 mL/min to fill the column first and then synthetic hydrolyzed urine was pumped into the column at the same speed. Samples were collected every 5 min for the first 2 h then every 20 min for the next 4 h, and analyzed for NH_4^+ concentration via an ammonia analyzer. An initial column experiment was performed using fresh clinoptilolite. In subsequent adsorption-regeneration cycles, the used clinoptilolite was regenerated with 1 mol/L NaCl in the same column. All column tests were run until clinoptilolite was saturated with NH_4^+, and then the adsorbent was regenerated.

Since POP was synthesized on a lab scale, the limited amount of POP lead to the development of column tests using less amount of adsorbent. The POP column was designed based on the constant diffusivity (CD) rapid small scale column test (RSSCT) method [42,43] to scale down the clinoptilolite column so the results can be compared between the POP and clinoptilolite column tests [44]. Up-flow continuous adsorption experiments with POP were performed in a 3 mL syringe (0.86 cm diameter, 6.5 cm length), packed with 0.05 g POP, and filled up with DI water. Synthetic hydrolyzed urine was pumped through the syringe at a speed of 0.37 mL/min for 8.25 min. Samples were collected every 10 s for the first 2 min, then collected every 20 s for the last 6.25 min. The regeneration process was performed in the same syringe using 1 mol/L NaCl (see Figure S2 for setup and Table S2 for design parameters).

Column tests of adsorption and regeneration cycles provided experimental data to calibrate and validate the integrated adsorption and regeneration model, which considers liquid axial dispersion, film mass transfer, and intra-particle diffusion [38]. It can predict the adsorption breakthrough curve, removal and recovery efficiency for multiple adsorption-regeneration cycles. The validated model was used to predict the performance of clinoptilolite and POP for multiple cycles. The parameters required for the integrated adsorption and regeneration model include adsorbent properties (adsorbent size, porosity, density, intra-particle diffusivity, and external mass transfer coefficient), column configuration (bed height, bed diameter, bed volume, and bed porosity), and flow and operation condition (superficial velocity, empty bed contact time, and regenerant feed concentration). The parameters needed for modeling adsorption and regeneration of NH_4^+ on clinoptilolite and POP are provided in Table S1 and Table S2, respectively. To explore the mass transport mechanisms of the adsorption using clinoptilolite and POP, Biot (Bi) number was calculated with the following expression [45]:

$$Bi = \frac{R \bullet k_l}{\varepsilon \bullet D_s \bullet D_g} \tag{7}$$

where D_g is the ratio between mass of solute in adsorbent phase versus mass of solute in solution, $D_g = \frac{\rho_b \bullet q_m}{\varepsilon \bullet c_i}$; ρ_b is the bulk density of the bed, kg/m^3; q_m is the maximum capacity, mg/g; c_i is influent concentration, mg/L; ε is the bed porosity; R is the particle radius, m; k_l is the liquid phase mass transfer rate coefficient, m/s; D_s is the intra-partial diffusion coefficient, m^2/s.

In this study, the absolute average deviation (AAD) was used to quantify the difference between experimental data and model predicted data. In a laboratory scale, if AAD $\leq$ 0.1, it indicates the predicted data generally agrees with the experimental data [46].

2.6. Analytical methods

Samples were filtered by 0.45 μm filters (Whatman® membrane) and measured on the same day the test ended. Each sample (0.1 mL) was diluted by a factor of 100. This preparation is necessary to ensure that the NH_4^+ concentration was less than 100 mg/L for testing. Timberline-2800 Ammonia & Nitrate analyzer was used to measure the NH_4^+ concentration. The ammonium chloride (NH_4Cl) stock solution and 1 mg/L, 5 mg/L, 10 mg/L, 50 mg/L, 80 mg/L, and 100 mg/L NH_4Cl standard solutions were prepared and stored at 4 °C until they were used for calibration in tests.

