Recovery of Ammonium from Aqueous Solutions Using ZSM-5

*Michael J. Manto, Pengfei Xie, Mitchell A. Keller, Wilhelm E. Liano, Tiancheng Pu, Chao Wang**

Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218, United States. Email: chaowang@jhu.edu; Fax: +410 516 5510; Tel: +410 516 5843

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Abstract. The demand of reactive nitrogen (N), such as ammonium (NH_4^+) and nitrate (NO_3^-), continues to increase for fertilizer applications as the population grows, but the Haber Bosch (H-B) process currently employed for industrial N fixation is challenged by low efficiency and high energy consumption. Here we report on the investigation of ZSM-5 as a superior sorbent for the recovery of ammonium from aqueous solutions. Fast capture and release of ammonium (NH_4^+) have been achieved with >90% overall efficiency of recovery using synthetic solutions of NH_4Cl and NaCl, respectively. The ZSM-5 sorbent has also been found to be recyclable and sustain high recovery efficiencies after multiple capture-release cycles. The capture of N has been further studied systematically in dependence of the dose of sorbent and reaction temperature, based on which the mechanism, thermodynamics and kinetics of ion exchange are discussed. Compared to other ion-exchange materials, the ZSM-5 zeolite exhibits superior selectivity for capturing ammonium in the presence of competing cations ($NH_4^+ >> Ca^{2+} > Mg^{2+} > K^+ > Na^+$) and demonstrates high efficiency of recovery in real wastewater streams.

1. Introduction

Nitrogen (N) is an essential element for life.[1] Its reactive forms, such as ammonium (NH_4^+) and nitrate (NO_3^-), are widely applied as fertilizers to promote the growth of plants.[2] Although N constitutes almost 80% of the terrestrial atmosphere, reactive N is limited in soils and the supply of biologically accessible N to plants relies on the N fixation from air. Atmospheric dinitrogen (N_2) can be converted into reactive N by leguminous crops or lightning. Most reactive N today (>70%) is produced via the artificial chemical synthesis of ammonia (NH_3), i.e., the Haber-Bosch (H-B) process.[3-4] While the demand of N fertilizers continually escalates with the growing population, the industrial H-B process is however challenged by the low conversion of N_2, high energy consumption and large carbon footprint.[5-6] This single process accounts for 1-2% of global energy consumption today, and moreover, the energy efficiency of modern H-B plants is approching its theoretical limit.[7]

A significant portion (as high as >80% in certain cases[8]) of the reactive N applied to farmland is lost into water. The runoffs from agriculture as well as other anthropological discharges from municipal and industrial wastewaters cause the enrichment of reactive N in ponds, lakes and rivers. This leads to eutrophication, threatening the survival of aquatic species and jeopardizing sources of clean water.[8-10] Traditionally, chemical precipitation is used to remove NH_4^+ and other contaminates during wastewater treatment. Although feasible for implementation, this approach may only be viable for nutrient-rich streams,[11-12] and the struvite derived from direct chemical precipitation is usually contaminated by toxic substances and not aimed for reuse.[13-14] Both the need for tuning the solution pH and the separation of solid products also add expenses and complexity to the operations.[15-16] For that reason, ion exchange has been extensively studied for improving the efficiency of nutrients recovery from wastewater[11,17-18], which can be integrated with anaerobic digestion[19-20] and/or chemical precipitation[21-22] to produce clean and valuable

products. Previous accounts have described the use of commercialized acidic[23-27] and basic[21,28] resins for cation exchange with dissolved NH_4^+; however, such sorbents have several disadvantages, including calcium sulfate fouling in acidic resins, inadvertent adsorption of organic molecules and organic contamination from the resins. Recent research has turned to zeolites as alternatives, owing to their structural robustness, tunable and selective adsorption properties, employment of naturally abundant elements and environmental compatibility.[29-30] Natural zeolites such as clinoptilolite,[22-23,31-33] wollastonite,[36] sepiolite[37] and others[36,38-39] have been shown to be effective in capturing the dissolved N from synthetic solutions and wastewater. Some of these studies have demonstrated controlled release of captured N utilizing acidic[22-23] or basic[36] regeneration solutions exhibiting ~90 – 100% release for synthetic ion exchange resins[22-23] and ~45 – 80% release for zeolites.[23,32] However, more effective sorbents with improved capturing capacity, efficiency of release, and specificity are yet to be developed.[40-41]

Here we report on the investigation of ZSM-5 nanocrystals as a sorbent for the recovery of ammonium from aqueous solutions. Zeolite Socony Mobil-5 (ZSM-5) is an aluminosilicate with the general chemical formula of $Na_nAl_nSi_{96-n}O_{192}$-$16H_2O$. Isomorphous substitution of Si^{4+} by Al^{3+} in the framework induces a negative charge, giving rise to the intrinsic capability for cation adsorption.[42-43] The kinetics and capacity of NH_4^+ adsorption/desorption on ZSM-5 have been systematically studied in dependence of the mass loading of sorbent and temperature using synthetic solutions. The results are fitted into different transport models and isotherms, based on which the mechanism of NH_4^+ ion exchange is discussed. Finally, the selective capture of ammonium in the presence of competing cations and from complex media such as real wastewater are also demonstrated.

