Ammonium and Potassium Removal from Real Hydrolyzed Urine Using Natural Zeolites

by

Urusha Regmi

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Graduate Supervisory Committee:

Treavor Boyer, Chair
Anca Delgado
Kerry Hamilton

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ABSTRACT

The goal of this research was to study the effect of dilution on ammonium and potassium removal from real hydrolyzed urine. The performance of two natural zeolites, clinoptilolite and chabazite, was studied and compared using batch equilibrium experiments at four dilution levels: 100%, 10%, 1% and 0.1% (urine volume/total solution volume). Further, the sorption behavior of other exchangeable ions (sodium, calcium and magnesium) in clinoptilolite and chabazite was studied to improve the understanding of ion exchange stoichiometry. Ammonium and potassium removal were highest in undiluted urine samples treated with clinoptilolite. This is a key finding as it illustrates the benefit of urine source separation. Chabazite treated samples showed the highest ammonium and potassium removal at an undiluted level at lower doses. At higher doses, potassium removal was similar in undiluted and 10% urine solutions whereas ammonium removal was the highest in 10% urine solutions. In general, chabazite showed higher ammonium and potassium removal than clinoptilolite. The result showed that ion exchange was stoichiometric in solutions with higher urine volumes.

DEDICATION

I would like to dedicate this thesis to my parents who always encouraged me to pursue my dreams.

ACKNOWLEDGMENTS

I am thankful to all the wonderful people who supported me throughout my graduate school journey. The support and input of my committee members has been invaluable in the completion of this thesis.

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This would not have been possible without some very special people in my life. I am beyond lucky to have very encouraging parents who made it possible for me to pursue this degree. I would also like to mention Dr. Netra Chettri and Dr. Nalini Chettri, two very special people who have been like parents to me and my friends who made this journey seamless.

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CHAPTER 1

INTRODUCTION

Urine source separation has gained considerable attention as a sustainable approach to wastewater management that emphasizes nutrient recovery and recycling. According to recent studies, other potential benefits of this technique include water conservation (O'Neal & Boyer, 2013), improved effluent quality and reduced energy demand of wastewater treatment plants (Wilsenach & van Loosdrecht, 2003). Urine accounts for less than 1% of the total wastewater volume (Larsen & Gujer, 1996) but contributes approximately 80% nitrogen (N), 50% phosphorus (P) and 50% potassium (K) to its total nutrient load (Beler-Baykal, Allar, & Bayram, 2011). NPK are essential fertilizers that aide plant growth and crop yield (Yagoub, Ahmed, & Mariod, 2012). Direct application of urine can however have undesirable effects like increase in soil salinity and conductivity, loss of nutrients to plants and the environment, and crop failure (Karak & Bhattacharyya, 2011). As a more viable alternative, the nutrients in source-separated urine can be recovered as concentrated products through physical-chemical processes such as precipitation, air stripping and adsorption for further use.

Nitrogen in fresh urine is mostly in the form of urea (Beler-Baykal et al., 2011). Upon storage, urea in fresh urine is naturally hydrolyzed by microbial urease enzyme to ammoniacal nitrogen (NH_3/ NH_4^+) as shown in Equation (1)(Udert, Larsen, Biebow, & Gujer, 2003):

$$NH_2(CO)NH_2 + 2H_2O \leftrightarrow NH_3 + NH_4^+ + HCO_3^- \qquad (1)$$

Thus, the form of nitrogen in hydrolyzed urine is predominantly ammoniacal nitrogen. Ion exchange is a very effective technique employed in ammonium (NH_4^+) removal and recovery. Among the various natural zeolites, which are naturally occurring cation exchange materials, chabazite and clinoptilolite have demonstrated high ion-exchange capacities and affinities for ammonium (Hedström, 2001). Thus, clinoptilolite and chabazite can be used to remove ammonium in urine and the exhausted zeolites can further be used as slow release fertilizers (de Campos Bernardi et al., 2016). This approach can also eliminate the common problem of nitrogen loss due to ammonia volatilization faced in current agricultural practices where urea is used as a fertilizer (de Campos Bernardi et al., 2016). Additionally, potassium ions (K^+) in the urine can also be removed simultaneously owing to the high affinity of clinoptilolite and chabazite towards it (Hedström, 2001). The generalized equation for cation exchange in zeolites is given below:

$$Z^- : A^+ \; + \; B^+ \leftrightarrow Z^- : B^+ \; + \; A^+ \qquad (3)$$

In the above equation, Z^- represents the zeolite framework, A^+ represents the exchangeable cations present in the zeolite which participate in a stoichiometric exchange with the aqueous cation B^+.

The successful application of natural and modified zeolites in removal of ammonium from wastewater has been well documented (Booker, Cooney, & Priestley, 1996; Cooney, Booker, Shallcross, & Stevens, 1999; Hedström & Amofah, 2008; Khosravi, Esmhosseini, Jalili, & Khezri, 2012; Thorntona, Pearceb, & Parsons, 2007; Wang & Peng, 2010; Wasielewski, Rott, Minke, & Steinmetz, 2018; Widiastuti, Wu, Ang, & Zhang, 2011). The effect of the presence of competing ions on ammonium adsorption to clinoptilolite is known from a study conducted on an Italian groundwater treatment facility (Vocciante et al., 2018). Previous studies on ammonium and potassium removal and recovery from human urine using zeolites have focused on undiluted urine and primarily investigated clinoptilolite (Allar-Emeka & Beler-Baykal, 2017; Allar & Beler Baykal, 2015; Beler-Baykal et al., 2011; Beler-Baykal, Bayram, Akkaymak, & Cinar, 2004; Beler Baykal, Kocaturk, Allar, & Sari, 2009; Ganrot, Dave, & Nilsson, 2007; Lind, Ban, & Byden, 2000; Z. & G., 2004). The ammonium removal study performed by Beyler-Baykal in undiluted hydrolyzed urine using a fixed bed column packed with clinoptilolite showed up to 97% removal. Up to 88% of the removed ammonium was subsequently recovered using tap water giving an overall efficiency of 86%. The ammonium exhausted clinoptilolite when applied to *Ficus elastica*, a landscape plant, had similar effects as a synthetic fertilizer on the growth of the plant (Beler-Baykal et al., 2011). The effect of initial ammonium loadings on transfer of ammonium and potassium in undiluted hydrolyzed urine to preconditioned clinoptilolite in a column setting has been investigated. The results of this study showed that while there was no significant variation up to 10 mgNH_4^+/g clinoptilolite and 15 mgNH_4^+/g clinoptilolite on ammonium and potassium removal respectively, higher loadings led to lower removal efficiencies (Beler Baykal et al., 2009). Beyler-Baykal analyzed nutrient removal and recovery from pH-adjusted diluted urine solutions using preconditioned clinoptilolite in a column setting. The preconditioning was done using 1M of NaCl to convert the clinoptilolite to its sodium form. The study showed that samples with different percentages of urine, but the same initial loading had similar ammonium and potassium removal efficiencies (Kocatürk & Baykal, 2012). In the same study, it was observed that nutrient loaded clinoptilolite showed similar yield, measured as the dry mass, to chemical fertilizers when applied to flowerpots with grass (Kocatürk & Baykal, 2012).

The review of relevant literature highlights several gaps that this research seeks to fill. In conventional practices of wastewater treatment, urine is mixed with flush water and other waste streams that dilute and contaminate the nutrients. The effect of dilution on ammonium and potassium removal efficiency from urine using zeolites has been investigated in only one previous study as discussed above (Kocatürk & Baykal, 2012). The prospect of nutrient removal from urine using chabazite has not been addressed previously. Additionally, the study of sorption behavior of cations in literature is limited to ammonium and potassium; the characterization of other exchangeable ions in the zeolites has not been done in detail.

The main goal of this research was to investigate the effect of dilution on ammonium and potassium removal from real urine. Additional objectives were to (1) compare the performance of clinoptilolite and chabazite in ammonium and potassium removal, (2) investigate the sorption behavior of other exchangeable ions (sodium, calcium and magnesium) in clinoptilolite and chabazite to improve the understanding of ion exchange stoichiometry, (3) compare real urine results with previously available synthetic urine results to determine if synthetic urine can be used as a substitute for real urine in future studies. The objectives were accomplished using batch equilibrium tests.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

2.1.1. Zeolites

The two natural zeolites used in this work were clinoptilolite and chabazite. The zeolites were supplied by St. Cloud Mining, USA. The composition and properties of the zeolites used are listed in Tables S1 and S2 in Supplementary Material (SM), as reported by the supplier. The zeolites were used as received and were measured and dosed on a dry mass basis for all experiments.

2.1.2. Real hydrolyzed urine

Real urine samples were collected from male and female volunteers over a period of 8 hours and stored in a plastic barrel for three months. The extent of urea hydrolysis was monitored periodically and determined to be 90% at the end of the storage period as per total nitrogen, ammonia, and urea measurements. The hydrolyzed urine was then stored in collapsible polyethylene terephthalate containers to minimize headspace for ammonia volatilization.

2.1.3. Dilutions

The hydrolyzed urine was used undiluted (i.e., 100% urine) and at the following dilution levels (i.e., volume urine per volume total solution): 10, 1, and 0.1% (v/v). Dilutions in the study were done using tap water from a building which does whole-building water softening using cation exchange. Tap water was used for dilutions to replicate practical scenario where flushing is done used tap water in urinals. Tap water was collected at the time of each experiment and had the cation composition as shown in Table 2.1. Table 2.2 shows the initial cation concentrations of undiluted and diluted urine solutions used in equilibrium studies.

Table 2.1 – Composition of tap water used for dilutions in equilibrium studies. The column headings represent different dilution levels.

Component	100%[a,b]	100%[a,c]	10%[a,b]	10%[a,c]	1%[a,b]	1%[a,c]	0.1%[a,b]	0.1%[a,c]
NH_4^+	0.34	0.41	0.48	1.48	0.31	0.41	1.65	1.10
Na^+	271	258	309	222	295	180	312	317
K^+	6.70	24.7	9.67	7.46	4.36	2.07	2.70	2.40
Mg^{2+}	0.13	0.16	0.31	0.23	0.18	0.11	0.33	0.33
Ca^{2+}	0.68	0.79	1.80	1.44	0.89	0.68	1.14	1.19

[a] Measured; mg/L
[b] Clinoptilolite equilibrium study.
[c] Chabazite equilibrium study.

Table 2.2 – Composition of undiluted (100%) and diluted (10, 1, and 0.1%) urine solutions. The column headings represent different dilution levels.

Component	100%[a,b]	100%[a,c]	10%[a,b]	10%[a,c]	1%[a,b]	1%[a,c]	0.1%[a,b]	0.1%[a,c]
NH_4^+	5640	5220	647	583	63.7	53.2	6.86	6.60
Na^+	1800	1844	465	306	315	185	312	264
K^+	1336	1328	143	141	18.9	14.5	4.84	4.24
Mg^{2+}	0.31	0.32	0.26	0.24	0.19	0.16	0.30	0.22
Ca^{2+}	1.93	1.90	1.53	1.53	1.04	0.82	1.24	1.03

[a] Measured; mg/L
[b] Clinoptilolite equilibrium study.
[c] Chabazite equilibrium study.

