

Supply information:

1.1 Adsorption isotherms

The batch adsorption experiments were carried out at different temperatures of 303K. The concentrations of ammonia solutions were 3000mg/L. The 1g (x) Fe-Z was added to the 100mL ammonia solution in a 250mL beaker. The beaker was continuously stirred for 3h to reach equilibrium at 250rpm. Then samples were filtered with 0.45µm membrane filter and the ammonia concentration of remaining solution was measured.

Freundlich model supposes that uptake or adsorption of ammonia occurs on the heterogeneous surface by monolayer adsorption¹. The equation of this model is described following like this¹:

$$q_e = k_f (c_e)^{1/n} \quad (2-1)$$

The Freundlich equation can be linearized by taking logarithms and constants can be determined. The above equation can be linearized as follows:

$$\log(q_e) = \log k_f + 1/n \log(c_e) \quad (2-2)$$

Where k_f and $1/n$ are Freundlich constants and they are related with adsorption capacity and adsorption intensity, respectively. The initial concentrations of ammonia were varied and adsorbent dose was the same in order to determine the equilibrium isotherms.

The Langmuir model supposes that adsorption of ammonia happens on the homogeneous surface by monolayer adsorption instead of interaction between adsorbed ions¹. The model is described in the following equation form:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (2-3)$$

The above equation can be also linearized by the following process:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (2-4)$$

Where q_e denotes the amount adsorbed at equilibrium and was calculated based on Eq.(1).

q_{\max} is the Langmuir constant, which is equal to the adsorption capacity. The parameter K_L represents the Langmuir adsorption equilibrium constant and C_e is the equilibrium

concentration.

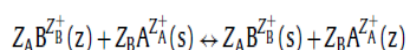
The essential features of the Langmuir isotherm can be expressed by the dimensionless constant separation factor R_L ²:

$$R_L = \frac{1}{1 + kC_0} \quad (2-5)$$

Where C_0 (mg/L) is initial concentration of adsorbate and k is the Langmuir constant (L/mg). There are four meanings for R_L values and they are as follows: favorable adsorption, $0 < R_L < 1$; unfavorable adsorption, $R_L > 1$; linear adsorption, $R_L = 1$; irreversible adsorption, $R_L = 0$.

1.2 Ion exchange isotherm

The ion exchange process can be described by the equation as follows:



Where Z_A, Z_B are the charges of the cations A and B. The symbol 'z' and 's' refer to the zeolite and solution phases, respectively. The thermodynamic equilibrium constant K_a is calculated from the following equation³:

$$\ln K_a = \frac{Z_B - Z_A}{Z_A Z_B} + \int_0^1 \ln K_e dA \quad (2-6)$$

K_a can be obtained through plotting the plot of $\ln K_a$ versus A_z , where K_c is the kielland coefficient.

The free energy of exchange ΔG can be obtained by the following equation⁴

$$\Delta G = \frac{-RT}{Z_A Z_B} \ln K_a \quad (2-7)$$

The sodium ions of zeolite can be changed with ammonia ions and the equivalent fraction of ammonia ions in the solution (A_s) and in the zeolite phase A_z can be calculated by

$$A_s = \frac{C_e}{C_0} \quad (2-8)$$

$$A_z = \frac{V}{ME} (C_0 - C_e) \quad (2-9)$$

Where C_0 and C_e are the initial and equilibrium concentrations of ammonia in the aqueous solution (mg/L), respectively. The E is the CEC of zeolite (mgNH₄⁺/g), V is the volume of aqueous solution (L), and M is the mass of (x) Fe-Z.

$$\text{Kielland coefficient } K_c = \frac{A_z(1-A_s)}{(1-A_z)A_s} \quad (2-10)$$

In addition, Eqs.(2-12) and (2-13) can be expressed as ⁵

$$\ln K_a = \int_0^1 \ln K_c dA_z \quad (2-11)$$

$$\Delta G = -RT \ln K_a \quad (2-12)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2-13)$$

1.3 Adsorption kinetics

The batch adsorption experiments were carried out at different initial ammonia concentrations of 1000, 2000 and 3000 mg/L, respectively. The 100mL ammonia solution was mixed with 1g (x) Fe-Z in a 50mL beaker. The beaker was continuously stirred (250rpm) at initial pH 7.0 and the temperature of 303K. The samples were taken out and filtered with the 0.45 μ m membrane filter to analyze the current ammonia concentration at selected time intervals (0.33, 0.66, 1, 1.33, 1.66, and 2.0 hours).

