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Research Article

Selective Adsorption of Adenosine and Guanosine by a β -Cyclodextrin/Layered Double Hydroxide Intercalation Compound

A film of carboxymethyl- β -cyclodextrin-intercalated Zn–Al layered double hydroxide (CMCD–LDH) was investigated for selective adsorption of the nucleosides adenosine (A) and guanosine (G). The effects of pH value and adsorption time on the adsorption behavior were studied. The CMCD–LDH film shows a higher selectivity for G than A under identical conditions of G and A, which results from the ability of selective recognition of the interlayer CMCD. The kinetic studies show that adsorption of A and G by the CMCD–LDH film can be described satisfactorily by the slab diffusion model. Both the values of diffusion coefficient (D) and adsorption capability (q_e) of G by the CMCD–LDH film are larger than those of A, demonstrating the selective adsorption of the CMCD–LDH film for nucleosides. Due to its easy preparation and manipulation, this film is expected to be successfully applied in the field of selective adsorption and separation.

Keywords: Adsorption, Product properties, Selectivity, Separation techniques, Thin films

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1 Introduction

As the constructing units of nucleic acids, nucleosides are involved in a large number of biochemical processes. Because of their important biological effects, nucleosides and their derivatives are widely used for the manufacture of medicaments. Mixtures of various nucleosides often arise both in the isolation of nucleosides from biological raw material and in the case of their chemical modification. For the separation of such nucleoside mixtures, some usual methods have been applied, e.g., mass spectrometry (MS) [1], high-performance liquid chromatography (HPLC) [2], electrochemical impedance spectroscopy (EIS) [3], and capillary electrophoresis (CE) [4]. However, drawbacks of these methods still exist: in some cases, complete separation of the modified nucleosides was not achieved or partial destruction of some unstable compounds occurred. Recently, a new trend of designing artificial sieves and filters and their promise for the separation of biomolecules has been reviewed [5]. Many attempts have also been made to develop a technique that enables sensitive detection and selective separation of biomolecules and biomarkers within a short period of time [6–8], but most of these techniques

lack the capability to selectively separate the target molecules from a complex biomolecule analyte [9].

β -Cyclodextrin (β -CD) is a cyclic oligosaccharide with seven glucose units and can form an inclusion complex with some molecules through a host-guest interaction. Since the inside surfaces of the CD's cavities are hydrophobic, CD tends to form inclusion complexes with certain compounds whose molecular size and structure match with CD's cavities. In the last few years, the study of enantioselective separation of nucleosides with CDs has attracted much attention in the field of analytical research. Wang et al. explored the possibility of improving the separation of adenine and guanine using CDs as an additive of capillary electrophoresis [10]. Wang and co-workers proposed a simple and reliable method based on an electrochemical technique with β -CD-incorporated carbon nanotube-modified electrodes for simultaneous or individual determination of guanine and adenine [11].

Recently, layered double hydroxides (LDHs) have received considerable attention due to their potential technological applications [12–17]. LDHs are a class of anionic clays which can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ [18], where M^{II} and M^{III} are di- and trivalent metal cations, respectively. LDHs have positively charged layers and a wide variety of charge-balancing anionic species (A^{n-}). Numerous studies show that LDHs have a wide range of applications in industry, e.g., as catalyst precursors, ion exchangers, adsorbents for environmental contaminants, and substrates for the immobilization of biological materials

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[19–26]. Recently, Choy et al. synthesized hybrids of the modified CD intercalated into LDHs (CMCD–LDH) and elucidated the configuration of interlayer CD [27]. Mohanambe and Vasudevan reported the adsorption of iodine and naphthalene by CMCD–LDH [28, 29]. Recently, we have studied the properties of CMCD–LDH as the confined nanocage and investigated the enantioselective adsorption of racemic 1-phenyl-1,2-ethanediol molecule by CMCD–LDH powder and film [30–32]. However, the separation of nucleoside mixtures by CD-functionalized LDHs remains a challenge and has not been previously reported.

