



## Research on mechanism of perfluorooctanoic acid adsorption by calcined CuAl-carbonate layered double hydroxide

Yuechao Wu, Yulin Wang\*, Jianguang Li, Huiming Zeng, Feng Lin, Haijie Ben, Mingping He, Zhenqiang Dong, Wanli Xu, Liang Lv\*

College of Chemical and Materials Engineering, Quzhou University, 78 Jiu Hua Da Dao, Ke Cheng District, Quzhou City, Zhejiang 324000, China, Tel. +86 570 8026667; Fax: +86 570 8026667; email: Lianglv\_buct@126.com (L. Lv), csu\_lin@163.com (Y. Wang)

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### ABSTRACT

A novel adsorbent of CuAl-carbonate layered double hydroxide (CuAl-LDH) was synthesized by coprecipitation method and applied to remove redundant perfluorooctanoic acid (PFOA) from water. The physical and chemical properties of as-prepared CuAl-LDH and CuAl-CLDH were investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and Fourier-transform infrared (FT-IR) analysis. The TEM results and XRD analysis confirm that CuAl-LDH presents the crystalline nature and CuAl-CLDH owns memory effect. The FT-IR analysis indicates that PFOA can be removed through entering interlayer of CuAl-CLDH. In order to understand the adsorption process profoundly, the mechanism was studied by adsorption thermodynamics and kinetics. The results indicate that the CuAl-CLDH can be effectively utilized to remove PFOA from water, where the maximum adsorption quantity (1,526.1 mg/g) could be achieved and the adsorption equilibrium could be reached in 2 h. The thermodynamic data are well-fitted to the Freundlich isotherm model while pseudo-second-order model provides better correlation of the kinetic data. From the thermodynamic analysis, the adsorption process is exothermic and spontaneous. Based on TEM, XRD and kinetic analysis, the memory effect probably takes an important part in early adsorption phase while chemisorption may control the adsorption rate at the second adsorption phase. Because of the excellent adsorption quantity showed by CuAl-CLDH, they are anticipated to remove PFOA from water in pollution control.

*Keywords:* Perfluorooctanoic acid; CuAl-LDH; CuAl-CLDH; Adsorption thermodynamics; Adsorption kinetics

### 1. Introduction

The extensive utilization of perfluorinated compounds (PFCs) in industrial applications and daily life [1] for decades has given rise to their global distribution in environment and biological accumulation in humans [2–5]. Perfluorooctanoic acid (PFOA) as one foremost PFCs of concern has been found in soil and groundwater worldwide [2,3,5–9]. The concentration of PFOA observed in drinking water at many spots has exceeded the advisory limitation

of 0.07 µg/L provided by United States Environmental Protection Agency [10]. Among the various frequent treatments for environmental pollution [11–14], adsorption is the most widely adopted technique due to its simple operation and low cost. Hence, the development of novel adsorbents with high removal efficiency has attracted considerable interest for treatment of PFOA-contained waste water.

Layered double hydroxides (LDHs), one kind of anionic clay with similarly lamellar structure but different properties,

\* Corresponding authors.

are effective ion exchangers/adsorbents for removal of a variety of anionic pollution for their high specific surface area and porosity. The calcination of LDHs at 450°C–500°C will convert into calcined layered double hydroxides (CLDHs) with removal of interlayer water, anions and hydroxyl groups [15,16]. The CLDHs then are able to recover the lamellar structure after they are exposed to PFOA aqueous solution. During the process, water is adsorbed to regenerate hydroxyl groups and PFOA are imported into the interlayer galleries. This phenomenon is known as “memory effect”.

Compared to MgAl-CLDH, it is noticed that the application of CuAl-CLDH for the removal of pollution is limited since the cations with specific  $d^n$  configurations may exhibit particular coordination preferences which militate against the formation of LDHs phases [17]. Therefore, the objectives in this study are synthesis of CuAl-CLDH and its mechanism for the adsorption of PFOA from water. The thermodynamics and kinetics during adsorption process have been examined for further research.

## 2. Materials and methods

### 2.1. Reagents and chemicals

The starting materials  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and NaOH in this study were purchased from Xilong Scientific Co., (China),  $\text{Na}_2\text{CO}_3$  was obtained from Zhejiang Hanoun Chemical Technology Co., (China), PFOA was purchased from Shanghai Macklin Biochemical Co., Ltd., (China). All the chemicals were analytical grade and used without further purification. The water used was deionized and decarbonated. A 0.6648 g/L PFOA stock solution was prepared and other PFOA test solutions were prepared through subsequent dilution of the stock solution.