The adsorption kinetics can be described by the power function adsorption kinetics model and adsorption kinetics model. The equations of adsorption kinetics are as follows ⁶:

$$\text{The pseudo-first-order model} \quad \ln(q_e - q(t_i)) = \ln q_e - k_1 t \quad (2-14)$$

$$\text{The pseudo-second-order model} \quad \frac{t}{q(t_i)} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2-15)$$

$$\text{Intra-particle diffusion model} \quad q(t_i) = k_3 t^{1/2} + C \quad (2-16)$$

Where k_1 (1/min) is the rate constant of pseudo-first-order equation. k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order equation. k_3 (mg g⁻¹ min^{1/2}) is the rate constant of intra-particle diffusion and C (mg/g) is a constant that is about the thickness of the boundary layer. q_e and $q(t_i)$ (mg/g) are the amount of ammonia adsorbed at equilibrium and at time t_i , respectively. The amount of adsorption at equilibrium q_e was calculated based on Eq.(1). The adsorption of TC at time t_i , $q(t_i)$ (mg/g) was calculated from the equation as follows ⁶:

$$q(t_i) = \frac{(C_0 - C_{t_i})V_0 - \sum_2^{i-1} C_{t_{i-1}}V_s}{m}$$

Where C_0 and C_{t_i} (mg/L) are the initial ammonia concentration and the ammonia concentration at time t_i , respectively. V_0 and V_s (L) are the volume of the bulk ammonia solution and the volume of the sample taken out every time for current ammonia concentration analysis, respectively. The m (g) is the mass of the (x) Fe-Z.

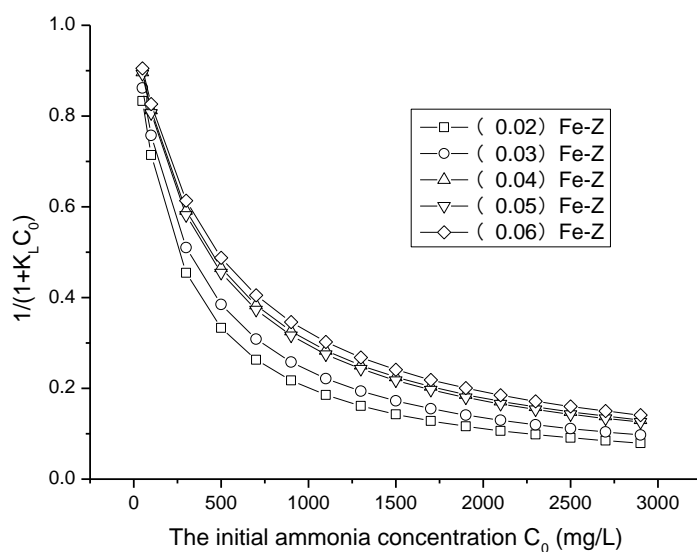


Fig. 1 Variation of separation factor (R_L) as a function of initial ammonia concentration

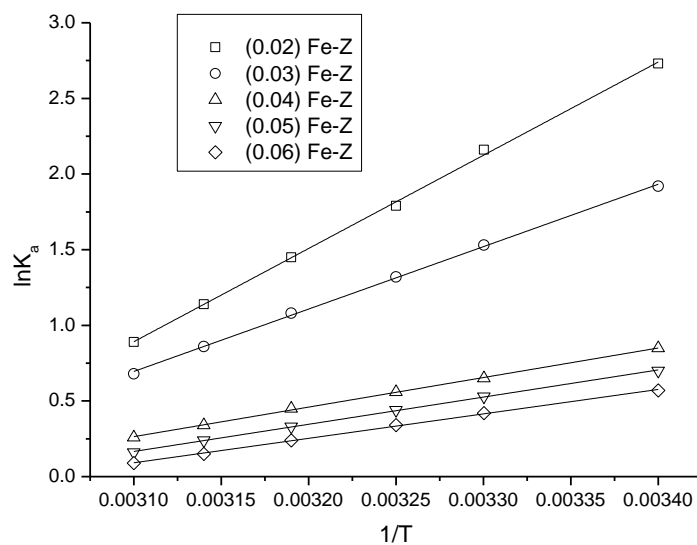


Fig.2 Variation of thermodynamic equilibrium constant $\ln K_a$ as a function of the temperature $1/T$

References

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