2.7. Material cost analysis

The prices for different adsorbents and the regeneration chemical were considered in an initial material cost analysis. The material cost was normalized by the total amount of NH_4^+ removed, which depended on the adsorption capacity (see Eq. 8). The adsorption capacity was calculated by graphical integration of area above the breakthrough curve in each cycle (q_i in mg/g) from either column tests or the model simulations.

$$P = \frac{P_a \bullet m_a + P_r \bullet m_r}{\sum m_a \bullet q_i} \times 1000 \tag{8}$$

where P is the material cost, USD/g; P_a is adsorbent price, USD/g; m_a is the mass of adsorbent, g; P_r is NaCl price, USD/g; m_r is the mass of NaCl used in regeneration process, g; q_i is the adsorption capacity in cycle i, mg/g. The price of NaCl used in the regeneration studies was 63.10 USD/kg (Sigma-Aldrich, US). The price of clinoptilolite was estimated by full truckload shipment, from the St. Cloud Zeolite Company, as 445 $/ton. The price of POP was estimated as 2100 $/kg based on the amount and the price of the chemicals used in the lab-scale synthetic process. The POP price can be highly uncertain due to the different production scale and the estimated price was very conservative.

3. Results and discussion

3.1. Adsorption rate

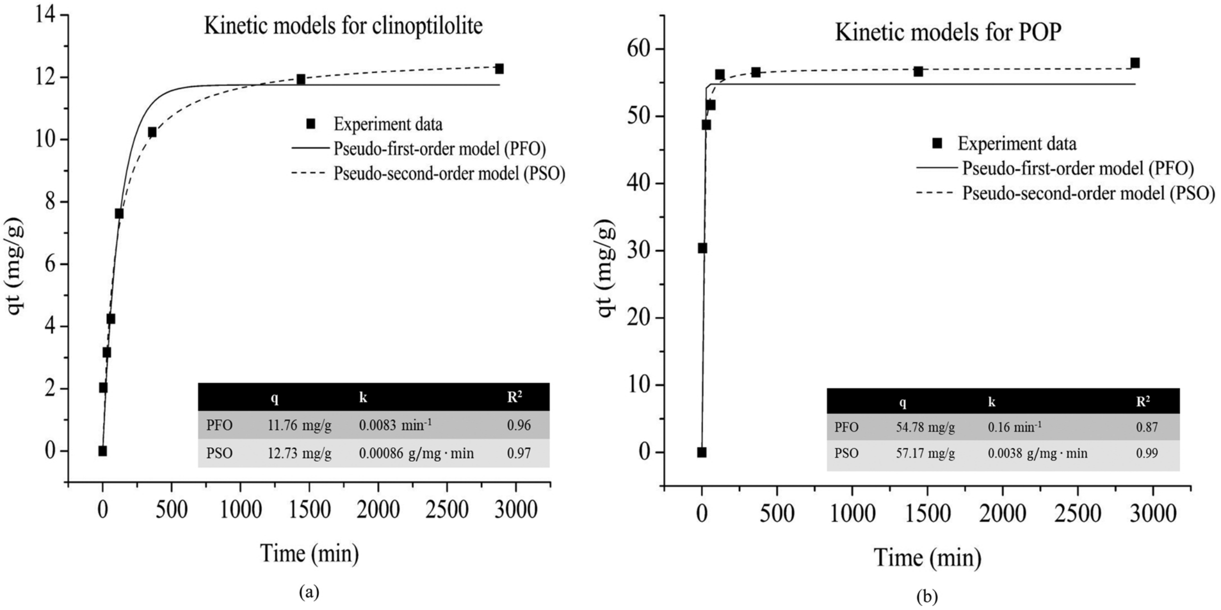
Fig. 1 shows the adsorbent phase concentration of NH_4^+ over time calculated based on the NH_4^+ concentration in synthetic hydrolyzed urine (average values of the samples from triplicate trials) (see Figure S3 in supplementary information). As can be seen, the adsorption of NH_4^+ using clinoptilolite was rapid in the first 2 h, giving a removal of 74% of initial NH_4^+. The adsorption then reached equilibrium at around 6 h in batch studies. For POP, most of the NH_4^+ was adsorbed within 5 min to 1 h of the experiment and the equilibrium was reached at about 2 h. The fast removal of NH_4^+ at the initial period is attributed to the abundant active sites on the surface of the adsorbents. When the active sites on the surface are nearly saturated, the rate of adsorption becomes dominated by pore diffusion of NH_4^+ onto the inner surface of the adsorbent, leading to slower removal of NH_4^+ and finally to equilibrium.

