

Adsorption Thermodynamics, Kinetics and Mechanism of Calcium(II) Ions onto Kaolinite Clay in Coal Slime Water

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Slime water is a highly concentrated micro-solid-liquid suspension-dispersion system which is mainly consisted of kaolinite and other clay minerals. The existence of these fine clay particles is one of the reasons why slimes water is difficult to clarify. In this work, the adsorption thermodynamics, kinetics and mechanism of Ca^{2+} onto kaolinite clay were systematically investigated through batch adsorption experiments, theoretical analysis, characterization of sorbents and field trial. The results show that the adsorption nature of Ca^{2+} onto kaolinite is spontaneous and exothermic. The adsorption data follow Langmuir isotherms. The possible adsorption mechanism is that CaOH^+ in the system reacted with $\equiv\text{SiOH}$ and $>\text{AlOH}$ groups appeared in the surface of kaolinite. Sorption is mainly controlled by pseudo-second-order kinetics. The main advantages of calcium salt as coagulant are good selective, low-cost and high efficiency in precipitating kaolinite particles from slime water systems.

Key Words: Kaolinite, Calcium ion, Adsorption, Coal slime water.

INTRODUCTION

The coal preparation consumes large amount of water, as cleaning 1 ton of coal needs about 3 tons of water circulating. With the increase of raw coal output and selected ratio, quantities of water needed and waste water produced in coal cleaning process are rapidly increasing. If the waste water which we called slime water wasn't effectively treated and was reused circularly, it will cause serious resource waste and environmental pollution. But it is very difficult to settle the slime water, especially for the extreme difficult to clarified slime water systems. Now the extreme difficult to clarified slime water systems occupy about half in total slime water in china. So the treatment of slime water is an important step in coal processing plants, which affects directly the coal quality, economic and environmental efficiency¹.

Slime water is a highly concentrated micro-solid-liquid suspension-dispersion system which is mainly consisted of clay minerals, such as kaolinite, illite and montmorillonite. The existence of these fine clay particles, especially kaolinite clay, is one of the main reasons why slimes water is difficult to clarify². In recent years, many kinds of flocculation ways have been investigated for precipitating kaolinite particles from slime water³⁻⁶, but for difficult clarified slime water systems, the system didn't clarify completely after large amount of flocculants were used. Mineral coagulant (mainly gypsum)

has excellent sedimentation effects in difficult clarified slime water systems and has been applied in large scale in china⁷, but the reasons why gypsum (effective composition is Ca^{2+}) has excellent sedimentation effects on fine clay particles in the slime water have little been reported in literatures. In this paper, we investigated the adsorption thermodynamics and kinetics of Ca^{2+} onto kaolinite clay and proposed the possible special adsorption mechanism in order to solve the clarification problems of difficult clarified slime water and instruct production process.

EXPERIMENTAL

All chemicals used were of analytical-laboratory grade and were purchased from Fu Chen Chemical Reagent Factory, Tianjin, China.

Kaolinite samples used were provided by China kaolinite Co. (Suzhou, Jiangsu, China). Particles of kaolinite were passed through a 200-mesh sieve and were dried at 105 °C. BET-specific surface area measured by N_2 adsorptions is 17 $\text{m}^2 \text{g}^{-1}$.

The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 1 g (weighs accurately) of kaolinite with 100 mL (measures accurately) of Ca^{2+} solution under natural pH conditions with electrolyte concentration of 0.2 mol/L at a constant speed of 200 rpm in thermostatic oscillation box. After an oscillating time, the suspensions were centrifuged for

10 min at 1500 rpm. The supernatants were collected and analyzed for calcium ions concentration.

Stock solutions of calcium were prepared from CaCl_2 . Working solutions of Ca^{2+} were prepared from the stock solution to the desired concentrations for each experimental run. The accurate concentrations were measured with calcium ion electrode.

Adsorption capacity of kaolinite was calculated as:

$$q_t = \frac{40(C_0 - C_t)V}{1000m} \quad (1)$$

where q_t (mg/g) is the adsorption capacity. C_0 is the initial Ca^{2+} concentration and C_t (mmol/L) is the Ca^{2+} concentration. V (mL) is the volume of the solution and m (g) is the mass of kaolinite.