2. Materials and methods

2.1. Chemicals

Ammonium chloride (NH_4Cl, ACS grade, VWR), calcium chloride dihydrate ($CaCl_2$-$2H_2O$, ACS reagent, $\geq$ 99%), magnesium chloride hexahydrate ($MgCl_2$-$6H_2O$, ACS reagent, 99.0-102.0%, Sigma-Aldrich), potassium chloride (KCl, ACS grade, VWR), sodium chloride (NaCl, $\geq$ 99.0%, Fisher). Deionized water (with a resistance of ~18.2 MΩ) was collected from an ELGA PURELAB flex apparatus.

2.2. Synthesis and characterization of ZSM-5

Commercial NH_4-ZSM-5 (Alfa Aesar, Si/Al = 11.5) was calcined at 450 °C for 4 h in static air to convert it into H-ZSM-5, which was used as the sorbent for ion exchange. Scanning electron microscopy (SEM) images were taken on a JEOL 6700F field emission electron scanning microscope operated at 10.0 kV. X-ray diffraction (XRD) patterns were obtained from a PANalytical X'Pert^3 X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). The Al content was determined by XRF on a Bruker-AXS S4 Explorer. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2010 and the samples were degassed under vacuum for 4 h at 300 °C. Specific surface area (SSA) was calculated according to the Brunauer-Emmett-Teller (BET) theory.

2.3. Ion exchange

Synthetic solutions of NH_4^+ (containing 1 g of N per litter, or 1 g-N/L, which has a pH of 5.6 ± 0.1) were prepared by dissolving NH_4Cl in deionized water. A specified amount of ZSM-5 sorbent was added to 10 mL of this solution and the obtained mixture was stirred at 700 rpm for up to 3 h for N capture. After the capture, the sorbent was removed from the NH_4Cl solution by

centrifugation and re-dispersed in brine water (10 g-NaCl/L) to release the captured N. At specific times during the N capture and release processes, aliquots of the reaction solution were extracted from the mixtures and centrifuged to remove the sorbents. The resulting supernatants were treated with an indophenol assay[44-45] to determine the concentration of NH_4^+ (see the Supplementary Material for more details of the assay). Absorption spectra were collected on a Thermo Scientific GENESYS 10S UV-Vis spectrometer. The amounts of N captured and released were determined by calculating the difference in N concentration between the initial solution and the collected supernatants. Various concentrations of NaCl, KCl, $CaCl_2$ or $MgCl_2$ were added to the NH_4Cl solutions to study the competing cation effect. For wastewater treatment, the activated sludge (obtained from the Back River Wastewater Treatment Plant in Baltimore, MD) was centrifuged to remove the solid residues, with the supernatant being used to study the capture of ammonium. The results presented in the discussion represent the averages of at least three independent repeats.

3. Results and discussion

3.1. Preparation of ZSM-5 nanocrystals

Commercial NH_4-ZSM-5 nanocrystals with a Si/Al molar ratio of 11.5 is converted into H-ZSM-5 via calcination at 450 °C in air.[46-47] Hereby the zeolites are denoted as M-ZSM-5, where M represents the adsorbed cation (e.g., NH_4^+, H^+, Na^+, etc.). The obtained product has a typical size of a few hundred nanometers and the particles possess irregular polyhedral shapes (Fig. 1a and b). The major peaks exhibited in the XRD pattern can be indexed to the MFI type of framework (JCDPS No. 37-0359), confirming that the crystal structure of the zeolite remains intake during the sorbent preparation (Fig. 1c). The specific surface area is estimated by the Brunauer–Emmett–Teller (BET) analysis to be ~376 m^2/g, which is similar to previously reported results on

comparable materials (Fig. 1d).[46-47] The pore volume is calculated to be ~0.163 cm^3/g by using the t-plot method.[48]

3.2. N capture and release in synthetic solutions

The capture and release of ammonium (NH_4^+) are examined using solutions of NH_4Cl and NaCl, respectively. Fig. 2a shows a series of UV-Vis spectra collected over the course of N capture. The NH_4Cl solution was sampled at different times (0-3 h) and treated with the indophenol assay,[44-45] resulting in an absorption peak at 640 nm with the intensity proportional to the concentration of ammonium (see the Supplementary Material for more details of the assay). This peak dissipates as the time of capture increases, indicating the removal of NH_4^+ from the solution and its uptake by the ZSM-5 sorbent. Utilizing a pre-established calibration curve (Fig. S1), the concentrations of residual NH_4^+ in the solution are quantified and are observed to follow the amount of adsorbed N during the process of capture (Fig. 2b).

With the given amount of dissolved N (10 mg), the efficiency of N capture is highly dependent on the dose of sorbent, with more N captured as dose increases (Fig. 3a). The efficiency of N capture (the ratio between the captured N and the total amount in the initial solution) varies from ~44% to ~98% as the applied dose of sorbent increases from 1 to 50 g/L (Fig. 3b). The dependence of capture efficiency on the loading of sorbent translates into the change of N uptake with the amount of applied sorbent (Fig. 3c). A maximum uptake of ~440 mg-N/$g_{zeolite}$ is observed when 1 g/L of sorbent is applied, suggesting the potential of the ZSM-5 sorbent for achieving high capacity of N sorption. N capture via ZSM-5 is also evaluated by varying solution pH in the range of 5.5 – 9.5. The fraction of N removed decreases at increasing pH (Fig. S2).