As mentioned before, PFO and PSO kinetic models were applied to investigate the adsorption rate of NH_4^+ onto clinoptilolite and POP. As shown in Fig. 1, the PSO model was a better fit to the experimental data for both adsorbents based on the R^2 value, which suggests the surface adsorption involving chemisorption as the rate-limiting step for the removal of NH_4^+. The adsorption behavior may involve valency forces through the sharing or exchange of electrons between NH_4^+ and the adsorbent [35]. The corresponding PSO rate constant k_2 for POP is 0.0038 g/mg•min, which is more than four times faster than clinoptilolite. The faster adsorption of NH_4^+ onto POP can be attributed to the POP's large surface area and hierarchical pore structure [20]. Mesopores allow for a high flux, which greatly accelerates the mass transfer of the NH_4^+, thereby improving its adsorption rate.

3.2. Adsorption capacity

Batch isotherm studies were conducted to determine the maximum adsorption capacity of NH_4^+ in the synthetic hydrolyzed urine on clinoptilolite and POP. The isotherm studies evaluated the effect of clinoptilolite and POP dose on NH_4^+ removal in the period of 6 h and 2 h, respectively (see Figure S4 in supplementary information). The removal of NH_4^+ increased with the increase of adsorbent dose due to an increase in the adsorptive surface area and the availability of more active adsorption sites [47]. The relationship between q_e and c_e were investigated using the Langmuir and Freundlich isotherm models as shown in Fig. 2. It can be seen that the experimental data for clinoptilolite and POP fit better to the Langmuir isotherm than to the Freundlich model based on the R^2 value. This indicated that homogenous monolayer adsorption occurred on clinoptilolite and POP with finite adsorption sites [47]. The maximum adsorption capacity determined using the Langmuir model was 74.96 mg/g for POP, which is around five times higher than clinoptilolite. This is due to the large surface area and the number of active sites of the POP. Clinoptilolite has a maximum adsorption capacity of 15.42 mg/g that is similar to the capacity of 15.44 mg/g reported from the previous study on NH_4^+ removal from source-separated urine [48]. POPs have been used in previous studies to remove water contaminants, including heavy metals and organic pollutants. The adsorption capacities of 1216 and 1045 mg/g were reported for removing mercury and methyl orange, respectively [23,49]; however, there is no prior study on NH_4^+ removal using POPs. In terms of NH_4^+ removal, the POP has outperformed several commercial adsorbents that have a maximum capacity of 40 mg/g [50–52]. One of the commercial adsorbents, Dowex Mac 3, had a higher maximum adsorption capacity of 155 mg/g than POP. This might be because Dowex Mac 3 has a higher density of active groups due to its aliphatic resin structure and macropores [18].

Through the post-synthetic modification process, strong acid sulfonic groups serve as very binding sites to undergo adsorption with NH_4^+ in solution. Compared with clinoptilolite, POP has a higher surface area and large amount of readily available binding sites. POP is thus an ideal candidate to extract NH_4^+ from urine as a sustainable source of nitrogen. Given that sulfonic acid is a strong acid, the cation exchange process will prefer to coordinate to NH_4^+ cations over Na^+ resulting in a rapid ion-exchange process. Further, utilizing ion-exchange is beneficial given the ease in ammonium extraction using a solution of NaCl resulting in adsorbent regeneration for multiple cycles,



(a) (b)

Fig. 1. Pseudo-first-order and pseudo-second-order kinetics for NH_4^+ adsorption on (a) clinoptilolite and (b) POP.