2.2. Experimental methods

Batch equilibrium tests were conducted using clinoptilolite and chabazite at urine volume percentages of 0.1, 1, 10, and 100% for 1 d as this was determined to be sufficient time to reach equilibrium from the kinetic study (Cribbs and Boyer, unpublished). Varying dose of zeolite was added to 100 mL urine solution in 125 mL amber glass bottle as shown in Table 2.3. For each dose, the ratio of zeolite mass to urine volume was the same across all urine volume percent. Due to size constraint of the sample bottles, doses higher than 500 g/L were not tested for undiluted urine samples. Control samples included tap water with zeolite, urine without zeolite, and tap water without zeolite at each urine volume percent for all experiments. Samples were placed on a Thermo Scientific™ MaxQ™ 2000 and 3000 Benchtop Orbital Shakers at 200 rpm for mixing. Samples were generated in triplicate and diluted as described previously. The ambient laboratory temperature was 24°C.

Table 2.3 – Experimental matrix for equilibrium studies.

Urine (v/v)	Zeolite dose (g/L)						
100%	200	300	400	500	–	–	–
10%	20	30	40	50	70	90	110
1%	2	3	4	5	7	9	11
0.1%	0.2	0.3	0.4	0.5	0.7	0.9	1.1

2.3. Analytical methods

Samples from the equilibrium tests were filtered using 0.45 µm filters (Environmental Express) before being measured for pH and conductivity using Orion Versastar Pro-advanced Electrochemistry meter. The meter was calibrated for pH with pH 4, 7 and 10 buffer solutions and for conductivity with 100 µScm^{-1}, 1413 µScm^{-1}, 12000 µScm^{-1}, 50000 µScm^{-1} and 100000 µScm^{-1} standards prior to use. Total nitrogen (TN) concentration of samples was measured using the Shimadzu Total Nitrogen Measuring Unit Analyzer (TNM-L). All samples were stored in tightly capped amber bottles to avoid ammonia loss due to volatilization at 4 °C during storage periods prior to analysis. The cation concentrations (magnesium, sodium, potassium and calcium) were measured using Inductively Coupled Plasma (ICP) optical emission spectrometer (Thermo Fisher iCap 6000 ICP-OES). All measurements were done in duplicates.

CHAPTER 3

RESULTS AND DISCCUSSION

In this section, sample names correspond to the percentage of urine present in their total volume. For example, 10% urine solutions refer to samples with 10% urine and 90% tap water, i.e., the urine has been diluted by a factor of 10 (DF=10).

Table 3.1 – Practical scenarios represented by the dilution factors used in the study.

Dilution factor (DF)	Urine (v/v)	Description	Examples of Corresponding Scenarios
1	100%	Undiluted urine	Waterless urinals and no-mix toilets(O'Neal & Boyer, 2013)
10	10%	Moderate flush water volume in urinals and toilets	
		DF = 3.5	High – efficiency urinals(O'Neal & Boyer, 2013)
		DF = 21	Standard urinals(O'Neal & Boyer, 2013)
100	1%	Moderate dilution with grey water(Larsen & Gujer, 1996)	-
		DF = 66	1.4 L/person/d of urine diluted by 91.3 L/person/d of greywater(O'Neal & Boyer, 2013)
		DF = 188	1.4 L/person/d of urine diluted by 262 L/person/d of wastewater(O'Neal & Boyer, 2013)
1000	0.1%	-	Urine typically represents <1% of total wastewater (Larsen & Gujer, 1996)

Figures 3.1, 3.3, 3.5, 3.6, 3.8, 3.10 show the results of the equilibrium studies with real urine where normalized concentrations of total nitrogen, potassium and sodium for all dilution levels are plotted against zeolite doses normalized by the percentage of urine in the solution for comparison across different dilution levels. In this section, dose values will correspond to the normalized zeolite doses. For example, a dose of 500 g/L in 10% urine solutions will correspond to a dose of 50 g/L. All plots are the average of triplicate samples and the error bars represent one standard deviation. The concentrations of different cations present in the tap water used for dilutions are tabulated in Table 2.1. Table 2.2 lists the initial TN concentrations in undiluted and diluted urine solutions used in the equilibrium studies. It is assumed that the urine was completely hydrolyzed, and all the nitrogen was in the form of ammonium. Although this assumption is inaccurate, as the pH of hydrolyzed urine is 9.3 at which ammoniacal nitrogen is distributed to ammonia and ammonium, the decrease in TN concentrations can be used as a surrogate for the decrease in ammonium concentrations as only ammonium takes part in the ion exchange.

Results of equilibrium studies with clinoptilolite are discussed in Section 3.1 followed by chabazite studies results in Section 3.2. In each subsection of sections 3.1 and 3.2, real urine results are discussed followed by discussion of previously available synthetic urine data for the purpose of comparison of real and synthetic urine behaviors.

The synthetic urine study used for comparison of nutrient removal in real urine with removal in synthetic urine was performed in University of Florida, Gainesville. The synthetic hydrolyzed urine composition and recipe was based on previous literature

(Sendrowski & Boyer, 2013). The pH of synthetic hydrolyzed urine was 9.5 and was prepared with ACS purity chemicals in deionized (DI) water and stored in collapsible polyethylene terephthalate containers to minimize head space for ammonia volatilization. The experiments with synthetic urine were performed at the same dilution levels as real urine experiments. The dilutions were performed using DI water in the kinetic study and using tap water in the equilibrium study. All samples consisted of 125 mL amber bottles with screw cap and contained 100 mL of urine solution. All experiments were performed on an Innova 2000 Platform Shaker at 200 rpm, samples in triplicate, and diluted as described previously. The ambient laboratory temperature was 24°C. The equilibrium time determined from the kinetic study was 24h and, thus, was the time used in the equilibrium study with real urine. The synthetic urine samples in kinetic study were measured for TN using a Shimadzu TOC-V_{CPH} total organic carbon analyzer with a TNM-1 total nitrogen measuring unit. The synthetic urine samples in equilibrium study were measured using ion chromatography (IC) for NH_4^+, K^+, Na^+, Mg^{2+}, and Ca^{2+}. Samples were generated in triplicate and measured in duplicate as with real urine study. All concentrations were reported as the mean value of triplicate samples (Cribbs and Boyer, *unpublished*). The results of this study are presented in the Appendix.

3.1. Equilibrium studies with Clinoptilolite

3.1.1. Effect of dilution on ammonium removal

Ammonium (NH_4^+) was removed from all real urine solutions treated with clinoptilolite. For up to a dose of 500 g/L clinoptilolite, removal was the highest at undiluted level (DF=1) (Fig. 3.1). The highest removal observed in undiluted urine solutions was 66% for a dose of 500 g/L clinoptilolite which corresponded to an initial ammonium loading of 5.12 mg/g. Up to 97% ammonium removal was observed in a previous study with clinoptilolite treated undiluted urine (Beler-Baykal et al., 2011). The clinoptilolite was preconditioned with NaCl to attain the sodium form and the initial ammonium loading was 3 mg/g (Beler-Baykal et al., 2011). Since initial ammonium loading has no effect on removal efficiencies up to 10 mg/g (Beler Baykal et al., 2009), the higher removal observed in the previous study was likely due to the preconditioning of clinoptilolite as the sodium form has a higher ammonium exchange capacity . Another reason for the difference could be the use of TN as an indicator of ammonium concentrations as it is a measurement of all the nitrogen species in urine solutions, including ammonia, which is not removed by ion exchange. It was observed that, in general, ammonium removal in undiluted and 10% urine solutions increased with increase in clinoptilolite dose. With increasing dose, more sites are available for ammonium exchange which can be attributed to the increasing removal. The reason for the low removal and irregular trends observed in 0.1% and 1% urine solutions could be the very high sodium concentrations in the tap water which was used for dilutions. The high sodium concentration in the tap water used in this study was likely due to sodium release during the softening of building water. Clinoptilolite shows the following order of selectivity towards the different cations present in urine solutions used in this study: $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$ (Hedström, 2001). The presence of high sodium concentrations in 0.1% and 1% urine solutions can thus affect the ammonium uptake of clinoptilolite. The highest ammonium removal observed across all doses was 73% which was achieved for 10% urine solution with 110 g/L clinoptilolite. Figure 3.2 shows the plot of ammonium loadings on clinoptilolite (solid phase concentration) at different doses against the ammonium concentrations of the treated urine solutions (liquid phase concentration). The highest ammonium loadings on the exhausted clinoptilolite observed across different doses were 10.2 mg/g, 7.2 mg/g, 11.4 mg/g and 11.5 mg/g for 0.1%, 1% 10% and undiluted urine solutions respectively. These were observed at 200 g/L clinoptilolite in 0.1%, 10% and undiluted urine solutions and at 300 g/L clinoptilolite in 1% urine solutions.

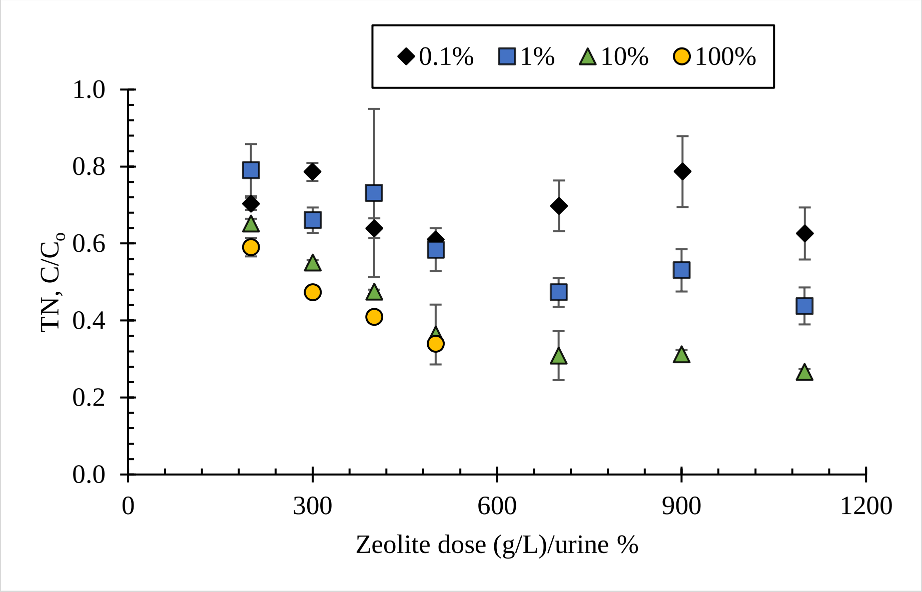

Figure 3.1 – Reduction in aqueous ammonium (NH_4^+-N) concentration by clinoptilolite sorption as function of zeolite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial NH_4^+ concentration, C_o, given in Table 2.

