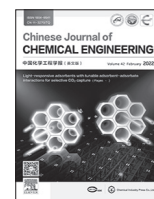




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Full Length Article

Additive manufacturing of sodalite monolith for continuous heavy metal removal from water sources



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ABSTRACT

Herein, we present a simple strategy for preparing monolithic sodalite adsorbents *via* sequential additive manufacturing and post-treatments. In detail, the method includes (i) 3D printing of cylindrical monoliths using clay as the base material; (ii) thermal activation of the 3D-printed clay monoliths by calcination (to produce reactive alumina and silica species and enable mechanical stabilization); (iii) conversion of the activated clay monoliths to hierarchical porous sodalite monoliths *via* hydrothermal alkaline treatment. Parametric studies on the effect of calcination temperature, alkaline concentration and hydrothermal treatment time on the property of the resulting materials (such as phase composition and morphology) at different stages of preparation was conducted. Under the optimal conditions (*i.e.*, calcination temperature of 850 °C, NaOH concentration of 3.3 mol·L⁻¹, reaction temperature of 150 °C, and reaction time of 6 h), a high-quality pure sodalite monolith was obtained, which possesses a relatively high BET surface area (58 m²·g⁻¹) and hierarchically micro-meso-macroporous structure. In the proposed application of continuous removal of heavy metals (chromium ion as the model) from wastewater, the developed 3D-printed sodalite monolith showed excellent Cr³⁺ removal performance and fast kinetics (~98% removal efficiency within 25 cycles), which outperformed the packed bed using sodalite pellets (made by extrusion).

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1. Introduction

Heavy metal ions, such as Cr³⁺ and Pb²⁺ released from industrial and agricultural activities, are considered to be one of the most dangerous pollutants to various water sources [1]. Adsorption processes employing porous materials such as activated carbons, zeolites, porous polymers and metal–organic frameworks (MOFs) are effective and efficient for addressing the metal pollution issues in water sources and wastewater [2].

Zeolite is a class of aluminosilicate materials with three-dimensional (3D) microporous networks [3–5]. Due to the isostructural substitution of Si⁴⁺ by Al³⁺ in non-siliceous zeolites, the intrinsic charge of the zeolite framework is negative. Accordingly, exchangeable cations, such as H⁺ and Na⁺, are present in their frameworks to neutralize the charge [6,7]. The cation exchange

property of zeolites makes them ideal candidates for adsorption applications such as heavy metals removal from aqueous media [8]. Accordingly, many studies have been conducted to evaluate the performance of different zeolite-based adsorbents in adsorption applications such as removal of heavy metals [9,10] and ammonia [11]. Among different zeolitic frameworks, sodalite (SOD, with a molecular formula of Na₈Al₆Si₆O₂₄Cl₂ and pore aperture of 0.26 nm) is alkali resistant and hydrothermally stable [12], which is a suitable framework material for adsorption applications in aqueous media [13].

Sodalite zeolite is commonly hydrothermally synthesized using commercial chemicals, such as tetraethyl orthosilicate and aluminum isopropoxide as the silicon and aluminum source, which is less economical. Alternatively, cheap silicon and/or aluminum sources, such as clays, volcanic glasses, rice husks, diatoms and fly ashes, can also be used as the starting materials for zeolite synthesis which can reduce the cost of the resulting zeolites significantly [14,15]. To date, clay has been used to synthesize many types of zeolites, such as Linde Type A, X, Y, P, 4A, NaA,

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cancrinite, sodalite, hydroxydodalite and faujasite [16,17]. Although clay can be used as the starting materials for synthesizing different types of zeolites, it is difficult to obtain pure phase zeolites due to the harsh synthesis conditions. Therefore, the conditions of thermal and hydrothermal treatments of clay need to be tailored to tune the dominant crystalline phase in the final products [18].

Packed bed configurations, which employ particles/pellets/beads of porous adsorbents, are commonly used for adsorption applications for treating water/wastewater [19–21]. However, attrition of the adsorbent particles and the pressure drop issue, especially at high flowrates, are problematic which may cause the secondary contamination of the treated stream and high energy penalty [22–25]. To address these issues experienced by the conventional packed beds, structured adsorbents were developed such as monoliths [26–28]. The monolithic structure can allow high flowrate applications with the reduced pressure drop and improved mass and heat transfer [29–32], as well as being mechanically strong. These merits make monolithic adsorbents promising for developing efficient capture technologies. Computer-aided additive manufacturing, that is, 3D printing, has been demonstrated as a powerful tool for manufacturing complex geometries flexibly and precisely, which has promoted significant innovation in fields of biomedical engineering, energy, catalysis and environmental applications [33]. Efforts have been made to improve design and fabrication of structured materials with high specific surface area, a network of broad pores, interconnected porosity and tunable heteroatom compositions, which allow more facile access of the active sites [34–38]. The ‘ink’ used by 3D printing can be customized with different functional materials, including various porous materials, such as zeolites [39,40], porous polymers, metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) [41]. For example, Yu *et al.* [40] developed a facile ‘3D printing and zeolite soldering’ strategy to construct mechanically robust binder-free zeolite monoliths with hierarchical structures, which was used as a superior configuration for CO₂ capture. Thus, it is clear that the manufacture of monolithic adsorbents with hierarchical porous structures *via* 3D printing can be an attractive strategy to boost the performance of adsorbents [12,42].