Release of the captured N is crucial for the recovery of nutrients and for the development of cost-effective, reusable sorbent materials. To desorb the ammonium anions, the ZSM-5 sorbents

are isolated from the NH_4Cl solution and re-dispersed in a brine solution. The Na^+ cations exchange with the adsorbed NH_4^+, and the ammonium released into the brine solution is again analyzed by using the indophenol assay. Fig. 3e presents the percentages of N (relative to the captured amount) released during the desorption process using 10 ml of NaCl solution (10 g/L). Nearly complete release (~92 – 97%) is observed independent of the sorbent dose. By comparing the time-dependent capture and release (Fig. 3 a and d), it can be seen that the latter exhibits a flatter curve at the initial stage (e.g., up to 1 h). This observation indicates lower rates of desorption than adsorption, which will be further elucidated in the following discussion about the kinetics. Varying the concentration of the NaCl solution used for regeneration (Fig. S2) shows that less N is released and that the rate of desorption decreases in more diluted solutions. It should be pointed out that the ammonium may also be released in acidic electrolytes, such as applying HCl and phosphate to produce $(NH_4)H_2PO_4$ or $(NH_4)_2HPO_4$ which can be used as fertilizers directly.[11,14-15]

Recyclability of ZSM-5 is further studied by applying ZSM-5 to successive capture and release processes in synthetic solutions. Fig. 4a-b show the mass-specific sorption and desorption of N over 20 capture-release cycles, respectively, using 30 g/L of sorbent. Over the course of the recyclability analysis from cycle 1 to cycle 20, the capacity of N sorption only dropped slightly from 30.0 ± 1.0 to 22.8 ± 2.0 mg-N/$g_{zeolite}$. The trend of N desorption exhibits similar behavior, decreasing from 29.0 ± 1.0 to 16.2 ± 1.2 mg-N/$g_{zeolite}$. These results demonstrate that the ZSM-5 zeolite can be reused for multiple capture-release cycles, which is an important merit of cost-effective sorbents for practical applications.

It is interesting to notice the rather consistent trends of N sorption and desorption from the recyclability studies (Fig. 4a-b). This finding suggests that the recyclability of the ZSM-5 sorbent may be mainly limited by the release of captured N, which is better visualized by the overlapped

trends of release and recovery efficiencies over the course of the capture-release cycles (Fig. 4c). The release efficiency represents the ratio between the released and the captured N, while the recovery efficiency refers to the net percentage of the N recovered per capture-release cycle from the NH_4Cl solution. It is found that the two efficiencies exhibit similar trends depending on the number of cycles, with the release efficiency dropping from ~97% to ~71% and the recovery efficiency from ~90% to ~68% throughout the 20 cycles. It is thus postulated that some ammonium cations get trapped within the pores of ZSM-5 (due to, for example, hydrogen bonding between NH_4^+ and the framework oxygen[49-51]) during release and block the active sites for cation adsorption in the successive adsorption, causing the loss of uptake capacity.

3.3. Kinetics of ammonium sorption

The capture of N was further carried out at different temperatures to investigate the kinetics of ammonium sorption. This was done by applying 30 g/L of ZSM-5 sorbent to 10 mL of NH_4Cl solution (1 g-N/L) at 5 – 95 °C. Fig. 5a presents the dependence of N sorption on time at the various temperatures. The time-dependent sorption consistent exhibits a three-stage behavior, namely a rapid increase during the initial ~15 min, followed by a leveling-off regime, and then a plateau at time beyond. Throughout the capturing process, higher capacities of sorption were observed at higher temperatures. Noticeably, it took less time to reach the equilibrium, as indicated by the plateau in the sorption curves, at a higher temperature, e.g., <1 h at 95 ^oC versus ~2 h at 5 ^oC (Fig. 5a). The equilibrium uptake was also found to increase slightly as the temperature was raised, which suggests shift of equilibrium for the ion exchange reaction (see the following discussion).

The three-stage behavior observed in the sorption kinetics is indicative of a diffusion-controlled process during the N capture.[52-53] The two kinetic regimes observed in sorption with

rapid increase and leveling-off can be ascribed to film and pore diffusion, respectively (Fig. 5a). According to the intra-particle diffusion (IPD) model,[54-56] the time-dependent sorption (Q_t) can be fit by the following equation

$$Q_t = kt^{0.5} + C \quad (1)$$

Fig. 5b shows the comparison of fitted pore (k_p) and film (k_f) diffusion coefficients at the various temperatures. For all the temperatures of capture, k_p is generally much smaller than k_f, indicating that the diffusion through the micropores within the zeolites is limiting the rate of sorption. It is interesting to find that, while k_f increases with temperature, k_p exhibits rather weak (or even negative) dependence on temperature. The former is typical for molecular diffusion in liquid phase and consistent with the previously reported cation diffusion in zeolites.[57-58] The latter phenomenon is likely a result of the Knudsen diffusion of ammonium through the micropores of zeolites, which could exhibit lower diffusion coefficient at higher temperatures due to the enhancement of Brownian motion and increase of collisions between the ions and the zeolite framework.[59-62]

3.4. Ion-exchange mechanism

Cation exchange on zeolites is generally believed to be associated with the Brønsted acid sites introduced by the substitution of Si^{4+} by Al^{3+}.[29,43,63] When H-ZSM-5 is used for N capture, the ion-exchange reaction can be written as (Scheme 1)

$$\equiv Al{-}O\cdots H + NH_4^+ \rightarrow \equiv Al{-}O\cdots NH_4 + H^+ \quad (2)$$

This reaction is associated with the release of protons to the solution, as confirmed by the observed change of solution pH from 5.6 to 3.5 during the first capture step of the recyclability study (Table 1). In the subsequent capture and release cycles, the ion exchange involves Na^+ and the reaction can be written as (Scheme 1).