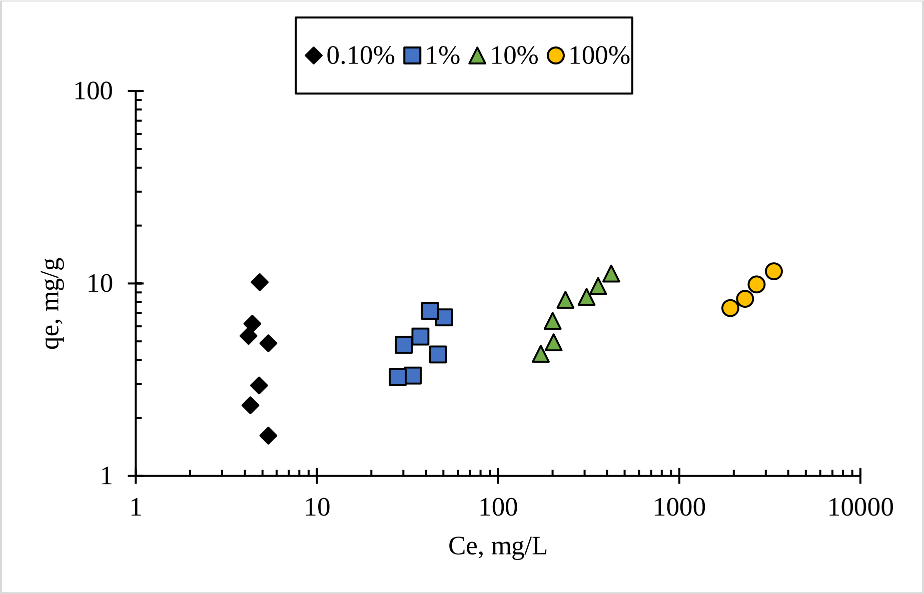

Figure 3.2 – Equilibrium ammonium sorption to clinoptilolite for undiluted and diluted urine solutions; solid-phase concentration, qe; solution concentration, Ce. Legend gives percent urine by volume. Data are mean value of triplicate samples.

Ammonium removal trends observed in real urine varied from synthetic urine trends. Up to a dose of 500g/L zeolite, ammonium removal in synthetic urine using clinoptilolite increased with increase in dose with highest removal in 1% urine solutions at each dose. The same trend did not continue for higher doses. The highest ammonium removal in synthetic urine was 71% which was observed for 1% urine solution treated with 500 g/L zeolite. The ammonium loadings on clinoptilolite were higher in synthetic urine than real urine. The highest loadings observed were 21.4 mg/g in 0.1%, 42.6 mg/g in 1%, 25.0 mg/g in 10% and 29.9 mg/g in undiluted urine solutions, all with 200 g/L clinoptilolite. The differences in diluted real and synthetic urine solutions were likely due to the change in experiment location and use of different sources of tap water (Cribbs and Boyer, *unpublished*).

3.1.2. Effect of dilution on potassium removal

As with ammonium removal results in real urine (Section 3.1.1.), the highest potassium (K^+) removal in real urine studies was observed in undiluted urine samples for up to a dose of 500g/L clinoptilolite (Fig. 3.3). Potassium removal increased with increase in clinoptilolite dose in 10% and undiluted urine solutions as expected due to increased availability of exchange sites (one sample among the 300g/L triplicate samples in 10% urine was removed due to very high variability). Potassium was released for all 0.1% urine solutions as well as 1% urine solutions with clinoptilolite doses lower than 900g/L. At lower doses, the available sites were likely occupied by ammonium due to which potassium removal could not be achieved. The highest potassium removal was observed in undiluted (58%) and 10% urine (57%) solutions with 500g/L and 1100g/L clinoptilolite respectively. In a previous study with NaCl preconditioned clinoptilolite, up to 89% and 55% potassium removal was observed in undiluted and 30% urine solutions (Kocatürk & Baykal, 2012). The reason for the high difference in potassium removals in undiluted urine solutions is not known. The highest potassium loadings were 1.17 mg/g and 1.63 mg/g in 10% urine solutions with 500g/L clinoptilolite, and undiluted urine solutions with 400 g/L clinoptilolite, respectively (Fig 3.4). In theory, clinoptilolite is more selective towards potassium than ammonium owing to the smaller hydration radius of potassium ions. However, comparing to ammonium removal results in Section 3.1.1., clinoptilolite was more selective towards ammonium in this study than potassium when used to treat real urine. The reason for this could be the higher concentration of ammonium in the urine solutions leading to a higher concentration gradient between the solid and liquid phase, thus favoring ammonium removal.

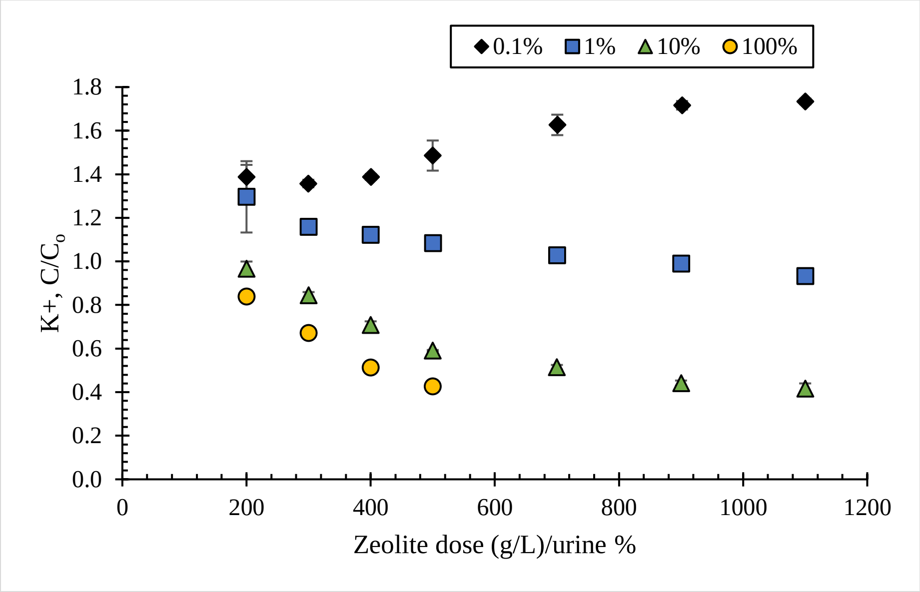

Figure 3.3 – Change in aqueous potassium (K^+) concentration by clinoptilolite sorption/desorption as function of zeolite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial K^+ concentration, C_0, given in Table 2.

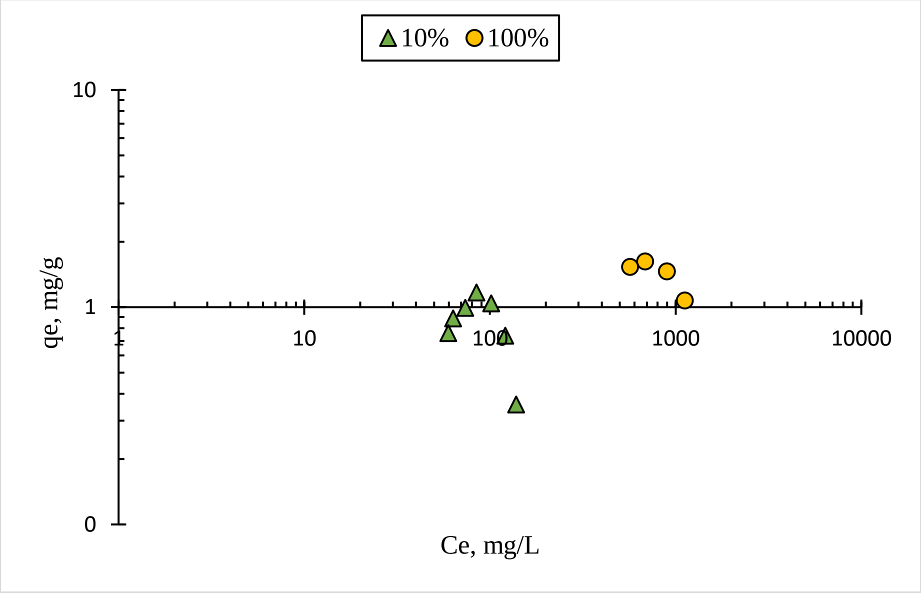

Figure 3.4 – Equilibrium potassium sorption to clinoptilolite for undiluted and diluted urine solutions; solid-phase concentration, qe; solution concentration. Legend gives percent urine by volume. Data are mean value of triplicate samples.

Potassium behavior in real and synthetic urine were similar as discussed in this paragraph. In synthetic urine studies, potassium was released in all 0.1% urine solutions and 1% urine solutions treated with doses lower than 500 g/L clinoptilolite. Potassium removal in 10% and undiluted urine solutions were comparable and increased with increasing clinoptilolite dose. The maximum potassium removal achieved was 57% for 10% urine solution treated with 1100 g/L zeolite. The highest potassium loadings observed were 1.16 mg/g and 1.54 mg/g in 10% urine solutions with 400 g/L clinoptilolite and undiluted urine solutions with 200 g/L clinoptilolite respectively. Ammonium removal was higher than potassium removal in synthetic urine studies as well (Cribbs and Boyer, *unpublished*).

3.1.3. Characterization of exchangeable ions

It is important for charge neutrality to be maintained during ion exchange. Thus, the exchange of ions is analyzed in units of meq/L rather than their concentrations. Ammonium removal in 0.1% urine solutions were in the range of 0.08 meq/L to 0.14 meq/L. Consequently, it was expected that change in sodium in units of meq/L would also be in a comparable range to maintain electroneutrality. Due to limitations in instrumental accuracy, corresponding sodium changes in units of mg/L could not be accurately detected as the initial sodium concentration in the urine solutions was very high. Thus, results for 0.1% urine solutions are not discussed in this section. In 1%, 10% and undiluted urine solutions, the primary cations that exchanged with ammonium and potassium were sodium and calcium. Magnesium concentrations remained essentially constant in all the studies. While both sodium and calcium were released, sodium release was higher by at least an order of magnitude at all dilution levels. At each dose, sodium release was higher for urine solutions with a higher urine volume percent (Fig. 3.5). This was in coherence with predicted results as the concentration of ammonium and potassium was higher in urine solutions with a higher urine volume percent (Table 1); thus, requiring more sodium ions to be released for their removal. Figure 3.11 shows the plot of released against removed ions during ion exchange which were in comparable magnitude in 1%, 10% and undiluted urine solutions suggesting stoichiometric exchange.