Here we report a method for preparing sodalite monoliths and the application of sodalite monoliths to the removal of heavy metal (such as chromium) ions under continuous-flow conditions. Specifically, 3D printing was used to prepare the pristine clay monoliths, which were then thermally and hydrothermally treated to be converted to sodalite monoliths. The key process parameters including calcination temperature (of the pristine clay monolith), alkaline concentration and crystallization time (of the hydrothermal treatment of the pristine/calcined monoliths) were systematically investigated to understand their effects on the property of the resulting materials. Under the optimum treatment conditions (*i.e.*, calcination temperature of 850 °C, and alkaline concentration of 3.3 mol·L^{−1} at 150 °C for 6 h hydrothermal treatment), the SODM (sodalite monolith) was obtained with the pure sodalite phase and preserved mechanical strength. The SODM possessed a hierarchical porous system and high ion-exchange capacity, and showed good performance in adsorbing the model heavy metal ions from synthetic wastewater.

2. Materials and Methods

2.1. Materials

Natural clay was purchased from Alladin Chemical Reagent Co., Ltd). Sodium hydroxide (NaOH) and chromium chloride

hexahydrate (CrCl₃·6H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2. Synthesis of SODMs

2.2.1. Additive manufacturing of clay monoliths

Homogenous clay paste was formulated by blending commercial clay (80% (mass)), hydroxypropyl methylcellulose (HPMC, 2% (mass), as the binder) and deionized water (18% (mass)) to give the suitable plasticity and rheological property to facilitate extrusion molding. The paste was then loaded into a syringe (250 ml, with a 0.60 mm nozzle) and used as the ink by a ceramic 3D printer (SYNO-Source1418, China). The configurations of monolith were designed using the Simplify 3D software, and the clay monoliths were built layer-by-layer *via* material jetting. After the additive manufacturing, the printed clay monolith was dried at 100 °C for 12 h, and calcined for 2 hours, in which the temperature was varied to investigate its effect on the mechanical strength.

2.2.2. Conversion of clay monoliths to SODM

To convert the 3D printed clay monoliths into sodalite monoliths, the clay monolith (~3.0 g) was immersed in NaOH solution (60 ml) with different concentrations of 1.9, 2.3, 2.9 and 3.3 mol·L^{−1}. Then the hydrothermal treatment was carried out in a Teflon-lined stainless autoclave (100 ml) at 150 °C for different durations (from 3 to 24 h). Finally, the obtained monolith was washed with deionized water, dried at 100 °C, and calcined at 550 °C for 6 h. The resulting samples were denoted as SODM-*x*-*y*M-*z*, in which *x* is the calcination temperature (of the clay monolith), *y*M is the concentration of NaOH solution (*M* is the abbreviation for molarity, mol·L^{−1}) and *z* is the time of hydrothermal treatment. The information of the samples above is listed in Table S1 in the Supplementary Material, and relevant characterization techniques employed are presented in SI as well. Schematic diagram of the manufacturing process of the monolith adsorbents is shown in Fig. 1.

2.3. Adsorption of heavy metal ions

The selected SODM (*i.e.*, SODM-850 °C-3.3 M-6 h, diameter of 25 mm, thickness of 5 mm, and mass of 2 g) was assessed under continuous cyclic conditions at 25 °C to evaluate its performance for adsorption of heavy metal ions (*i.e.*, chromium ion, Cr³⁺) from synthetic wastewater, as shown in Fig. 2. During the adsorption experiments, a peristaltic pump was used to flow the synthetic wastewater (total 1500 ml) containing 100 mg·L^{−1} Cr³⁺ through the monolith adsorbent bed at 15 ml·min^{−1} (the estimated contact time between the solution and the adsorbent was about 0.1 s). The adsorption experiment was performed cyclically for total 25 cycles, in details, the solution was fully passed through the adsorbent bed, and the performance of adsorption was analyzed by measuring the initial and final concentration of Cr³⁺ in the solution. After that, the procedure with the treated solution was repeated (total 25 cycles). The adsorption capacity of the monolith was evaluated by studying its removal efficiency of chromium ion (%) and total amount adsorbed (mg metal ion per gram of adsorbent), which are defined as Eqs. (1) and (2).

$$\text{Removal efficiency} = (C_i - C_t)/C_i \times 100\% \quad (1)$$

$$\text{Total amount adsorbed} = (C_i - C_t)V/m \quad (2)$$

where *C_i* (mg·L^{−1}) is the initial concentration of the heavy metal ions, *C_t* (mg·L^{−1}) is the concentration of the heavy metal ions at time *t* (min), *V* (ml) is the volume of the synthetic wastewater, and *m* (g) is the mass of the adsorbent.

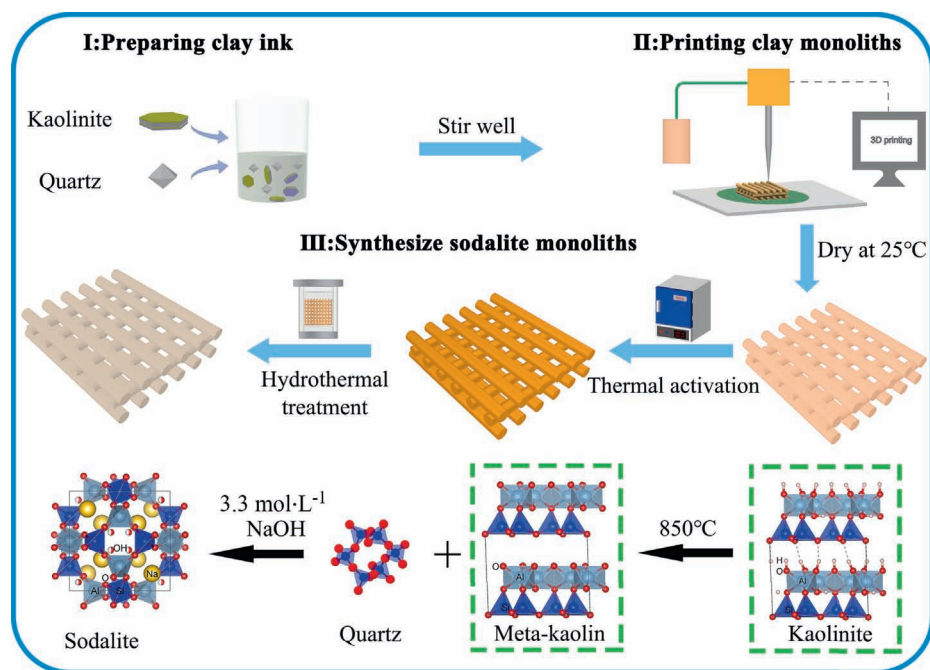


Fig. 1. Schematic of fabrication procedure of 3D-printed sodalite monoliths.

