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Activation and adsorption performance of sewage sludge carbon for CO₂: unusual enhancement effect of HF treatment[†]

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To understand the dependence of activation processes of sludge carbons on CO_2 adsorption, five sludge carbons (SC_1 - SC_5) were prepared by direct pyrolysis, pyrolysis-citric acid (CA) activation, pyrolysis-(CA + $ZnCl_2$) activation, pyrolysis-(CA + $ZnCl_2$ + KOH) activation and pyrolysis-(CA + $ZnCl_2$ + KOH)-HF activation, respectively. It was unexpectedly found that the features of SC_5 were very different from the others. Its specific surface area reached as high as 2654 mg g⁻¹, being 4.2, 12.0, 71.5 and 88.4 fold that of SC_4 , SC_2 and SC_1 , correspondingly. Moreover, many ultramicropores and C-F groups were formed, in addition to the intended desilication. These microstructural changes lead to a great adsorption capacity of 215.2 mg g⁻¹ for CO_2 , which was 2.5, 8.9, 26.9 and 40.6 fold that of SC_4 , SC_3 , SC_2 and SC_1 , respectively. The significant increase of the surface area was attributed to the combined activation effect of HF chemical etching on SC and the expansion of d002 interlayers of SC due to the physical action of SiF_4 gas in HF activation. And, the enhancement of CO_2 adsorption was demonstrated to be due to the formation of extensive CO_2 -philic expanded interlayer space-type micropores and C-F functional groups in SC_5 activated by HF.

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Environmental significance

The preparation of super sludge carbon was investigated. It was found that HF post-treatment of sludge carbon could act as a novel activation process which could result in a great improvement on its performance. In addition to removing its impurities, HF activation could turn common activated SC into super sludge carbon with a surface area of 2654 m² g⁻¹ and many C-F functional groups. Its CO_2 adsorption capacity reached 215.2 mg g⁻¹, which was 40.6 fold that of unactivated sludge carbon. These findings provided a new and facile way to upgrade the performance of sludge carbons for capturing CO_2 gas.

1. Introduction

It has been recorded that the global CO_2 concentration has been increasing from 270 ppm during the pre-industrial revolution to more than 385 ppm nowadays.¹ Increasing emissions of CO_2 gas have received worldwide concern

^b Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-Sen University, no. 135, Xingang Xi Road, Guangzhou 510275, P. R. China owing to their climate effects.² The importance and urgency of carbon emission reduction have been broadly recognized. Therefore, various capture technologies have been developed, such as absorption,^{3–5} adsorption,^{6,7} membrane separation,⁸ *etc.* Among them, chemical absorption with alkanolamine solutions offers higher capture efficiency for CO_2 ,⁵ but it also suffers from various disadvantages, such as high equipment corrosion rates, high energy consumption in regeneration, and need a large absorber,⁹ *etc.* Physical adsorption technologies based on porous materials possess the potential to overcome these disadvantages. In the recent years, extensive efforts have been directed to developing porous adsorbents with great physical adsorption capacity for CO_2 , such as molecular sieves, zeolites, activated carbon, metal organic frameworks, *etc.*^{10–13}

Among the porous CO_2 adsorbents, porous carbons prepared from waste biomass have attracted more attention because they are inexpensive and easily generable, compared with other solid adsorbents. More importantly, they possess



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[†] Electronic supplementary information (ESI) available: Supplementary figures: CO_2 adsorption models of SC_5 . Packing density photos of SCs. SEM/HRTEM images, F mapping of SC_5 , and BET surface area of SC activated by different concentrations of HF. Adsorption selectivity (CO_2/N_2) and CO_2 adsorption isotherms of SC_4 and SC_5 . The temperature of sludge carbon-containing suspended slurry before and after adding HF. Supplementary table: CO_2 adsorption capacities of various carbon materials. See DOI: 10.1039/d1en00037c