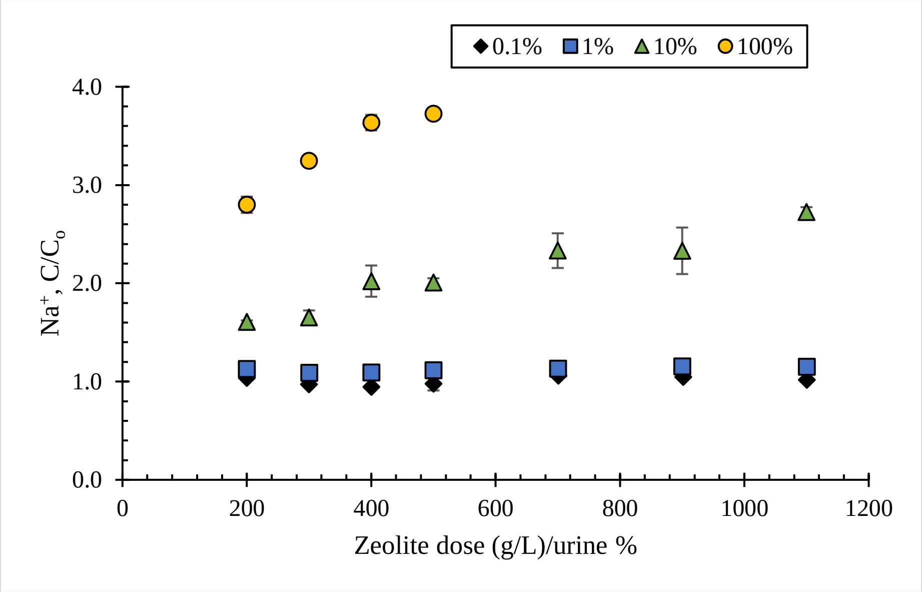

Figure 3.5 – Change in aqueous sodium (Na^+) concentration by clinoptilolite desorption as function of clinoptilolite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial Na^+ concentration, C_0, given in Table 3.

Similar to real urine, sodium was the primary cation that exchanged with ammonium and potassium in synthetic urine solutions. Magnesium and calcium measurements in 10% urine solutions showed high variability; thus, will not be discussed in this section. Magnesium and calcium were not present in undiluted urine. Clinoptilolite showed magnesium removal in synthetic urine. The removal increased with increase in clinoptilolite dose and was higher in 1% than in 0.1% urine solutions. Sodium release increased with increasing zeolite dose and increasing urine volume present. In summary, clinoptilolite showed removal of ammonium > potassium with sodium release in 100% urine, whereas clinoptilolite showed removal of ammonium > calcium > magnesium with sodium and potassium release in 0.1% urine (Cribbs and Boyer, *unpublished*).

3.2. Equilibrium studies with Chabazite

3.2.1. Effect of dilution on ammonium removal

Ammonium removal was the highest in 10% urine solutions at all chabazite doses higher than 300g/L. Similar to clinoptilolite studies, the highest ammonium removal was observed for 10% urine solutions with 1100g/L chabazite (Fig.3.6). Removal was the lowest in 0.1% urine solutions in general for the same reason as discussed in Section 3.1.1. However, the maximum removal was 5% higher in chabazite treated solutions. The reason for this could be the higher cation exchange capacity (CEC) of chabazite as a result of higher substitution of Si by Al in the aluminosilicate framework. Removal in 1% and 10% urine solutions increased with increasing chabazite dose as a result of higher availability of exchange sites. The highest ammonium loadings were 9.59 mg/g, 7.38 mg/g, 14.3 mg/g and 15 mg/g in 0.1%, 1%, 10% and undiluted urine solutions respectively all of which were observed at 200 g/L chabazite dose. Compared to clinoptilolite, ammonium loadings in 10% and undiluted urine solutions were higher on chabazite. The plot of solid phase ammonium concentration against liquid phase ammonium concentration in real urine is shown in Figure 3.7.

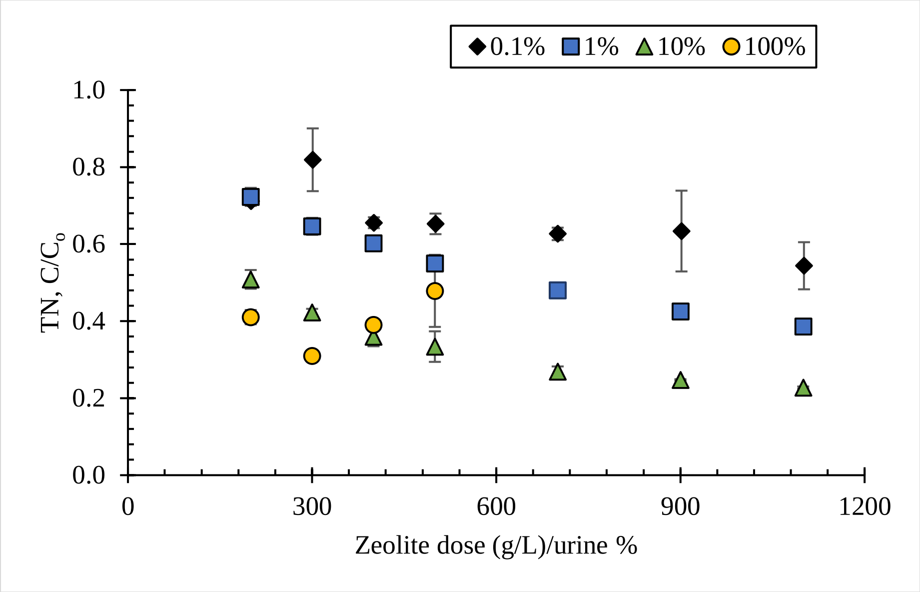

Figure 3.6 – Reduction in aqueous ammonium (NH_4^+) concentration by chabazite sorption as function of zeolite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial NH_4^+ concentration, C_o, given in Table 2.

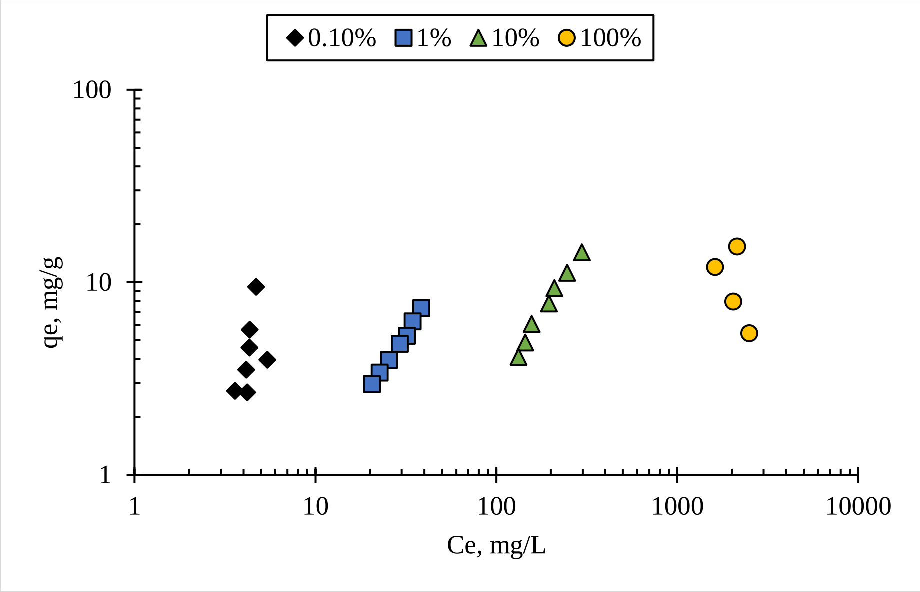

Figure 3.7 – Equilibrium ammonium sorption to chabazite for undiluted and diluted urine solutions; solid-phase concentration, qe; solution concentration, Ce. Legend gives percent urine by volume. Data are mean value of triplicate samples.

The results of chabazite studies discussed above varied from synthetic urine data as discussed here. Up to a dose of 500g/L, the highest ammonium removal was observed in undiluted urine solutions. Ammonium removal increased with increase in zeolite dose up to 400g/L in 0.1%, 1% and 10% urine after which there was a significant decrease in the removal. Compared to real urine, the highest removal was 5% greater in synthetic urine, observed in 10% urine solutions with 1100g/L chabazite. The highest ammonium loadings were 32.5 mg/g, 23.9 mg/g, 33.3 mg/g and 38.7 mg/g in 0.1%, 1%, 10% and undiluted urine solutions which were all significantly higher than in real urine solutions (Cribbs and Boyer, *unpublished*).

3.2.2. Effect of dilution on potassium removal

Chabazite removed potassium in all the real urine solutions with an exception of 0.1% urine solutions treated with 200g/L and 300g/L zeolite. This could be due to occupancy of exchange sites by removed ammonium at lower doses. Similar to clinoptilolite studies, potassium removal up to 500g/L dose was highest at undiluted level; the only exception being 10% urine solutions treated with 500g/L dose which had an equal removal. The highest removal across all doses, 82%, was observed for undiluted urine solution with 300g/L zeolite. Increased removal with increasing zeolite dose was observed only in 1% urine solutions. The highest potassium loadings on chabazite were 0.55 mg/g, 2 mg/g, 4.64 mg/g and 5mg/g for 0.1%, 1%, 10% and undiluted urine solutions. Thus, potassium loading, and removal were higher for urine solutions treated with chabazite compared to clinoptilolite due to its higher cation exchange capacity. The plot of solid phase potassium concentration against liquid phase potassium concentration is shown in 3.9. Although chabazite is theoretically more selective towards potassium than ammonium owing to the smaller hydrated radius of potassium, in units of meq/L, ammonium removal was at least an order of magnitude higher than potassium removal in chabazite treated urine solutions. The reason for this could be the higher concentration of ammonium in the urine solutions, creating a higher concentration gradient driving the removal in favor of ammonium uptake.

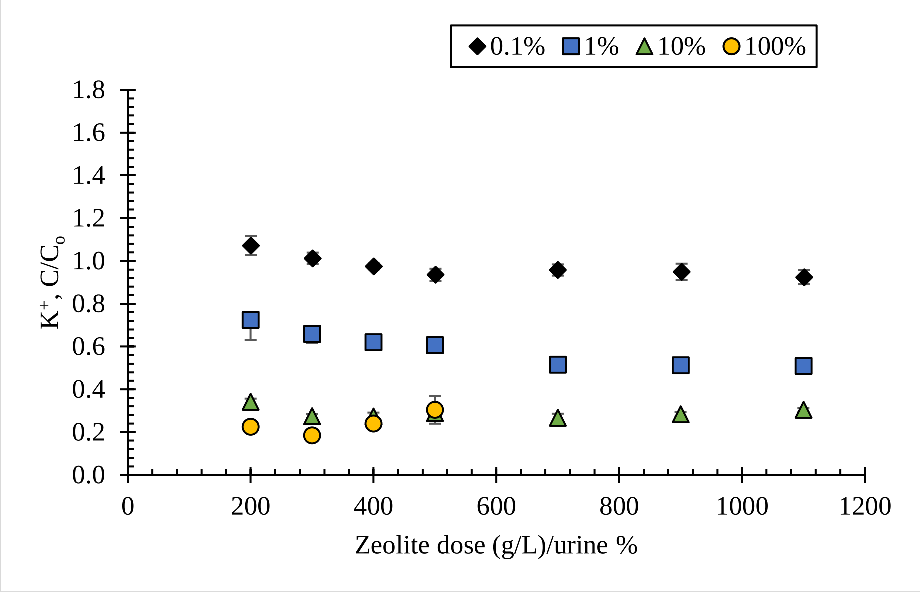

Figure 3.8 – Change in aqueous potassium (K^+) concentration by chabazite sorption/desorption as function of zeolite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial K^+ concentration, C_0, given in Table 2.

