Ammonium adsorption by chabazite zeolite-tuff from swine manure for soil amendment

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INTRODUCTION AND AIM OF THE WORK

The need to improve fertilizer use efficiency (FUE) is one of the major challenges for modern agriculture and environmental sustainability. Animal manures, especially in liquid form, represent very important organic fertilizers but their very high availability of nutrients, especially in the form of NH_4^+, stimulates soil microbial activity leading to rapid N transformations and significant losses from the soil in the form of NO_3^- and N GHG gasses, causing severe environmental pollution. A valid methodology for contrasting this phenomenon is the use of (zeolitites, ZEO), particular rocks with high zeolite content (>50%) in the treatment of zootechnical liquid manure (ZLM). These rocks are particularly efficient as sorbent of cationic species and hence their use can lead to a significant reductions of NH_4^+ concentration. Then, once «charged» of NH_4^+, ZEO can be applied as soil amendments and act as slow release fertilizer.

While ZEO NH_4^+ sorption from synthetic solutions is a well investigated field, actually there is a lack of knowledge regarding his sorption behavior in **real ZLM**.
The aim of this work is to deeply characterize NH_4^+ adsorption by a chabazite-rich ZEO (CHA) quarried in center Italy, in contact with ZLM, in particular with swine manure. A series of batch experiments were conducted in order to define the equilibrium isotherms, kinetic models and thermodynamic parameters.

MATHERIALS

CHA — 2 grain size selected
- Granular (0.7–2.0 mm), **CHAg**
- μ-sized (< 20 μm), **CHAμ**

Both dried at 105 °C

SM* — centrifuged at 4000 rpm for 8 min.
- Centrifuged swine manure, **CSM**

* Initial pH = 8.07
Initial NH_4^+ = 3140 mg L^{-1}

EXPERIMENTAL SETUP AND CALCULATIONS

ISOTHERMS

- Batch experiments with different masses of CHA mixed with CSM for 20 h.
- pH barely varied during the experiment thus no pH correction was conducted.
- Air stripping evaluated by performing blanks.

TEMPERATURES	BEST MODELS	LINEAR EQUATIONS
13, 20, 37 °C	Harkins-Jura →	$\frac{1}{q_e^2} = \beta\, In(C_e) + \alpha$
CHA DOSAGES	Freunlich →	$q_e = K_F \times C_e^{1/n}$
0.5, 1, 3, 5, 8, 12 g	Langmuir →	$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}}$

KINETICS

- Batch experiments with a specific mass of CHA mixed with CSM based on CSM initial NH_4^+ content.
- Only data sufficiently far from equilibrium were considered:
  F(t) < 85 %, F(t) = q(t)/q_e
- Temperature fixed at 20 °C.
- The experiments were conducted in 3 replicates.

BEST MODELS	LINEAR EQUATIONS
Pseudo-Second Order →	$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{h}$
Intraparticle Diffusion →	$q_t = K_{ID}t^{0.5} + C$
Elovich →	$q_t = \frac{2.3}{\alpha} In(t+t_0) - \frac{2.3}{\alpha} In(t_0)$

THERMODYNAMICS

METHODS APPLIED	LINEAR EQUATIONS
van't Hoff equation →	$In(K_{eq}) = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R}$
Gibbs-Helmholtz →	$\Delta G = \Delta H - T\Delta S$

- NH_4^+ were measured with an Ion Selective Electrode (ISE) Orion 95-12 connected to an Orion 4star pH-ISE benchtop (Thermo Fisher).

Mathematical symbols in order of appearence

q_e: equilibrium adsorption capacity $(mg\ g^{-1})$
C_e: equilibrium concentration $(mg\ L^{-1})$
α, β: Harkins-Jura constants
K_F: Freundlich constant
K_L: Langmuir constant
q_{max}: maximum adsorption capacity $(mg\ g^{-1})$
q_t: adsorption capacity at time t $(mg\ g^{-1})$
h: initial adsorption rate $(mg\ g^{-1}\ min^{-1})$
t: time (min)