Based on our previous work on the separation of chiral isomers [31, 32], herein we report a study on the direct separation of nucleotides by the CMCD–LDH film. Adenosine (A) and guanosine (G) were selected as the model target molecules, and the CMCD–LDH film was synthesized by the method of in situ crystallization on a porous anodic alumina (PAO)/aluminum substrate. After optimization of the separation conditions, the selective adsorption of nucleoside mixtures by the CMCD–LDH film was achieved. Moreover, the slab diffusion model was successfully validated in this work. Due to the easy preparation and manipulation of the CMCD–LDH film, this work not only provides helpful information for better understanding of the molecular recognition mechanism of nucleosides by β -CD-intercalated LDH, but also develops a novel and simple method for selective adsorption and separation of mixed nucleosides.

2 Experimental

2.1 Reagents

Adenosine, guanosine, and β -CD were purchased from Aldrich. Aluminum metal sheet was generously supplied by Shanghai Jing Xi Chemical Technology Co. Ltd. (purity: > 99.5%, thickness: 0.7 mm). Other chemicals, including $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NH_4NO_3 , NH_4OH (1%), and chloroacetic acid, were of analytical grade and used without further purification.

2.2 Preparation

2.2.1 Synthesis of Carboxymethyl- β -Cyclodextrin, CMCD (3.6)

CMCD (3.6) was synthesized according to the procedure described previously [33], and the average number of carboxylate groups per β -CMCD was calculated by ^1H NMR [34].

2.2.2 Preparation of the CMCD–LDH Film

The CMCD–LDH film was prepared according to the method reported previously by our group with some modifications [32]. The porous anodic alumina (PAO) film was fabricated by anodizing an aluminum metal sheet for 50 min in a thermostatic bath of 1 M H_2SO_4 at 25 °C and with a thickness of

0.7 mm. PAO/Al was used as both the substrate and the sole source of aluminum. The CMCD–LDH film was prepared as follows: 0.01 mol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.06 mol of NH_4NO_3 , and 0.001 mol of CMCD were dissolved in deionized water, and pH was adjusted to 6.5 by adding diluted ammonia (1% NH_4OH). Then the PAO/Al substrate was placed vertically in the solution at 70 °C for 48 h to obtain the CMCD–LDH microcrystals grown on the surface of the substrate. Finally, the substrate was taken out, rinsed with water, and dried at room temperature. Based on the difference between the initial and final mass of the substrate, the weight of the CMCD–LDH film per unit area of the substrate was calculated to be $3.66 \times 10^{-2} \text{ kg/m}^2$.

2.2.3 Adsorption Experiments

Nucleoside adsorption experiments were carried out using a batch method. The effects of pH value and reaction time were investigated, and the effect of reaction time was used to determine the kinetic model of nucleoside adsorption. A series of 100 mL nucleoside solutions (concentration: 1 g/L for A or G; pH 5, 6, 7, 8, 9, respectively) were added to Erlenmeyer flasks, and the structured CMCD–LDH film (with an area of 10^{-4} m^2) was immersed into the solution. The flasks were then placed in a water bath at a temperature of 303 K and gently shaken for a specific time period to reach adsorption equilibrium. For quantitative analysis, standard calibration curves of A and G were prepared by means of a UV-vis spectrophotometer at $\lambda = 260 \text{ nm}$. The amount of nucleotide adsorbed by the CMCD–LDH film was calculated by the difference between the initial (C_0) and equilibrium concentration (C_f) per kg of LDHs adsorbent: $q_e = (C_0 - C_f) \times V/m$.

An adsorption experiment was then carried out to measure the adsorption selectivity of the CMCD–LDH film. The prepared CMCD–LDH films were immersed into the mixture solutions (containing equal amounts of A and G) with different concentrations for 48 h to reach adsorption equilibrium. Afterwards the A and G concentrations in the solutions were analyzed by HPLC.

2.3 Characterization

Powder X-ray diffraction (XRD) data were recorded by a Shimadzu XRD-6000 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 30 mA, a scanning rate of 2° min^{-1} , and a 2θ angle ranging from 3° to 60° . The morphology of the CMCD–LDH film was investigated by using a scanning electron microscope (SEM: Hitachi S-4700). Room-temperature FT-IR spectra were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$, with 2 cm^{-1} resolution and 32 individual scans on a Bruker Vector22 Fourier transform spectrometer using the KBr disk method. The UV-vis spectrophotometer (Shimadzu UV-2501PC) was employed to measure the absorbance spectra of compounds in the 200–400 nm wavelength range. The concentrations of A and G in the solutions, before and after the adsorption experiments, were determined by UV-vis spectroscopy at a wavelength of 260 nm.