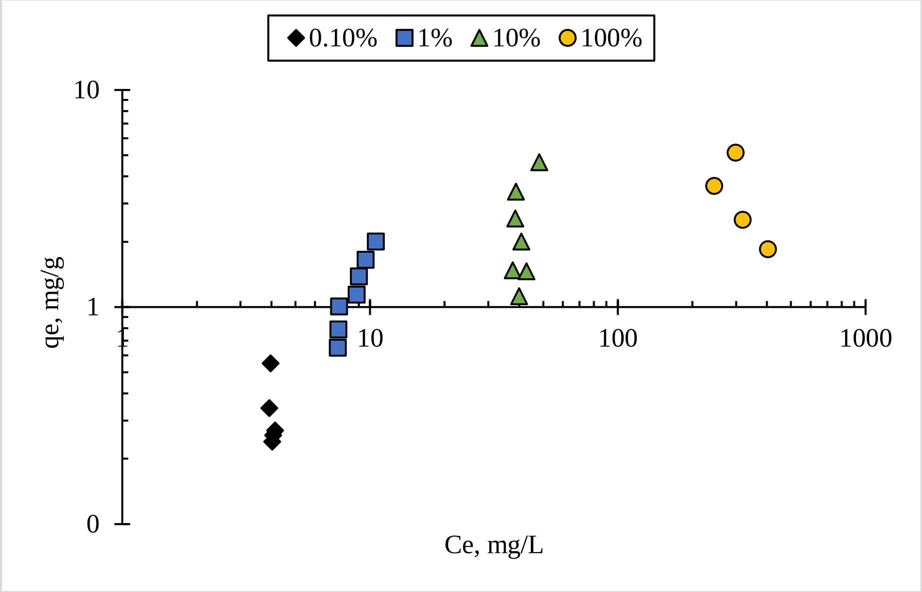

Figure 3.9 – Equilibrium potassium sorption to chabazite for undiluted and diluted urine solutions; solid-phase concentration, qe; solution concentration. Legend gives percent urine by volume. Data are mean value of triplicate samples.

Chabazite removed potassium from all synthetic urine solutions. In general, the highest removal at each dose was observed in 10% urine solutions. Removal increased with increasing dose in 0.1% urine solutions with a significant increase from 400 g/L to 500 g/L dose. This could be accountable for the decrease in ammonium removal observed at doses higher than 300 g/L in 0.1% urine solutions (Section 3.2.1.). Up to 82% potassium removal was achieved in 10% urine solutions with 900 g/L chabazite. The highest potassium loadings observed in synthetic urine were 3.34 mg/g, 5.49 mg/g, 6.84 mg/g and 6.31 mg/g for 0.1%, 1%, 10% and undiluted urine solutions respectively. These values corresponded to chabazite doses of 500 g/L for 0.1% urine solutions and 200 g/L in 1%, 10% and undiluted urine solutions (Cribbs and Boyer, *unpublished*).

3.2.3. Characterization of exchangeable ions

The results of 0.1% urine solutions are not discussed in this section due to very high sodium concentrations. Ammonium and potassium exchanged with calcium, magnesium and primarily with sodium in chabazite studies with real urine. The release of sodium and magnesium was the highest in undiluted urine solutions (Fig. 3.10) while calcium release was highest in 10% urine solutions at all doses. Compared to clinoptilolite studies, chabazite released more sodium in undiluted and 1% urine solutions. Figure 3.11 shows the plot of removed against released ions. The combined magnitude of calcium, magnesium and sodium release was higher than combined removal of ammonium and potassium for all doses in 1% urine solutions and lower in 10% urine solutions in general . Undiluted urine solutions showed a more linear relationship between released and removed ions suggesting stoichiometric exchange.

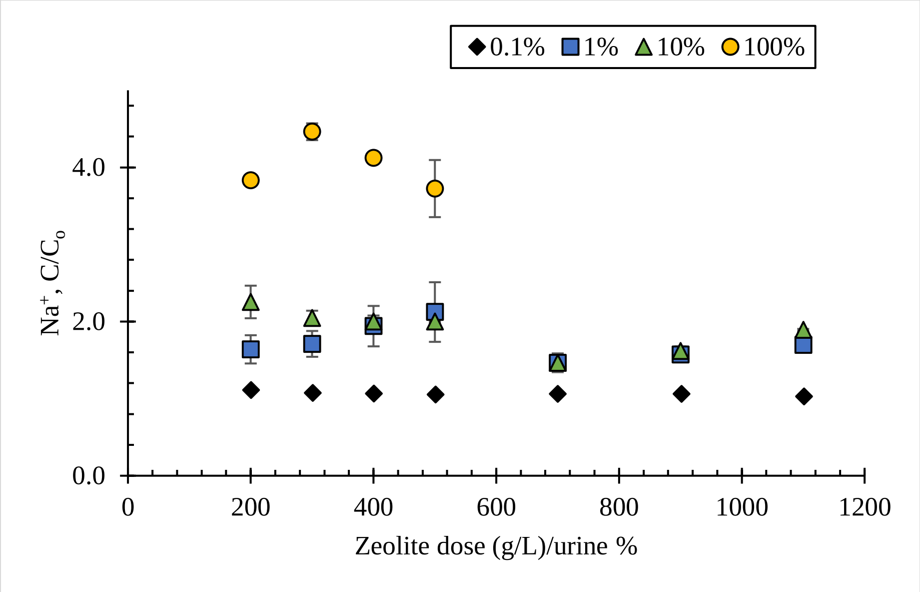

Figure 3.10 – Change in aqueous sodium (Na^+) concentration by chabazite desorption as function of chabazite dose normalized by percent urine by volume at equilibrium. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation. Initial Na^+ concentration, C_0, given in Table 3.

In synthetic urine however, chabazite removed ammonium, magnesium and calcium and potassium in exchange with sodium in 0.1% and 1% urine solutions. Magnesium and calcium were not present in undiluted urine solutions and showed high variability in 10% urine solutions; thus, are not discussed in this section. Sodium release increased with increased zeolite dose for all urine solutions (Cribbs and Boyer, *unpublished*).

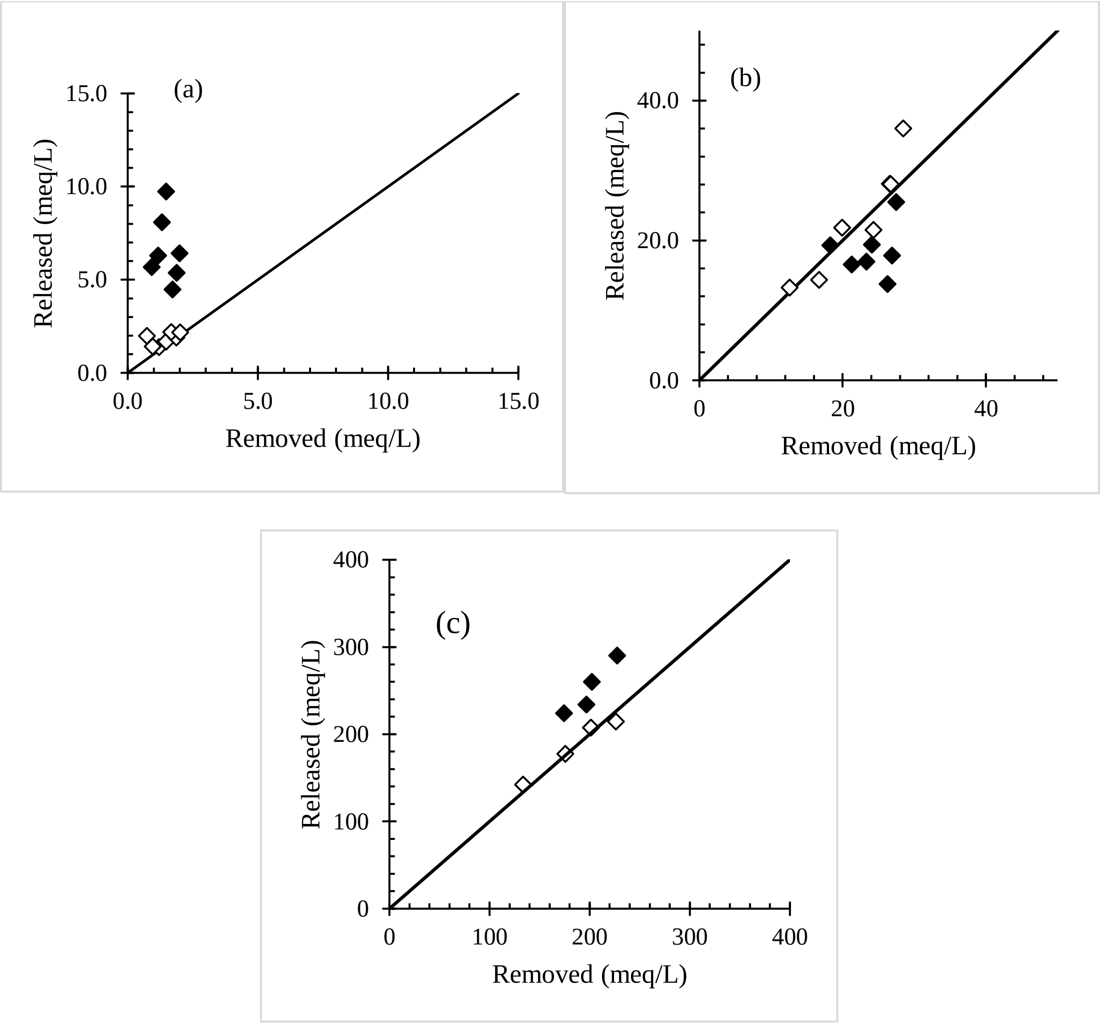

Figure 3.11 – Exchange of cations in urine solution for counterions in zeolite framework: (a) 1%, (b) 10% and (c) 100% urine solutions. Open symbols show clinoptilolite; closed symbols show chabazite; solid line shows y = x. Data are mean of triplicate samples.

