Supplementary Information for

Removal of ammonium from swine wastewater using synthesized zeolite from fly ash

Hui Tang ¹, Xiaoyi Xu ^{2,*}, Bin Wang ¹, Chenpei Lv ¹, Dezhi Shi ^{1,*}

¹ Key Laboratory of Three Gorges Reservoir Region's Eco-Environment, Ministry of Education, Chongqing University, Chongqing, 400045, China.

² School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou, 215001, China.

Contents:

Section 1. Description of adsorption kinetics model Section 2. Description of adsorption isotherms model Section 3. Description of adsorption thermodynamics Section 4. Supplementary table and figure of contents

Number of supplemental tables: 2 Number of supplemental figures: 4

Section 1. Description of adsorption kinetics model

The adsorption kinetics can typically determine the contact time required for the adsorbent to reach its maximum adsorption capacity during the equilibrium phase. The results of our kinetics experiment were analyzed using pseudo-first-order (Equation 1) and pseudo-second-order kinetics models (Equation 2): [1,2]

$$ln(q_e - q_t) = ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{2}$$

where qe and qt are adsorption capacity (mg/g) at equilibrium, and time t (min), and k_1 (1/min) and k_2 (g/(mg/min)) are the adsorption rate constant of the pseudo-first-order and pseudo-second-order models, respectively.

Section 2. Description of adsorption isotherms model

Adsorption isotherm refers to a curve that reflects the relationship of amount of solute q_e , at constant temperature in a certain volume of solution, adsorbed on the unit mass by adsorbent and the corresponding equilibrium concentration of the solution C_e [3]. The Freundlich isotherm model [4] explains that the surface properties of the adsorbent is heterogeneous and the multilayer adsorption occurs on the surface. The Langmuir model [5] illustrates the surface properties of the adsorbent is homogeneous and the monolayer adsorption occurs on the surface. The ammonium adsorption equilibrium isotherm was analyzed by the Freundlich mathematical models (Equation 3) and Langmuir (Equation 4), which are expressed as follows:

$$q_e = k_f C_e^{1/n} \tag{3}$$

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \tag{4}$$

$$R_L = \frac{1}{1 + k_l C_0} \tag{5}$$

where q_m is the maximum ammonium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), n is the heterogeneity factor, R_L is a dimensionless separation factor, and k_f , k_l are the Freundlich, Langmuir constants, respectively.

Section 3. Description of adsorption thermodynamics

The thermodynamics parameters, including Gibbs free energy (ΔG°), enthalpy variation (ΔH°), and entropy variation (ΔS°) can be calculated by Gibbs and Van't Hoff equations according to the experimental data for ammonium adsorption onto zeolite at different temperatures [6,7]:

$$K_c = \frac{C_{ad,e}}{C_e} \tag{6}$$

$$\Delta G^{\circ} = -RT \ln K_{\rm c} \tag{7}$$

$$\ln K_{\rm c} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(8)

In which k_c is the equilibrium constant; $C_{ad,e}$ (mg/L) denotes the NH₄⁺ amount adsorbed on the adsorbent per liter of the solution at equilibrium; R (8.314 J/mol/K) is the universal gas constant and T(K) is the temperature. A straight line will yield when (ln K_c) was plotted against (1/T), ΔH° and ΔS° can be obtained from its slope and intercept.

Section 4. Supplementary Table and Figure of contents

Table S1. The kinetic model parameters for ammonium adsorption of synthetic zeolite.

Table S2. Ammonia nitrogen adsorption capacities of various zeolites.

Figure S1. XRD of synthetic zeolite. (Y) zeolite Y, (P) zeolite P, (F) faujasite, (Q) quartz.

Figure S2. FTIR spectrum of synthetic zeolite.

Figure S3. Equilibrium isotherm fitted to the Langmuir and the Freundlich models (25 °C).

Figure S4. Fitting of ammonium removal efficiency in simulated wastewater.

Parameters		Initial Ammonium Concentration (mg/L)			
		20	100	300	500
Pseudo-first-order	<i>q</i> e	1.85	7.70	17.50	20.91
	<i>k</i> 1 (1/min)	0.060	0.120	0.260	0.200
	r^2	0.420	0.376	0.213	0.930
Pseudo-second-order	$q_e(\mathrm{mg/g})$	2.00	8.36	18.54	21.29
	<i>k</i> ₂ (g/(mg/min))	0.041	0.014	0.008	0.008
	r^2	0.999	0.999	0.999	0.999

Table S1. The kinetic model parameters for ammonium adsorption of synthetic zeolite.