HPLC was conducted on a Waters liquid chromatograph equipped with a 1525 binary pump and a 2695 photodiode array detector from Waters Corporation (Milford, MA). A and G were separated and analyzed by using an Atlantis d-C18 column (4.6 mm \times 250 mm, 5 μ m) (eluting solvent: water/methanol 85:15 v/v). The flow rate was 0.7 mL/min and the chromatographic peaks were measured at a wavelength of 260 nm to facilitate the detection of nucleosides.

3 Results and Discussion

3.1 Characterization of the CMCD-LDH Film

The XRD patterns and FT-IR spectrum of the CMCD-intercalated LDH film are shown in Figs. S1 and S2 (Supporting Information). In Fig. S1, the sequence of strong (003), (006) reflections at low angle and the (012) reflection at high angle for the film indicate formation of a well-crystallized hydrotalcite-like LDH phase. Compared with the ZnAl-LDH film (d_{003} = 0.887 nm) [35], the basal distance (d_{003}) of the CMCD-LDH film is 1.568 nm, increasing by 0.681 nm after the intercalation of CMCD. Taking into account the dimensions of the β -CD molecule and the basal distance of the CMCD-LDH film, the CMCD anions can only adopt a monolayer arrangement with their cavities axis perpendicularly to the LDH layer and carboxymethyl groups on adjacent CD molecules attached alternately to the upper and lower LDH layer surfaces. This is in accordance with the arrangement reported in our previous research of a CMCD-LDH sample [31].

In the FT-IR spectrum of CMCD-LDH (see Fig. S2b), the absorption at 2990 cm^{-1} is due to the stretching vibration of $-\text{CH}_2$. Two absorption peaks at 1606 cm^{-1} and 1422 cm^{-1} are attributed to the asymmetric and symmetric stretches of carboxylate $-\text{COO}^-$, respectively. A band at 1026 cm^{-1} is assigned to the absorption of C-O-C of glucose units. Compared with the pristine CMCD (see Fig. S2a), a red-shift of 10 cm^{-1} for the asymmetric stretching vibration of $-\text{COO}^-$ in the CMCD-LDH can be observed. This spectral change is expected for the formation of hydrogen bonding between the carboxylate and the hydroxyl in the LDH layer.

The morphology of the PAO/Al substrate and CMCD-LDH film was characterized by scanning electron microscopy (SEM). As can be seen from Fig. 1a, the top view of the PAO/Al substrate displays a porous structure. After the in situ growth process, the curved hexagonal facets of the LDH microcrystal perpendicularly to the surface of the substrate were

observed (see Fig. 1b), indicating the successful immobilization of the CMCD-LDH film on the substrate. This is in agreement with the results of XRD and FT-IR. The edge-view of the CMCD-LDH film (see Fig. 1c) clearly shows only a thin film of the LDH crystals fabricated on the PAO/Al substrate with a thickness of about 4.5 μ m. In this film, the ab-plane of the hexagonal LDH microcrystals is perpendicular to the substrate, with sufficient exposure of the edges of LDH crystals to the outside, which is favorable for the adsorption of solute from solutions.

3.2 Adsorption Behavior of the CMCD-LDH Film

Solid state UV-vis spectroscopy was used to further investigate the adsorption behavior of the CMCD-LDH film. Fig. 2 shows the UV-vis spectra of the CMCD-LDH film, A, G, and the adsorption products (CMCD-LDH-A, CMCD-LDH-G), respectively. The spectra of the adsorption products CMCD-LDH-A (see Fig. 2b) and CMCD-LDH-G (see Fig. 2e) display a broad absorption band, which are in accordance with the characteristics of A (see Fig. 2d) and G (see Fig. 2g). The results indicate that A and G were adsorbed by the CMCD-LDH film, respectively. Compared with the pristine A and G, the absorption bands of the products CMCD-LDH-A (see Fig. 2b) and CMCD-LDH-G (see Fig. 2e) shifted to a lower wavelength for about 10 nm, respectively. To further verify the adsorption of A or G into the cavity of CMCD by the CMCD-LDH film, the UV-vis spectra of the inclusion complexes CMCD-A and CMCD-G are also presented (see Figs. 2c and f). It should be noted that a similar blue-shift of A or G also occurred, which can be attributed to the inclusion of A or G within the β -CD hydrophobic cavity. Therefore, based on our previous work and the results above, it can be concluded that adsorption of A or G by the CMCD-LDH film occurs not only on the surface of LDH, but also within the cavity of intercalated CMCD.