Adsorption isotherms were studied on Ca^{2+} solutions with varying concentrations from 5-80 mmol/L at four different temperatures, 5, 15, 25 and 35 °C, which selected according to the application temperature range in actual coal slime water. The adsorbent dose was 1 g/L.

Adsorption kinetics was studied on 5.458 mmol/L initial Ca^{2+} concentration at 10 and 20 °C for a certain time of 0-3 h, respectively.

Field trials were performed in Xingtai coal preparation plant in Shanxi province, China.

Detection method: Elemental compositions of kaolinite surface before and after adsorption were analyzed using X-ray photoelectron spectroscopy analysis (XPS). XPS analyses were performed in PHI-5300/ESCA with a monochromatic aluminum K_{α} X-ray source. All spectra were obtained in fixed analyzer transmission mode with pass energies of 80 and 20 eV being used for the survey and high-resolution scans, respectively. Elemental compositions were calculated from peak areas obtained from the survey spectra using the appropriate sensitivity factors after subtraction of a linear background.

RESULTS AND DISCUSSION

Adsorption isotherm: Fig. 1 illustrates the effects of Ca^{2+} concentration onto the adsorption capacity at 5, 15, 25 and 35 °C, respectively. As shown, the equilibrium adsorption capacity increases promptly with increasing Ca^{2+} concentration at low Ca^{2+} concentration stage and reaches maximum value and then the adsorption capacity remains unchanged. This indicates that the surface of kaolinite doesn't adsorb any adsorbates when all active surface sites are occupied. The adsorption capacity decreases with the rise in temperature, showing exothermic nature of the adsorption process. A maximum calcium adsorption capacity of 3.127 mg/g was achieved with Ca^{2+} concentration of 39.2182 mmol/L at 5 °C.

The linear forms of Langmuir isotherm⁸ (2) and Freundlich isotherm⁹ (3) are as:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where C_e (mmol/L) is the equilibrium concentration, q_e (mg/g) is the equilibrium adsorption capacity, Q (mg/g) is the maximum

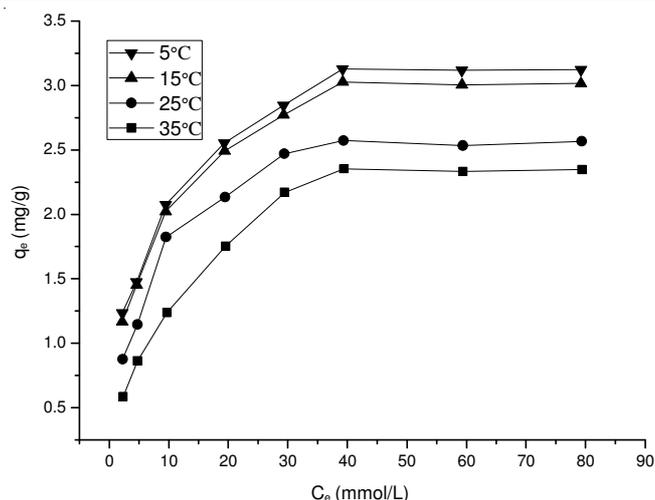


Fig. 1. Effects of Ca^{2+} concentration on the adsorption capacity at different temperatures

adsorption capacity of sorbent, b (L /mmol) is the Langmuir constant expressing the adsorption ability. K_F is the empirical constant of Freundlich isotherm and n is the empirical parameter related to the intensity of adsorption.

Isotherm constants for each model were determined from the slope and intercept of the linearized plot of the respective isotherm equations. For example, Q and b were calculated from the slope and intercept of the linearized plot C_e/q_e vs. C_e shown in Fig. 2. Table-1 shows the values of various isotherm constants and their corresponding correlation coefficients (R^2) at different temperatures. Excellent fitting lines for Langmuir isotherm equation were obtained at all experimental temperatures studied. The Q values at different temperatures are close to the experimental equilibrium adsorption capacities and the maximum theoretical Q value is 3.361 mg/g at 5 °C, which was little higher than experimental values (3.127 mg/g). The higher R^2 values indicate the applicability of Langmuir isotherm. The results show that the adsorption process of Ca^{2+} onto kaolinite is mainly monolayer adsorption.

