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Recovery of ammonium from aqueous solutions using ZSM-5

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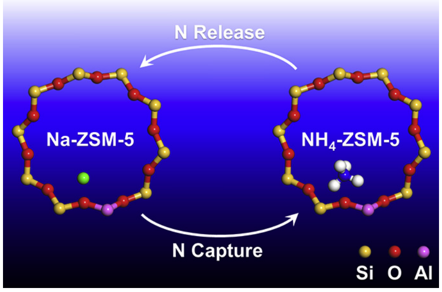
HIGHLIGHTS

- Develop ZSM-5 zeolite as a highly efficient sorbent for capture and release of ammonium.
- Achieve ~90% recovery of ammonium from synthetic solutions and ~80% from real wastewater streams.
- Study the mechanism, thermodynamics and kinetics of the ion exchange reaction on ZSM-5 systematically.
- Demonstrate superior selectivity than the other sorbents for ammonium in the presence of competing cations.
- Demonstrate recyclability of the sorbent in both synthetic and real wastewater solutions.

GRAPHICAL ABSTRACT



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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 sorbent exhibits superior selectivity for capturing ammonium in the presence of competing cations ($NH_4^+ \gg Ca^{2+} > Mg^{2+} > K^+ > Na^+$) and demonstrates high efficiency of ammonium recovery from real wastewater streams.

1. Introduction

Nitrogen (N) is an essential element for life (Greenwood and Earnshaw, 1997). Its reactive forms, such as ammonium (NH_4^+) and nitrate (NO_3^-), are widely applied as fertilizers to promote the

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growth of plants (Black, 1984). 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 (Bodirsky et al., 2014; Smil, 1992). While the demand of N fertilizers continually escalates with the growing population, the industrial H–B process is challenged by the low conversion of N_2, high energy consumption and large carbon footprint (Cherkasov et al., 2015; Smil, 2004). This single process accounts for 1–2% of global energy consumption today, and moreover, the energy efficiency of modern H–B plants is approaching its theoretical limit (Matassa et al., 2015).

A significant portion (as high as >80% in certain cases) of the reactive N applied to farmland is lost into water (Lewis et al., 2011). 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 (Elser et al., 2007; Lewis et al., 2011; Tilman et al., 2001). 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 (Kumar and Pal, 2015; Liu et al., 2011), and the struvite derived from direct chemical precipitation is usually contaminated by toxic substances and not aimed for reuse (Darwish et al., 2016; Mehta et al., 2015). Both the need for tuning the solution pH and the separation of solid products also add expenses and complexity to the operations (Batstone et al., 2015; Doyle and Parsons, 2002). For that reason, ion exchange has been extensively studied for improving the efficiency of nutrients recovery from wastewater (Beaton et al., 2017; Hedstrom, 2001; Liu et al., 2011), which can be integrated with anaerobic digestion (Amini et al., 2017; Gao et al., 2014) and/or chemical precipitation (Liberti et al., 1981; Lind et al., 2000) to produce clean and valuable products. Previous accounts have described the use of commercialized acidic (Ancuta et al., 2005; Gefeniene et al., 2006; Mumford et al., 2008; Tarpeh et al., 2017; Wirthensohn et al., 2009) and basic (Leakovic et al., 2000; Liberti et al., 1981) 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 (Ali et al., 2012; Wang and Peng, 2010). Natural zeolites such as clinoptilolite (Beler-Baykal et al., 2011; Erbil et al., 2011; Guo et al., 2008; Lind et al., 2000; Tarpeh et al., 2017; Wen et al., 2006), wollastonite (Lind et al., 2000), sepiolite (Balci and Dincel, 2002) and others (Karapinar, 2009; Lei et al., 2008; Lind et al., 2000) 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 (Liberti et al., 1981; Lind et al., 2000) or basic (Lind et al., 2000) regeneration solutions exhibiting ~90–100% release for synthetic ion-exchange resins (Lind et al., 2000; Tarpeh et al., 2017) and ~45–80% release for zeolites (Beler-Baykal et al., 2011; Tarpeh et al., 2017). However, more effective sorbents with improved capturing capacity, efficiency of release, and specificity are yet to be developed (Thornton et al., 2007; Zhang et al., 2007).

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 $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$. Isomorphous substitution of Si^{4+} by Al^{3+} in the framework induces a negative charge, giving rise to the intrinsic capability of adsorbing cations (Chu and Dwyer, 1983; Manto et al., 2017). 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 ($CaCl_2\cdot 2H_2O$, ACS reagent, ≥99%), magnesium chloride hexahydrate ($MgCl_2\cdot 6H_2O$, ACS reagent, 99.0–102.0%, Sigma-Aldrich), potassium chloride (KCl, ACS grade, VWR), sodium chloride (NaCl, ≥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 ($\lambda = 1.5406$ 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 liter, or 1 g-N L^{-1}, 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^{-1}) 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 (Solorzano, 1969; Weatherburn, 1967) 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.