

# Reduction of Nitrogen Load in a Zootechnical Wastewater Using a Natural Chabazite Zeolite: An Investigation on Sorption Mechanisms <sup>†</sup>

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<sup>†</sup> Presented at the 4th EWaS International Conference: Valuing the Water, Carbon, Ecological Footprints of Human Activities, Online, 24–27 June 2020.

Published: 3 September 2020

**Abstract:** The use of zeolite-rich tuffs is a valid method for recovering nitrogen from wastewaters. This paper aims at describing the  $\text{NH}_4^+$  adsorption processes of an Italian chabazite zeolite tuff used for the treatment of raw liquid swine manure. The effects of temperature, grain size and contact time were investigated. The isothermal analysis showed a multilayer adsorption behavior, well explained by the Harkins–Jura model, while kinetics was explained by pseudo-second-order, Elovich and intraparticle diffusion models. This study highlighted the complexity of the adsorption process from raw liquid manure, as well as the significant differences between tested particle sizes of the same zeolite tuff.

**Keywords:** ammonium adsorption; pig manure; natural zeolite tuff; chabazite; isotherm; kinetic; thermodynamic; wastewaters; agriculture

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## 1. Introduction

The use of natural zeolite-rich tuffs for wastewater treatment is recognized as a valid method to reduce the inorganic cationic species like  $\text{NH}_4^+$ . Then, once saturated by  $\text{NH}_4^+$ , the zeolite tuff can be reused and employed as soil amendment or as growing media with many important advantages, as demonstrated by recent works [1–4].

The adsorption mechanisms of  $\text{NH}_4^+$  from synthetic solutions prepared in laboratory were deeply investigated during the past twenty years [5–7]. However, a detailed description of  $\text{NH}_4^+$  adsorption from a real zootechnical wastewater is, up to now, totally missing. Furthermore, most of the studies were conducted using clinoptilolite or heulandite tuffs, while chabazite ones were investigated far less.

In this paper, various experiments (following, as closely as possible, the procedures indicated by Wasielewski et al. [8]) are illustrated, with the aim to deeply characterize the adsorption mechanisms of  $\text{NH}_4^+$  by an Italian chabazite-rich tuff (CHA) from a raw liquid swine manure. The experiments included the evaluation of temperature, contact time and particle size effects.

## 2. Materials and Methods

### 2.1. Materials, Experimental Design and Analytical Methods

The CHA was quarried in central Italy (Sorano, Grosseto province) and was purchased by Verdi S.p.a. company. The physico-chemical characteristics and the mineralogical composition of the used CHA is reported in Malferrari et al. [9]. Two grain sizes were selected for the experiments, a granular one ( $>0.7$  and  $<2.0$  mm; CHAg) and a  $\mu$ -sized one ( $<62$   $\mu\text{m}$ ; CHA $\mu$ ); both were dried at  $105$   $^{\circ}\text{C}$  for 24 h before the beginning of the experiments.

The liquid swine manure was obtained from a local farmer in a 25 L tank. To improve the homogeneity of the liquid manure (rich in suspended solids), the sample was centrifuged at 4000 rpm for 8 min. The supernatant was collected to obtain the liquid phase for the experiments (centrifuged swine manure, CSM). The initial CSM's pH was  $8.07 \pm 0.03$ , while  $\text{NH}_4^+$  concentration was  $3140 \pm 45$   $\text{mg L}^{-1}$ .

Isothermal adsorption experiments have been carried out at 13, 20 and  $37$   $^{\circ}\text{C}$ . Seven dosages of CHA, ranging from 0.5 to 12 g, were mixed with 50 mL of CSM into plastic bottles in three replicates and stirred in an orbital shaker at 200 rpm for 20 h. Samples without CHA were included (blanks) in order to evaluate the air stripping effect. Since pH measurements barely varied between 8.07 and 8.48 (optimum pH range for the adsorption of  $\text{NH}_4^+$  by zeolites found by [10]), we decided not to further investigate the pH effects and to not buffer the CSM. After 20 h of shaking, the mixtures were centrifuged at 4000 rpm for 8 min and analyzed for their  $\text{NH}_4^+$  concentration with an Ion Selective Electrode (ISE) Orion 95-12 connected to an Orion 4star pH-ISE benchtop (Thermo Fisher).  $\text{NH}_4^+$  equilibrium adsorption capacity ( $q_e$ ,  $\text{mg g}^{-1}$ ) was determined by Equation (1):

$$q_e = \frac{(C_0 - (C_0 - C_b) - C_e) * V}{m} \quad (1)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial  $\text{NH}_4^+$  concentration,  $C_b$  ( $\text{mg L}^{-1}$ ) is the  $\text{NH}_4^+$  concentration in blanks after 20 h,  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration at equilibrium,  $V$  (L) is the volume of CSM and  $m$  (g) is the mass of the sorbent (CHA).