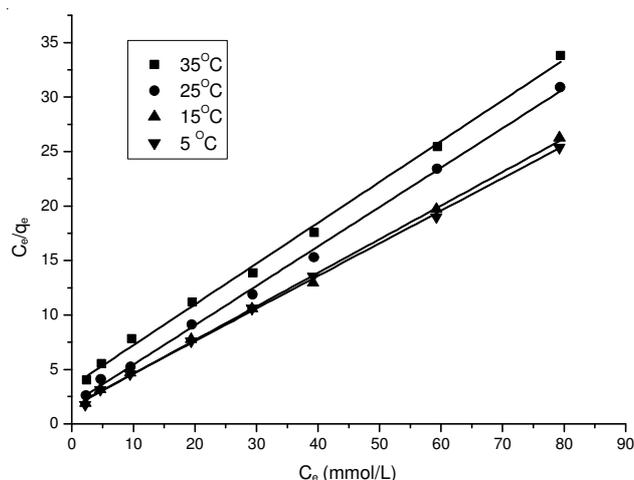


Fig. 2. Plot of the Langmuir isotherm for Ca^{2+} onto kaolin at different temperatures

Adsorption thermodynamics investigations: Thermodynamic parameters associated with the adsorption, namely

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS OF CALCIUM SORPTION ONTO KAOLINITE

Temperature (°C)	Langmuir			Freundlich		
	Q (mg/g)	b (L/mmol)	R ²	n	K _F [(mg)(L/mmol) ^{1/n}]	R ²
35	2.679	0.1105	0.99332	2.393	0.4570	0.94166
25	2.764	0.1994	0.99754	3.156	0.7559	0.89745
15	3.240	0.2034	0.99811	3.521	0.9918	0.94089
5	3.361	0.1975	0.99784	3.547	1.0303	0.94553

standard free energy change (ΔG° kJ mol⁻¹), standard enthalpy change (ΔH° kJ mol⁻¹) and standard entropy change (ΔS° J mol⁻¹ K⁻¹), were calculated from the variation of thermodynamic distribution coefficient K_d with changes of temperature. K_d for the adsorption reaction can be defined as:

$$K_d = \lim_{C_e \rightarrow 0} \frac{C_s}{C_e} \quad (4)$$

where C_s (mmol/g) is the Ca²⁺ concentration on the surface of kaolinite, C_e (mmol/mL) is the Ca²⁺ concentration in the equilibrium suspension, the K_d can be calculated by plotting $\ln(C_s/C_e)$ vs. C_e and extrapolating C_e to zero¹⁰.

The free energy of sorption process is given as:

$$\Delta G^\circ = -RT \ln K_d \quad (5)$$

The values of ΔH° and ΔS° can be calculated from the slope and intercept of a plot of $\ln K_d$ vs. $1/T$ as:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

The calculated values of thermodynamic parameters are shown in Table-2. The negative values of ΔG° confirm the spontaneous nature of calcium sorption. The value of ΔH° is negative indicating that the sorption process is exothermic in nature. So increasing temperature will be disfavor of the adsorption which is coincident with the result of experiment 3.1. The negative value of ΔS corresponds to a decreased degree of freedom in the system as a result of adsorption of Ca²⁺, as well as decreased randomness at the solid-solution interface reflecting principally the extra translational entropy.

TABLE-2
THERMODYNAMIC PARAMETERS
AT DIFFERENT TEMPERATURES

T (K)	K_d	ΔG° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (KJ mol ⁻¹)
308	9.974	-5.890		
298	13.464	-6.442	-42.825	-19.156
288	18.174	-6.944		
278	22.198	-7.165		

Adsorption kinetics: The kinetics of adsorption process of Ca²⁺ onto kaolinite was also studied (Fig. 3). The rates of adsorption of Ca²⁺ onto kaolinite are very fast at the beginning (0.5 h), then become slow with increase in time because more and more adsorbent surface sites were occupied by the adsorbate molecule/ion. Finally the equilibrium reached.