Adsorption kinetics was studied as well, in which the pseudo-first-order and pseudo-second-order models, as Eqs. (3) and (4), were used to study the experimental data.

$$\ln(q_e - q_t) = \ln q_e - K_F t \quad (3)$$

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

where, q_e ($\text{mg}\cdot\text{g}^{-1}$) and q_t ($\text{mg}\cdot\text{g}^{-1}$) are adsorption capacity at equilibrium and time t (min), respectively. K_F (min^{-1}) and K_S ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively.

3. Results and Discussion

3.1. Thermal activation of the pristine clay prior to hydrothermal treatment

The transformation of clay to sodalite zeolite is enabled by the process of dissolution and recrystallization [43]. The property of the starting material and the condition of hydrothermal treatment are key parameters which can influence the dissolution and recrystallization process, and thus the property of the resulting materials. Kaolinite is one of the main constituents of kaolin, and its structure consists of silicon-oxygen tetrahedral sheets joined alternately to alumina octahedral sheets, which makes it stable and resistant to acids and alkalis. Therefore, when using kaolin as the starting material to synthesize zeolite, calcination at high temperatures is necessary to enable the thermal dehydroxylation of kaolinite to form metakaolin with the partially disordered crystalline structure [44], which can be more reactive during the hydrothermal treatment for the formation of zeolites [45]. In this work, the pristine clay was calcined at 400, 650, 850 and 1200 °C, respectively, to study the effect of calcination temperature on its phase composition. Fig. 3(a) shows the XRD patterns of the pristine clay and the clays calcined at different temperature from 400 to 1200 °C, in which the pristine clay shows the primary phases of kaolinite (with the characteristic diffraction peaks at 2θ of 9.36°, 12.3°, 25.16° and 28.1°) and quartz (2θ at 20.89°, 26.67°, 36.60°, 39.49° and

42.49°). After the calcination at 650 °C, the diffraction peak of kaolinite disappeared, which is accordance to the results reported previously by Barrer [46] that metakaolin was produced by dihydroxylation process after calcination between 700 °C and 1000 °C. A further increase of calcination temperature to 1200 °C led to the formation of mullite (diffraction peaks at 16.49°, 30.94°, 33.22° and 33.25°), which is unfavorable to the following dissolution and recrystallization process because mullite is insoluble in alkaline solution [47]. The phase transition of the pristine clay under thermal treatment was also found by the thermogravimetric analysis and derivative thermogravimetry (TGA/DTG), as presented in Fig. 3(b), which suggests that the transition of kaolinite to metakaolin started at ~492 °C. The mass loss of the pristine clay under the thermal condition of TGA can be described as: (i) the initial mass loss of about 0.7% at <400 °C could be attributed to the release of the absorbed water; (ii) the mass loss of about 5.6% at 400–850 °C was the result of the structural decomposition of kaolinite (i.e., dehydroxylation) [48]; and (iii) the final mass loss of ~6.6% in range of 850–1500 °C could be due to the phase transformation into mullite.

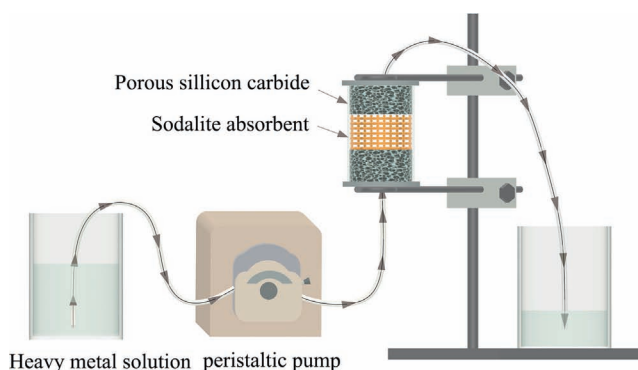


Fig. 2. Schematic of the experimental rig for adsorption of heavy metals on the structured adsorbent from wastewater.