206 $$\equiv Al{-}O\cdots NH_4 + Na^+ \leftrightarrow \equiv Al{-}O\cdots Na + NH_4^+ \quad (3)$$

207 Again, this reaction is confirmed by the measured changes of solution pH, i.e., decreasing from
208 6.9 to 5.7 – 5.8 after the release of ammonium into the NaCl solution and increasing from 5.6 to
209 6.7 after the capture of ammonium from the NH_4Cl solution (Table 1). It is noticed that silanol
210 groups may be present on ZSM-5 and also contribute to cation exchange,[64] but that mechanism is
211 unlikely to play a significant role in the present study carried out in acidic or neutral solutions, as
212 also suggested by the observation of lower N capture efficiency at increasing solution alkalinity
213 (Fig. S2).

214 However, it is necessary to point out that the molar ratio between the captured N and the
215 number of Al sites present in the sorbent can go beyond one. The dose-dependent studies (Fig. 3c)
216 shows that the N/Al ratio increases as the amount of applied sorbent is reduced and goes above 1
217 at the doses of <30 g/L (for the given 10 mL of NH_4Cl solution with 1 g-N/L). The cation
218 exchangeable capacity (CEC) of the ZSM-5 sorbent was estimated to be ca. 1.45 $mmol/g_{zeolite}$,
219 based on the X-ray fluorescence (XRF) analysis[65] of Na-ZSM-5 with H^+ completely substituted
220 by Na^+ (comparable with the previously reported value for this material[66]). Thereby the
221 observation of much higher uptake of ammonium than the CEC on the ZSM-5 sorbent is likely
222 also a result of the formation of hydrogen bond between NH_4^+ and the framework oxygen,[49-51]
223 which could have trapped extra NH_4^+ cations in the micropores of the zeolite during the capturing
224 process. As mentioned above, it is postulated that the same mechanism caused the capacity
225 degradation observed in the recyclability studies.

226 Fitting the capacity of sorption, Q_{eq}, and residual concentration of N, C_{eq}, at equilibrium
227 with isotherms enables further corroboration of the N sorption mechanism.[23,33-34,39-41] Fig. 6b
228 presents the isotherm derived from the mass loading-dependent capturing experiments carried out

at room temperature, with the parameters used for fitting summarized in Table 2. It can be seen that the Langmuir isotherm, associated with monolayer adsorption, only fits well when the equilibrium concentration (C_{eq}) is low, e.g., <200 mg-N/L, which is corresponding to the regime with N/Al ≈ 1 at high sorbent doses (e.g., >30 g/L in Fig. 6a). In the high-C_{eq} regime, the Freundlich and Redlich-Peterson isotherms outperform the Langmuir isotherm in fitting. Overall, the Redlich-Peterson isotherm, considered a hybrid approach derived from both of the Langmuir and Freundlich isotherms and other sorbate-sorbate interactivity principles, exhibits the best fitting to the experimental data (R^2 = 0.957).[39] This suggests that a hybrid monolayer-multilayer behavior occurs, with the distribution dependent on the equilibrium concentration of ammonium, namely more Langmuir-type of adsorption at low concentrations and multilayer-dominant situation at high concentrations. This finding is well in line with the above analysis derived from the N/Al ratios.

3.5. N capture and release in complex media

After studying the N capture and release in synthetic solutions, we aim to further demonstrate the potential application of the zeolite sorbent for N recovery in practical conditions. For that purpose, the ZSM-5 sorbent was applied to capture ammonium from synthetic solutions in the presence of competing cations and recovery of ammonium from real wastewater containing a bevy of inorganic and organic impurities.

Previously, the effects of coexisting cations have been extensively studied in the ion exchange for N recovery, with the primary focus placed on the competing adsorption of Na^+, K^+, Ca^{2+}, Mg^{2+} etc. that are commonly present in wastewater.[23-24,31,33,38-39,41] To examine these effects on the capture of N using ZSM-5, 20 – 100 mmol/L of Na^+, K^+, Ca^{2+} and Mg^{2+} were added to the NH_4Cl solution (1 g-N/L or 71.4 mmol-N/L), and the capacity of N sorption was measured at the various cation concentrations (Fig. 7a). It was found that introduction of these cations had

252 insignificant impact on the capacity of N sorption at relatively low concentrations. At equimolar
253 or higher concentrations of cations, the capacity had ~10 – 15% of drop, with Ca^{2+} exhibiting the
254 largest impact. From the results about competing cations, it can be derived that the affinity to the
255 ZSM-5 sorbent follows the trend: $NH_4^+ >> Ca^{2+} > Mg^{2+} > K^+ > Na^+$. The observed trend for metal
256 cations is consistent with the calculated binding energies of metal cations on ZSM-5,[67] whereas
257 the much stronger affinity of ammonium could also be attributed to the formation of hydrogen
258 bond with the framework oxygen.[49-51] It is noticed that the overall order of ion exchange observed
259 on ZSM-5 differs from those reported on natural zeolites (e.g., $K^+ > NH_4^+ > Ba^{2+} > Na^+ > Ca^{2+}$ on
260 clinoptilolite).[29] This difference can be attributed to the unique framework structure of ZSM-5 and
261 thus highlights the superiority of using ZSM-5 as sorbent for N recovery.