### 2.2. Preparation of CuAl-LDH and CuAl-CLDH

CuAl-LDHs sample was acquired through co-precipitation method. The mixed solution of NaOH and  $\text{Na}_2\text{CO}_3$  was prepared as precipitant and the nitrates were dissolved in deionized water according to molar ratio of  $n_{\text{Cu}}:n_{\text{Al}} = 4:1$ . Under constant and intensive stirring, solution of precipitant was added dropwise into mixed solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  at 65°C and pH = 10. After stirring for 24 h, raw products were subsequently treated through crystallization, centrifugation, cleanse and drying at 80°C for 24 h in the air oven.

CuAl-CLDH sample was obtained after calcination of as-prepared CuAl-LDH at 450°C for 6 h.

### 2.3. Characterization of CuAl-LDH, CuAl-CLDH and CuAl-CLDH after adsorption

The crystalline structures of CuAl-LDH, CuAl-CLDH and CuAl-CLDH after adsorption were characterized by X-ray diffraction analyzer (D8 Advance), the surface morphologies of the samples were detected using transmission electron microscopy (TEM; Tecnai G2 F20), the functional groups in the samples were monitored with Fourier-transform infrared (FT-IR; Nicolet iS50) spectra.

### 2.4. Adsorption experiments

In this part, the concentration of PFOA solution was measured by high performance liquid chromatography (HPLC). Batch adsorption researches were processed as follows: 0.1 g CuAl-CLDH was added into 30 mL PFOA solution with different initial concentration. The thermodynamics of adsorption was investigated at initial concentration of 125, 250, 500, 1,000 and 2,000 mg/L, respectively. The temperatures required for thermodynamics of adsorption were 25°C, 35°C, 45°C, 55°C and 65°C, respectively. The time required was 6 h. The kinetics of adsorption was investigated at initial concentration of 500 mg/L, the temperatures required for kinetics of adsorption were 25°C, 35°C, 55°C and 65°C, respectively. The samples were taken at 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 270, 300, and 360 min, respectively.

The quantity of PFOA adsorbed at equilibrium ( $q_e$ ) can be calculated by Eq. (1), where  $q_e$  is the adsorption quantity (mg/g) at equilibrium, and  $C_0$  and  $C_e$  are the initial concentration and concentration at equilibrium (mg/L), respectively.  $V$  is the volume (mL) of PFOA solution, and  $m$  is the mass (g) of adsorbent used.

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

The quantity of PFOA adsorbed at time  $t$  ( $q_t$ ) can be calculated by Eq. (2), where  $q_t$  is the adsorption capacity (mg/g) at time  $t$  and  $C_t$  is the concentration at time  $t$  (mg/L).

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

## 3. Results and discussion

### 3.1. Characterization of CuAl-LDH, CuAl-CLDH and CuAl-CLDH after adsorption

#### 3.1.1. TEM analysis

The surface morphologies of CuAl-LDH, CuAl-CLDH and CuAl-CLDH after adsorption are shown in Fig. 1.

We can see from Fig. 1A and B that the morphology of CuAl-LDH is confirmed to be nanosheet and the surface of CuAl-LDH platelets are smooth. However, the sizes of CuAl-LDH platelets are not uniform. From Fig. 1C and D, it is found the disappearance of nanosheet structures, which may be caused by destruction of organized layered structure after calcination. Meanwhile, the formation of mesoporous holes in the basal planes can also be observed in these two figures, which is a typical phenomenon for calcination of LDHs at 450°C. Fig. 1E and F obviously show that CuAl-CLDH after adsorption has partially recovered to the original organized lamellar structure. It also could be noticed that the layered structure is not as clear as that in Fig. 1A and B. To some extent, the result of TEM analysis has confirmed the “memory effect”.

#### 3.1.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction (XRD) patterns of CuAl-LDH, CuAl-CLDH and CuAl-CLDH after adsorption.