For the kinetic experiments, CHA was added to 0.5 L of CSM at a ratio of 0.1 g per mg  $\text{NH}_4\text{-N}$  in the batch ( $\approx 122$  g) and mixed at a constant temperature of  $20$   $^{\circ}\text{C}$ , at a speed of 400 rpm, for 420 min. An aliquot of 10 mL was sampled at periodic intervals (5, 10, 20, 30, 45, 60, 120, 180, 270, 360 and 420 min) and immediately centrifuged at 4000 rpm for 4 min in order to separate the sorbent from the liquid fraction and stop the sorption processes. The batch volume was continuously reduced due to sampling, but it can be assumed that no change in the ratio of sorbent mass to the volume of CSM occurred because of the homogeneity of the mixture. Experiments were carried out in triplicates and a batch without zeolite (blank) was also included in the kinetic experiments in order to evaluate the air stripping effect.  $\text{NH}_4^+$  concentration at time  $t$  ( $C_t$ ,  $\text{mg L}^{-1}$ ) was measured by ISE electrode as in the isothermal adsorption experiments. The time-dependent  $\text{NH}_4^+$  loadings ( $q_t$ ,  $\text{mg g}^{-1}$ ) were calculated by Equation (1) replacing  $q_e$  and  $C_e$  with  $q_t$  and  $C_t$ , respectively. At 420 min, we considered that a "near-equilibrium" condition was achieved, thus it was assumed that  $q_{t,420} \approx q_e$ .

### 2.2. Data Analysis and Calculations

The equilibrium data were tested within the Harkins–Jura, Freundlich and Langmuir isotherms.

The Harkins–Jura linear isotherm can be expressed by Equation (2) [11]:

$$\frac{1}{q_e^2} = \beta \ln(C_e) + \alpha \quad (2)$$

where  $q_e$  is the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium sorbate concentration ( $\text{mg L}^{-1}$ ), and  $\alpha$  and  $\beta$  are constants; in particular,  $\beta$  is linked to the specific surface area of the sorbent.

The Freundlich model is reported by Equation (3) [12]:

$$q_e = K_F \times C_e^{1/n} \quad (3)$$

where  $K_F$  ( $L \text{ g}^{-1}$ ) is the Freundlich constant and  $n$  is the adsorption capacity.

The Langmuir model [13] in its linear form can be expressed by Equation (4):

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L} \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (4)$$

where  $q_{\max}$  ( $\text{mg g}^{-1}$ ) is the maximum monolayer adsorption capacity and  $K_L$  is the Langmuir constant ( $L \text{ mg}^{-1}$ ).

Kinetic data were analyzed applying pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion (ID) and Elovich equations.

The PFO [14] can be described by Equation (5) [15]:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1}{2.303} t \quad (5)$$

where  $q_e$  and  $q_t$  are the equilibrium adsorption capacity and the adsorption capacity at time  $t$  ( $\text{mg g}^{-1}$ ), respectively,  $t$  is the contact time (min) and  $k_1$  is the PFO rate constant ( $\text{min}^{-1}$ ).

The PSO proposed by Ho et al. [16] is expressed in linear form by Equation (6):

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{h} \quad (6)$$

where  $h$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{ min}^{-1}$ ). From the experimental data, it is possible to calculate  $h$  when  $q_t/t$  approaches 0:  $h = k_2/q_e^2$ , where  $k_2$  is the PSO rate constant [17].

The ID is a diffusion-controlled process described by Equation (7) [18]:

$$q_t = K_{ID} t^{0.5} + C \quad (7)$$

where  $K_{ID}$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{ min}^{-0.5}$ ) and an intercept  $C$  proportional to the thickness of the boundary layer, as reported by [19].