262 Real wastewater contains a wide range of organic and biomolecular contaminants in
263 addition to competing ions. (Bio)fouling caused by these contaminants has been recognized to be
264 one of the major challenges for the applications of ion-exchange sorbents for wastewater
265 treatment.[29,63] To demonstrate its potential for practical applications, the ZSM-5 sorbent has been
266 used to recover N from the anaerobic digestion effluents obtained from the Back River Wastewater
267 Treatment Plant in Baltimore, MD. After removing the sludge by centrifugation, the supernatant
268 was analyzed to contain ~38.4 mg of dissolved ammonium per liter. The ZSM-5 sorbent achieved
269 91% of capture efficiency and 89% of release efficiency, corresponding to an overall efficiency of
270 ~90% for N recovery from this solution (Fig. 7b). Moreover, the ZSM sorbent was also found to
271 be capable of sustaining the high recovery efficiencies throughout multiple capture-release cycles
272 for the wastewater solutions. The recovery efficiency dropped by merely <10% over five cycles,
273 indicating that ZSM-5 is potentially resistant to fouling by the organic and biomolecular
274 impurities.

4. Conclusion

We have investigated ZSM-5 as sorbent for the recovery of ammonium from aqueous solutions. Fast capture and release of ammonium (NH_4^+) have been achieved with >90% overall efficiency of recovery using synthetic solutions of NH_4Cl and NaCl, respectively. The ZSM-5 sorbent has also been shown to be recyclable and sustain high recovery efficiencies after multiple capture-release cycles. Systematic studies of the N sorption process at different mass loadings of sorbent and reaction temperatures reveal hybrid mono- and multi-layer adsorption, with the distribution between these two models depending on the equilibrium concentration of ammonium, and diffusion-controlled kinetic performance, with the Knudsen diffusion of ammonium through the micropores of zeolites identified to be the rate-limiting factor. Moreover, the ZSM-5 sorbent has been demonstrated to be selective for capturing ammonium in the presence of competing cations, with the affinity following the order $NH_4^+ >> Ca^{2+} > Mg^{2+} > K^+ > Na^+$, and efficient in recovering ammonium from real wastewater streams. Our work highlights the great potential of synthetic zeolites as sorbents for efficient recovery of valuable nutrients from wastewater and other aqueous solutions.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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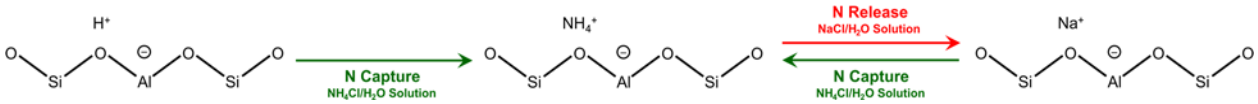
295 **Scheme 1.** Proposed ion exchange mechanism for N recovery.

296 

297 **Table 1.** Measured solution pH during initial and subsequent capture and release cycles.

Cycle	Solution	Stage	pH
First Capture-Release Cycle	NH_4Cl/H_2O	Before Capture	5.6 ± 0.1
		After Capture	3.5 ± 0.1
	$NaCl/H_2O$	Before Release	6.9 ± 0.1
		After Release	5.7 ± 0.1
Subsequent Capture-Release Cycles	NH_4Cl/H_2O	Before Capture	5.6 ± 0.1
		After Capture	6.7 ± 0.1
	$NaCl/H_2O$	Before Release	6.9 ± 0.1
		After Release	5.8 ± 0.1

298

299 **Table 2.** Equations and fitting parameters of the N sorption isotherms.

Isotherm	Equation	Parameters			Coefficient of Determination (R^2)
Langmuir	$Q_{eq} = \frac{Q_m K_L C_{eq}}{1 + K_L C_{eq}}$	K_L	Q_m		0.864
		0.00588 L/mg-N	161.3 mg-N/g		
Freundlich	$Q_{eq} = K_F C_{eq}^{\ n}$	K_F	n		0.944
		0.651	0.994		
Redlich-Peterson	$Q_{eq} = \frac{aC_{eq}}{1 + bC_{eq}^{\ n}}$	a	b	n	0.957
		0.801	0.051	0.021	