The pseudo-first-order (7)¹¹ and pseudo-second-order (8)¹² models were employed to explain the solid/liquid adsorption.

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \quad (7)$$

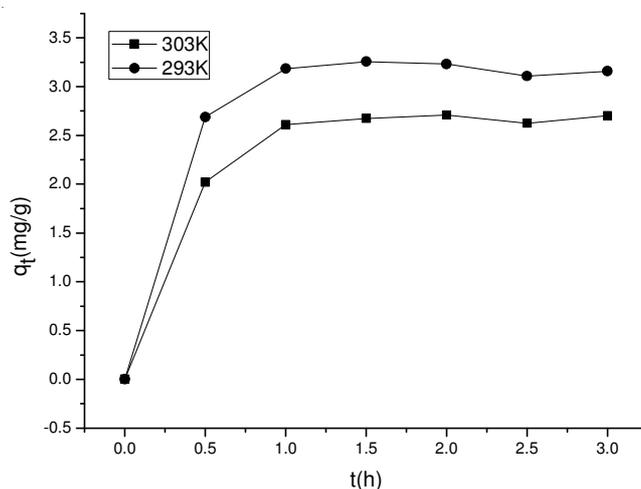


Fig. 3. Adsorption kinetics curves for the adsorption of Ca²⁺ on kaolin at 293 and 303 K

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity of Ca²⁺ adsorbed at equilibrium and at time t (h), respectively. k_1 (h⁻¹) is the rate constants of pseudo-first-order. The values of the rate constants (k_1) were obtained from the slope of the straight-line plots of $\ln(q_e - q_t)$ vs. t at different temperature. k_2 (g/(mg h)) is the rate constant of pseudo-second-order. The values of q_e (1/slope) and k (slope²/intercept) of the pseudo-second-order equation can be found out by plotting t/q_t vs. t shown in Fig. 4.

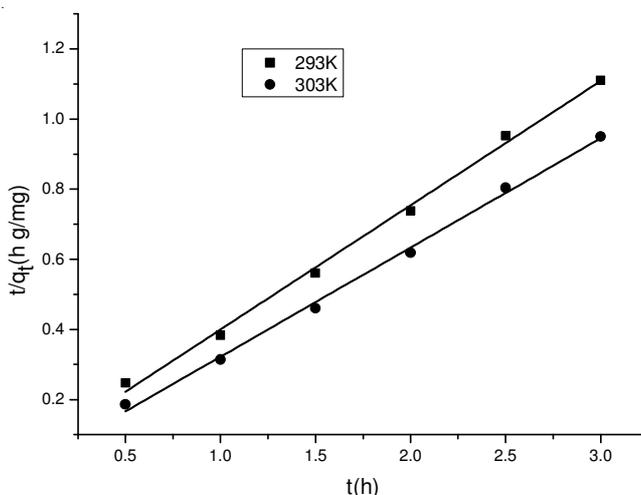


Fig. 4. Pseudo-second-order plot of Ca²⁺ on kaolin at 293 and 303 K

The rate constants (k_1 and k_2) and correlation coefficients (R^2) fitting to two models present in Table-3. The high values

TABLE-3
ADSORPTION KINETICS EQUATIONS SIMULATE
OF Ca²⁺ AT DIFFERENT TEMPERATURES

T (K)	Pseudo-first-order		Pseudo-second-order	
	k ₁ (h ⁻¹)	R ²	k ₂ (g/(mg h))	R ²
293	0.880	0.3130	8.299	0.9989
303	0.185	0.5000	12.859	0.9927

of R²₂ (0.9989, 0.9927) for all temperatures indicate that the adsorption data fit well to pseudo-second-order kinetics for the entire adsorption process.