The results of this study show that ammonium and potassium removal from real urine using zeolites depends on the urine solution composition. This is in contrast with the findings of a previous study which showed that for the same initial ammonium loading, similar ammonium and potassium removal in all urine solutions with different percent of urine volume in them (Kocatürk & Baykal, 2012). As seen in urine solutions with high dilution factors, the presence of high sodium concentrations interfered with the nutrient removals. This supports the idea that urine should be collected separately instead of being mixed with wastewater before going to treatment plants.

CHAPTER 4

CONCLUSION

The main focus of this study was to study the effect of dilution on ammonium and potassium sorption on two natural zeolites, clinoptilolite and chabazite, for their removal from human urine. Experiments were conducted at four dilution levels and the behavior of exchangeable ions was also studied to gain a better understanding of the removal mechanism.

Ammonium and potassium removal in real urine were highest in undiluted urine samples treated with clinoptilolite. This is a key finding as it illustrates the benefit of urine source separation rather than treatment after dilution in the distribution system or at a wastewater plant. However, difference in ammonium removal in undiluted and 10% urine solutions was less than 15% across all doses. Thus, clinoptilolite can be effective in ammonium removal in buildings which have both waterless and moderate flush urinals. In general, chabazite showed better ammonium and potassium removal in real urine studies compared to clinoptilolite. Ammonium and potassium removal in chabazite treated urine solutions were in general highest in undiluted urine solutions at lower doses. For doses higher than 300 g zeolite/ % urine, chabazite showed comparable potassium removal in undiluted and 10% urine solutions but ammonium removal was higher in 10% urine solutions. However, doses higher than 500 g/L were not used in this study which limits our knowledge about zeolite behavior at higher doses. Since sodium release in chabazite studies was high, its implication in the treated water use should be considered. It was also observed that the difference in potassium removal in 10% and undiluted urine solutions treated with chabazite showed less than 15% or less difference. Thus, chabazite is suitable for potassium removal in buildings with both waterless and moderate flush urinals.

Although literature suggests similarity in real and synthetic urine sorption behavior, synthetic urine trends varied from real urine and overestimated ammonium removal, and ammonium and potassium loadings on chabazite at equilibrium in chabazite studies. Thus, it is advisable to use real urine in further ion exchange studies. Subsequent experiments should be conducted using real urine in column tests at the bench and pilot scale for at DF = 10 and undiluted level as highest removals were observed at these dilution levels. Additional experiments should be conducted to evaluate regeneration and recovery of ammonium from urine for fertilizer production.

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APPENDIX A

SUPPLEMENTARY TABLES

Table S1: Chemical composition by percent mass of clinoptilolite and chabazite. [a]

Zeolite	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	Na_2O	K_2O	CaO	TiO_2	P_2O_5	LOl
Clinoptilolite	66.73	10.27	0.86	0.04	0.51	3.03	3.59	1.77	0.11	0.00	13.09
Chabazite	68.10	18.59	2.84	-	0.75	8.32	1.12	0.27	-	-	-

[a] From supplier.

Table S2 : Physical-chemical properties of clinoptilolite and chabazite. [a]

Zeolite	particle diameter (μm)	pore diameter (Å)	pore volume cm^3/g	surface area (m^2/g)	particle density (g/cm^3)	Si/Al ratio	Ion-exchange Capacity (meq/g)
Clinoptilolite	297-420	4.0	0.029	≤ 800	2.2-2.4	5.1	1.85
Chabazite	297-420	4.3	0.468	520.95	1.73	3	2.50

[a] From supplier.

Table S3 : pH measurements of clinoptilolite and chabazite treated urine solutions

Zeolite dose(g/L) / % urine	100%[a]	100%[b]	10%[a]	10%[b]	1%[a]	1%[b]	0.1%[a]	0.1%[b]
200	9.30	9.01	9.38	9.14	9.19	8.96	8.13	8.10
200	9.31	9.13	9.38	9.34	9.19	8.99	8.20	8.04
200	9.31	9.02	9.37	9.12	9.20	8.99	8.20	8.00
300	9.41	8.93	9.44	9.38	9.24	9.04	8.17	7.93
300	9.40	8.64	9.45	9.27	9.25	9.00	8.17	8.00
300	9.39	8.77	9.45	9.30	9.23	9.02	8.14	8.01
400	9.47	8.84	9.54	9.30	9.30	9.08	8.28	8.01
400	9.47	8.86	9.52	9.04	9.20	9.03	8.31	8.08
400	9.47	8.90	9.51	9.11	9.29	9.02	8.27	8.01
500	9.52	9.14	9.59	9.03	9.32	9.07	8.30	8.03
500	9.53	9.03	9.57	8.64	9.33	9.03	8.18	8.00
500	9.53	9.10	9.59	8.94	9.31	9.07	8.20	8.02
700			9.63	8.91	9.36	9.06	8.24	8.04
700			9.63	8.58	9.38	9.03	8.29	8.08
700			9.61	8.47	9.37	9.07	8.22	8.00
900			9.67	8.64	9.38	9.04	8.20	8.04

900			9.67	8.69	9.36	9.07	8.24	8.04
900			9.67	8.41	9.39	9.07	8.33	8.07
1100			9.67	8.43	9.43	9.02	8.20	8.01
1100			9.67	8.28	9.39	9.07	8.26	8.02
1100			9.10	8.42	9.41	9.04	8.24	8.08
-	9.09	9.11	9.08	9.07	9.08	8.85	8.21	8.09
-	9.09	9.11	9.07	9.07	9.08	8.85	8.21	8.00
-	9.10	9.11	9.05	9.07	9.08	8.85	8.11	7.90

[a] Clinoptilolite equilibrium study.
[b] Chabazite equilibrium study.

Table S4 : Conductivity measurements of clinoptilolite and chabazite treated urine solutions.

Zeolite dose(g/L) / % urine	100%[a,c]	100%[b,c]	10%[a,d]	10%[b,c]	1%[a,d]	1%[b,d]	0.1%[a,d]	0.1%[b,d]
200	19.40	34.69	5008	6.02	1900	2180	2013	1134
200	30.32	34.29	5018	5.78	1869	2100	2024	1047
200	30.09	35.19	5058	6.05	1899	2114	2009	1032
300	29.60	36.22	5035	6.18	1854	2106	2022	1036
300	29.88	36.15	5069	6.30	1864	2236	2013	1047
300	29.00	36.21	5045	6.31	1869	2226	2009	1032
400	28.58	36.32	5059	6.77	1866	2178	2004	1030
400	28.89	36.51	5101	6.95	1834	2223	2031	1028
400	29.24	36.16	5109	7.13	1863	2257	2000	1035
500	28.70	32.71	5133	7.64	1830	2282	2027	1021
500	28.50	34.82	5096	8.23	1831	2356	2031	1024
500	28.56	33.62	5122	8.05	1842	2304	2021	1018
700			5159	8.66	1870	2438	2032	1019
700			5213	9.09	1836	2542	2019	1020
700			5192	9.57	1868	2427	2021	1014
900			5232	10.02	1835	2648	2026	1015
900			5263	10.18	1866	2566	2015	1004
900			5327	10.55	1846	2576	2032	1026
1100			5293	11.40	1899	2717	2013	1001
1100			5329	11.95	1872	2727	2034	1008
1100			5237	11.67	1900	2742	2029	1019
-	33.31	32.49	5387	5.38	1852	2044	2027	1007
-	33.10	32.11	5416	5.42	1857	2011	2044	997
-	33.05	32.23	5457	5.38	1870	1991	2033	993

[a] Clinoptilolite equilibrium study.
[b] Chabazite equilibrium study.
[c] Measured, mS/cm.
[d] Measured, µS/cm.

APPENDIX B

SUPPLEMENTARY FIGURES

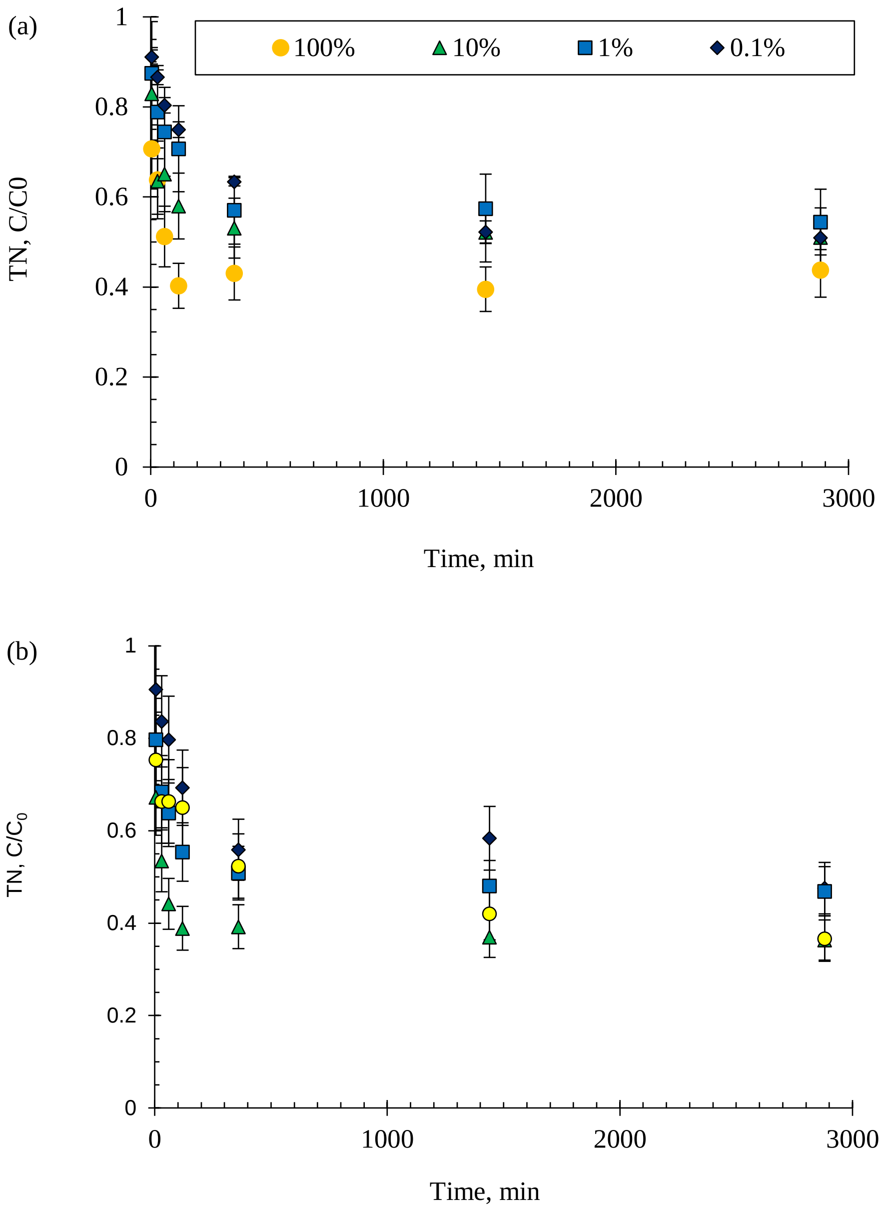

Figure S1 – Reduction in aqueous total nitrogen (TN) by zeolite sorption as function of mixing time at 200 rpm in synthetic urine (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation.