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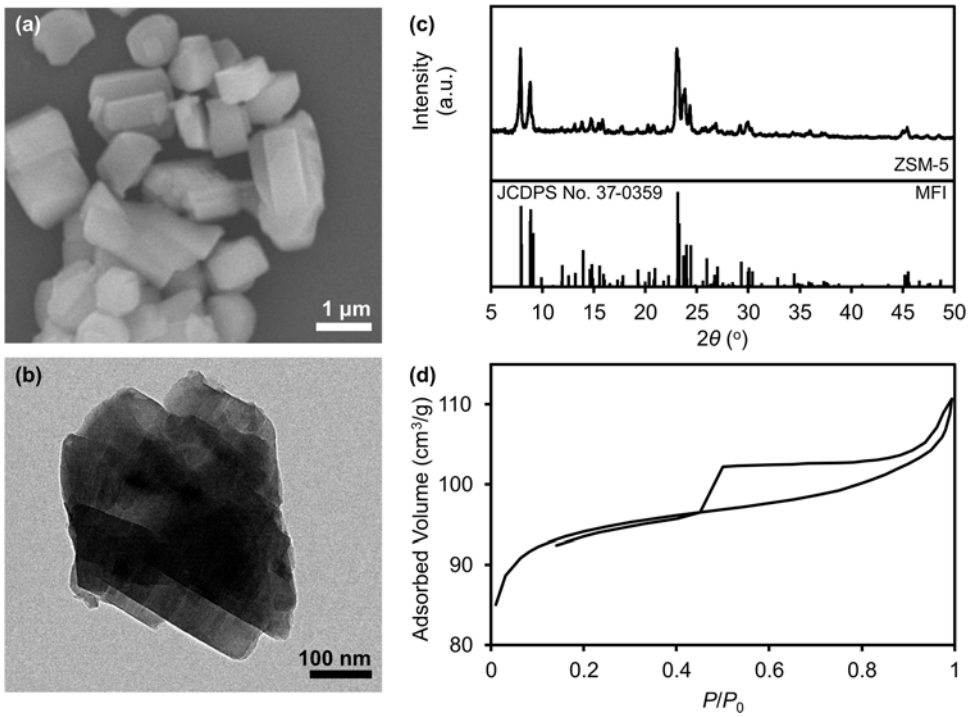
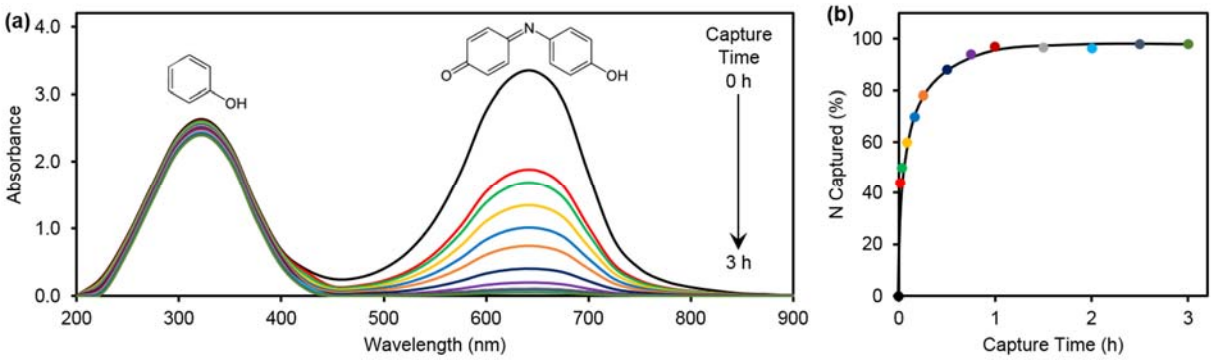


301

302 **Fig. 1.** (a) SEM and (b) TEM images of ZSM-5 nanocrystals. (c) XRD pattern of the as-prepared