The Elovich model can be expressed in linear form by Equation (8) [15].

$$q_t = \left(\frac{2.3}{\alpha}\right) \ln(t + t_0) - \left(\frac{2.3}{\alpha}\right) \ln(t_0) \quad (8)$$

where  $\alpha$  is the initial adsorption rate constant [20]. The dimensionless form of the Elovich equation (Equation (9)) permits the calculation of  $R_E$ , which is an approaching-equilibrium parameter, proportional to the tendency of the system to achieve equilibrium conditions [21].

$$\frac{q_t}{q_{\text{ref}}} = R_E \ln \left( \frac{t}{t_{\text{ref}}} \right) + 1 \quad (9)$$

Thermodynamic parameters were calculated using the van't Hoff relation (Equation (10)) [22]:

$$\ln(K_{\text{eq}}) = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R} \quad (10)$$

where  $K_{\text{eq}}$  is the thermodynamic equilibrium constant,  $\Delta H$  is the enthalpy change ( $\text{J mol}^{-1}$ ),  $\Delta S$  is the entropy change ( $\text{J K}^{-1} \text{ mol}^{-1}$ ),  $R$  is the universal gas constant ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the temperature (K).  $K_{\text{eq}}$  has been derived by  $K_{\text{eq}} = \delta K_d$ , where  $K_d$  is the distribution coefficient ( $K_d = q_e/C_e$ ;  $\text{mL g}^{-1}$ ) [6,23], and  $\delta$  is the density of CSM ( $\sim 1.009 \text{ g mL}^{-1}$ ). The Gibbs free energy change ( $\Delta G$ ,  $\text{kJ mol}^{-1}$ ) was determined by the Gibbs–Helmholtz equation (Equation (11)):

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

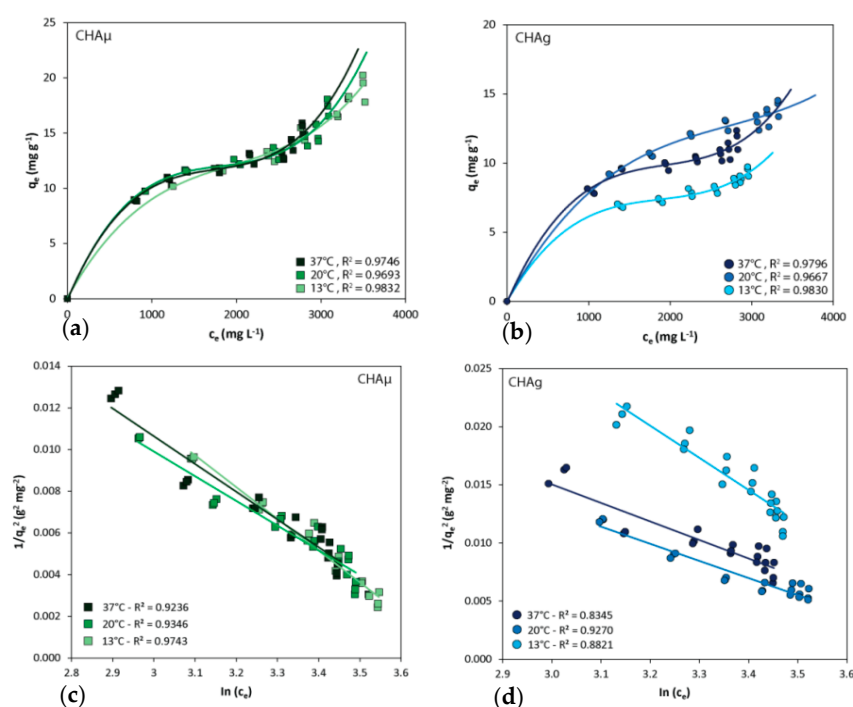
### 3. Results and Discussions

#### 3.1. Isotherms

Isotherm parameters are reported in Table 1, while equilibrium condition plots are reported in Figure 1.

**Table 1.** Parameters calculated by Harkins–Jura, Freundlich and Langmuir isotherms (Equations (2), (3) and (5), respectively) for CHA $\mu$  and CHAg, at temperatures T = 286, 293 and 307 K (13, 20 and 37 °C).