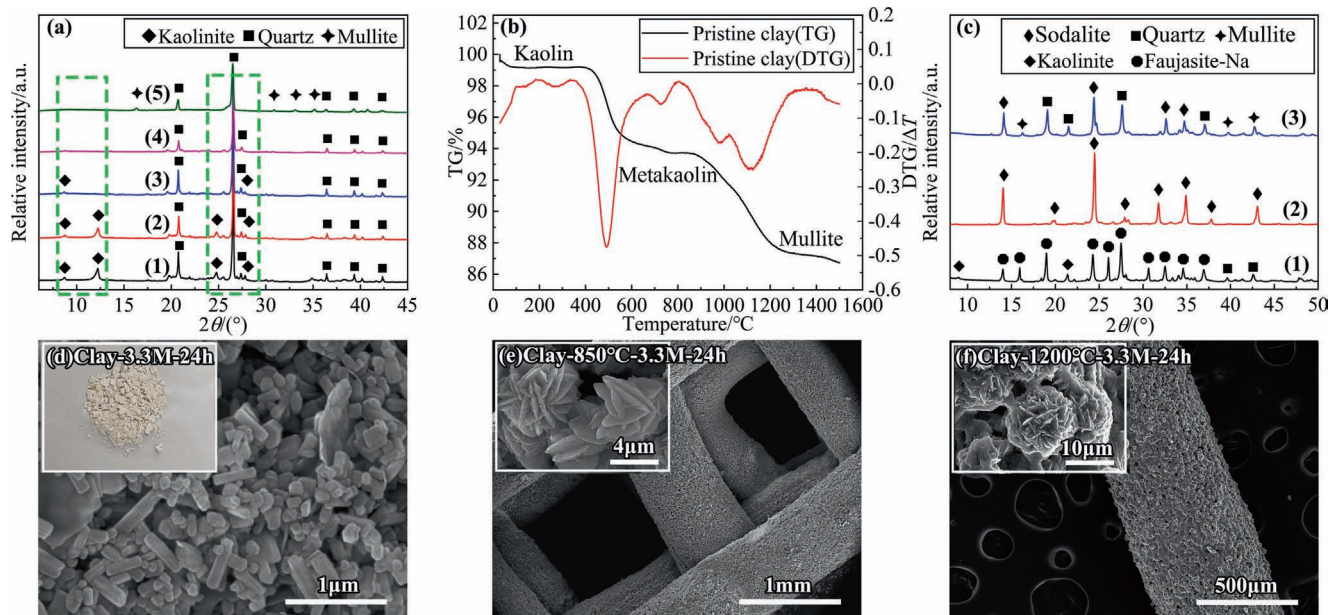


Fig. 3. (a) XRD patterns of the pristine and calcined clay, (1) pristine clay, (2) 400 °C, (3) 650 °C, (4) 850 °C, (5) 1200 °C; (b) TGA-DTG curve of the pristine clay; (c) XRD patterns of the pristine and calcined clay monoliths after the hydrothermal treatment with 3.3 mol·L⁻¹ NaOH solution at 150 °C for 24 h, (1) Clay-3.3 M-24 h, (2) Clay-850 °C-3.3 M-24 h, (3) Clay-1200 °C-3.3 M-24 h; (d) SEM image of the hydrothermally treated sample Clay-3.3 M-24 h (inset, photograph of the sample); (e) SEM images of the hydrothermally treated sample Clay-850 °C-3.3 M-24 h (inset, microscopic morphology of the sample); (f) SEM images of the hydrothermally treated sample of Clay-1200 °C-3.3 M-24 h (inset, microscopic morphology of the sample);

The effect of calcination temperature on the final monolith was studied under the fixed hydrothermal treatment condition (i.e., in 3.3 mol·L⁻¹ NaOH solution at 150 °C for 24 h). After the hydrothermal treatment, the 3D-printed pristine clay was converted to faujasite-Na, as evidenced by XRD and SEM analysis (i.e., the Clay-3.3 M-24 h sample in Fig. 3(c) and (d)). The mechanical strength of the resulting faujasite-Na monolith was also poor, that is, the monolith structure collapsed after the hydrothermal treatment (inset of Fig. 3(d)). Regarding the calcined clay monolith (at 1200 °C), although the geometrical shape of the monolith (i.e., the Clay-1200 °C-3.3 M-24 h sample) was maintained after the hydrothermal treatment, the resulting Clay-1200 °C-3.3 M-24 h monolith was only partially converted into sodalite, and quartz and mullite phases were still present (as shown in Fig. 3(c) and (f)), because mullite is stable in alkaline, which was found in the process of using calcined fly ash as starting materials to synthesize zeolite X [47].

After calcination at 850 °C, the pristine clay was converted to metakaolin, which could be fully transformed into the pure phase sodalite (i.e., the Clay-850 °C-3.3 M-24 h sample) after the hydrothermal treatment, as shown in Fig. 3(c) (XRD), with the maintained geometrical shape (as shown in Fig. 3(e)). This phenomenon was consistent with the previous results in the literature that the thermal activation of kaolin at a suitable temperature is the prerequisite to enable the aluminum species in it to participate in the dissolution and recrystallization process during the hydrothermal treatment, and high calcination temperatures led to the formation of mullite (Fig. 3(f)), which was stable in an alkaline environment [44,49].

3.2. Hydrothermal treatment of clay monoliths for phase transfer

As mentioned above, in the hydrothermal alkaline treatment, the dissolution–recrystallization mechanism is the key to convert the metakaolinite and/or quartz phase into zeolitic materials. Specially, dissolution of the phases was favored by high alkalinity,