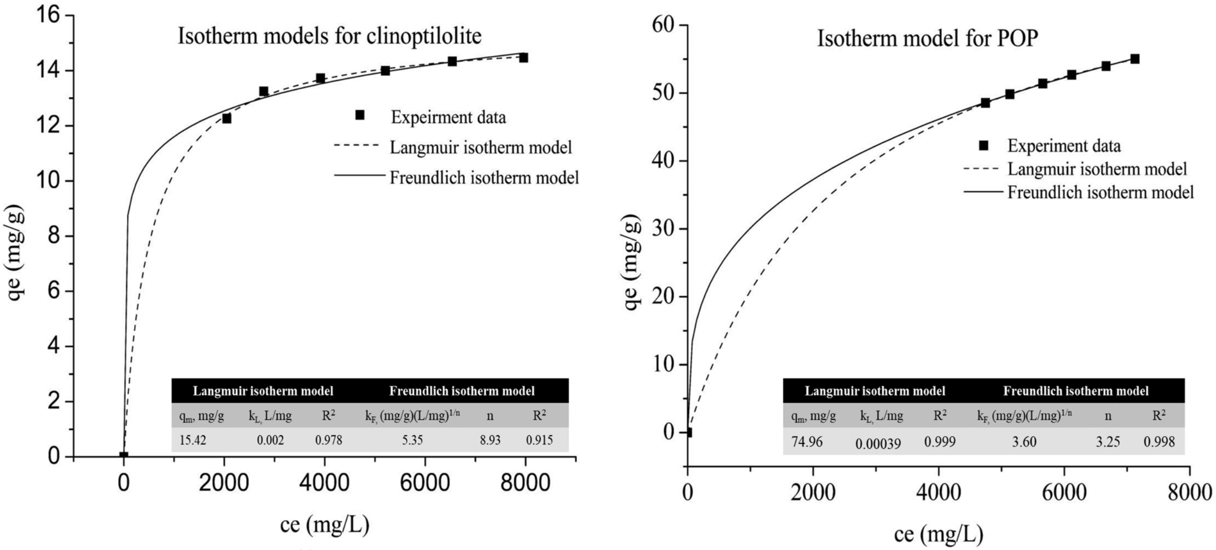
extending the lifetime of the material as well as reducing long-term costs.

3.3. Performance evaluation of multiple uses

The performance in terms of NH_4^+ removal and recovery from synthetic hydrolyzed urine using clinoptilolite and POP for multiple uses in continuous flow configuration was evaluated using the integrated adsorption and regeneration model. External mass transfer coefficient was calibrated with the experimental data from the first cycle and the model was validated using the experimental data from the 2nd and 3rd cycles as shown in Fig. 3. The computed AADs were less than 0.1 (see Table S3 in supplementary information), indicating the model predictions are in good agreement with the experimental data.

Once the model was calibrated and validated, it was used to simulate the performance of clinoptilolite and POP over multiple adsorption-regeneration cycles. The adsorption capacity and the regeneration efficiency calculated based on the simulated results are shown in Fig. 4. As can be seen, the regeneration efficiency and the capacity decreased with the number of cycles. The performance of clinoptilolite deteriorated significantly with a regeneration efficiency of 0.23 after 24 cycles. However, the regeneration efficiency for POP is still about 0.8 after 24 cycles, indicating POP can maintain its performance after multiple cycles.

To explore the significance of external mass transfer versus intra-particle mass transfer for two adsorbents, Bi number were calculated. Adsorption is governed by external mass transfer (Bi < 10), intra-particle mass transfer (Bi > 10), or both (Bi ~10) [53]. In this study, the value of Bi number for POP is 11.7, indicating that intra-particle mass transfer is the rate controlling step for the adsorption process of NH_4^+ on the POP. This may be due to the large surface area and specific pore structure of the POP. Compared with POP, the value of Bi number for clinoptilolite is lower, less than 10, suggesting the external film diffusion controls the adsorption rate rather than intra-particle diffusion.



(a) (b)

Fig. 2. Freundlich and Langmuir isotherms for NH_4^+ adsorption on (a) clinoptilolite and (b) POP.