303 ZSM-5 compared to the MFI framework. (d) Measured N_2 adsorption profile for ZSM-5.

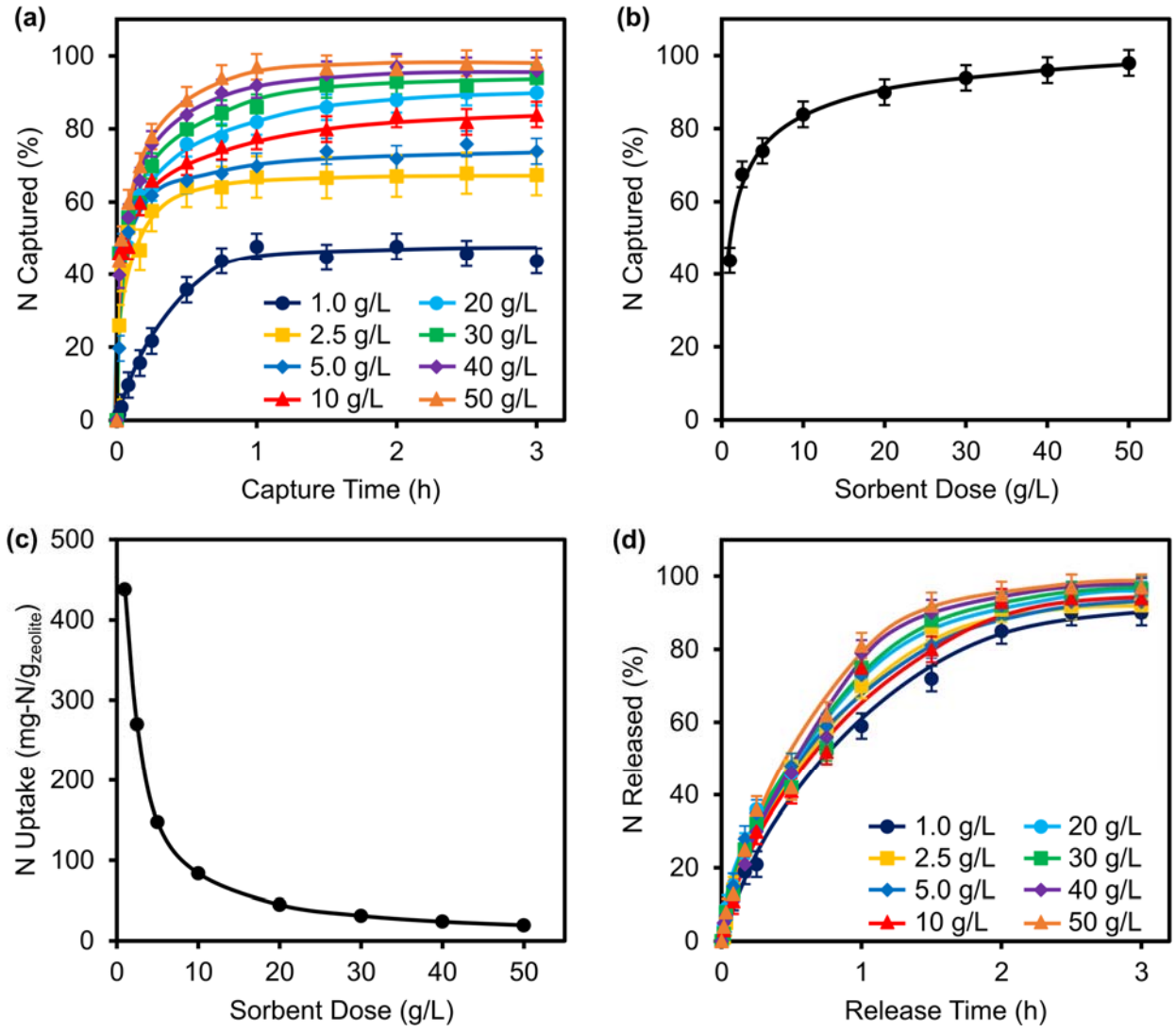


304

305 **Fig. 2.** (a) Typical UV-Vis spectra collected over the course of N capture using the indophenol

306 blue assay. (b) Time-dependent N capture efficiency of the ZSM-5 sorbent (50 g/L in 1 g-N/L

307 NH_4Cl) derived from the spectra shown in (a).



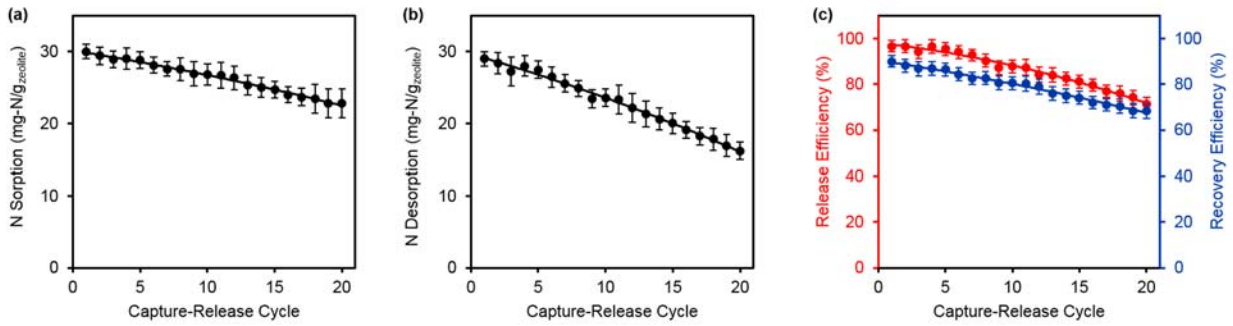
308

309 **Fig. 3.** Dependence of N capture and release on the dose of sorbent: (a) Time-dependent capture,

310 (b) achieved efficiency of N capture at equilibrium, (c) calculated capacity of N sorption and (d)

311 time-dependent release.

312

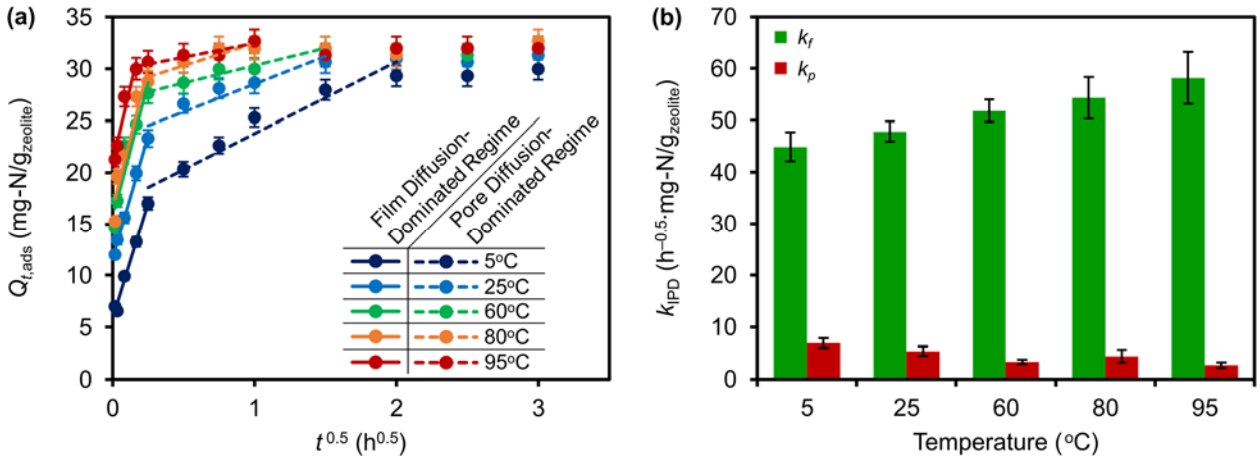


313

314 **Fig. 4.** Recyclability of the ZSM-5 sorbent for N recovery using 30 g/L of sorbent: (a) Capacity of

315 N sorption and (b) desorption over 20 capture-release cycles. (c) Overlapped trends of release and

316 recovery efficiencies throughout the capture-release cycles.