which could enable more silicon and aluminum species to participate in the following recrystallization process [21,43]. Since the optimum calcination temperature for the clay monolith has been established at 850 °C, in the following investigation, the concentration of NaOH solution was varied from 1.3 to 3.3 mol·L⁻¹ during the hydrothermal treatment (of the pristine and calcined clay monoliths at 850 °C) to study its effect on the resulting monoliths. As shown in Fig. 4(a) (XRD patterns) and Table S1, it can be seen that the crystalline phases of the resulting materials from the hydrothermal treatment (at 150 °C for 24 h) with the NaOH concentration of 1.3, 2.3 and 2.9 mol·L⁻¹ were the mixed analcime and sodalite phases, along with quartz. Conversely, when 3.3 mol·L⁻¹ NaOH solution was used, the monolith with the pure sodalite was obtained. The effect of alkalinity of the system (i.e., the NaOH concentration) on zeolitization is also evidenced by the corresponding SEM analysis, as shown in Fig. 4(b)–(e). The morphology of the resulting materials changed from the composite of large analcime crystals and small sodalite crystals to the solely small sodalite crystals with an increase in the NaOH concentration (at 150 °C for 24 h). With the appropriate NaOH concentration identified, the treatment time was further investigated, which was varied from 3 to 24 h. According to XRD analysis (Fig. 4(f)), the treatment time of 3 h was not sufficient to complete the phase transformation, that is, the unreacted quartz phase (from the pristine clay) was still present in SODM-850 °C-3.3 M-3 h. By extending the hydrothermal treatment time ≥6 h, pure sodalite monolith could be successfully obtained. According to the SEM morphologies shown in Fig. 4(g)–(j), the crystal size of sodalite increased (from 2–3 μm to 6–7 μm) by prolonging the treatment time from 6 h to 24 h. Since the ideal conditions of calcination (of the 3D printed clay monolith at 850 °C) and hydrothermal treatment (of the calcined clay monolith in 3.3 mol·L⁻¹ NaOH solution at 150 °C for 6 h) were identified for producing pure sodalite monolith. The corresponding sample of SODM-850 °C-3.3 M-6 h was discussed and characterized further for its properties [42].

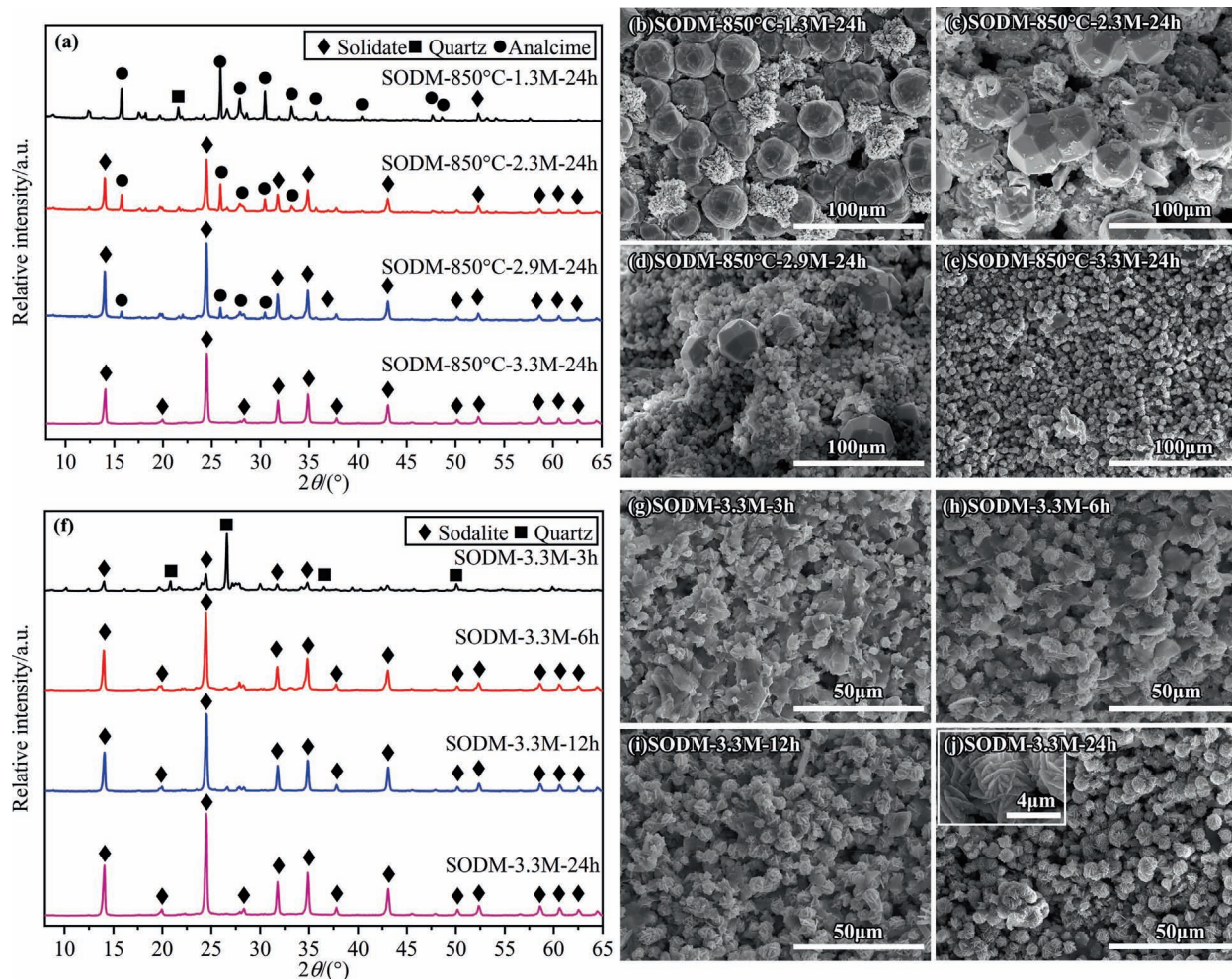


Fig. 4. (a) XRD patterns of monoliths obtained from the hydrothermal treatment (of the clay monolith calcined at 850 °C) with different NaOH concentrations; (b–e) SEM images of the samples in (a); (f) XRD patterns of monoliths obtained from the hydrothermal treatment (of the clay monolith calcined at 850 °C) with 3.3 mol·L⁻¹ NaOH and different times; (g–j) SEM images of SEM images of the samples in (f).