3.2.1 Effect of Solution pH Value

It has been reported that the solution pH value imposes a significant influence on the analysis and separation of nucleosides [36]. The adsorption experiments in this work were carried out in the pH value range of 5–9. Fig. 3 displays the adsorption capacity of the CMCD-LDH film for A and G with different initial pH values. As can be seen from Fig. 3, the adsorption

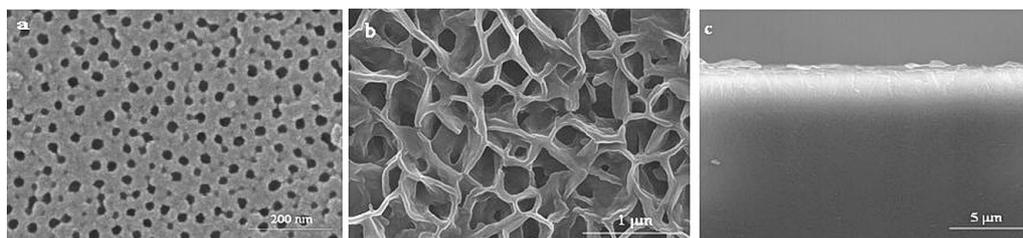


Figure 1. SEM images of (a) the PAO/Al substrate, (b) the surface-view of the CMCD-LDH film on PAO/Al substrate, (c) the edge-view of the CMCD-LDH film on PAO/Al substrate.

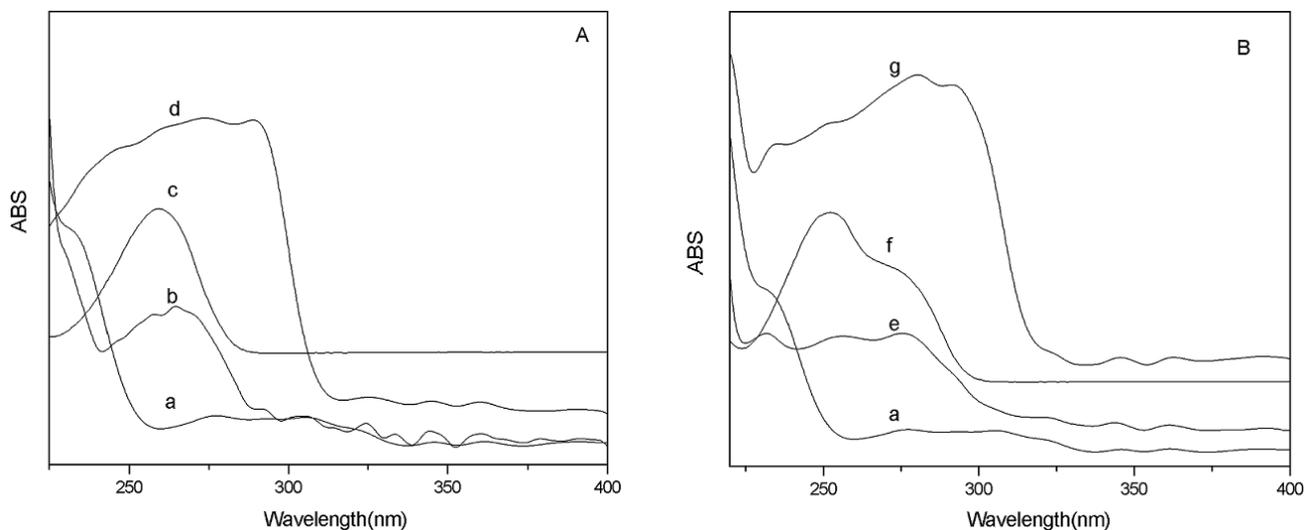


Figure 2. (A) UV-vis spectra of (a) the CMCD-LDH film, (b) the adsorption product of CMCD-LDH-A, (c) CMCD-A, (d) A. (B) UV-vis spectra of (a) the CMCD-LDH film, (e) the adsorption product of CMCD-LDH-G, (f) CMCD-G, (g) G.