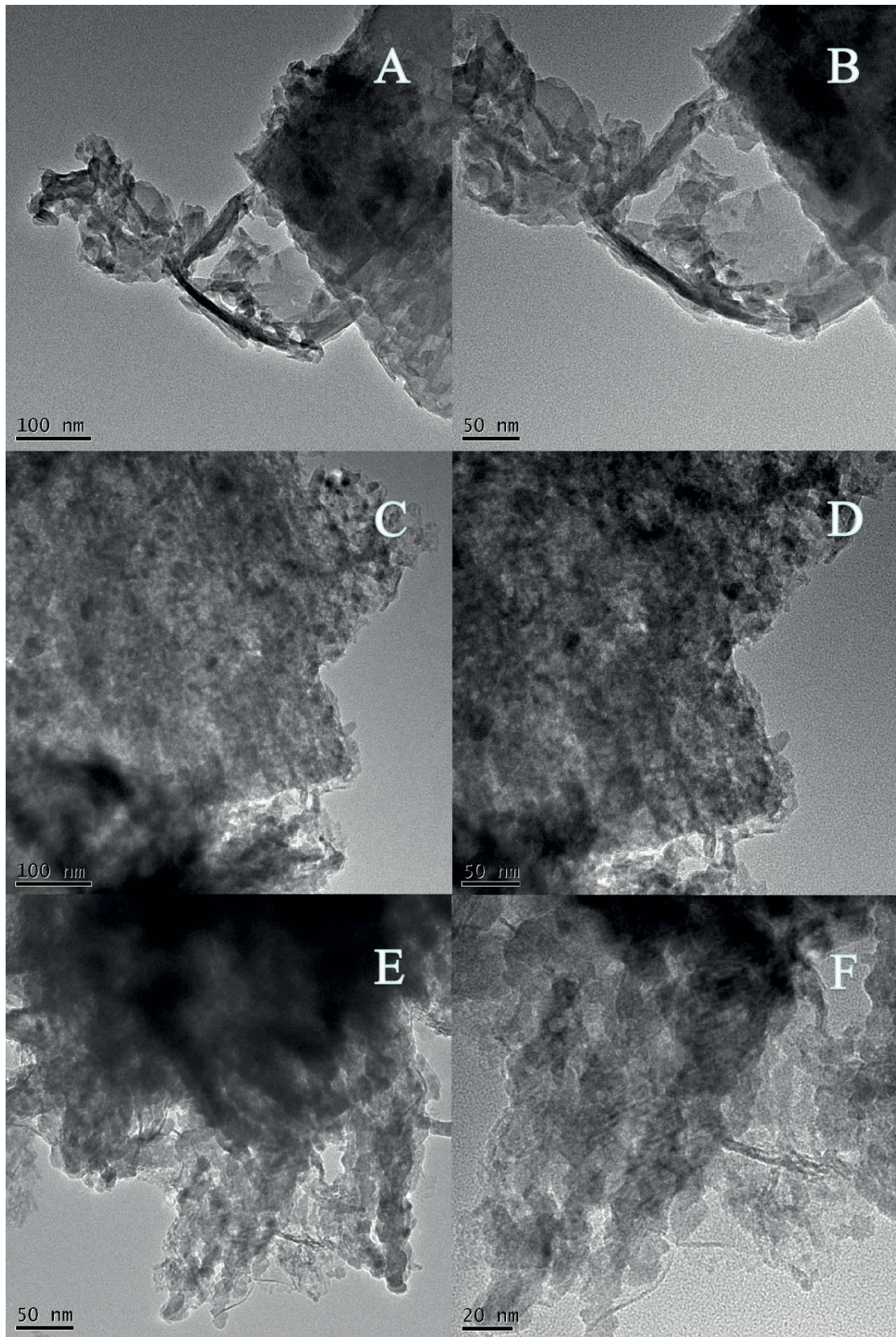


Fig. 1. Transmission electron microscopy (TEM) micrographs of CuAl-LDH (A, B), CuAl-CLDH (C, D) and CuAl-CLDH after adsorption (E, F).

