



Super adsorption capability of rhombic dodecahedral Ca-Al layered double oxides for Congo red removal

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ABSTRACT

In this work, a novel rhombic dodecahedral structure of Ca-Al-layered double hydroxides (Ca-Al-LDHs) was synthesized by a two-phase solvothermal method. Subsequently, Ca-Al layered double oxides (Ca-Al-LDOs) were obtained by calcinating Ca-Al-LDHs at 600 °C which maintained the rhombic dodecahedral structures well. The morphologies of as-obtained samples were characterized by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The phase structure and elemental composition were analyzed by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. Fourier transformed infrared (FT-IR) spectra were performed to confirm the existence of LDH structures. The Ca-Al-LDOs exhibited high adsorption rates and superb adsorption capacities for removal of Congo red (CR) from aqueous solution. The maximum adsorption capacities of Ca-Al-LDOs towards CR reached to 1536.1 mg g⁻¹, which is extremely higher than most of hydrotalcite-like materials. The adsorption process of Ca-Al-LDHs and Ca-Al-LDOs were described by the Langmuir isotherm model and pseudo-second-order model well. The adsorption mechanisms mainly dominated by electrostatic adsorption, ion exchange process, hydrogen bonding interactions and surface complexation. This general strategy afforded a wide possibility to prepare a novel and advanced LDOs adsorption material for water treatment.

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1. Introduction

Organic contaminants in polluted water have become a serious environmental issue and received wide attention [1]. Among various organic pollutants, organic dyes are main pollutant source in water due to their wide applications in industries and uncontrolled emissions [2]. The direct discharge of wastewater containing organic dyes can lead to serious environmental pollution, intensify water crises and even harm human beings. Thus, diverse technologies have been developed to remove organic dyes such as adsorption [3], membrane filtration [4], photochemical degradation [5], flocculation [6], and ozonation techniques [7]. Among these methods, adsorption is a promising method because of its high efficiency, relatively low cost and simple operation [8]. A variety of

adsorbents have been prepared to remove the dyes in wastewater such as carbon-based nano materials [9], graphene oxide [10], industrial waste [11], and polymer resins [12]. The selection and fabrication of adsorbents played a vital role in the adsorption technology. Generally, desirable adsorbents should be efficient, stable, low-cost, and environment-friendly. However, the low adsorption capability and recyclability of these adsorbents are main obstacles to apply them in water treatment. Hence, developing a new adsorbent with excellent adsorption capability, along with low production cost is currently still an important issue for basic research as well as practical applications.

The general formula of layered double hydroxides (LDHs) can be expressed by $[M_1^{2+}_x M_2^{3+}_{3-x}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metals respectively, and A^{n-} represents the n-valent anion [13]. Furthermore, LDHs are also known as anionic clays, have been reported as a potential adsorbent for removing anionic pollutants from wastewater, which can be attributed to their layered structure, high porosity, and interlayer

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anion mobility of its A^{n-} host [14]. In recent years, plenty of literature have reported application of binary LDHs on the adsorption of dyes and heavy metal ions, such as Ni-Fe-LDHs [15], Ni-Al-LDHs [16], and Mg-Fe-LDHs [17]. These LDHs with desirable morphologies have been widely researched, because of their fantastic porous structure and structural stability. Many researchers have tried to utilize calcined [18], intercalated [19] and modified [20] methods to further improve LDHs adsorption performance. Calcination treatment contributes to reducing the aggregation of LDHs and enhance the surface defects of materials. For example, Li et al. [21] have confirmed that calcination of polydopamine decorated Mg-Al-LDHs nanoflakes could greatly improve adsorption capacity of toxic metals and anionic dyes. The Mg-Ni-Al-LDOs derived from Mg-Ni-Al-LDHs prepared with a co-precipitation method have depicted a better adsorption performance for removal of methyl orange than the uncalcined LDHs, which has been researched by Hassina's group [22].

Two-phase solvothermal method is a novel synthetic route to prepare some nanocrystals with special morphologies [23]. Some of the $Mg(OH)_2$ and $AlOOH$ nanostructures and their derivatives with excellent adsorption properties synthesized with two-phase solvothermal method have been reported by our group [24,25]. In this work, the novel rhombic dodecahedral Ca-Al-LDHs was fabricated by a two-phase solvothermal process. After calcination treatment, the rhombic dodecahedral Ca-Al layered double oxides (LDOs) were obtained. The Ca-Al-LDHs and Ca-Al-LDOs were used as adsorbents for adsorption of Congo red (CR) from aqueous solution to and compared its adsorption properties. Furthermore, the XRD and FT-IR techniques were investigated to evaluate the interaction mechanism of CR with the Ca-Al-LDHs and Ca-Al-LDOs.

2. Experimental section

Materials: All chemicals were of analytical grade and used as received without any further purification. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, 99.0%) was purchased from Tianjin Yaohua Chemical Reagents Co., Ltd. Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.0%) was purchased from Tianjin Hongyan Chemical Reagents Co., Ltd. Sodium hydroxide (NaOH, 96.0%) was purchased from Tianjin Baishi Chemical Reagents Co., Ltd. Sodium oleate ($C_{18}H_{35}COONa$ or NaOA, 98%) was purchased from Tokyo Chemical Industry Co., Ltd. Absolute n-hexane and ethanol were purchased from Tianjin Baishi Chemical Reagents Co., Ltd. Thermostat oil bath was purchased from Jin Yi Instrument Co., Ltd., China. All the deionized water (with resistivity up to $18.2 M\Omega/cm$) was prepared by a UPC-III-40L pure Ultrapure Water System (China). The autoclave were purchased by Anhui Kemi Machinery Technology Co., LTD and the pressure of the autoclave was approximately 10.2 Mpa when the temperature reached $180^\circ C$.

2.1. Preparation of Ca-Al-LDHs and Ca-Al-LDOs

In a typical synthesis process, 2 mmol of $Ca(NO_3)_2 \cdot 4H_2O$ (0.472 g), 1 mmol of $Al(NO_3)_3 \cdot 9H_2O$ (0.375 g) and 7 mmol of NaOA (2.132 g) were added to the solution containing 20 mL of absolute ethanol, and 30 mL of n-hexane. The mixed solution was stirred at $70^\circ C$ for 1 h at about 600 rpm by using a thermostat oil bath (DF-II). Then 10 mL of 0.7 M sodium hydroxide aqueous solution was added and the mixture was stirred for 1 h. After cooled to room temperature, then sealed in a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at $180^\circ C$ for 24 h, the obtained white precipitate of Ca-Al-LDHs was washed and centrifuged in a TG-20G centrifuge (Kate laboratory equipment Co., Ltd, Yancheng, China) for 8 min at 10000 rpm with anhydrous alcohol and n-hexane three times, respectively. Finally, the washed Ca-Al-LDHs were dried at $60^\circ C$ for 12 h. The as-synthesized sample was heated at $600^\circ C$ for 2 h in a muffle furnace to obtain Ca-Al-LDOs. The synthesis of these materials is illustrated in Fig. 1.