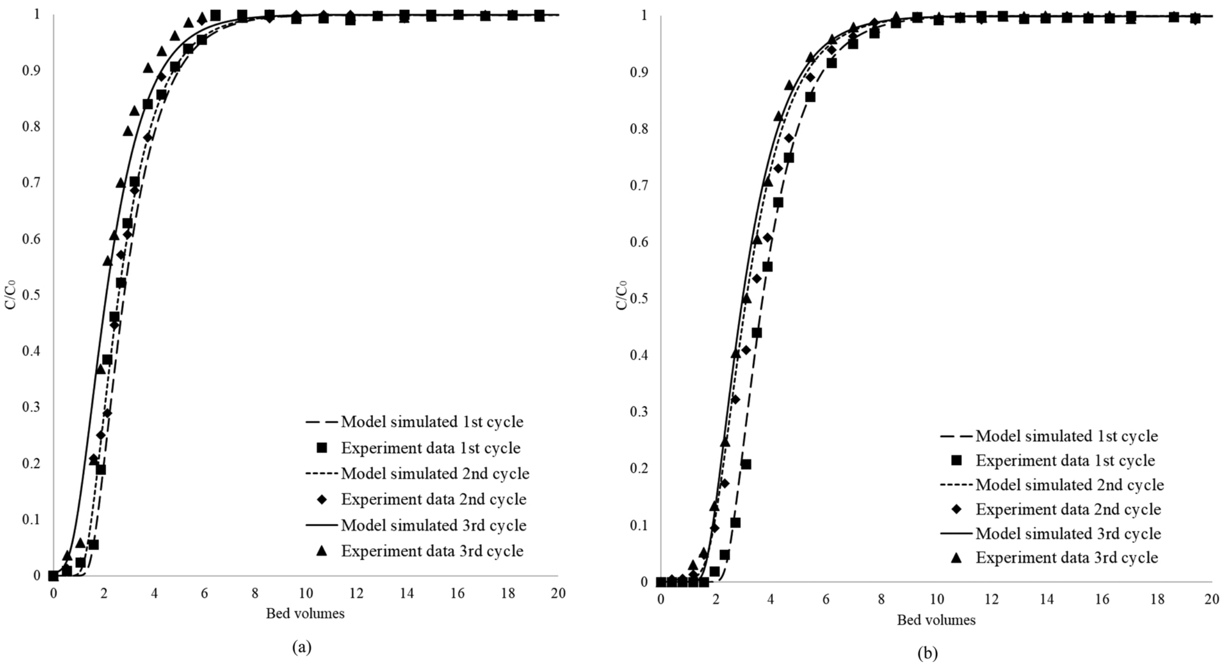


Fig. 3. Experimental and simulated breakthrough curves for NH_4^+ adsorption on (a) clinoptilolite and (b) POP.

3.4. Cost assessment

The material cost for clinoptilolite and POP applications were determined by the chemical cost, adsorption capacity, and regenerant cost, according to Eq. 8. The simulated adsorption capacity of clinoptilolite and POP for each adsorption-regeneration cycle. If clinoptilolite and POP are used for a single time, the treatment would cost 1.97 \$/g NH_4^+ and 37.62 \$/g NH_4^+, respectively. This is due to the high adsorbent cost for POP as it was synthesized at lab scale. The adsorbent cost for POP decreased significantly from cycle 1–24 as shown in Fig. 5 due to its high adsorption capacity and regeneration efficiency.

This preliminary cost analysis indicates that the high adsorption capacity of POP cannot compensate the high adsorbent cost. However, POP can be competitive to clinoptilolite with multiple uses if the production of POP can be scaled up and the price can be reduced to 300 \$/kg. In addition, there are many factors that were not considered in this analysis, such as the reactor size and costs, the quality of recovered nutrient, fertilizer prices, and the disposal cost of used adsorbents. The results may be different if those factors are taken into consideration for a more in-depth cost analysis.

4. Conclusion

In this study, the potential of clinoptilolite and POP for removing and recovering NH_4^+ from synthetic hydrolyzed urine was investigated based on lab-scale experiments, process modeling, and preliminary cost analysis. Compared with clinoptilolite, POP has a high adsorption rate and capacity in removing NH_4^+. The adsorption reached equilibrium at 2 h and 6 h for POP and clinoptilolite, respectively. The maximum exchange capacity for clinoptilolite and POP is 15.42 mg/g and 74.96 mg/g, respectively. After 24 adsorption-regeneration cycles, the regeneration efficiency of POP is predicted to be 80% with a high capacity around 50 mg/g. The high capacity and regeneration efficiency of POP, however, are not able to compensate the high material cost to make POP economically competitive to clinoptilolite. The production of POP has to be scaled up in the future to investigate the potential applications of POP in nutrient removal and recovery.