Paper

the dual environmental benefits of waste utilization and CO₂ fixation.^{14,15} A wide range of waste biomass has been used to prepare carbon materials as CO₂ adsorbents. They include nut shells (almond shell, coconut shell, etc.), food residues (coffee grounds, bagasse, celtuce leaves, etc.), wood residues (sawdust, poplar anthers, etc.), marine macroalgae and so on. Some of these bio-carbons possess excellent performance. For example, the CO₂ adsorption capacities of bio-carbons derived from jujun grass, Camellia japonica and celtuce leaves were 215.6 mg g^{-1} , g^{-1} 220.0 mg g^{-1} , g^{-1} and 193.6 mg g^{-1} ,¹⁷ respectively. However, there have been only a few reports about sewage sludge carbons (SCs) as CO₂capture materials, even though sewage sludge is one of the most produced waste biomass in the world and research on SC as an adsorbent has started in as early as the 1970s.¹⁸ Their CO₂-adsorption capacities (about 60 mg g^{-1}) are much lower than those of the above bio-carbons,¹⁹⁻²¹ but J. M. d. Andrés et al. found that the CO2-adsorption capacity of activated sludge carbon was about 4 fold that of unactivated sludge carbons.¹⁹ This situation stimulated us to continuously improve the CO₂ adsorption performance of SCs by activation, etc.

As we have known, the adsorption performance of porous carbons is intensively correlated with not only their surface area but also pore structure, etc.²² However, the specific surface area of SCs derived from direct pyrolysis was generally smaller than 60 m² g⁻¹.²³ Recently, it was reported that composite activation is one of the effective ways to increase their surface areas and to enrich the pore structure of carbon materials as well.²⁴⁻²⁶ Considering that ZnCl₂ and KOH have been widely used as a chemical activator to generate mesopores and micropores, and CA can effectively form macropores in co-pyrolysis with sludge,²⁷⁻³⁰ we started to investigate the pore-forming effect of their composite activation in order to prepare SCs with hierarchical pore structures, because hierarchical structures are generally favorable for both thermodynamics and kinetics of CO₂ adsorption.31 In addition, sewage sludge generally contains higher minerals than usual biomass and these minerals block the pores of SCs, possibly resulting in a low specific surface area as well. Thus, acid washing activation with HCl is a common post-treatment process for SCs.32 It can effectively remove many minerals, such as CaO, Al₂O₃, etc., but it cannot take out SiO2. It is commonly the most abundant mineral in SCs; thus, its removal could possibly increase the porosity of SCs. Considering that HF has been used to facilitate desilication of many materials,^{33,34} in this project, HF post-treatment was used to remove silicon from SCs to further increase their surface areas.

This paper mainly explored the dependence of these activations on the CO_2 adsorption of SCs. Special efforts were done to understand the remarkable enhancement effect and mechanism of HF activation on the CO_2 adsorption performance of SCs. The main aim of this investigation was to develop effective porous SC materials for CO_2 adsorption.

2. Materials and methods

2.1. Material and reagents

The sludge was dewatered sewage sludge containing about 80% H_2O from the secondary sedimentation tank of the Chencun wastewater treatment plant in Guangdong, China. The content of ash, volatile and fixed carbon of the dried sludge was 42.4%, 44.1%, and 13.5%, respectively. For the ash, the content of main mineral elements Al, Fe, Si, and Ca was 3.6%, 2.1%, 9.7% and 3.4%, respectively. The purity of the used HF, CO₂ and N₂ is 40%, 99.99% and 99.9995%, individually.

2.2. Preparation of the SCs

 SC_1 was prepared by pyrolysis of sewage sludge. Concretely, 20.0 g of dried sewage sludge ground and sieved with a 200 mesh screen was placed into a ceramic ark, heated in a furnace at a rate of 10 °C min⁻¹ to 650 °C in the presence of N_2 and held for 3 h.¹⁹ After cooling to room temperature, the resulting product (yield: 61.8%) was ground to less than 200 mesh. The meshed powder was washed with a HCl solution and rinsed with deionized water until its pH reached 7.³² The washed product (yield: 35.5%) was dried at 105 °C overnight in an oven and then ground using a pestle with a porcelain mortar and sieved with a 200 mesh screen, unless otherwise specified.

 SC_2 , SC_3 and SC_4 were prepared by pyrolysis-activation in which the pyrolysis was the same as that for SC_1 . The used activators were 100 ml solutions containing 20 g CA, 20 g CA-20 g ZnCl₂ and 20 g CA-20 g ZnCl₂-60 g KOH, respectively. They were stirred with the sludge for 2 h to form homogeneous sol-gels before pyrolysis, unless otherwise specified. SC_5 was obtained by the further activation of 10 g SC_4 soaked in 30 ml solution of 10 mol L⁻¹ HF, at 30 °C for 9 h. The yields of SC_2 -SC₅ were 35.4%, 32.8%, 26.5%, and 16.8%, respectively. The aim of the activation is to desilicate SC_4 *via* reaction (1):^{35,36}

$$SiO_2 + 4HF = SiF_4(gas) + 2H_2O$$
 (1)