2.2. Characterization of Ca-Al-LDHs and Ca-Al-LDOs

The crystal structure of the as-synthesized products were determined by a Rigaku D/max-ga X-ray diffractometer (XRD) at a scanning rate of $6^\circ \cdot min^{-1}$ using Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) in 2θ ranging from 10° to 80° . The morphologies and microstructures of the obtained particles were characterized with a transmission electron microscopy (TEM, HitachiH-600). The synthesized nanocrystals were observed with field-emission scanning electron microscope (FESEM) on a Hitachi SU-8000 field emission electron microscope operating at 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo XPS ESCALAB 250Xi instrument with an Al K_{α} (1486.8 eV) X-ray source. The specific surface area and pore size distribution were obtained by the nitrogen adsorption-desorption isotherms and via the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method. Nitrogen adsorption-desorption measurements were performed on a Micromeritics ASAP 2020 physisorption instrument at 77 K. Fourier Transform Infrared Spectrum (FT-IR) of the samples were taken in KBr pellets by using a Bruker EQUINOX-55 spectrometer (Bruker Optics Inc., Germany) within the range of $4000-400 cm^{-1}$. The concentrations of CR in aqueous solutions were acquired with the use of a UV-vis spectrophotometer (UV-2450PC, Shimadzu, Japan).

2.3. Adsorption experiment

Typically, the adsorption kinetic experiments were conducted by adding 20 mg adsorbent to 100 mL of $100 mg L^{-1}$ CR solution at natural pH (ca.7) under rate of stirring 800 rpm at room

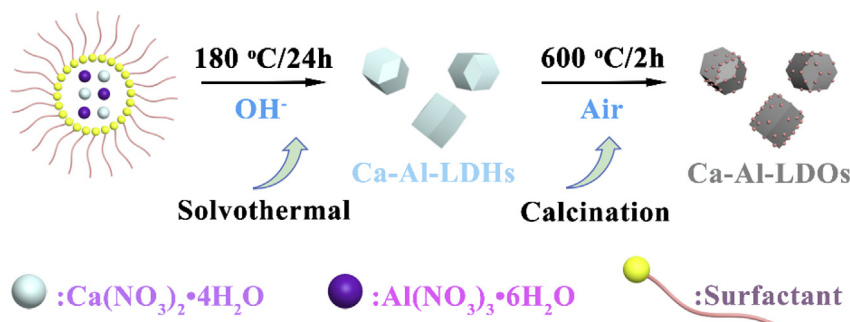


Fig. 1. Schematic illustration of the synthesis and calcination of Ca-Al-LDHs and Ca-Al-LDOs.

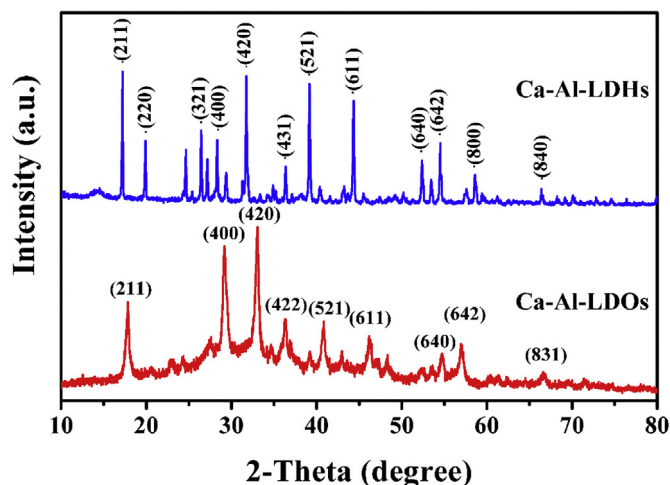


Fig. 2. XRD pattern of obtained Ca-Al-LDHs and Ca-Al-LDOs.

temperature (303 ± 2 K). At different time intervals, approximately 3 mL of aqueous solution were taken from the suspension, and the adsorbent were separated from the solution were centrifuged in a TGL-16C centrifuge (Shanghai Anting Instrument Factory, Shanghai, China) at 10000 rpm for 3 min. UV–vis adsorption spectra (UV-2450 PC) was used to analyze the concentration of CR remained in the upper clean solution at the maximum absorption wavelength of 490 nm. The adsorption capacity of the adsorbents at time t , q_t (mg g^{-1}), was also calculated:

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

where C_t is the concentration of CR at contact time t (mg L^{-1}), V (L) is the volume of the CR solution and m (g) is the weight of adsorbents.

To evaluate the maximum adsorption capacity of the as-prepared material for CR, 2 mg of as-prepared sample was added to a 10 mL of CR solutions with different concentration ($30\text{--}300 \text{ mg L}^{-1}$) at natural pH (ca.7). The adsorption isotherm was obtained by varying the equilibrium CR concentrations C_e (mg L^{-1}) with stirring for 48 h at room temperature (303 ± 2 K). The amount of CR adsorbed on the sample at equilibrium q_e (mg L^{-1}) was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 (mg/L) is the initial CR concentration, V (L) is the volume of the CR solution and m (g) is the mass of the Ca-Al-LDHs or Ca-Al-LDOs.

The recyclability of the adsorbent was evaluated by repetition of adsorption/calcination cycles using the same Ca-Al-LDOs sample. A constant Ca-Al-LDOs dosage of 200 mg L^{-1} was placed in 100 mg L^{-1} CR solutions at room temperature (303 ± 2 K) and kept in contact for 12 h. The used Ca-Al-LDOs powder was calcined and reused in the same conditions. This procedure was repeated six times and the adsorption capacity was calculated for each cycle. All the experimental data were the average of triplicate determinations. The relative errors of the data were about 5%.