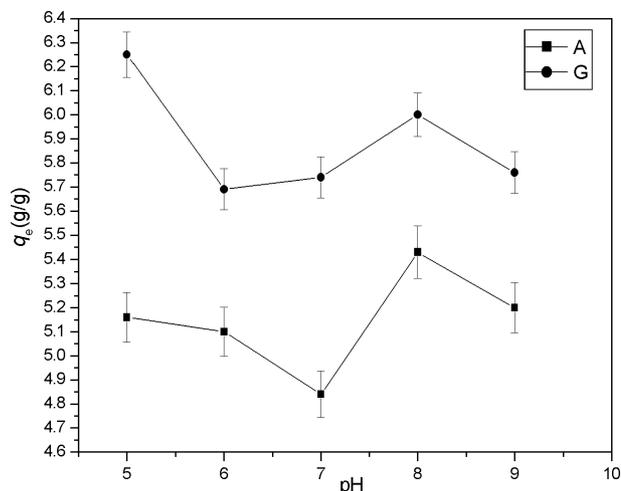


Figure 3. Effect of solution pH on the adsorption capacity of A and G by the CMCD-LDH film.

capacity of the CMCD-LDH film varies with the change of pH. The highest adsorption was observed at pH 8 for A, while it occurred at pH 5 for G. It is interesting to note that the largest difference in the adsorption capacity between G and A was obtained at pH 5. Therefore, the optimal separation of mixtures of nucleosides can be achieved at pH 5 when they are in a competitive environment.

The dissociation process equilibrium of A and G in solution can be expressed in Fig. 4, and the distribution coefficient δ of A and G can be calculated by the pH and pK_a values. It was found that G is a neutral molecule at pH 5 ($\delta_1 = 100\%$), while A has a small amount of positively charged molecules ($\delta_0 = 3.1\%$, $\delta_1 = 96.9\%$). It is well known that CDs show stronger inclusion with neutral guest molecules than cations, accounting for a larger adsorption capacity for G than that of A at pH 5.

3.2.2 Selective Adsorption of A and G by the CMCD-LDH Film

HPLC was used to measure the amount of A and G in the remaining solution after adsorption equilibrium has been reached. The CMCD-LDH film (with an area of $2 \times 10^{-4} \text{ m}^2$) was immersed into a mixture solution of A and G (equal amounts of A and G, pH 5) with different total concentration and then shaken for two days in a water bath at 303 K. The amount of nucleotide adsorbed by the CMCD-LDH film was calculated by the difference between the initial and equilibrium concentrations. The adsorption capacities with different total concentration of A and G were plotted and are shown in Fig. 5a. It can be seen that the adsorption capacities of the CMCD-LDH film for both A and G increased clearly with increasing the original concentration. A comparison between the adsorption curves of A and G demonstrates that the CMCD-LDH film shows preferential adsorption for G than for A.

To further verify that the selective adsorption of the CMCD-LDH film is related to the hydrophobic cavity of CD, a comparison study was carried out under the identical condition, i.e., the adsorption experiments were performed in the mixture solution of equal amounts of A and G by the ZnAl- NO_3 LDH film. The results show that there is no selective adsorption between A and G by the ZnAl- NO_3 LDH film (see Fig. 5b). Therefore, the selective adsorption of nucleoside molecules onto the CMCD-LDH film could be attributed to a stronger recognition capability of CMCD toward G, while the recognition for A is relatively weak. As can be seen from Fig. 4, the structures of A and G are similar except that a C=O group exists in G. In this work, it can be expected that both the charge and structure of the guests influence the host-guest interactions, and thus play important roles in the adsorption of G and A by CMCD. As a result, the selective adsorption of G by the CMCD-LDH film can be attributed to a multiple recognition of CMCD host toward G molecules, which gives a stronger van der Waals and hydrophobic interactions.