2.3. Characterization and analysis of the SCs

The morphologies of the SCs were obtained using a scanning electron microscope (SEM, JEOL, JSM-6330F) with an energy dispersive X-ray spectrometer (EDS, Inca300 Oxford). X-ray diffraction (XRD) spectra of the SCs were determined with a D-MAX 2200 VPC diffractometer (Rigaku Corporation, Japan) with Cu K α radiation at 40 kV and 30 mA. High resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2010HR. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 Thermo-VG Scientific system. Raman spectra were obtained on a Renishaw Raman microscope (Renishaw inVia, UK) with a 633 nm laser. The pore characterizations of the SCs were performed by physical adsorption of N₂ at 77 K using an auto-adsorption system (Autosorb-6, Quantachrome, US) and a mercury intrusion porosimeter (AutoPore IV 9500,

Micromeritics Instruments Co.). Prior to analysis, the samples were ground, sieved with a 200 mesh sieve, and then heated at 200 °C for 2 h in a vacuum environment. The CO₂/N₂ adsorption selectivity was measured using а gas chromatograph (GC-2014C, SHIMADZU) with a flame ionization detector (FID). Adsorption energy (E_2) of CO₂ on the SCs was calculated using density functional theory (DFT) and the Vienna ab initio simulation package (VASP)37 with the projector augmented wave (PAW) method³⁸ and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).³⁹ For convenience, the SCs were simplified as bilayer graphene and single-layer graphene containing hydroxyl, epoxy and C-F groups. The adsorption models are shown in Fig. S1.† The adsorption energy (E_a) was defined as $E_{\text{carbon-CO}_2} - [E_{\text{carbon}}]$ + $E_{\rm CO_2}$], where $E_{\rm carbon-CO_2}$ is the total energy of carbon with adsorbed CO₂. E_{carbon} and E_{CO_2} are the energies of the virgin carbon materials and CO2 molecules, respectively.

2.4. Adsorption experiments of CO₂

 CO_2 adsorption and desorption isotherms were measured on a Quantachrome Autosorb-iQ2-MP gas sorption analyzer from 0.01 bar to 1 bar. Prior to each adsorption experiment, the SC was degassed for 2 h at 250 °C and 0.01 bar to remove impurities from its pores. A CO_2 (15 vol%)–N₂ (85 vol%) binary mixed gas was used as a test sample for adsorption selectivity.^{40–44}

 CO_2 adsorption kinetic curves were gravimetrically determined using a NetzschTG-209 analyzer (NETZSCH-Gerätebau GmbH Co.) at 25 °C and 1 bar CO₂. The sorbent was first heated at 250 °C in N₂ flowing for 60 min to remove impurities from the pores. The measurements were repeated three times for each sample, and the average value was taken as the adsorption capacity. The uncertainty of the CO₂ adsorption results was estimated to be less than 2% in terms of standard error.

3. Results and discussion

3.1. Characterization of the SCs

Five sludge carbons (SC_1-SC_5) were derived from various processes. Apart from SC_1 obtained by direct pyrolysis, the other SCs were further activated by CA, CA + ZnCl₂, CA +

 $ZnCl_2 + KOH$ and $(CA + ZnCl_2 + KOH)$ -HF, respectively, in the process of pyrolysis or after pyrolysis. As expected, these activation processes considerably decreased the packing density (Fig. S2[†]) and changed the surface characteristics. As shown in Fig. 1, apart from SC1, the others displayed obvious porous textures, but their pore distribution was considerably different. For SC₂, no significant pores below 1 nm width were detected and the macropore volume over 50 nm pore size of SC₂ was much more than that of SC₁. This observation matched the view that CA is a desirable macroporefabricating agent.27,28 In terms of SC3 and SC4, rich mesopores and micropores were observed, in addition to the macropores, being consistent with the activating property of ZnCl₂ and KOH. Most notably, the BET specific surface area of SC₅ reached 2654 m² g⁻¹ (Table 1), which was 4.2, 12.0, 71.5 and 88.4 fold that of SC₄, SC₃, SC₂ and SC₁, respectively. Moreover, it demonstrates a hierarchical texture with more abundant pores (Fig. S3[†]). Such a significant increase exceeded our original expectation for HF treatment. The unexpected result denoted that HF could act as an effective activator of SC. The activation role was further confirmed by the great BET increase of SC1 activated by HF alone, compared with that of unactivated SC_1 (Fig. S4[†]).