3. Result and discussion

3.1. Ca-Al-LDHs and Ca-Al-LDOs phase structure

The crystal phase of the as-synthesized Ca-Al-LDHs and Ca-Al-LDOs samples examined by XRD as presented in Fig. 2, Twelve major diffraction peaks marked in blue color of the Ca-Al-LDHs sample are located at approximately 17.2° , 19.9° , 28.3° , 31.8° , 36.4° , 39.2° , 44.3° , 52.4° , 54.5° , 58.6° , and 66.4° . These peaks can be indexed to (211), (220), (321), (400), (420), (431), (521), (611), (640), (642), (800) and (840) planes of Katoite (JCPDS24-0217). After calcination at 600°C , the layered structure of Ca-Al-LDHs material

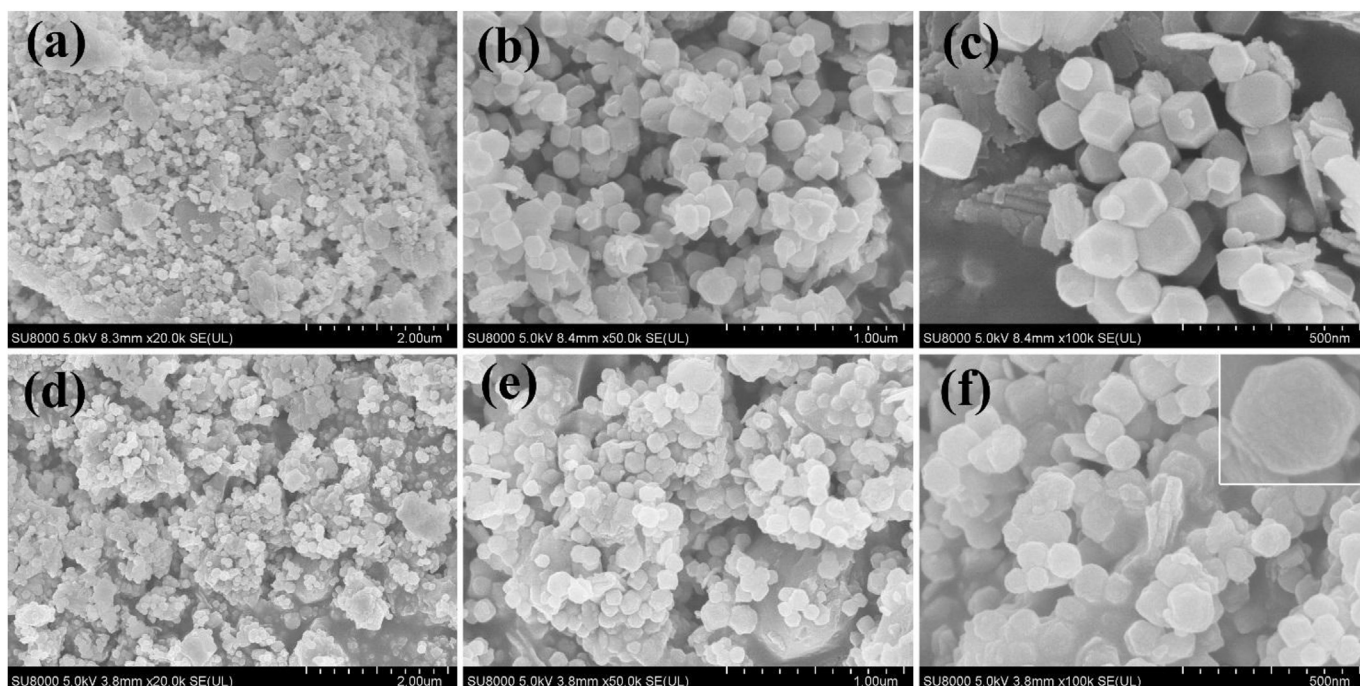


Fig. 3. Different magnification SEM images of (a)–(c) Ca-Al-LDHs, (d)–(f) Ca-Al-LDOs.

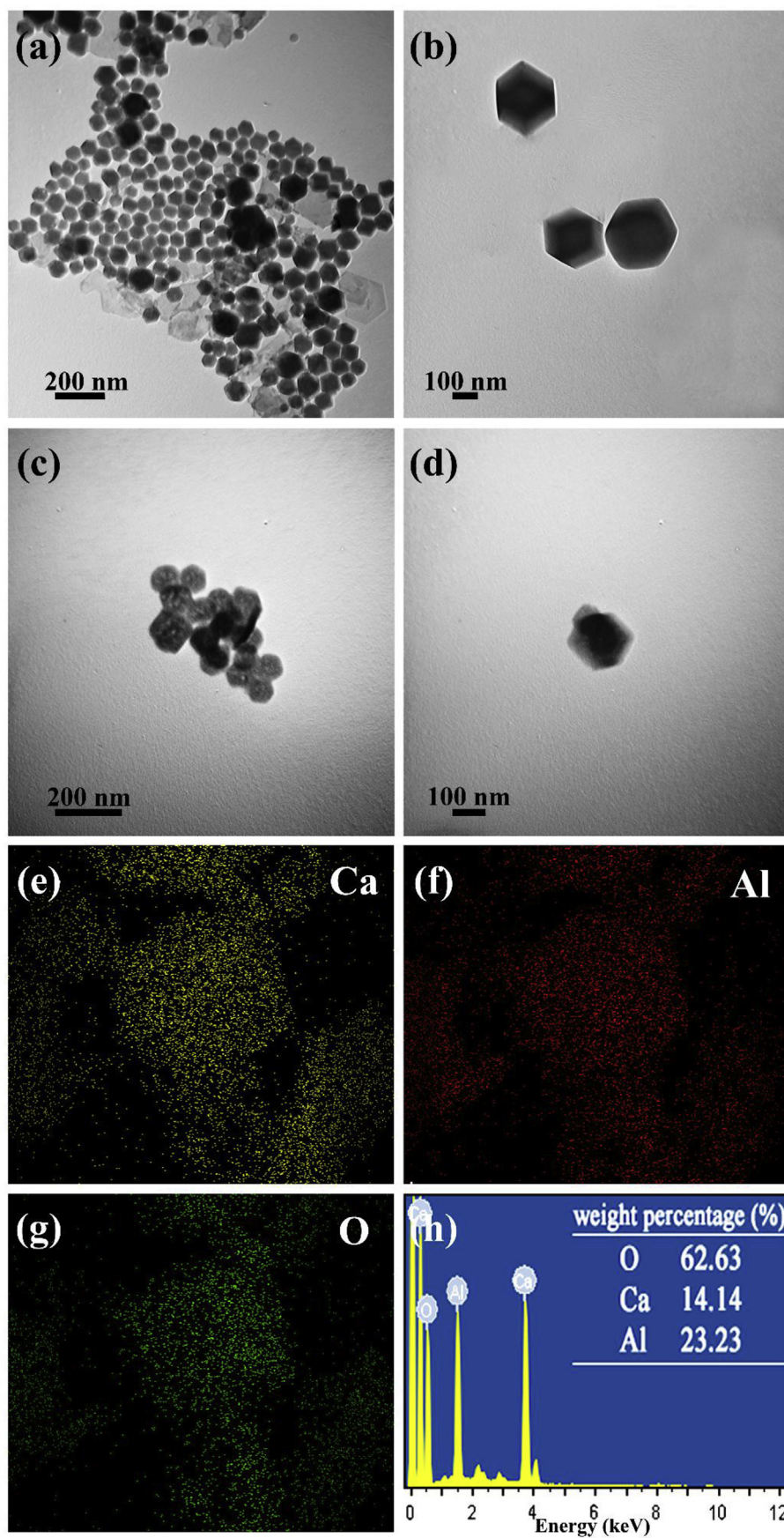


Fig. 4. TEM images Ca-Al-LDHs (a)–(b) and Ca-Al-LDOs (c)–(d); element mapping images of the Ca-Al-LDOs (e, f, g) and EDS pattern of Ca-Al-LDOs (h).