3.3. Properties of SODM

As shown in Fig. 5(a), 3D-printed SODMs with tailorable geometries was fabricated from the identified suitable conditions (*i.e.*, calcination temperature of the pristine clay monolith at 850 °C, hydrothermal treatment conditions of 3.3 mol·L⁻¹, 850 °C and >6 h). Notably, the obtained SODM of SODM-3.3 M-6 h with 15 channels per square inch (cps) was measured to have a compressing strength of 17.9 MPa (Fig. 5(g)), which is mechanically strong. According to SEM characterization, as shown in Fig. 5(b)–(d), that the morphology of the clay phase (of the 3D printed clay monolith) was clearly different from that in SODM-3.3 M-6 h. In detail, after the hydrothermal treatment, Fig. 5(c) and d shows that SODM-3.3 M-6 h was consisted of particles of 6–7 μm with the armadillo-like morphology which was assembled by crystalline sodalite sheets. Fig. 5(e) shows the SEM image of the cross-section of SODM-3.3 M-6 h. It suggests that the sodalite crystals were inter-growth to form a well-developed interconnected 3D network with open macroporosity, which could be beneficial to mass transfer of absorbates during adsorption [23,39,50].

TEM analysis was performed on SODM-3.3 M-6 h, as shown in Fig. 5(f). From the electron diffraction pattern of SODM-3.3 M-6 h (inset of Fig. 5(f)), one can see that the phase of SODM-3.3 M-6 h is highly crystalline, which was confirmed by XRD analysis as well (as shown in Fig. 5(h)). The powder XRD

patterns of the clay monolith and SODM-3.3 M-6 h were compared, which showed all the characteristic diffraction peaks of sodalite and confirmed the sodalite phase in SODM-3.3 M-6 h. Therefore, based on the consistent findings from SEM, TEM and XRD analyses, we confirmed that clay was converted to pure sodalite phase after the procedure developed. In addition, according to EDS analysis (as shown in Fig. 5(i) and Table S2), Na⁺ cations were present in the as-synthesized SODM-3.3 M-6 h monolith with the high concentration of about 16.2% (mass), which is comparable to the theoretical Na⁺ concentration of commercial sodalite (Na₈Al₆Si₆O₂₄Cl₂), suggesting a good ion exchange property for heavy metal removal in adsorption [12,42].

Fig. 6(a) shows the comparison of adsorption–desorption isotherms of the calcined clay monolith and SODM-850 °C-3.3 M-6 h by nitrogen (N₂) physisorption. The clay monolith is non-porous according to its type II adsorption isotherm and insignificant Brunauer-Emmett-Teller (BET) surface area of about 9 m²·g⁻¹. After the hydrothermal treatment with 3.3 mol·L⁻¹ NaOH solution (at 850 °C for 6 h), the obtained SODM-850 °C-3.3 M-6 h showed the type IV like isotherm. The adsorbed amount at the low relative pressure range is not significant which is reasonable since the kinetic diameter of N₂ (0.364 nm) is larger than the pore aperture of SOD (~0.26 nm), and hence the adsorption of N₂ molecules in the micropores of SOD was not hindered. At the relative pressure of > 0.8, the hysteresis loop was measured for SODM-850 °C-3.3