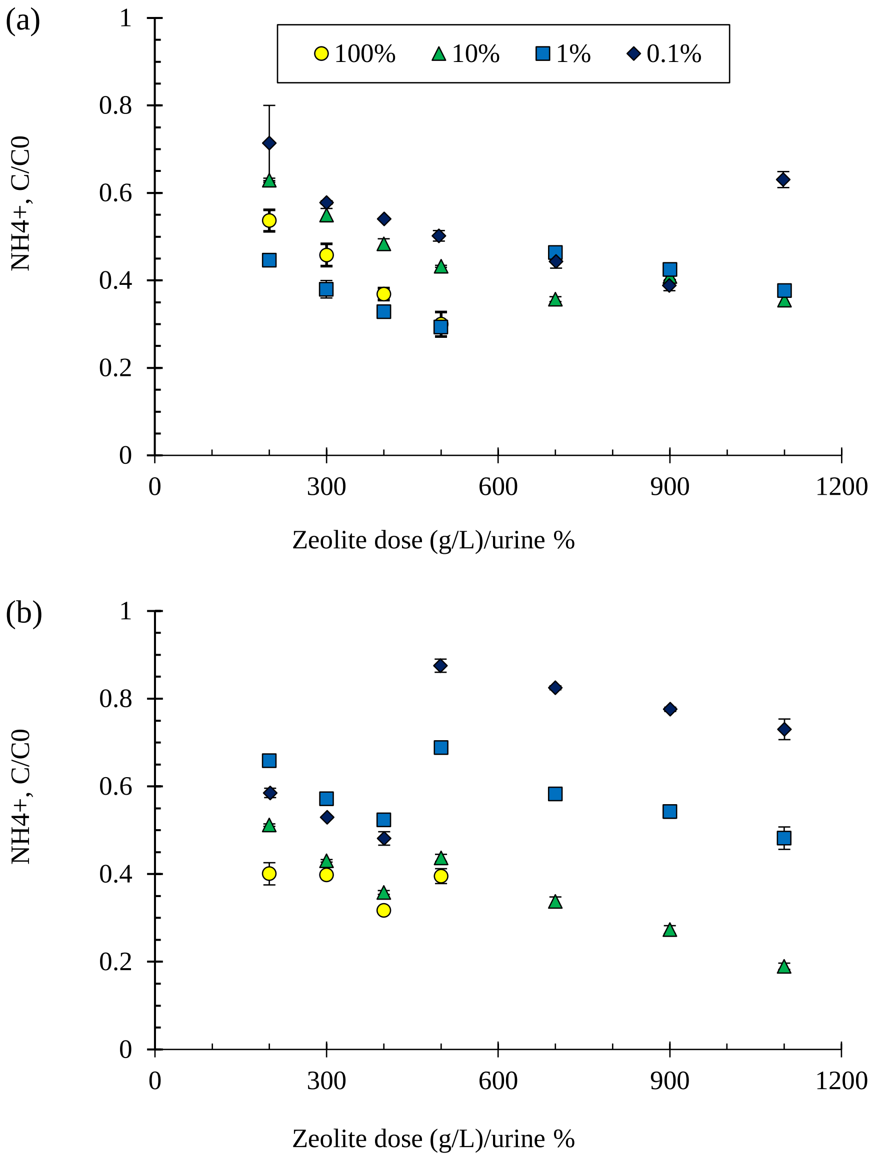

Figure S2 – Reduction in aqueous ammonium (NH_4^+) concentration by zeolite sorption as function of zeolite dose normalized by percent urine by volume at 1440 min equilibrium time and 200 rpm in synthetic urine: (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation.

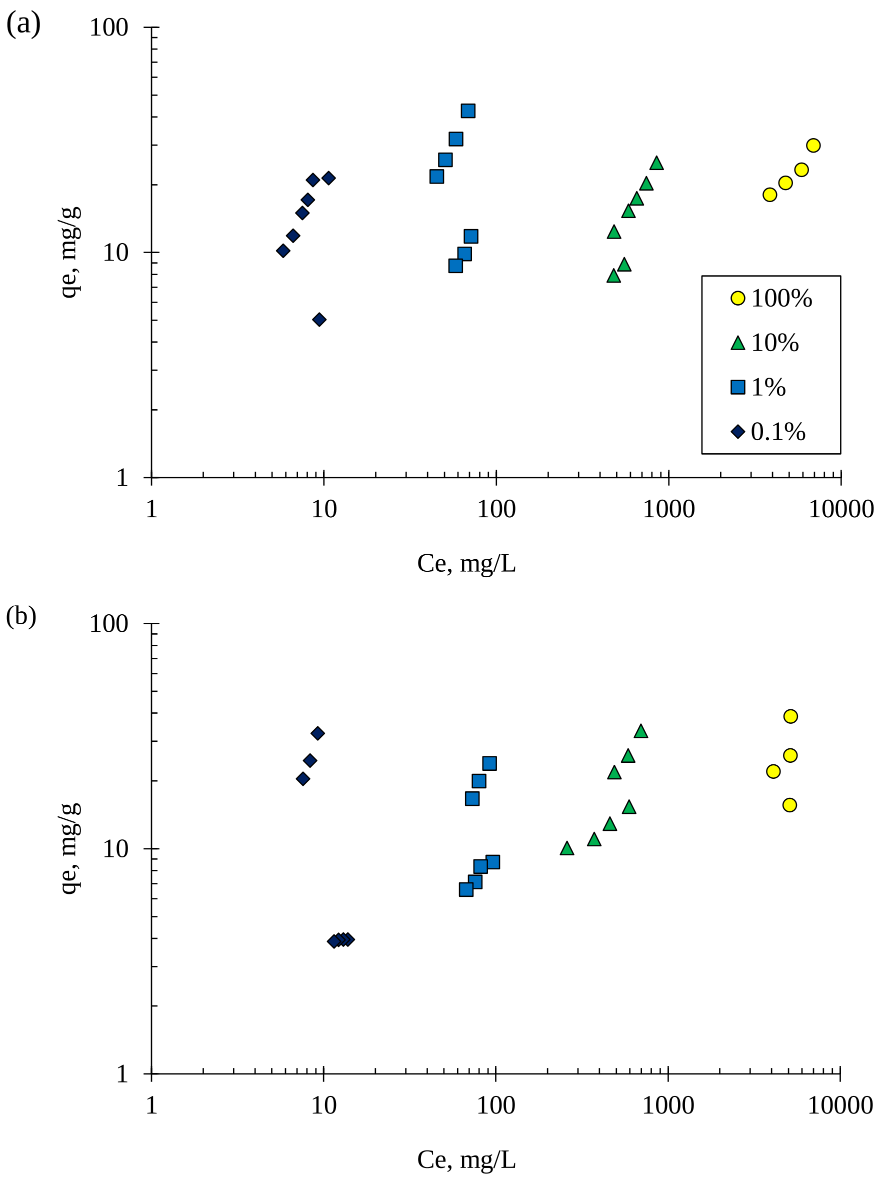

Figure S3 – Equilibrium ammonium sorption (as N) to zeolite for undiluted and diluted synthetic urine; solid-phase concentration, q_e; solution concentration, C_e: (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples.

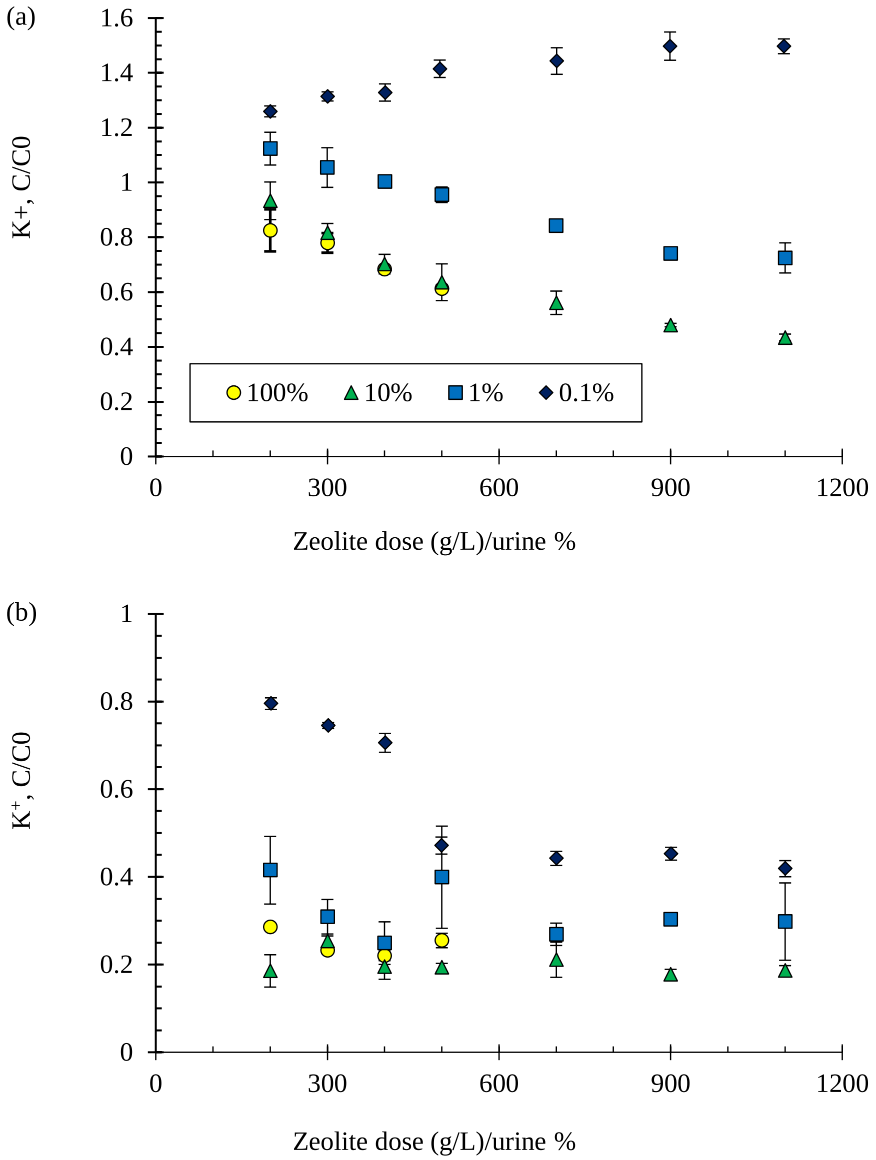

Figure S4 – Change in aqueous potassium (K^+) concentration by zeolite sorption/desorption as function of zeolite dose normalized by percent urine by volume at 1440 min equilibrium time and 200 rpm in synthetic urine: (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation.