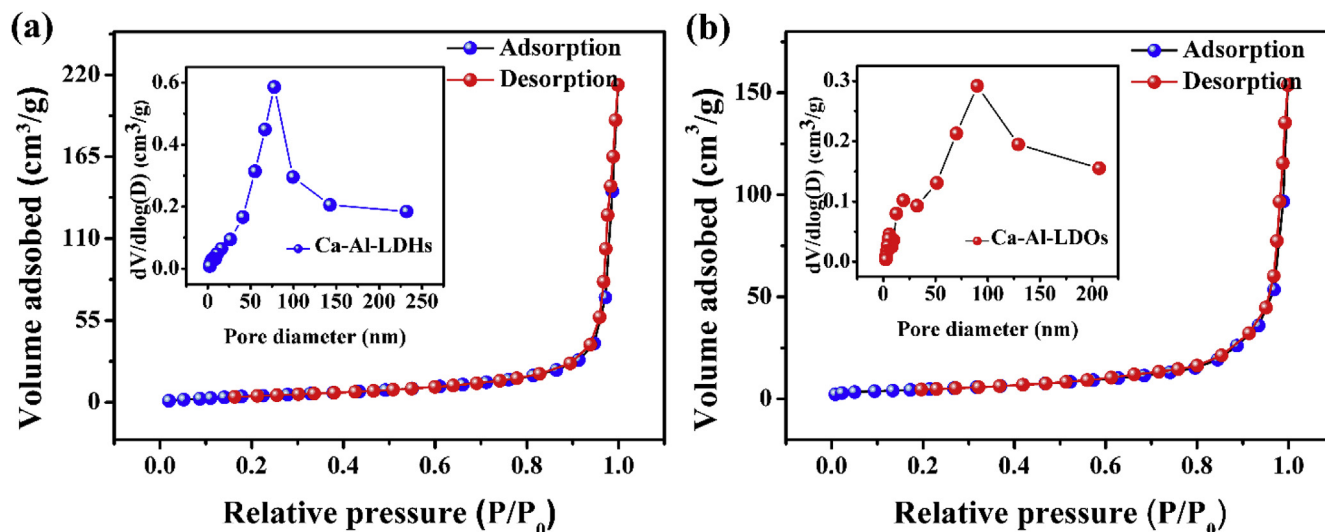


Fig. 5. N₂ adsorption-desorption isotherms of as-obtained Ca-Al-LDHs (a) and Ca-Al-LDOs (b); the corresponding BJH desorption pore size distributions curve (inset).

was changed into bimetallic oxide Ca-Al-LDOs. The Ca-Al-LDOs sample exhibited nine diffraction peaks located at approximately at 17.8°, 29.2°, 33.1°, 36.3°, 40.9°, 46.2°, 54.8°, 57.1° and 66.7° that corresponded to the (211), (400), (420), (422), (521), (611), (640), (642) and (831) planes of Mayenite (JCPDS 48-1882). No other peaks were observed, indicating the high purity of the obtained Ca-Al-LDHs and Ca-Al-LDOs.

3.2. Morphology and elemental composition

In order to characterize the microscopic architectures and composition of the as-obtained samples, SEM, TEM and EDS were employed. As shown in Figs. 3 and 4, the pristine Ca-Al-LDHs sample appears to be rhombic dodecahedral morphology, which exhibited an average diameter of 150 nm (Figs. 3c and 4b). The surface of the rhombic dodecahedral Ca-Al-LDHs is smooth from different view angles. As for the Ca-Al-LDOs sample is the same sizes (Figs. 3f and 4d), shows a mixture of the nanoparticle and rhombic dodecahedron morphologies, with the nanoparticles attaching on the rhombic dodecahedron. The energy dispersive X-ray spectroscopy (EDS) spectrum of the Ca-Al-LDOs (Fig. 4h) exhibited the presence of Ca, Al, and O elements and the corresponding weight percentages are 14.14%, 23.23%, and 62.63%, respectively. As displayed, Ca, Al, and O distribute homogeneously in the rhombic dodecahedron. This result corroborates that Ca-Al double metal oxide were successfully obtained.

3.3. Nitrogen adsorption-desorption isotherms

To obtain the Ca-Al-LDHs and Ca-Al-LDOs specific surface area and pore structure distribution, N₂ adsorption-desorption analysis was conducted. Fig. 5 displayed the Ca-Al-LDHs (Fig. 5a) and Ca-Al-LDOs (Fig. 5b) nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda pore size distribution (inset). The results indicate that the as-prepared samples adsorption amount at a relative pressure approach 1.0 increased dramatically, because of the filling of spaces in Ca-Al-LDHs and Ca-Al-LDOs. The pore size distribution of the Ca-Al-LDHs and Ca-Al-LDOs emerged as unimodal porosity, owing to the macropores with pore diameters of 77.68 nm and 89.96 nm, respectively. The N₂-BET surface area was 20.46 m²/g for Ca-Al-LDHs, and 17.30 m²/g for Ca-Al-LDOs. The Ca-Al-LDOs surface area is lower than Ca-Al-LDHs, which could be due to collapse of the sheets into large and dense aggregates upon calcination [26].

3.4. FTIR spectrum

Fourier transform infra red (FT-IR) spectra of Ca-Al-LDHs and Ca-Al-LDOs were performed and the results are shown in Fig. 6. The large and broad band observed at 3438 cm⁻¹ and 3661 cm⁻¹ can be attributed to O-H stretching vibration of interlayer water molecules and of OH groups [27,28], and the weak band of Ca-Al-LDHs at ca. 3000 cm⁻¹ is indication of the water molecules, which was attributed to the hydrogen-bond in the interlayer [29]. This weak band disappeared in Ca-Al-LDOs indicated that the interlayer anions were removed during the high temperature calcination process. The IR spectrum of Ca-Al-LDHs and Ca-Al-LDOs samples exhibits absorptions at 1428 and 1416 cm⁻¹ respectively, on account of the presence of intercalated NO₃⁻ anions [27]. The bands of Ca-Al-LDOs at 828 cm⁻¹ and 567 cm⁻¹ were attributing to metal-oxygen and metal-hydroxyl stretching [22,30,31].