Table S2. Ammonia nitrogen adsorption capacities of various zeolites.

	The Ammonium		
Types	Adsorption	Thermodynamic Model	Reference
	Capacity (mg/g)		
Natural zeolite	13.32	Langmuir	[8]
Modified zeolite	11.83	Langmuir	[9]
Modified zeolite	9.66	Langmuir	[11]
ZFA	28.65	Langmuir	[12]
ZFA	25.13	Langmuir	[13]
ZFA	23.15	Langmuir	[14]
ZFA	32.16	Langmuir	This research



Figure S1. XRD of synthetic zeolite. (Y) zeolite Y, (P) zeolite P, (F) faujasite, (Q) quartz.



Figure S2. FTIR spectrum of synthetic zeolite.



Figure S3. Equilibrium isotherm fitted to the Langmuir and the Freundlich models (25 °C).



Figure S4. Fitting of ammonium removal efficiency in simulated wastewater.

References

- 1. Lagergren, S.Y. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakad, Handlingar **1898**, 24, 1–39.
- 2. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. Proc. Biochem. 1999, 34, 451-465.
- Qi, L.; Teng, F.; Deng, X.; Zhang, Y.; Zhong. X. Experimental study on adsorption of Hg(II) with microwaveassisted alkali-modified fly ash. *Powder Technol.* 2019, 351, 153–158.
- 4. Freundlich, H. Über die adsorption in lösungen (adsorption in solution). J. Am. Chem. Soc. 1906, 5, 121–125.
- 5. Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Am. Chem. Soc. **1918**, 40, 1361–1403.
- 6. Lin, J.; Zhang, Z.; Zhan, Y. Effect of humic acid preloading on phosphate adsorption onto zirconium-modified zeolite. *Environ. Sci. Pollut. Res.* 2017, 24, 12195–12211.
- Yin, Q.; Zhang, B.; Wang, R.; Zhao, Z. Phosphate and ammonium adsorption of sesame straw biochars produced at different pyrolysis temperatures. *Environ. Sci. Pollut. Res.* 2018, 25, 4320–4329.
- 8. Millar, G.J.; Winnett, A.; Thompson, T.; Couperthwaite, S.J. Equilibrium studies of ammonium exchange with Australian natural zeolites. *J. Water Proc. Eng.* **2016**, *9*, 47–57.
- Wijesinghe, D.T.N.; Dassanayake, K.B.; Sommer, S.G.; Jayasinghe, G.Y.; Scales, P.J.; Chen, D. Ammonium removal from high-strength aqueous solutions by Australian zeolite. *J. Environ. Sci. Health Part a-Toxic/Hazard. Subst. Environ. Eng.* 2016, 51, 614–625.
- Song, H.; Wang, J.; Garg, A.; Lin, X.; Zheng, Q.; Sharma, S. Potential of Novel Biochars Produced from Invasive Aquatic Species Outside Food Chain in Removing Ammonium Nitrogen: Comparison with Conventional Biochars and Clinoptilolite. *Sustainability* 2019, *11*, 24.
- Stocker, K.; Ellersdorfer, M.; Lechleitner, A.; Lubensky, J.; Raith, J.G. Impact of concentrated acid, base and salt pretreatments on the characteristics of natural clinoptilolite and its ammonium uptake from model solution and real effluents. *Microporous Mesoporous Mat.* 2019, 288, 109553.
- Zhang, M.; Zhang, H.; Xu, D.; Han, L.; Niu, D.; Zhang, L.; Wensi, W.; Binghui, T. Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination* 2011, 277, 46–53.
- 13. Liu, Y.; Yan, C.; Zhao, J.; Zhang, Z.; Wang, H.; Zhou, S.; Wu, L. Synthesis of zeolite P1 from fly ash under solvent-free conditions for ammonium removal from water. *J. Cleaner Prod.* **2018**, *202*, 11–22.
- 14. He, H.; Xu, S.; Han, R.; Wang, Q. Nutrient sequestration from wastewater by using zeolite Na-P1 synthesized from coal fly ash. *Environ. Technol.* **2017**, *38*, 1022–1029.