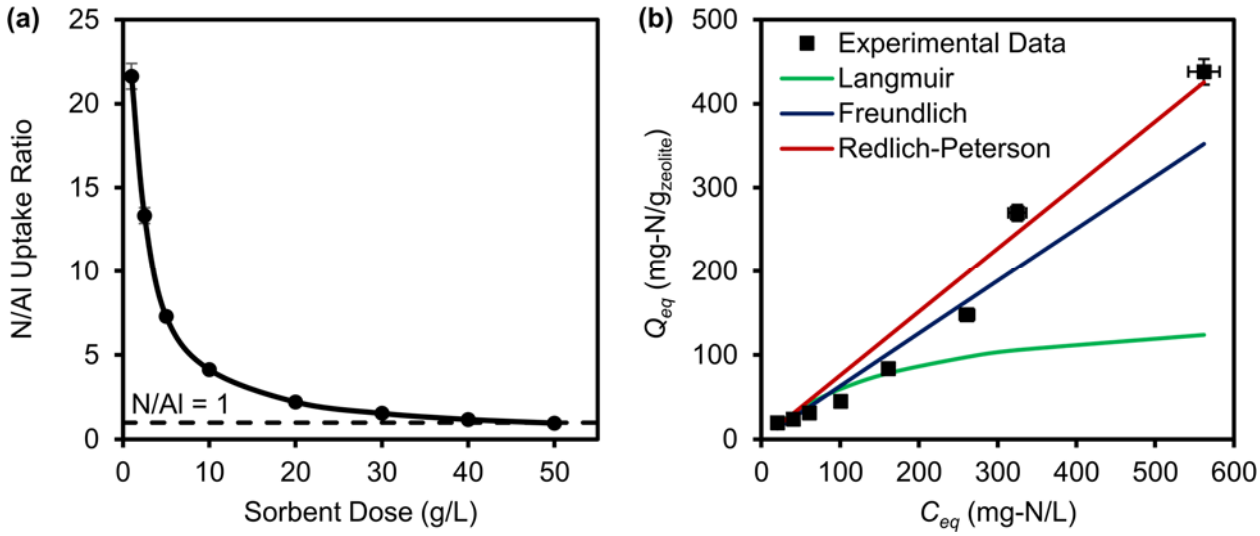


317

318 **Fig. 5.** (a) Time-dependent sorption at various temperatures (with 30 g/L of sorbent), with the

319 fitted film (k_f) and pore (k_p) diffusion coefficients using the intra-particle diffusion model

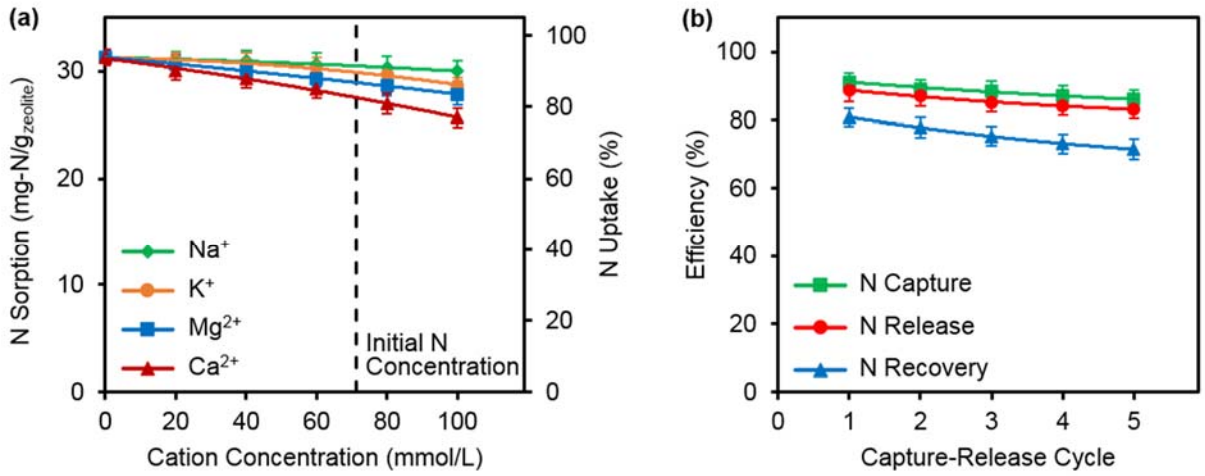
320 summarized in (b).



321

322 **Fig. 6.** (a) Calculated N/Al ratio for the N sorption at the various doses of sorbent. (b) Fitting for

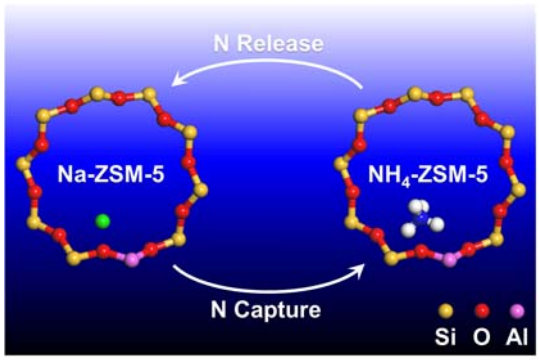
323 the measured equilibrium concentrations (C_{eq}) and uptake (Q_{eq}) with the three types of isotherms.



324

325 **Fig. 7.** (a) Using ZSM-5 for N capture in the presence of competing cations. (b) Efficiencies of N
326 capture, release and recovery from a real wastewater stream (containing 38.4 mg-N/L) by using
327 the ZSM-5 sorbent. The dose of sorbent is at 30 g/L in all cases.

328 **Table of Contents Graphic**



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