3.5. XPS spectrum

The chemical composition and chemical status of the Ca-Al-LDOs were investigated using X-ray photoelectron spectroscopy (XPS). The survey spectrum (Fig. 7a) revealed the presence of Ca, Al,

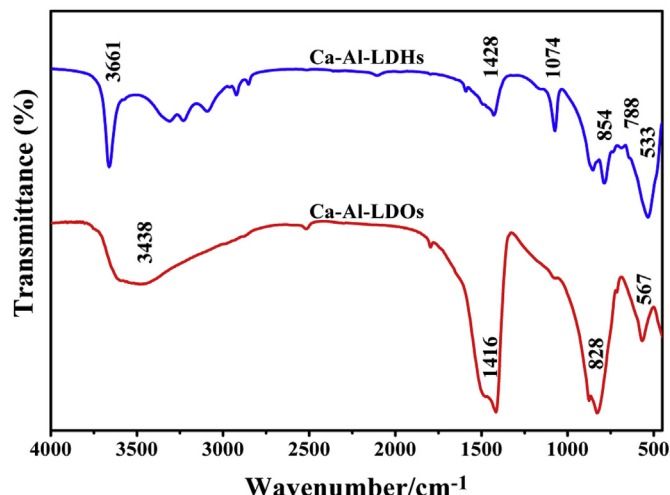


Fig. 6. FT-IR spectra of the Ca-Al-LDHs and Ca-Al-LDOs.

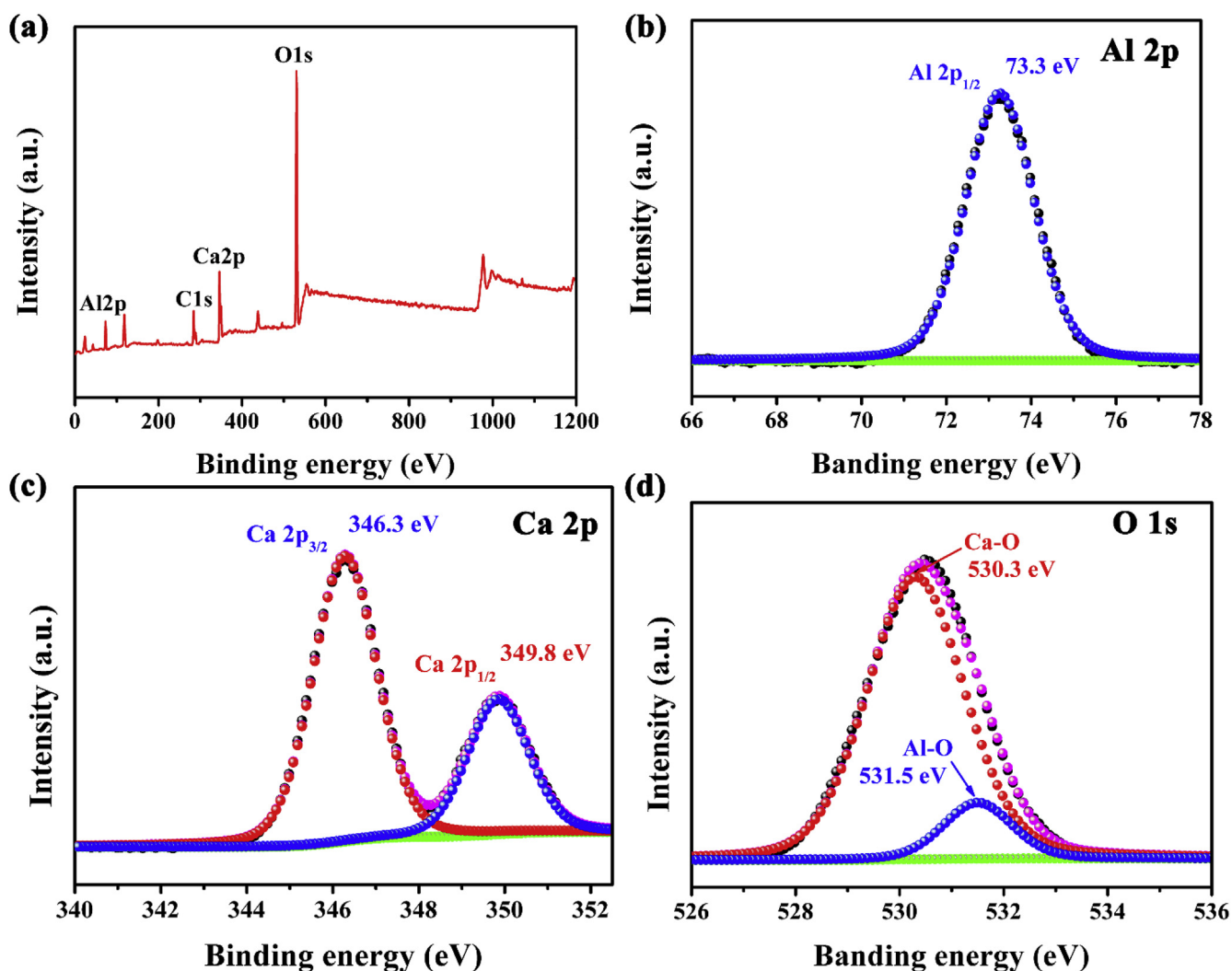


Fig. 7. XPS survey spectrum (a), high-resolution XPS spectra of Al 2p (b), Ca 2p (c), and O 1s (d) of the Ca-Al-LDOs sample.

O, and C: these were the predominant elements in the Ca-Al-LDOs. In Fig. 7b, the XPS spectra of Al species present one dominant peak at approximately 73.3 eV, which is ascribed to Al $2p_{1/2}$ of Al_2O_3 [32]. In Fig. 7c, the double peak characteristic of Ca 2p at 346.3 eV and 349.8 eV are corresponding to Ca $2p_{3/2}$ and Ca $2p_{1/2}$, respectively [33]. The high-resolution XPS spectrum of O 1s is shown in Fig. 7d, the two peaks at 530.3 and 531.5 eV corresponded to Ca–O, Al–O bonds [34]. The XPS analysis is consistent with the aforementioned EDS spectrum and powerful to demonstrate the bimetal mixed oxides in the Ca-Al-LDOs sample.

3.6. Adsorption kinetic and isotherm

Kinetic studies are essential for the evaluation of adsorption owing to this approach can describe the adsorption rate and elucidate the adsorption mechanism of sorption reactions [35]. The CR adsorption on Ca-Al-LDHs and Ca-Al-LDOs as an impact of contact time and room temperature are exhibited in Fig. 8. One could see that the Ca-Al-LDOs sample shown two-stepped kinetic and the single kinetic was observed for Ca-Al-LDHs. The speed of CR adsorbed by both Ca-Al-LDHs and Ca-Al-LDOs increases rapidly in ~25 min. The CR adsorption on Ca-Al-LDHs reached equilibrium state around 80 min, and then sustained the adsorption capacity.