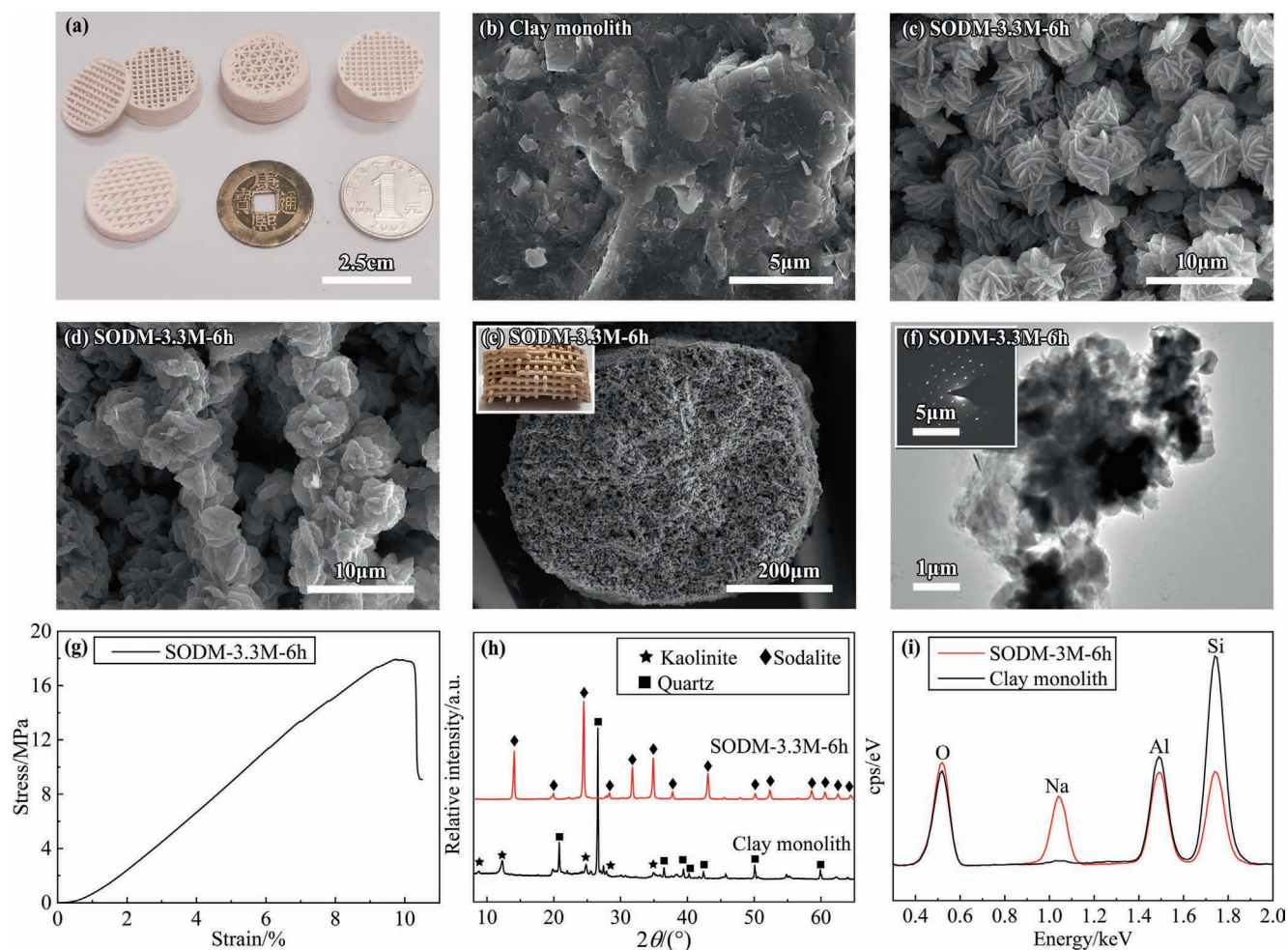


Fig. 5. (a) Digital photographs of 3D sodalite monoliths with tailorable geometries; (b) microscopic morphology of the calcined clay monolith by SEM after calcination at 850 °C; (c) and (d) microscopic morphologies of SODM-3.3 M-6 h; (e) cross-sectional view by SEM of SODM-3.3 M-6 h; (f) TEM characterization and electron diffraction pattern (inset) of SODM-3.3 M-6 h; (g) compressive strength curve of SODM-3.3 M-6 h; (h) XRD patterns and (i) EDS curves of the calcined clay monolith and SODM-3.3 M-6 h.

M-6 h, which suggests the N_2 adsorption on the external surface of SOD crystals and the presence of intercrystalline mesoporosity in SODM-850 °C-3.3 M-6 h. The BET surface area of SODM-850 °C-3.3 M-6 h was measured at $\sim 58 \text{ m}^2 \cdot \text{g}^{-1}$. Macroporosity of SODM-850 °C-3.3 M-6 h was probed by mercury porosimetry as well, as shown in Fig. 6(b), in which two types of macropores were found

at 60–800 nm and 60–350 μm, respectively, with a total pore volume of $0.62 \text{ ml} \cdot \text{g}^{-1}$. The macropores could be the results of the interparticle void among SOD crystal assembly. The presence of the hierarchical macro-/meso-/micro-pore system can improve the accessibility of the adsorbent surface to the substrates during adsorption. On the basis of the discussion above, under the

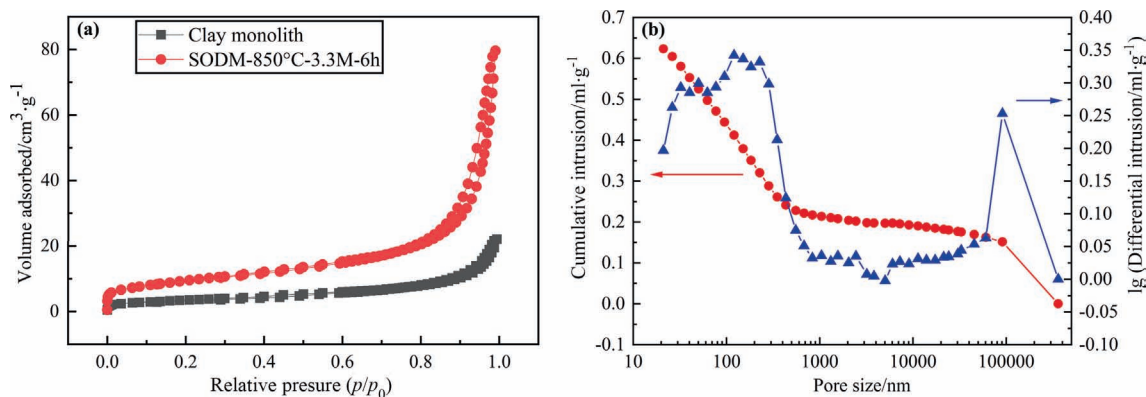


Fig. 6. (a) Nitrogen adsorption–desorption isotherms at $-196.15 \text{ } ^\circ\text{C}$ of the calcined clay monolith and SODM-850 °C-3.3 M-6 h; (b) mercury porosimetry analysis of SODM-850 °C-3.3 M-6 h.

appropriate conditions, the 3D printed clay monolith could be successfully transformed into a sodalite monolith.