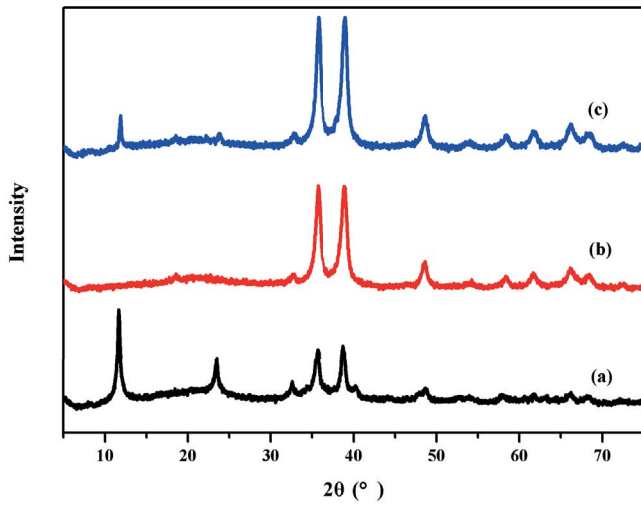


Fig. 2. X-ray diffraction (XRD) patterns of (a) CuAl-LDH, (b) CuAl-CLDH, and (c) CuAl-CLDH after adsorption.

The sharp and symmetric peaks in curve (a) indicating the crystalline nature of the sample. On the other hand, the  $2\theta$  angles at  $11.6^\circ$ ,  $23.3^\circ$ ,  $32.5^\circ$  and  $35.5^\circ$  are corresponding to the typical 003, 006, 009 and 012 crystal planes in LDHs, respectively. Moreover, the peaks at  $38.8^\circ$  and  $48.6^\circ$  belong to CuO and  $\text{CuAlO}_2$ , respectively. Compared with curve (a), the disappearance of peaks at  $11.6^\circ$  and  $23.3^\circ$  in curve (b) proves that the lamellar structure of CuAl-LDH has been destroyed in CuAl-CLDH. Meanwhile, the peaks in curve (b) around  $60^\circ$ – $70^\circ$ , which represent for  $\text{CuAlO}_2$ , are higher than that in curve (a), indicating the deformation of CuAl-LDHs after calcination as well. Ultimately, the recovery of peaks at  $11.6^\circ$  and  $23.3^\circ$  in curve (c) verifies “memory effect” from another point of view and demonstrates that PFOA can be removed from aqueous solution via entering interlayer of CLDH as well.

### 3.1.3. FT-IR analysis

As an effective technique for understanding groups in samples, FT-IR was adopted. Fig. 3 gives the FT-IR spectra of CuAl-CLDH and CuAl-CLDH after adsorption. The peaks appearing at  $1,204.81$  and  $1,148.07$   $\text{cm}^{-1}$  in curve (a) are assigned to the stretching vibration of C–F, indicating that PFOA can be adsorbed by CuAl-CLDH, which is corresponding to the results of XRD analysis.

### 3.2. Thermodynamic studies of PFOA adsorption

The adsorption isotherms are shown in Fig. 4. The increase in the temperature results in a decrease in PFOA adsorption quantity. This phenomena reveals that the process of PFOA removed by CuAl-CLDH is exothermic. The experimental data were fitted by Langmuir [Eq. (3)], Freundlich [Eq. (4)] and Langmuir–Freundlich (L–F) [Eq. (5)] isotherm models.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

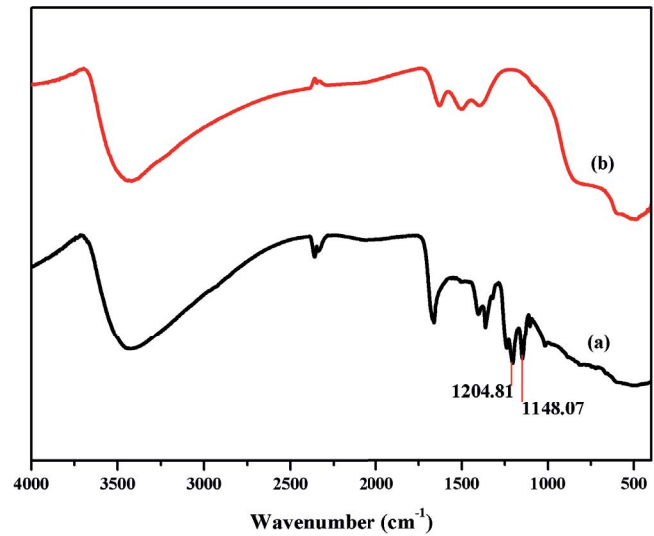


Fig. 3. FT-IR spectra of (a) CuAl-CLDH after adsorption and (b) CuAl-CLDH.