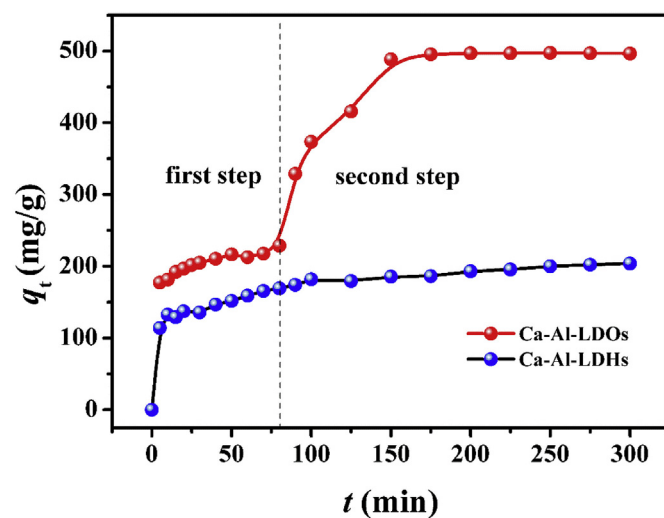


Fig. 8. Effect of contact time on the adsorption capacity of CR on the Ca-Al-LDHs and Ca-Al-LDOs samples (adsorbent dose = 200 mg L^{-1} ; CR concentration = 100 mg L^{-1}).

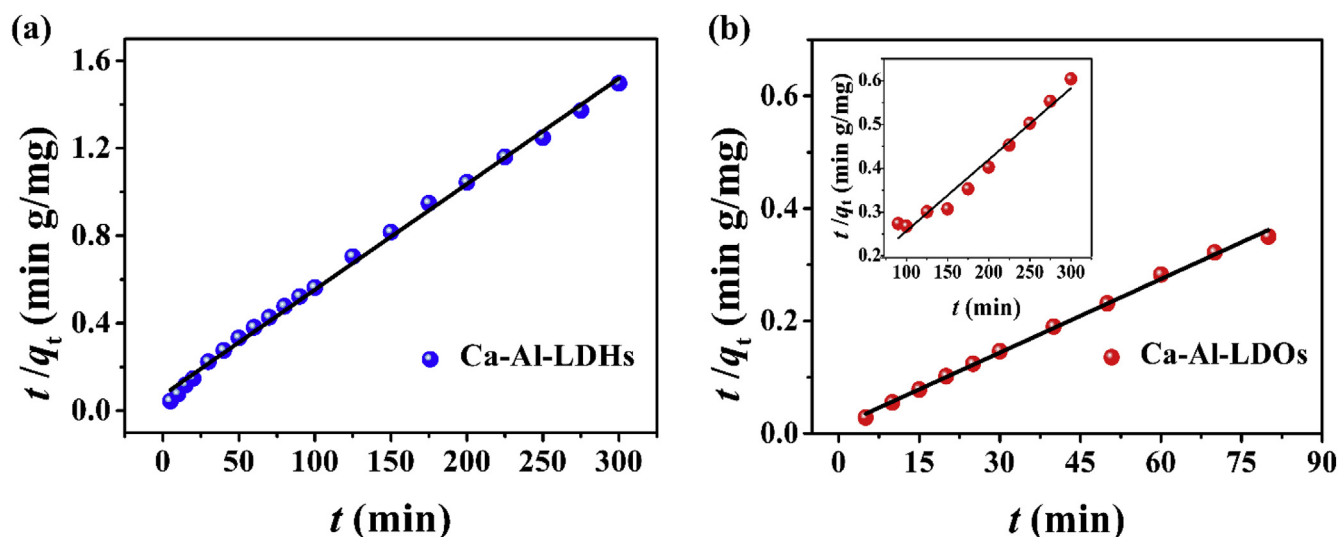


Fig. 9. The pseudo-second-order kinetic plots of CR adsorption on Ca-Al-LDHs (a) and Ca-Al-LDOs (b). The inserted curve is the second step of pseudo-second-order kinetic plots on Ca-Al-LDOs.

Table 1
Pseudo-first-order and pseudo-second-order kinetic model parameters of the as-obtained samples.

Samples	Pseudo-first-order model						Pseudo-second-order model					
	q_{e1} (mg/g)	q_{e2} (mg/g)	$K_{1,1}$ (min^{-1})	$K_{1,2}$ (min^{-1})	R_1^2	R_2^2	q_{e1} (mg/g)	q_{e2} (mg/g)	$K_{2,1}$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	$K_{2,2}$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R_1^2	R_2^2
Ca-Al-LDHs	203.7	-	0.01152	-	0.944	-	250	-	0.023×10^{-3}	-	0.997	-
Ca-Al-LDOs	228.6	498	2.4×10^{-4}	2.7×10^{-4}	0.915	0.779	229.4	613.5	1.5×10^{-3}	2.8×10^{-5}	0.997	0.968

Comparing to the adsorption of CR on Ca-Al-LDHs, the CR adsorption on Ca-Al-LDOs reached first equilibrium around 80 min, and then followed by a second increase of adsorbed CR, reaching a second plateau after 150 min. The first step was ascribed to the assimilate CR on the plenty and obtainable external surface adsorption sites. The second step on account of the adsorption of CR onto the inner surface adsorption sites, which are restricted by the internal particle diffusion mechanism [36].

To explain the adsorption mechanism on the Ca-Al-LDHs and Ca-Al-LDOs samples, the kinetics of CR adsorption were analyzed by two kinetic models, including pseudo-first-order [37] and pseudo-second-order kinetics [38], which were expressed as follows:

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (3)$$

$$t/q_t = 1 / (K_2 q_e^2) + t/q_e \quad (4)$$

where K_1 (min^{-1}) and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are signified kinetic adsorption rate constants of pseudo-first-order and pseudo-second-order models, q_e (mg/g) is the adsorption capacity at equilibrium and q_t (mg/g) is the adsorption capacity at time t (min), respectively. As shown in Fig. 9a and b, the fitting curves of the t/q_t versus t for adsorption of CR on the as-prepared samples display good linearity. From the calculated kinetic model constants (Table 1), it was apparent to notice that the Ca-Al-LDHs and Ca-Al-LDOs were better fitted by pseudo-second-order model than the pseudo-first-order model. It is worthy to note that the $K_{2,2}$ constant rate ($2.8 \times 10^{-5} \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) for Ca-Al-LDOs is much lower than the $K_{2,1}$ rate (1.5×10^{-3}). This finding is fully consistent with our interpretation of adsorption being limited by the intra particles diffusion.