3.4. Adsorption performance of SODM

The selected SODM, that is, SODM-850 °C-3.3 M-6 h, was assessed for its application as the structured adsorbent for removing heavy metal ions (Cr^{3+}) from the synthetic wastewater under cyclic conditions. As shown in Fig. 7, the total amount adsorbed of the SODM correlates with the cycle number (or the adsorption time) positively, that is, with an increase in the cycle number, the total amount adsorbed Cr^{3+} by SODM-850 °C-3.3 M-6 h increased. The adsorption of Cr^{3+} on the SODM showed a liner trend with adsorption cycles due to the relatively large ion gradient between the adsorbent and solution, and nearly 40% of Cr^{3+} was removed from the synthetic wastewater within 5-cycle adsorption. At the end of 25 cycles, about 98% removal efficiency was achieved by the SODM. The total amount adsorbed of SODM-850 °C-3.3 M-6 h (as mg Cr^{3+} adsorbed per unit mass, g, of the SODM) showed the similar trend to that of the adsorption efficiency, and the final adsorption capacity of the SODM reached $72.5 \text{ mg} \cdot \text{g}^{-1}$ after 25 cycles of adsorption, which was significantly higher than natural clay ($\sim 1.3 \text{ mg} \cdot \text{g}^{-1}$), kaolinite ($\sim 6.1 \text{ mg} \cdot \text{g}^{-1}$) and even clinoptilolite-type zeolite ($\sim 19.9 \text{ mg} \cdot \text{g}^{-1}$) [51]. To highlight the merits of SODM, comparative adsorption experiments using SODM and pelletized sodalite (prepared *via* extrusion, in packed-bed configuration) were performed. As shown in Fig. S1, the overall performance of structured SODM was much better than that of sodalite pellets. In the early stage of adsorption (<3 cycles), the removal efficiency of the two adsorbents was close, which could be attributed to adsorption occurring on the outer surface of the adsorbents. After that, SODM showed much improved adsorption efficiency than the pellets, which could be due to the hierarchical pore structure of SODM with the improved the accessibility of the adsorbent surface to the substrates during adsorption. Also, the SODM was saturated faster with 25 cycles and an adsorption efficiency of $\sim 98\%$ that the sodalite pellets, which required 40 cycles to reach saturation with a lower adsorption efficiency of $\sim 95.2\%$. Again, the findings supported the hypothesis of the improved microscopic mass transfer due to the structuring of sodalite (with the hierarchical pore structure). In conclusion, the measured high adsorption capacity can mainly be attributed to (i) the hierarchical pore structure of the SODM (which ensure the full usage of the active sites within the framework of sodalite), and (ii) its high ion exchange capacity. The latter was proved by

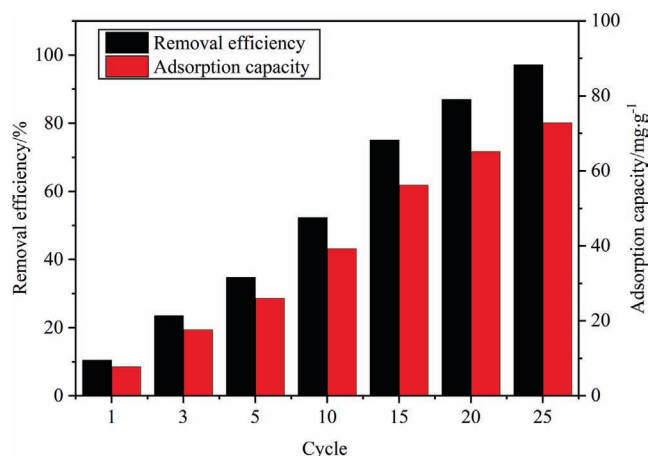


Fig. 7. Adsorption capacity and efficiency of SODM-3.3 M-6 h as a function of adsorption cycles.

the post-adsorption characterization of the SODM. As shown in Fig. S2, EDS line scan analysis of the SODM after 25 cycles of Cr^{3+} adsorption was performed. The results show that the Cr element distributed uniformly across the whole section of the SODM, which provided the convincing evidence of the enhanced accessibility due to the hierarchical pore structure, making all active sites available for adsorption.

Kinetic is one significant aspect in evaluating adsorption as a unit operation. In this work, the pseudo-first-order and pseudo-second-order models were used to study the equilibrium adsorption data of SODM (Fig. S3(a)). Relevant data fittings using the two models are shown in Figs. S3(b) and (c), respectively, with relevant constants (from fitting) presented in Table S3. According to the correlation coefficients, R^2 (Table S3), the pseudo-second-order model is the appropriate one compared to the pseudo-first-order model to describe the adsorption process over SODM. In detail, the rate-limiting step in heavy metal adsorption on SODM is the surface adsorption that involves chemisorption, possibly *via* ion exchange.

4. Conclusions

Here, a strategy was established to manufacture pure sodalite monoliths with a hierarchical pore system by converting 3D-printed clay monolith *via* calcination and hydrothermal alkaline treatment. The preservation of the crack-free body of the monolith, superior mechanical strength and ion-exchange capacity, as well as the developed hierarchical porous network, accounted for the good performance of the resulting sodalite monolith as the structured adsorbent for removing heavy metals from aqueous media under flow conditions. Systematic investigation revealed that the calcination temperature of the pristine clay monolith was a critical parameter to transform kaolinite in it to metakaolin, which could be subsequently transformed to the pure sodalite phase (by the hydrothermal alkaline treatment), and preserve the good mechanical strength of the resulting monolith. In addition, the optimum condition of only the premium concentration is benefitting to produce pure sodalite monolith. In this context, the optimum calcination condition was at 850 °C for 2 h, and that for the hydrothermal treatment was in $3.3 \text{ mol} \cdot \text{L}^{-1}$ NaOH at 150 °C for 6 h. This work presents a new strategy for developing structured zeolite monoliths from cheap raw materials, which can be applied to many fields such as adsorption and catalysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.12.016>.

Nomenclature

C_i	initial concentration, $\text{mg}\cdot\text{L}^{-1}$
C_t	concentration at time t , $\text{mg}\cdot\text{L}^{-1}$
K_F	pseudo-first-order rate constant, min^{-1}
K_S	pseudo-second-order rate constant, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$
M	the abbreviation for concentration unit sodium hydroxide solution, $\text{mol}\cdot\text{L}^{-1}$
m	the mass of the adsorbent, g
q_e	equilibrium adsorption capacity, $\text{mg}\cdot\text{g}^{-1}$
q_t	adsorption capacity at time t , $\text{mg}\cdot\text{g}^{-1}$
t	the adsorption time, min
V	volume, ml
W_t	mass concentration, %
θ	backswep angle, ($^\circ$)

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