K_{ID}: Intraparticle diffusion constant
C: intercept (graph q_t vs. $t^{0.5}$)
α: initial adsorption rate constant
K_{eq}: equilibrium constant
ΔH: free enthalpy change $(J\ mol^{-1})$
ΔS: free entropy change $(J\ K^{-1}\ mol^{-1})$
ΔG: Gibbs free energy change $(kJ\ mol^{-1})$
T: Temperature (K)
R: Universal gas constant $(J\ K^{-1}\ mol^{-1})$

RESULTS AND DISCUSSIONS

ISOTHERMS

CHAμ and CHAg showed L3 type curve (Fig.1), thus the formation of a multilayer bonding structure occurred.
There was no significative differences with respect to the temperatures tested for CHAμ, while temperatures has more relevant effects on CHAg.
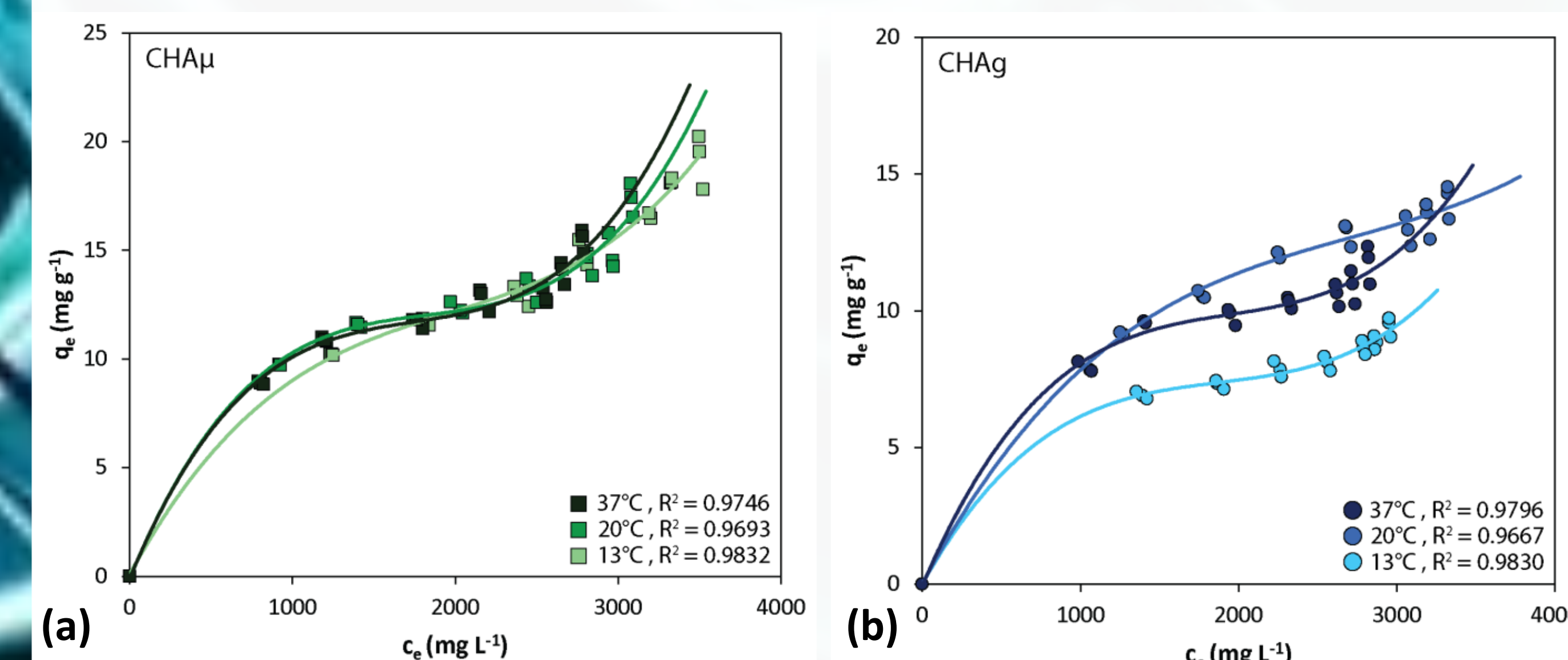Harkins-Jura was found to be the best isothermal model (Fig.2).