The adsorption isotherms on Ca-Al-LDHs and Ca-Al-LDOs were performed to investigate the adsorption capacity of the samples at varying initial concentrations of CR solution. Fig. 10 reveals the adsorption isotherms of CR on the obtained samples at room temperature. The Langmuir and Freundlich models were serve to analyze the experimental data. In general, the Langmuir model presumes that the adsorbed molecules are adhere to the adsorbent surface in a monolayer. The mathematical formula of the Langmuir isotherm could be represented as [39]:

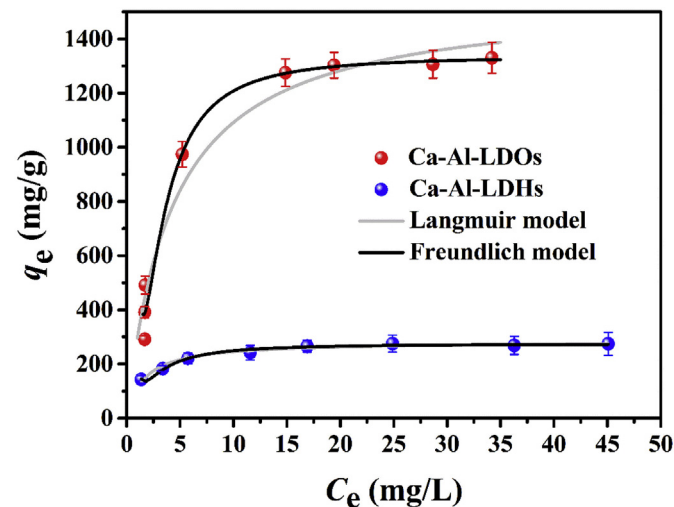


Fig. 10. Adsorption isotherms of CR on the Ca-Al-LDHs and Ca-Al-LDOs samples at room temperature (adsorbent dose = 200 mg/L).

Table 2

Adsorption isotherm parameters of the Ca-Al-LDHs and Ca-Al-LDOs samples.

	Langmuir model			Freundlich model			Sips model		
	Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F (mg^{1-n}/g)	n	R^2	K_s (L/g)	n_s	R^2
Ca-Al-LDHs	285.7	0.65	0.999	146.9	5.43	0.980	95.6	1.55	0.943
Ca-Al-LDOs	1536.1	0.22	0.986	327	2.27	0.981	222.8	1.69	0.982

$$C_e/q_e = 1/(K_L q_m) + C_e/q_m \quad (5)$$

where C_e (mg/g) and q_e (mg/g) are the equilibrium adsorption concentration and capacity, respectively; q_m (mg/g) is the theoretical maximum adsorption capacity, and K_L (L/mg) is the equilibrium constant of the Langmuir sorption.

The Freundlich isotherm used to describe the adsorption on heterogeneous surfaces. The Freundlich isotherm model equation could be expressed as [40]:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

where K_F [(mg/g)·(L/mg)^{1/n}] and n are empirical Freundlich constants, K_F is an indicator of the adsorption capacity, and $1/n$ is the correspond to the adsorption intensity. Sips isotherm is a combined form of Langmuir and Freundlich expression. The model is expressed as:

$$q_e = K_s C_e^{n_s} / (1 + a_s C_e^{n_s}) \quad (7)$$

where K_s (L/g) and a_s (L/mmol) is the Sips isotherm parameter, and n_s is the Sips parameter describe samples surface heterogeneity. The parameters calculated from the three models were summarized in Table 2. It can be seen that the adsorption isotherms of CR on Ca-Al-LDHs and Ca-Al-LDOs were well fitted by Langmuir model ($R^2 > 0.986$), which suggest that CR adsorption is in monolayer mode [41]. The K_L parameter value acquired for Ca-Al-LDHs samples was higher than that acquired for Ca-Al-LDOs, which corresponding to the lower energy requirement for the process using the calcined sample. The Langmuir isothermal theoretical maximum adsorption capacity for Ca-Al-LDOs was approximately 5 times higher than that of the Ca-Al-LDHs sample: 1536.1 mg g^{-1} and 285.7 mg g^{-1} at room temperature. Interestingly, the surface area of Ca-Al-LDOs is lower than that of Ca-Al-LDHs (Fig. 4), while the higher adsorption capacity of Ca-Al-LDOs. Specific surface areas cannot be considered the key parameter in determining as sorption onto adsorbents. The increase of adsorption capacity of Ca-Al-LDOs could be attributed to the abundant metal–oxide bonds (Ca–O and Al–O) and “memory effect”, which could provide more adsorption sites for CR adsorption on Ca-Al-LDOs. Table 3 shows the adsorption capacity of the

Ca-Al-LDOs sample compared with other adsorbents for CR removal.

3.7. Recyclability of the Ca-Al-LDOs

The good stability and good recyclability of adsorbents are critical factors for the practical applications. Therefore, it is important to highlight that the initial properties of Ca-Al-LDOs sample used in the adsorption experiments were recovered after thermal treatment at 600°C for 2 h under air flow. Under these conditions the adsorbed CR can be decompose, and the adsorbent is recycled. As shown in Fig. 11, six cycles of the activity were measured for prepared Ca-Al-LDOs. After the first use, the adsorption capacity reached 99.84, 98.36, 98.40, 96.63, 96.22 and 93.44% of the initial capacity. This small reduction in adsorption capacity indicates an important reuse property of the LDH memory effect. Other studies have also shown good recyclability for different LDH compounds and diverse anionic dye molecules [42,43].

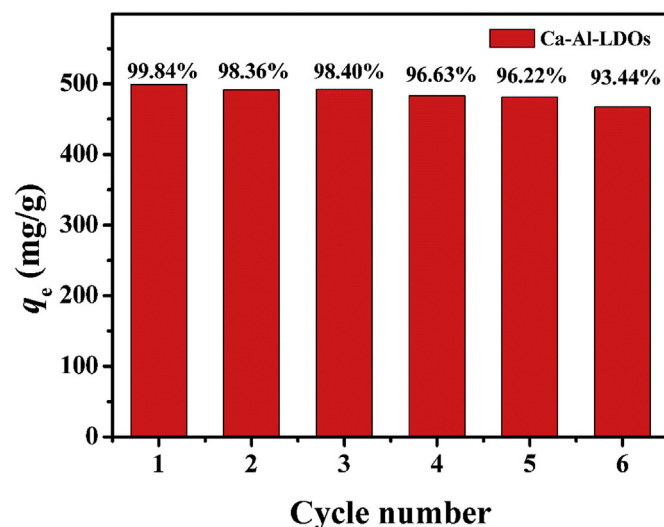
3.8. Adsorption mechanism

The mechanisms of CR adsorption onto the obtained rhombic dodecahedral structure samples have been investigated using FT-IR. The FT-IR spectra analysis of Ca-Al-LDHs and Ca-Al-LDOs before and after adsorption CR was presented in Fig. 12a. Obviously, it can be seen many new peaks appeared after CR adsorption on both Ca-Al-LDHs and Ca-Al-LDOs in the FT-IR spectra. The new band at 1050 and 1176 cm^{-1} on Ca-Al-LDOs with sorbed CR should be attributed to S–O and S=O vibrations of CR, which could conclude that the CR molecules were fastened on the functional group of Ca-Al-LDOs surfaces [44,45]. The O–H peak of Ca-Al-LDHs shifted from 3661 to 3482 cm^{-1} after CR adsorption, which indicates that hydrogen bond formed by surface O–H of Ca-Al-LDHs

Table 3

Comparison of the adsorption CR on Ca-Al-LDOs sample and previously reported materials.