Adsorption mechanism: Kaolinite consists of 1:1 Si-O tetrahedron and Al-O octahedron¹³. Si-O tetrahedron and Al-O octahedron share oxygen atoms. Inner and inner surface hydroxyl groups easily form hydrogen bonds, so the kaolinite structure is stable. The basal planes (00 $\bar{1}$ and 001) of kaolinite are constantly taken a little negative charge, due to the isomorphous substitution of Al³⁺ for Si⁴⁺ and Mg²⁺ for Al³⁺. So there are electrostatic attraction between Ca²⁺ and kaolinite, but it was not occupied dominant interaction in adsorption process because of the low isomorphous substitution quantities decided by the structure of kaolinite. The results of experiments and adsorption isotherm analyses (Section 3.1) also confirm this point.

As the normal pH value in the system is 6-9, Ca²⁺ may be converted to CaOH⁺ as shown in Fig. 5¹⁴. The surface charge of kaolinite becomes less negative and the surface of kaolinite particles appears a lot of ≡SiOH and >AlOH active groups. It is deduced that the hydroxyl group complexing reaction occurred as follows ((9), (10)) in adsorption process.

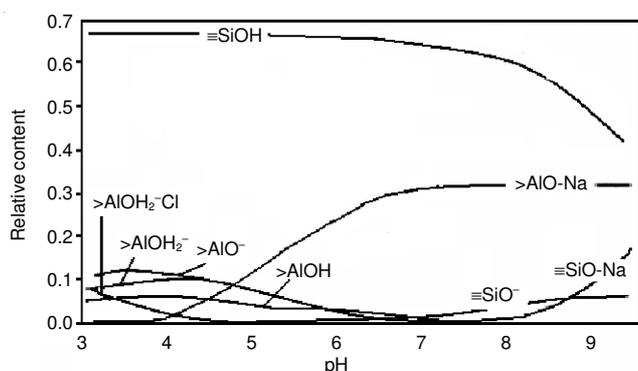
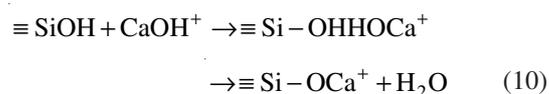
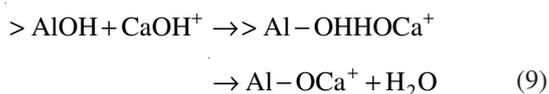


Fig. 5. Variation of the relative content of groups on kaolinite surface with pH value



It was suggested that the hydroxyl group complexing reaction plays a relatively important role compared to electrostatic interaction in adsorption process.

Table-4 gave the elemental relative composition of kaolinite surface before and after adsorption characterized by XPS. The calcium content in raw clay is very little, only occupied

TABLE-4
ELEMENTAL COMPOSITION (%) OF KAOLINITE
BEFORE AND AFTER ADSORPTION

	Si	Al	Mg	Ca	O
Raw clay	17.11	11.27	0	0.1	71.52
After adsorbed	18.62	8.53	1.08	1.09	70.68

0.1 % of total quantities, but it increased to 1.09 % after adsorbed indicating that calcium in the solution was adsorbed onto the kaolinite surface, which also demonstrated the occurrence of complexing reactions.

The special adsorption of Ca²⁺ onto kaolinite is crucial important for the selective aggregation and flotation in slime water system, especially for difficult clarified slime water systems. The quality of circulating water in coal preparation process affects the quality and ash of fine coal. Excess agents in circulating water can affect the flotation effects. The aggregating agents with poor selectivity precipitate coal and minerals at the same time and lead to ash decreasing in the tailings and fine coal lost. Calcium salt as aggregating agent can especially adsorb onto the surface of kaolinite and form the selective aggregation, which is in favour of quantifying agents and improving separation effects.

Conclusion

The adsorption nature of Ca²⁺ on kaolinite is spontaneous and exothermic. The adsorption data follow Langmuir isotherms. The possible adsorption mechanism is that CaOH⁺ in the system reacted with ≡SiOH and >AlOH groups appeared in the surface of kaolinite. Sorption is mainly controlled by pseudo-second-order kinetics.

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