Figure 1. C_e against q_e curves and relative R^2. *(a)* CHAμ, *(b)* CHAg
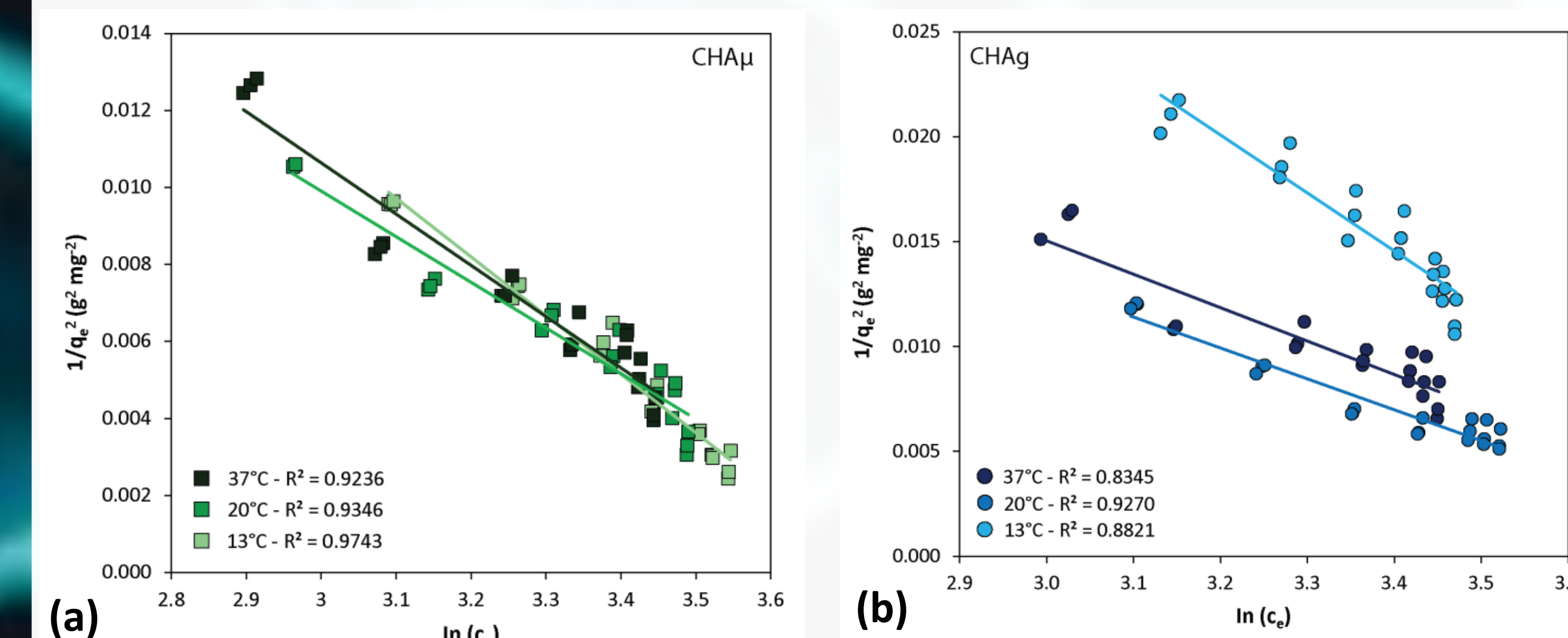