Adsorbents	Adsorbates	q_{\max} (mg/g)	References
Ca-Al layered double oxides	CR	1536.1	this study
Ca-bentonite	CR	107.4	[49]
γ - Al_2O_3 nanorods	CR	416.7	[50]
Activated carbon powder	CR	500	[51]
MgO (111) nanoplates	CR	303	[52]
Mg/Al LDH nanoflakes	CR	585	[21]
Hierarchical NiO nanosheets	CR	151.7	[53]
α - Fe_2O_3 nanoparticles	CR	254	[54]
Mg–Fe– CO_3 -LDH	CR	105	[55]
plate-like Mg–Al–LDH	CR	143.3	[56]
Ni/Mg/Al layered double oxides	CR	1250	[57]

**Fig. 11.** The recyclability of the Ca-Al-LDOs for the adsorption of CR.

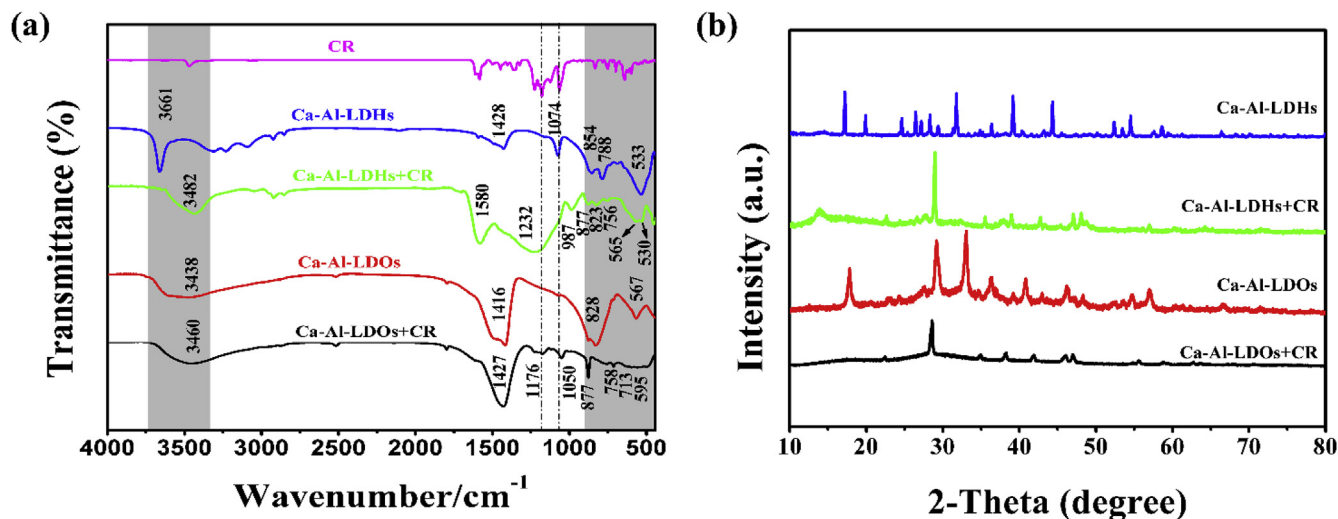


Fig. 12. The FT-IR spectra of Ca-Al-LDHs and Ca-Al-LDOs before and after CR adsorption and CR at 450–4000 cm⁻¹ (a). The XRD patterns of Ca-Al-LDHs and Ca-Al-LDOs before and after CR adsorption (b).

might participate in adsorption process [46]. The O-H peak of Ca-Al-LDOs had no clear change after CR adsorption, suggesting that hydrogen bonding did not participate in CR adsorption on Ca-Al-LDOs. It is clear to see that the peaks of Ca-Al-LDHs and Ca-Al-LDOs have obvious change after CR adsorption at 450–900 cm⁻¹. The peaks of metal-oxygen-metal and oxygen-metal-oxygen stretching were disappeared or shifted after adsorption, suggesting that the metal ions (Ca²⁺ and Al³⁺) were complexed with single and double sulfur (S–O and S=O) of CR on the functional group of Ca-Al-LDHs and Ca-Al-LDOs groups [47]. This phenomenon shows that CR adsorption on Ca-Al-LDHs and Ca-Al-LDOs might be attributed to surface complexation, ion exchange between the metal ions and dye anions.

Fig. 12b shows the XRD patterns of Ca-Al-LDHs and Ca-Al-LDOs adsorbents, meanwhile the Ca-Al-LDHs and Ca-Al-LDOs samples after adsorption of CR showed that many peaks disappeared. The XRD patterns of the adsorbents adsorption of CR have an evidence of crystalline state of adsorbents changing into amorphous state after adsorption, which suggests that the dye molecules diffuse into micropores and macropores of adsorbents. So one can conclude that adsorption of CR on Ca-Al-LDHs and Ca-Al-LDOs is mostly by chemisorption, which alter the structure of the layer space [48,57].

In addition, it can be concluded that the CR adsorption mechanism on Ca-Al-LDHs and Ca-Al-LDOs may be attributed to hydrogen bonding with oxygen or nitrogen, ion exchange and surface complexation. Furthermore, the Ca-Al-LDOs have a 3D hierarchically porous superstructure with nanoparticles, which may have facilitated rapid diffusion of CR molecules by serving as molecule-transport pathways, resulting in high adsorption of CR.

4. Conclusion

In summary, the Ca-Al-LDHs and Ca-Al-LDOs rhombic dodecahedral structures were prepared using facile synthetic methods and these samples have been studied as adsorbents for highly efficient uptake of CR. The Ca-Al-LDOs sample could be better fits with Langmuir isotherm model and the maximum adsorption capacity for CR was 1536.1 mg g⁻¹, which was significantly higher than Ca-Al-LDHs. The adsorption kinetics of Ca-Al-LDHs and Ca-Al-LDOs were both demonstrated to well follow the pseudo-second-order model. The adsorption of CR on Ca-Al-LDHs and Ca-Al-LDOs may be mainly attributed to hydrogen bonding with oxygen or nitrogen,

ion exchange and surface complexation. From the excellent adsorption capacity, the Ca-Al-LDOs can be serving as a kind of effective broad adsorbent for organic dyes as well as heavy metal ions, with a considerable application potential in wastewater treatment.

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