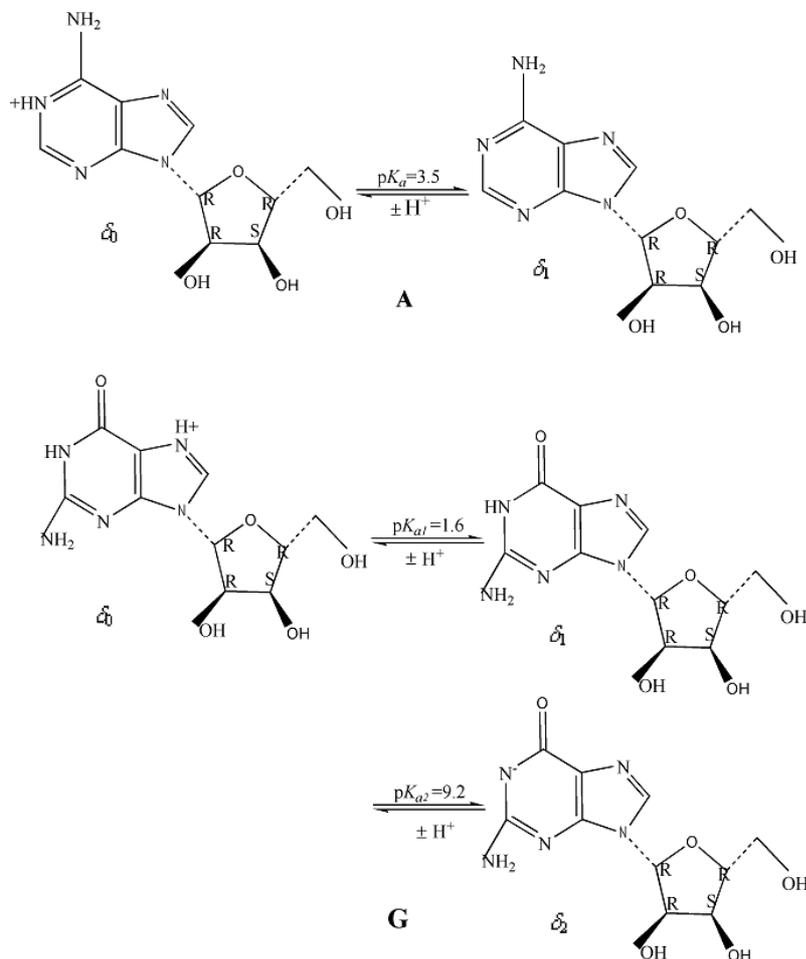


Figure 4. Dissociation process of A and G.

3.2.3 Study on the Diffusion Kinetics

The applied diffusion model of solid-liquid extraction, proposed by Crank [37], is derived from Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

The equation describes one component diffusion in a nonstationary monodimensional homogeneous system with the following initial and boundary conditions for the well-agitated unlimited volume of the bulk solution:

Initial conditions:

$$t = 0, -l - \frac{a}{2} < x < -\frac{a}{2} \text{ and } \frac{a}{2} < x < \frac{a}{2} + l, c = 0 \quad (2)$$

Boundary conditions:

$$t \geq 0, x = -l - \frac{a}{2}, c = c_0$$

$$t \geq 0, x = l + \frac{a}{2}, c = c_0 \quad (3)$$

Solving Eq. (1) with the conditions of Eqs. (2) and (3) gives:

$$F = \frac{q_t}{q_e} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2 \pi^2 t / 4l^2\} \quad (4)$$