Sorbent	Temp.	Harkins–Jura			Freundlich			Langmuir		
	T (K)	R <sup>2</sup> (-)	$\alpha$ (g <sup>2</sup> mg <sup>-2</sup> )	$\beta$ (g <sup>2</sup> L mg <sup>-3</sup> )	R <sup>2</sup> (-)	K <sub>F</sub> (L g <sup>-1</sup> )	n (-)	R <sup>2</sup> (-)	K <sub>L</sub> (L mg <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )
CHA $\mu$	286	0.973	0.057	−0.015	0.904	0.14	1.67	0.878	3.98 × 10 <sup>-4</sup>	29.5 (2.9)
	293	0.931	0.045	−0.012	0.853	0.66	2.55	0.860	10.27 × 10 <sup>-4</sup>	19.6 (1.0)
	310	0.920	0.051	−0.013	0.896	0.77	2.71	0.911	12.03 × 10 <sup>-4</sup>	18.1 (0.7)
CHAg	286	0.876	0.109	−0.028	0.826	0.45	2.68	0.798	9.12 × 10 <sup>-4</sup>	12.0 (0.7)
	293	0.937	0.057	−0.015	0.937	0.56	2.55	0.954	7.40 × 10 <sup>-4</sup>	18.9 (0.6)
	310	0.826	0.063	−0.016	0.826	0.95	3.23	0.843	13.03 × 10 <sup>-4</sup>	14.0 (0.6)



**Figure 1.** (a)  $q_e$  against  $C_e$  for CHA $\mu$  at 13, 20 and 37 °C; (b)  $q_e$  against  $C_e$  for CHAg at 13, 20 and 37 °C; (c)  $\ln(C_e)$  against  $1/q_e^2$  (Harkins–Jura isotherms, Equation (2)) for CHA $\mu$ ; (d)  $\ln(C_e)$  against  $1/q_e^2$  (Harkins–Jura isotherms, Equation (2)) for CHAg.

Both CHA $\mu$  and CHAg have shown curves of the L3 type in accordance with the classification proposed by Giles [24]. The presence of a “semi-flat” region (Figure 1a,b) in the middle of the curves means that a saturation condition is beginning to occur associated with the formation of a monolayer, but, at high  $C_e$  (right end of the curves), the increase in  $q_e$  demonstrates the renewed availability of exchange sites for NH<sub>4</sub><sup>+</sup> cations [24]. This behavior (multi-layer formation) has been observed for both CHA $\mu$  and CHAg and it starts at dosages  $\leq 6\%$  of CHA. The multilayer adsorption is not in agreement with Langmuir monolayer assumption [11] but it is in accordance with the other two models proposed, in fact, Harkins–Jura was found to be the best model ( $R^2$  between 0.826 and 0.973). Temperature seems to not significantly affect the sorption for CHA $\mu$  (Figure 1a,c), but it has a

more relevant effect in the case of CHAg (Figure 1b,d); in particular, the best adsorption performances were obtained at 20 °C, whereas the worst were obtained at 13 °C.

### 3.2. Kinetics

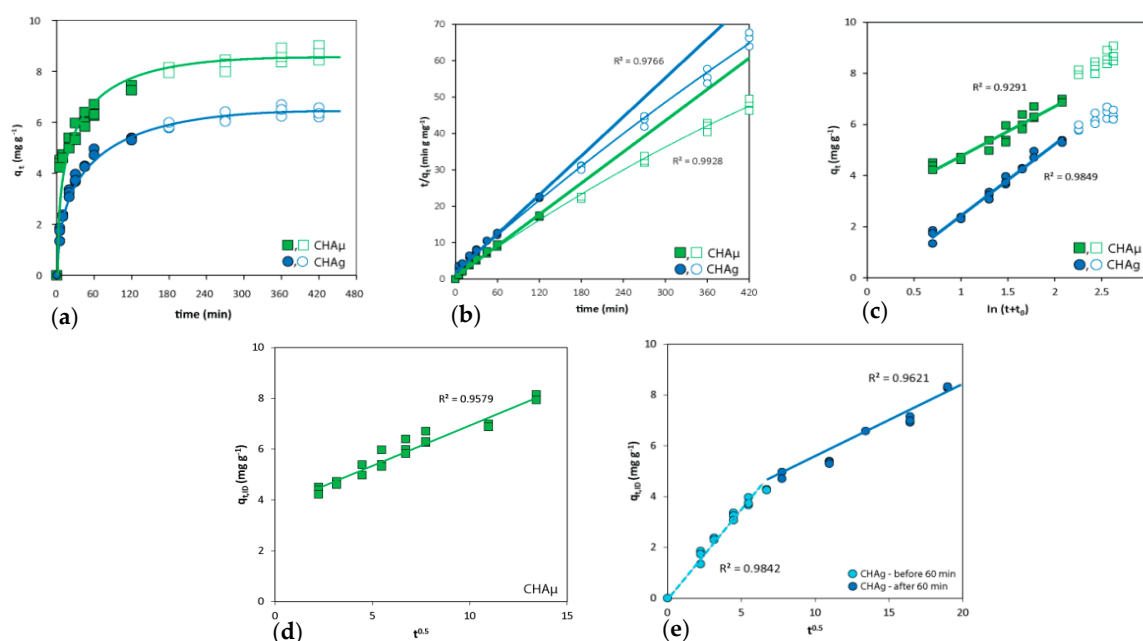
As pointed out by Simonin [25], in kinetic analysis, it is appropriate to take into account only data sufficiently far from equilibrium. For this reason, only data with a fractional uptake  $F(t) < 85\%$ , calculated as  $F(t) = q(t)/q_e$  [25], were chosen.