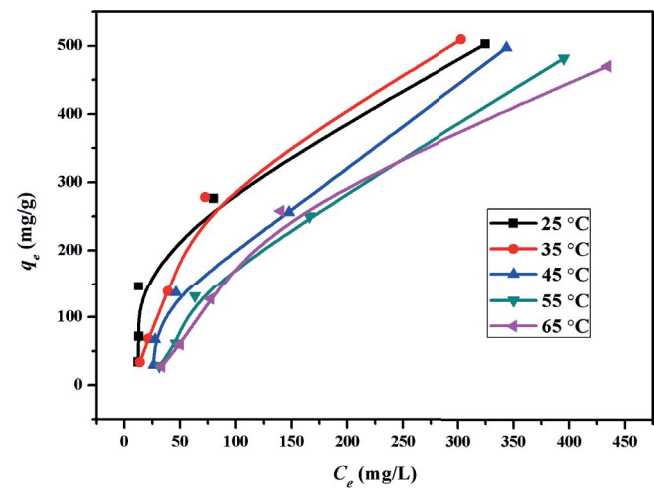


Fig. 4. Adsorption isotherms of PFOA adsorption onto CuAl-CLDH ( $V = 30$  mL;  $w_{\text{CuAl-CLDH}} = 0.1$  g;  $C_0 = 125, 250, 500, 1,000$  and  $2,000$  mg/L).

$$q_e = K_F C_e^n \quad (4)$$

$$q_e = \frac{q_m K_{L-F} C_e^n}{(1 + K_{L-F} C_e^n)} \quad (5)$$

where  $K_L$  is the Langmuir isotherm constant (mL/mg),  $K_F$  is the Freundlich isotherm constant,  $K_{L-F}$  is the L–F isotherm constant (mL/mg), and  $n$  is the adsorption intensity.

The fitted data by different models are compared in Table 1. It can be learned that the experimental data are better fitted by the Freundlich isotherm model than other two models. The results indicate that the active sites or pore structure of CuAl-CLDH maybe play an important role in removal of PFOA. Moreover,  $n$  is calculated

Table 1  
Langmuir, Freundlich and L-F constants for removal of PFOA by CuAl-CLDH

Temp. (°C)	Langmuir			Freundlich			L-F		
	$q_m$ (mg/g)	$K_L$ (L/mol)	$R^2$	$K_F$ (L/mol)	$n$	$R^2$	$q_m$ (mg/g)	$K_{L-F}$ (L/mol)	$R^2$
25	648.5	$1.02 \times 10^{-2}$	0.938	25.28	0.431	0.948	813.7	$1.44 \times 10^{-2}$	0.914
35	798.8	$5.99 \times 10^{-3}$	0.975	14.51	0.527	0.953	558.2	$7.87 \times 10^{-4}$	0.999
45	1,299.1	$1.78 \times 10^{-3}$	0.977	5.12	0.701	0.983	2,419.7	$1.51 \times 10^{-2}$	0.967
55	1,526.1	$1.17 \times 10^{-3}$	0.984	3.27	0.753	0.984	917.2	$8.88 \times 10^{-4}$	0.979
65	1,077.2	$1.82 \times 10^{-3}$	0.962	1.35	0.771	0.955	522.2	$6.58 \times 10^{-5}$	0.999

to be less than 1, which confirms that the removal of PFOA was favorable under the studied conditions.

On the other hand, based on the data acquired by fitting of Freundlich isotherm model, Gibbs energy change ( $\Delta G^\circ$ ), entropy change ( $\Delta S^\circ$ ) and enthalpy change in the adsorption process can be determined by Eqs. (6) and (7). Where  $R$  is molar gas constant (8.314 J/mol K),  $T$  is temperature (K), Results are shown in Table 2.

$$\Delta G^\circ = -RT \ln K \quad (6)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

Obviously, Gibbs energy change is negative, which indicates that the adsorption process is spontaneous.