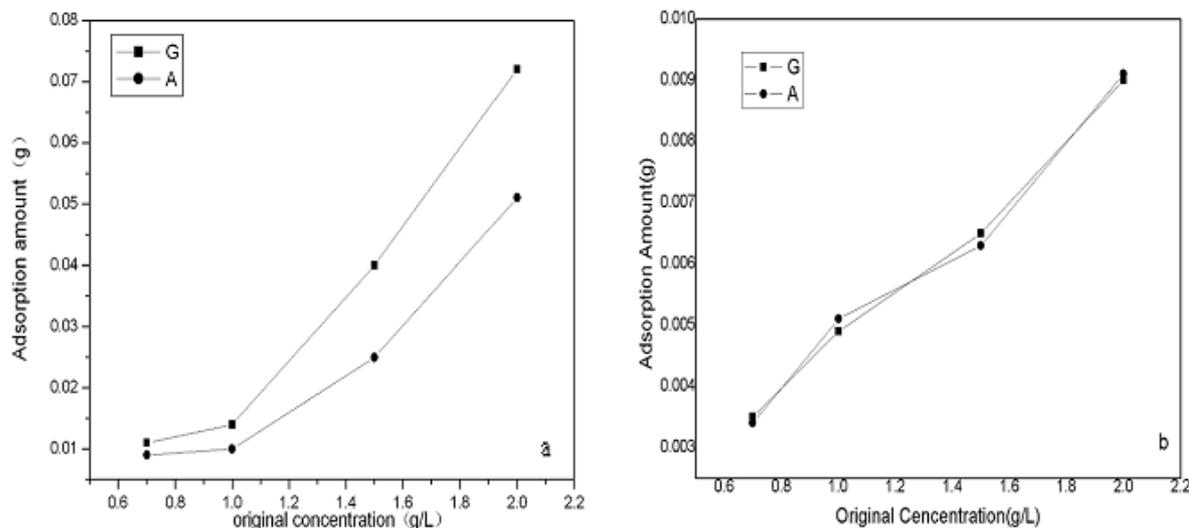


Figure 5. Selective adsorption results of A and G with different mixed concentrations: (a) by the CMCD-LDH film; (b) by the ZnAl-NO₃ LDH film.

where a is the thickness of the substrate, q_e is the amount of adsorbed adsorbate at equilibrium, D is the diffusivity, and l is the sample thickness.

In our experiment, as the film thickness is much lower than its diameter, the CMCD-LDH film can be considered as a monodimensional slab. Therefore, the active adsorption kinetics can be described by means of Eq. (4).

Based on Fick's law of diffusion, the curve-fitting plots are given in Fig. 6, and the parameters obtained for the diffusion are presented in Tab. 1. It can be seen from Tab. 1 that the adsorptions of both A and G by the CMCD-LDH film follow the slab diffusion model at pH 5, with satisfactory coefficients of 0.9905 (for G) and 0.9768 (for A), respectively. Both the values of diffusion coefficient (D) and adsorption capability (q_e) of G are larger than those of A, indicating that the CMCD-LDH film exhibits preferential selectivity toward G than A. Therefore, it can be expected that this structured film has prospective application in the field of selective adsorption and separation of nucleosides.

4 Conclusions

A novel property of the CMCD-LDH film for selective adsorption of adenosine and guanosine was studied in this work. The effects of pH value and reaction time on the adsorption were also investigated. The results indicated that the CMCD-LDH film shows preferential adsorption for G when G and A are in a competitive environment. This selectivity is due to the multiple recognition of the inter-CD cavity. The best separation of nucleosides by the CMCD-LDH film was achieved at pH 5. The slab diffusion model was used to study the dynamics of this system. The kinetic studies show that the adsorptions of both A and G by the CMCD-LDH film follow the slab diffusion model. The values of diffusion coefficient D and adsorption capability q_e of G are larger than those of A, indicating the selective adsorption of the CMCD-LDH film for nucleo-

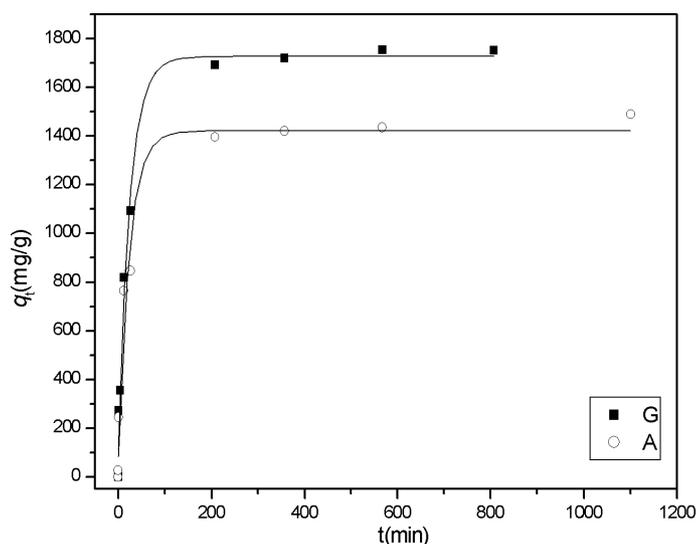


Figure 6. Adsorption curve-fitting plots of A and G by Fick's law of diffusion.

Table 1. Kinetic parameters for the adsorption of A and G by the CMCD-LDH film.

	Fick's law of diffusion		
	q_e (mg/g)	$D \times 10^{10}$ (m ² /s)	R^2
G	1727	2.691	0.9905
A	1421	2.575	0.9768

sides. It can be expected that this CMCD-functionalized inorganic layered film may have potential application in the biological separation field.

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