The PFO model showed bad correlation with respect to the other kinetic models applied, while the PSO model has shown high  $R^2$  values (Table 2), but the  $q_e$  calculated ( $q_{e,2}$ ) are slightly different from the real measured values (8.74 and 6.37  $\text{mg g}^{-1}$  for CHA $\mu$  and CHAg, respectively). The Elovich model has shown a good correlation with the experimental data, in particular regarding CHAg.  $R_E$  values indicate that CHAg approaches equilibrium conditions more slowly than CHA $\mu$ .

**Table 2.** Pseudo First Order, Pseudo Second Order and Elovich parameters (see Section 2.2 for detailed description) for CHA $\mu$  and CHAg and the relative  $R^2$  values.

Sorbent	PFO			PSO				Elovich		
	$R^2$ (-)	$k_1$ ( $\text{min}^{-1}$ )	$q_{e,1}$ ( $\text{mg g}^{-1}$ )	$R^2$ (-)	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_{e,2}$ ( $\text{mg g}^{-1}$ )	$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R^2$ (-)	$\alpha$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R_E$ (-)
CHA $\mu$	0.682	0.011	5.38	0.977	0.022	6.98	1.665	0.929	1.182	0.282
CHAg	0.890	0.015	4.86	0.993	0.014	5.60	0.566	0.985	0.820	0.524

The diffusion dynamics of  $\text{NH}_4^+$  have shown different behaviours between CHAg and CHA $\mu$  (Figure 2); in particular, the ID plot for CHA $\mu$  has shown only a straight line with an intercept C (Equation (7))  $\sim 4$ , while CHAg has clearly shown two ID lines, correlated with a rapid change of  $\text{NH}_4^+$  diffusion that begins after about 60 min after the contact with CSM.



**Figure 2.** Kinetic graphics. Full dots are  $F(t) < 85\%$  data (data considered in the kinetic analyzes); empty dots are  $F(t) > 85\%$  data (excluded from the model fitting): (a)  $q_t$  against  $t$ ; (b)  $t/q_t$  against  $t$  (PSO model, Equation (6)), only straight thick lines represent the PSO model while thinner lines also represent data excluded (with  $F(t) > 85\%$ ); (c)  $(t + t_0)$  versus  $q_t$  (Elovich model, Equation (8)); (d)  $t^{0.5}$  against  $q_{t,ID}$  (ID model, Equation (7)) for CHA $\mu$ ; (e)  $t^{0.5}$  against  $q_{t,ID}$  (ID model, Equation (7)) for CHAg; the graph shows two distinct regions with different ID parameters; the first is represented by light blue dots, while the second is represented by dark blue dots.

In the first region of the CHAg ID plot (Figure 2e), which represents about the first 60 min of contact with CSM, the intercept value was near zero ( $C = 0.17$ ), demonstrating that the adsorption is mainly governed by ID. Thus, during this first stage, external-surface adsorption and macropore diffusion occurs and a thin boundary layer develops. The thickness of this boundary layer is proportional to the  $C$  value and hence it was thin during the first 60 min [19].

After one hour, the adsorption layers thicken significantly ( $C = 2.24$ ), suggesting that the  $\text{NH}_4^+$  penetrates more slowly inside the internal structure and the micropores. This is validated by  $K_{\text{ID}}$  values that after 60 min are lower (slower diffusion) with respect to values calculated from the first hour (Table 3).

**Table 3.** ID parameters for CHA $\mu$  and CHAg; CHAg has two distinct patterns, before and after 60 min.

Sorbent		ID Model		
		$R^2$	$K_{\text{ID}}$	$C$
		(-)	( $\text{mg g}^{-1} \text{min}^{-0.5}$ )	( $\text{mg g}^{-1}$ )
CHA $\mu$		0.958	0.32	3.75
CHAg	before 60 min	0.984	0.63	0.17
	after 60 min	0.962	0.31	2.24

After about an hour of contact with CSM, the slope  $K_{\text{ID}}$  of CHAg reaches values similar to the one of CHA $\mu$  (0.31 and 0.32, respectively) (Table 3).