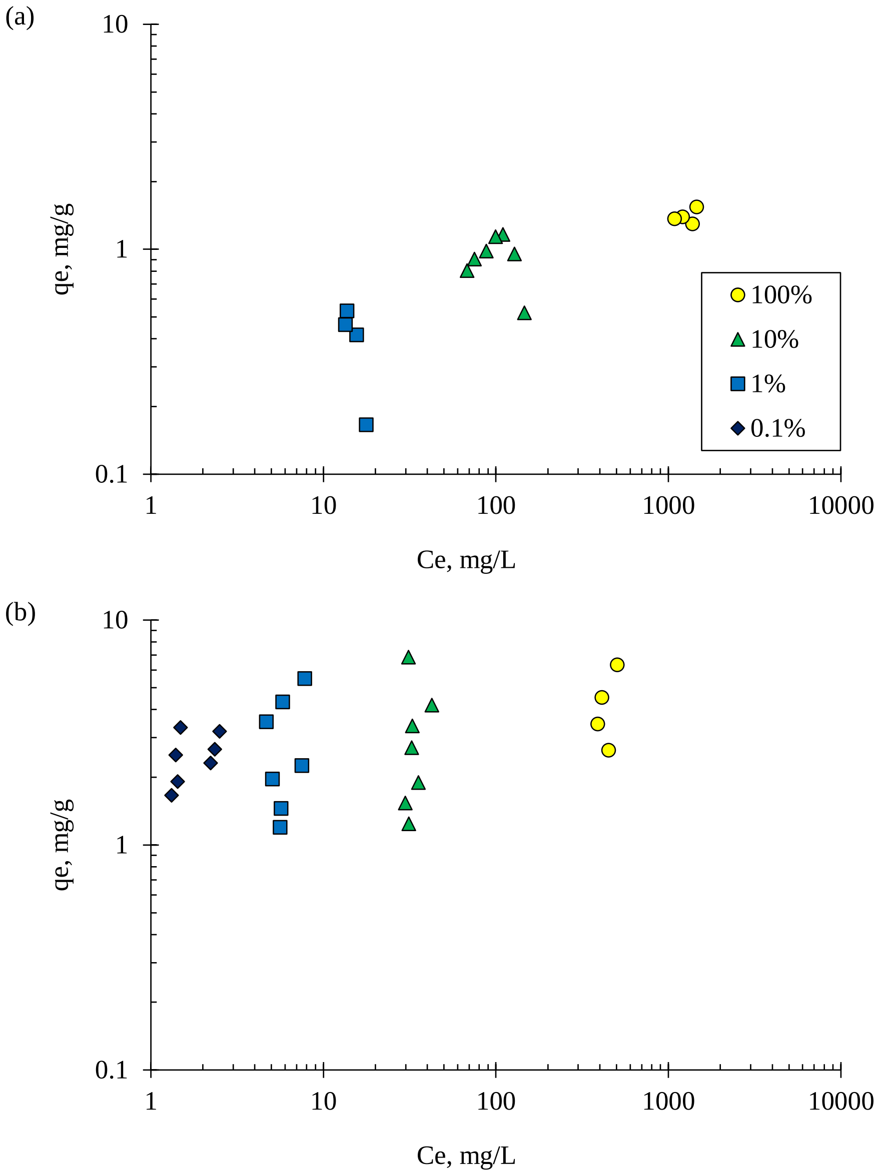

Figure S5 – Equilibrium potassium sorption to zeolite for undiluted and diluted synthetic urine; solid-phase concentration, q_e; solution concentration, C_e: (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples. There was no potassium sorption to clinoptilolite in 0.1% urine solution.

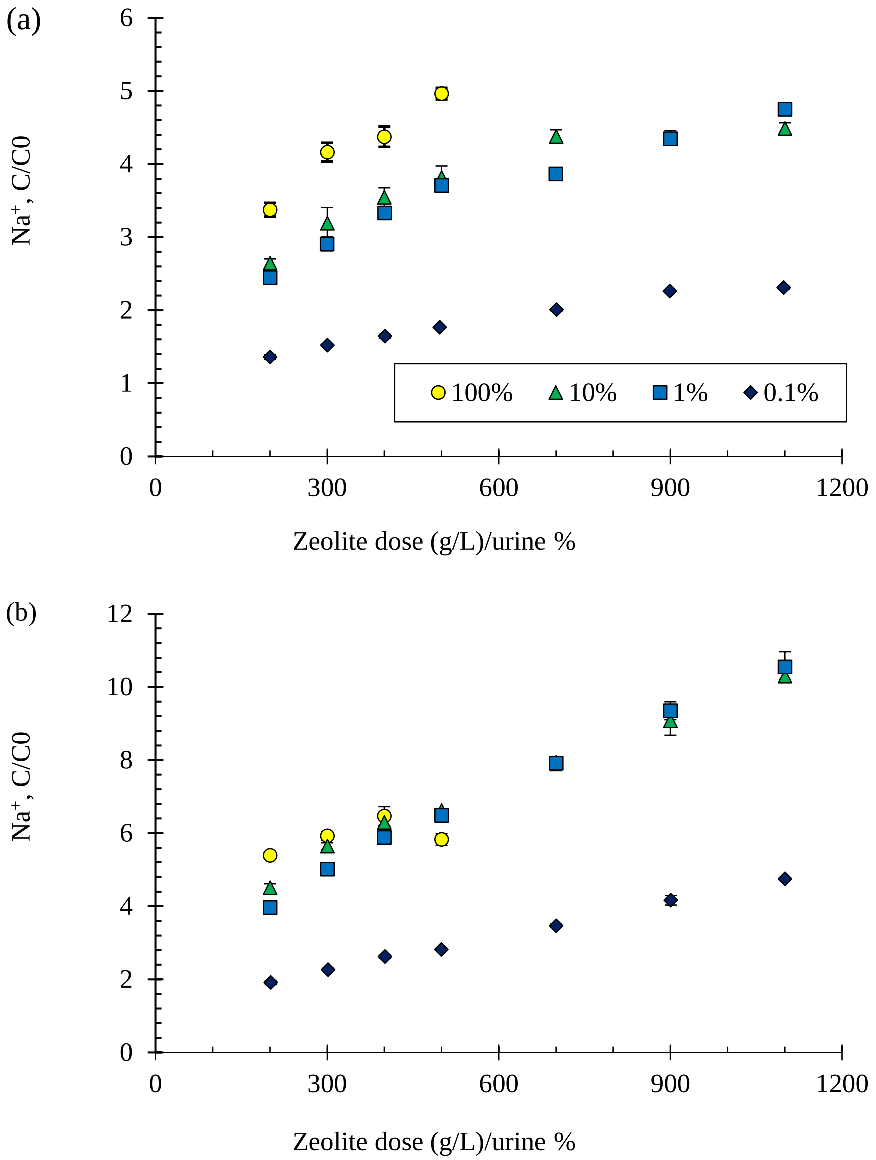

Figure S6 – Change in aqueous sodium (Na^+) concentration by zeolite desorption as function of zeolite dose normalized by percent urine by volume at 1440 min equilibrium time and 200 rpm in synthetic urine: (a) clinoptilolite and (b) chabazite. Legend gives percent urine by volume. Data are mean value of triplicate samples; error bars show one standard deviation.

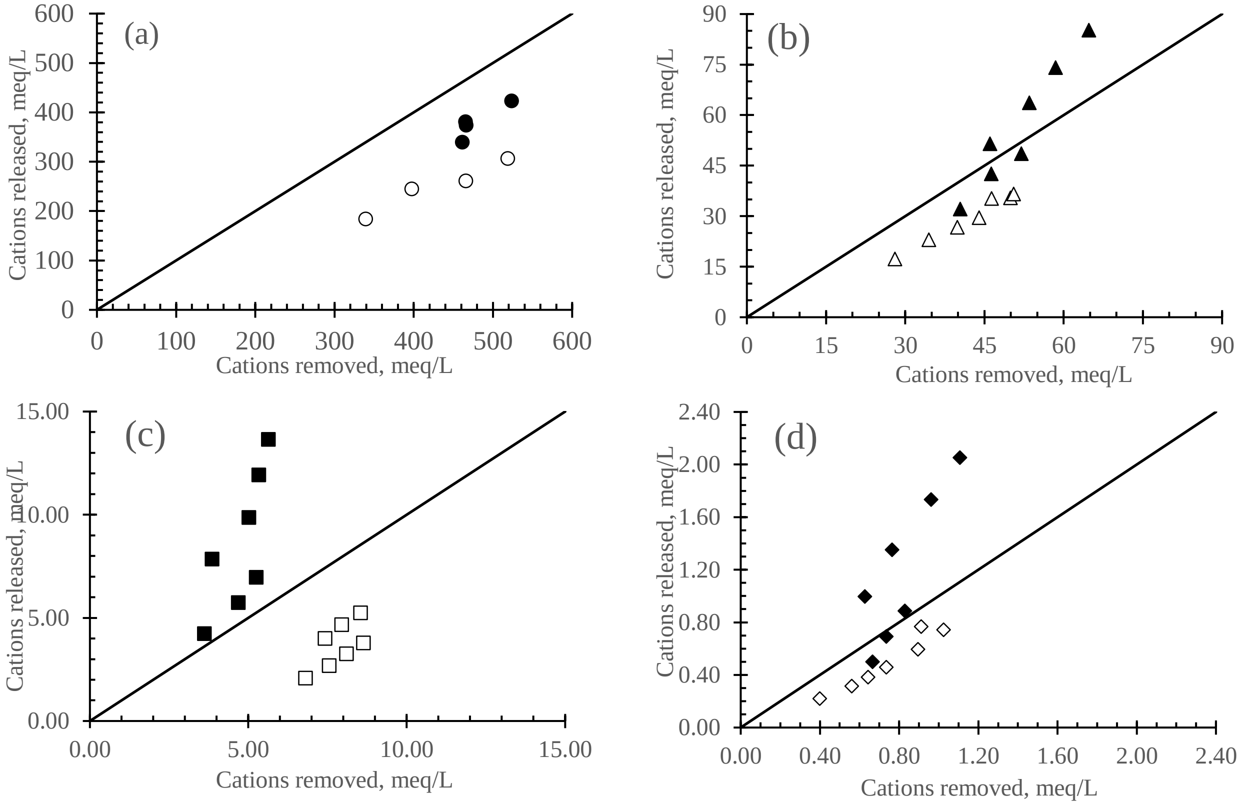

Figure S7 – Exchange of cations in urine solution for counterions in zeolite framework: (a) 100%, (b) 10%, (c) 1%, and (d) 0.1% (v/v) synthetic urine. Open symbols show clinoptilolite; closed symbols show chabazite; solid line shows y = x. Data are mean of triplicate samples.