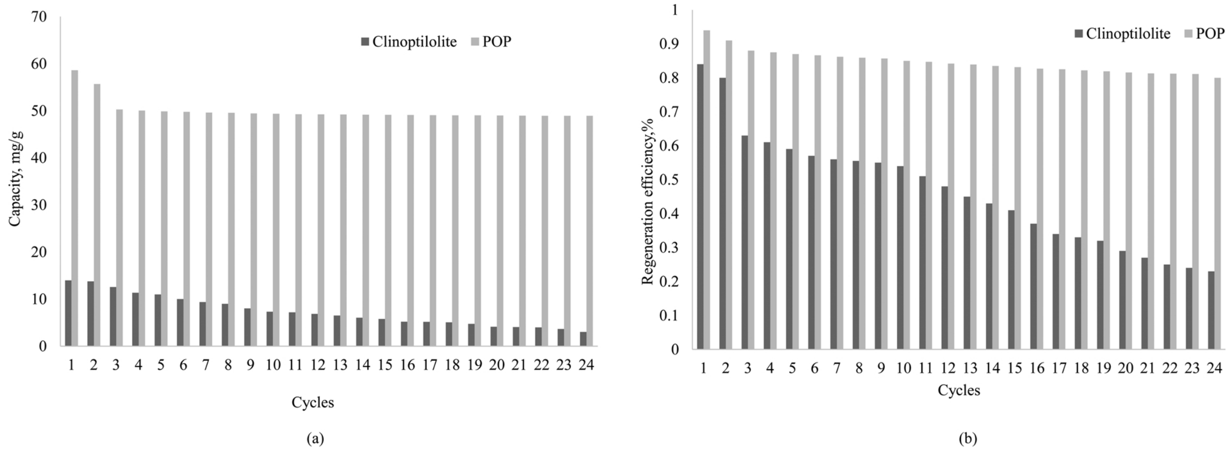


Fig. 4. Simulated results of multiple adsorption-regeneration cycles: (a) adsorption capacity; (b) regeneration efficiency*.
* Regeneration efficiency of the first cycle = (desorbed/adsorbed) × 100 %; Regeneration efficiency for the rest of cycles = (desorbed/total) × 100 %, where total = adsorbed + fouled.

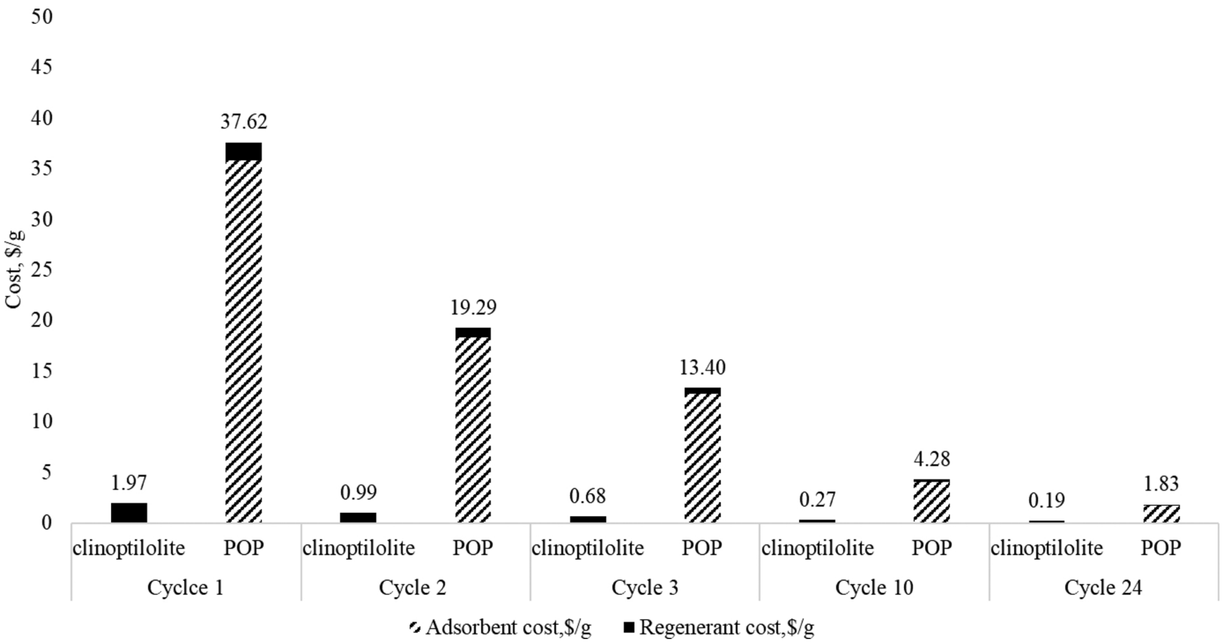


Fig. 5. Comparison of the material costs for clinoptilolite and POP applications in single and multiple adsorption-regeneration cycles.

CRediT authorship contribution statement

Yan Zhang: Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Briana Aguila:** Resources, Writing - original draft, Writing - review & editing. **Shengqian Ma:** Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Qiong Zhang:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2020.104296.

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