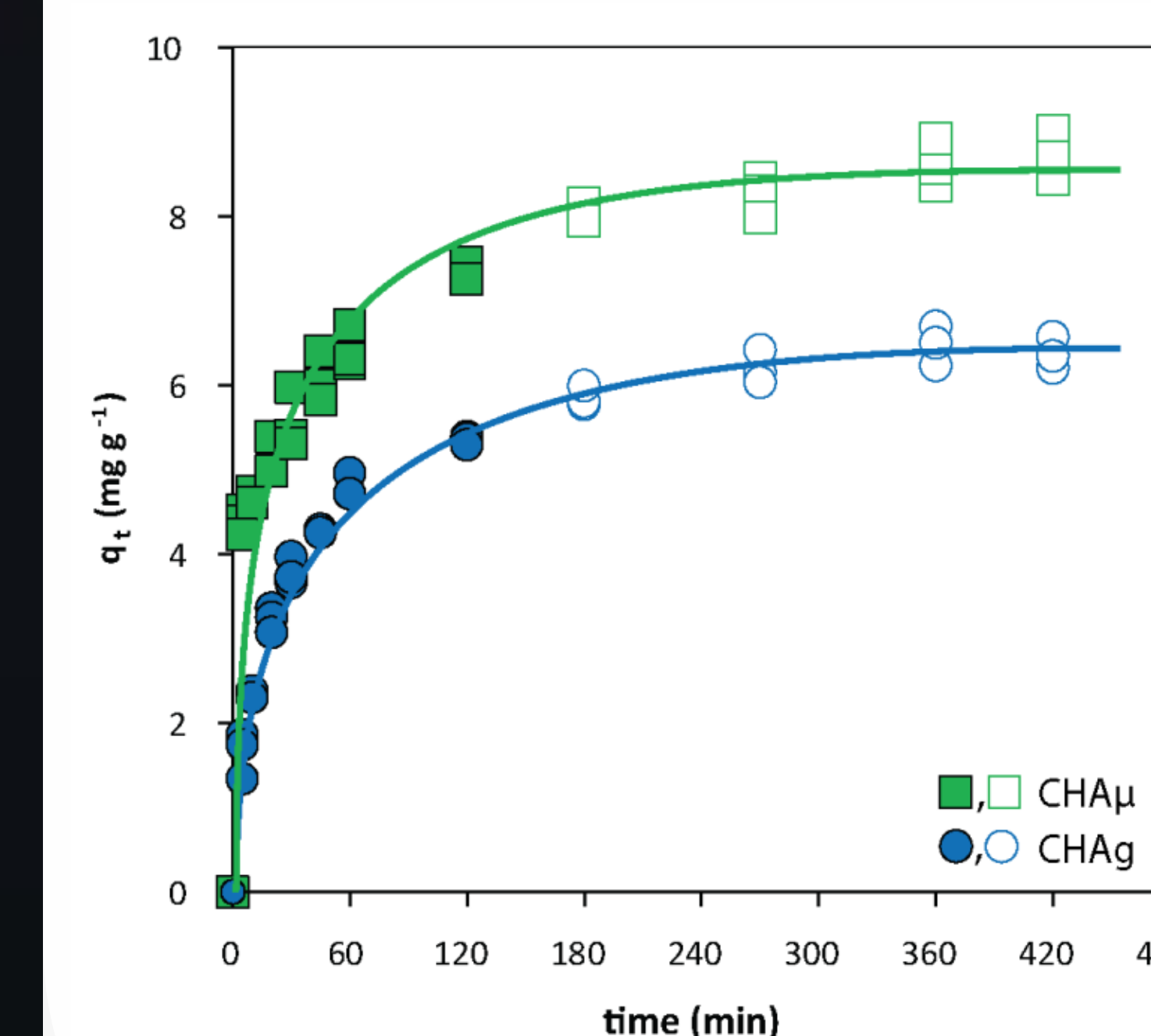**Figure 2.** Harkins-Jura isotherms and relative R^2. *(a)* CHAμ, *(b)* CHAg

KINETICS

NH_4^+ sorption for CHAμ and CHAg has shown differences in the sorption kinetics (Fig.3), in particular CHAμ adsorbed NH_4^+ more rapidly than CHAg and reaches higher equilibrium capacity.

Figure 3. q_t against t, empty dots are data not considered in kinetic analisys (F(t) > 85 %).