### 3.3. Kinetic studies of PFOA adsorption

The effect of reaction duration on adsorption quantity is presented in Fig. 5. It is seen that the adsorption of PFOA increase as the duration increases. Fig. 5 exhibits that the kinetics of PFOA adsorption can be divided into two phases: a fast adsorption phase and a slow adsorption phase. In order to investigate the rate-limiting step in the adsorption process, pseudo-first-order kinetic model [Eq. (8)] and pseudo-second-order kinetic model [Eq. (9)] were adopted to further analyze the effect of reaction duration on adsorption quantity under different temperature.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where  $k_1$  and  $k_2$  are for pseudo-first-order adsorption rate constant and pseudo-second-order adsorption rate constant, respectively. Therefore the data after nonlinear-fitted by the two models are summarized in Table 3.

By comparison, the adsorption data of PFOA by CuAl-CLDH fit better with pseudo-second-order kinetic model. This result suggests that the rate-limiting step in the adsorption process is the surface reaction, which also can be considered as chemisorption. Therefore the possible

Table 2  
Gibbs energy, enthalpy, and entropy changes for removal of PFOA by CuAl-CLDHs

Temp. (°C)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)
25	-8.007		
35	-6.853		
45	-4.321	-62.39	-181.54
55	-3.233		
65	-0.840		

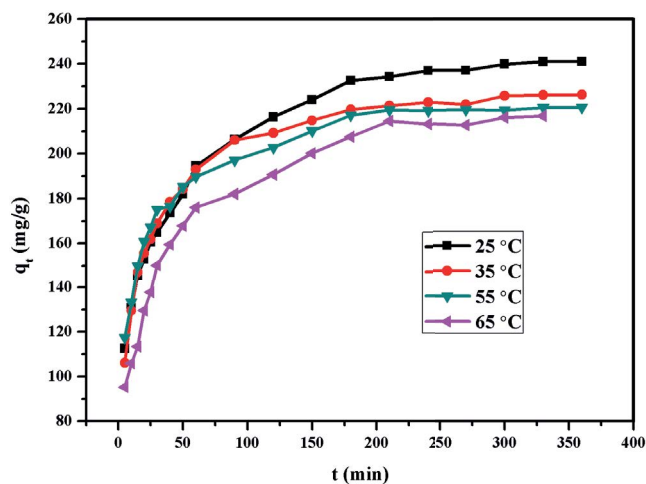


Fig. 5. Adsorption kinetic curves of PFOA adsorption onto CuAl-CLDH ( $V = 30$  mL;  $w_{\text{CuAl-CLDH}} = 0.1$  g;  $C_0 = 500$  mg/L).

mechanism of removal of PFOA by CuAl-CLDH can be described as: the fast adsorption phase is controlled by memory effect. Then the slow adsorption phase is controlled by chemisorption which probably involved the reaction between PFOA and active sites in CuAl-CLDH.

## 4. Conclusion

The CuAl-LDH and CuAl-CLDH with excellent adsorption quantity for PFOA can be successfully synthesized via coprecipitation method. The TEM analysis and XRD analysis demonstrate the crystalline nature of CuAl-LDH as well as the presence of memory effect. The FT-IR analysis

Table 3

Experimental conditions, parameters, regression coefficients ( $R^2$ ) of the two kinetics models for removal of PFOA by CuAl-CLDHs

Temp. (°C)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		$q_{e,cal}$ (mg/g)	$k_1 \times 10^{-2}$ (min <sup>-1</sup> )	$R^2$	$q_{e,cal}$ (mg/g)	$k_2 \times 10^{-4}$ (min <sup>-1</sup> )	$R^2$
25	241.0	223.4	6.07	0.710	250.0	2.83	0.999
35	226.2	212.2	7.37	0.779	232.0	4.12	0.999
55	220.4	206.3	9.10	0.706	226.2	4.80	0.999
65	216.6	201.5	5.26	0.802	225.7	2.89	0.999

proves the entrance of PFOA into interlayer of CuAl-CLDH. The mechanism of the adsorption process was studied by adsorption thermodynamics and kinetics. The adsorption thermodynamics of PFOA is well-fitted by the Freundlich isotherm model and the adsorption kinetics of PFOA can be perfectly fitted by the pseudo-second-order kinetic model. From the thermodynamic analysis, the adsorption process is exothermic and spontaneous; from the kinetic analysis, the adsorption process is controlled by memory effect at fast phase, which is corresponding to the results of TEM and XRD analysis, and the chemisorption is possibly involved at slow phase. The research on adsorption mechanism of PFOA by CuAl-CLDH will provide substantial foundation for further study and application.

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