For CHA $\mu$ , the high value of  $C$  ( $C = 3.75$ ) indicates the formation of an adsorption layer thicker than the one developed by CHAg in the second region of the graph ( $C = 2.24$ ) (Figure 2d,e).

A plausible hypothesis is that because of the considerably higher surface area of CHA $\mu$ , the formation of an adsorption layer is immediate because of a negligible macropore diffusion (too high  $C$  values for ID). However, from the data obtained, a very fast ID within the first 5 min cannot be totally excluded.

### 3.3. Thermodynamics

The thermodynamic parameters, reported in Table 4, show positive values for  $\Delta H$  for both CHA $\mu$  and CHAg, indicating endothermal conditions, with significantly higher values for CHAg. Because  $\Delta H > 0$ , the amount of energy in the liquid–solid adsorption surfaces increases during  $\text{NH}_4^+$  adsorption; thus, the  $\text{NH}_4^+$  cationic exchange processes need energy from the liquid phase in order to occur. While many authors have observed exothermic conditions ( $\Delta H < 0$ ) [6,22,26], others have calculated positive values of  $\Delta H$  [8,19]. In all these studies, the nature of the employed materials (zeolite tuff and solutions) varies significantly; this may explain the differences in thermodynamic parameters.

**Table 4.** Thermodynamic parameters for CHA $\mu$  and CHAg calculated by the isothermal data at the temperatures of 286, 293 and 310 K (13, 20 and 37 °C, respectively); see paragraph 2.5 for details.

Sorbent	Temperature	$\Delta H$	$\Delta S$	$\Delta G$
	(K)	( $\text{J mol}^{-1}$ )	( $\text{J K}^{-1} \text{mol}^{-1}$ )	( $\text{kJ mol}^{-1}$ )
CHA $\mu$	286	2124	13.7	−1.80
	293	2091	13.8	−1.96
	310	2146	13.6	−2.06
CHAg	286	2654	11.9	−0.74
	293	2343	13.0	−1.46
	310	2479	12.6	−1.42

$\Delta S$  is also positive, indicating that  $\text{NH}_4^+$  adsorption is a directional process and that the  $\text{NH}_4^+$  cations captured in the adsorption layers are in a more chaotic disposition with respect to the ones in

the liquid phase.  $\text{NH}_4^+$  adsorption is a spontaneous reaction ( $\Delta G < 0$ ) for all the temperatures investigated.  $\Delta G$  values are significantly lower for CHA $\mu$  than CHAg.

#### 4. Conclusions

In this work, the adsorption of  $\text{NH}_4^+$  from a raw liquid swine manure by chabazite-zeolite tuff was deeply characterized. The equilibrium curve was of the L3 type and demonstrated that, to obtain maximum adsorption by the zeolite tuff, it is necessary to use low dosages of adsorbant (<6%). A clear temperature effect was not observed for the  $\mu$ -sized one, while the granular one has shown deficient capacity at lower temperatures. Kinetic analyses have shown that the  $\mu$ -sized zeolite tuff approaches equilibrium faster than the granular one. ID plots have shown significant differences between the two grain sizes studied. For the granular one, the presence of two distinct regions in the graph demonstrates a change in diffusion dynamics during adsorption, with an initial rapid diffusion inside the macropores and on the external surfaces, followed by a slower diffusion inside the micropores.

The outcomes of this work highlighted the complexity of the sorption mechanisms in a complex matrix such as raw liquid manure in comparison to other studies performed on synthetic solutions. On the other hand, the studied Italian chabazite-zeolite tuff was confirmed as a valid material for the treatment of animal liquid manure and these data can be of high value for future application at the field scale.

**Author Contributions:** Conceptualization, G.G. and G.F.; methodology, G.G. and G.F.; formal analysis, G.G., G.F., V.M., N.T.; investigation, G.G.; resources, B.F. and M.C.; data curation, G.G.; writing—original draft preparation, G.G.; writing—review and editing, G.F., B.F., M.C.; supervision, G.F., M.C. All authors have read and agree to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** We gratefully thank the Miotto Giuliano company for the swine manure supply and Maurizio Bellettato (FerraraBio s.r.l.) for the furniture of the zeolite tuff.

**Conflicts of Interest:** The authors declare no conflict of interest.

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