In the case of CHAg (Fig.4a) diffusion through macro and mesopores was the main process during the first 60 minutes of contact. During this phase a thin NH_4^+ boundary layer were developed (thickness is proportional to the intercept C). After 1 hour the layer thickens significantly while NH_4^+ slowly penetrates inside the micropores.
For CHAμ diffusion is not so important as for CHAg, as demonstrated by the high value of the intercept, and just within the first minutes of contact CHAμ has developed an adsorption layer thicker than CHAg (Fig.4b).
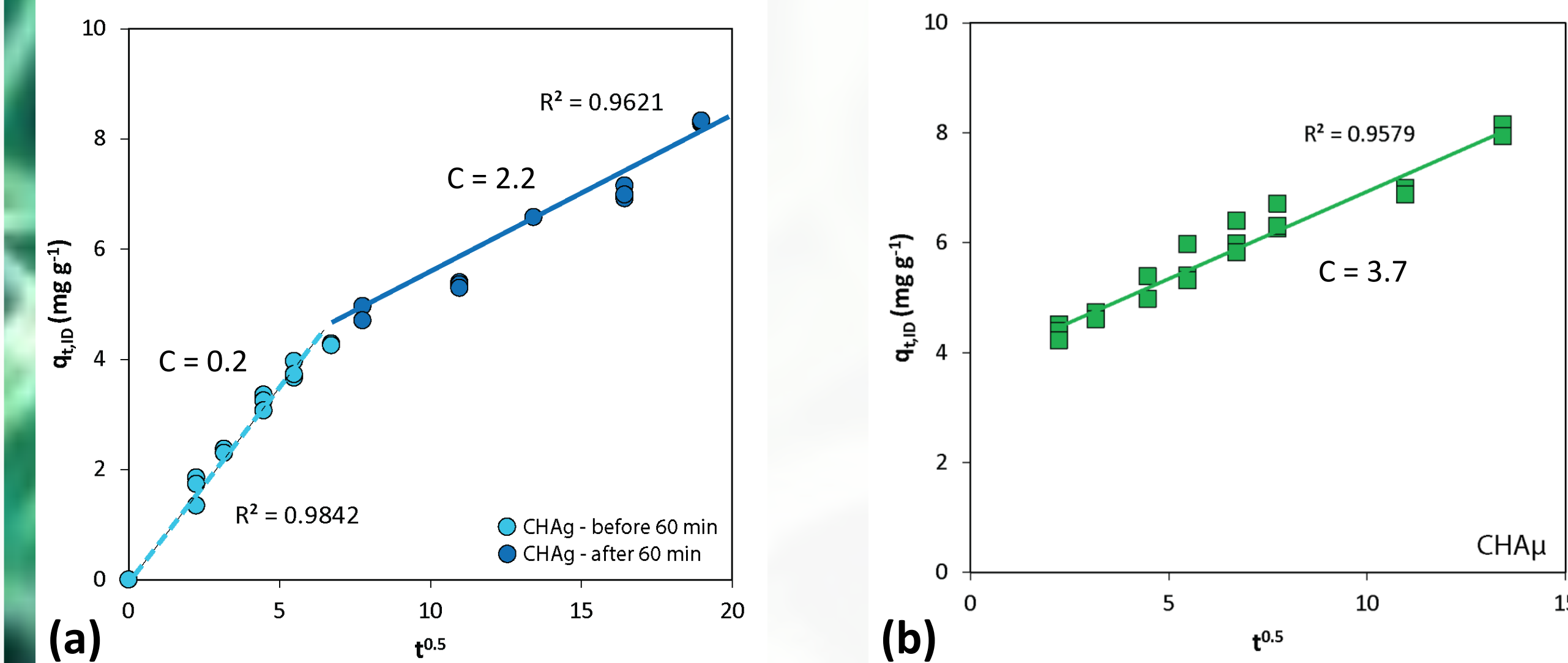

Figure 4. ID plots with R^2 and intercept C values. *(a)* CHAg, *(b)* CHAμ.

THERMODYNAMICS

ZEO size	ΔH (J mol⁻¹)	ΔS (J K⁻¹mol⁻¹)	ΔG (kJ mol⁻¹)
	Average values for 13, 20 and 37 °C		
CHAg	2492	12.5	-1.2
CHAμ	2120	13.7	-1.9

The adsorption was endothermic and spontaneous (ΔH > 0, ΔG < 0) and it was associated with an increase of the randomness in the interphase between the solid and the liquid phase (ΔS > 0).

CONCLUSIONS

In order to develop multilayer conditions and achieve maximum adsorption capacity ZEO should be applied at dosages < 6%. CHAg has performed better at higher temperatures. Kinetic analysis showed that CHAμ approaches equilibrium faster than the granular one and intraparticle diffusion was a relevant process for both.

The studied Italian chabazite-zeolitite was confirmed as a valid material for the treatment of zootechnical liquid manure and these data can be of high value for future applications at field scale.