The unusual BET specific surface area of SC₅ attracted us to further probe its other properties. Fig. 2A shows the XRD spectra of SC₄ and SC₅. Compared with the XRD spectra of SC₄, SC₅ showed no SiO₂ diffraction peaks while the diffraction peaks of it were at around 25.7° and 43.1°, while the diffraction peaks of SC5 at around 25.7 (corresponding to its crystal lanes $(002)^{45}$) were widen and enhanced. These changes demonstrated that HF activation could effectively remove SiO₂ from SC₄ and made it become heterogeneous with a turbostratic graphite-like structure.45 Although no peak related to F-containing compounds was observed in the XRD spectrum of SC₅, the EDS analysis indicated that its F elemental content increased from 0.0% to 2.3%, parallel to the removal of 4.9% Si, after HF activation. And these F species were evenly dispersed in SC₅ (Fig. S5[†]). Moreover, the XPS spectrum (Fig. 2B) displayed that these F species were incorporated in the carbon network rather than occurring in the form of HF or simple fluorine ions because there was a



Fig. 1 Pore size distribution of various SCs determined by N₂ adsorption (a) and Hg intrusion (b) (insert: N₂ adsorption-desorption isotherms of SCs).

Table 1 Surface characteristics and CO2-adsorption capacity of the various SCs

Sample	$S_{\rm BET} \left(m^2 \ { m g}^{-1} ight)$	$S_{ m micro} \left({ m m}^2 { m g}^{-1} ight)$	$V_{\rm total} \left({ m ml} { m g}^{-1} ight)$	$V_{ m micro} \left({ m ml} \ { m g}^{-1} ight)$	$V_{\rm meso} ({ m ml} { m g}^{-1})$	$V_{ m macro}{}^{a} \left({ m ml} \ { m g}^{-1} ight)$	CO_2 -Adsorption capacity (mg g ⁻¹)
SC ₁	30 ± 0.15	5 ± 0.02	0.131	0.002	0.129	0	5.3 ± 0.07
SC_2	97 ± 0.45	10 ± 0.04	0.841	0.003	0.109	0.729	8.0 ± 0.06
SC_3	223 ± 1	55 ± 0.34	0.505	0.066	0.153	0.286	24.1 ± 0.18
SC_4	600 ± 3	437 ± 2	0.718	0.164	0.246	0.308	87.0 ± 0.64
SC_5	2654 ± 13	1678 ± 8	4.033	0.644	0.809	2.580	215.2 ± 2.56

^{*a*} V_{macro} : the volume of intraparticle macropores.



strong F1s peak of C–F bonds at 686.37 eV in the spectrum.⁴⁶ The high-resolution XPS (Fig. 2C) of C1s revealed that these C–F bonds were diverse. In the range of 280–300 eV, there were three individual peaks of C1s at 284.88 eV, 293.43 eV and 296.18 eV. Among them, the first shoulder peak could be deconvoluted into four peaks with binding energies of 284.88 eV, 286.43 eV, 287.43 eV and 288.83 eV. They were consistent with the C1s bond energies of C–C, C–O,⁴⁷ semi-ionic C–F (ref. 48–50) and semi-covalent C–F,^{47,50,58} correspondingly. The other two peaks of C1s could be directly assigned to those of C–F covalent bonds with high energy.⁵¹ The occurrence of non-covalent and covalent C–F hybrid bonds indicated that SC₅ was a fluorinated carbon material with a non-holonomic graphite-like structure, *i.e.*, with numerous active groups and surficial defects.³⁸

The formation of these diverse C–F bonds was also somewhat unexpected because the original intention behind HF treatment was to desilicate SC₄. Moreover, the formation of C–F groups on the carbon surface was generally *via* the oxidation of F₂, XeF₂, *etc.*⁵⁰ However, some researchers found that HF which has no oxidability could etch carbon materials, but the mechanism of the etching process was not very clear.^{52,53} X. Yang *et al.* have once demonstrated that HF etching of graphene oxide occurred *via* epoxy addition, carbonyl addition and hydroxyl substitution (reactions (2)–(4)).^{54–56} Because there were many similar oxygenated groups, such as hydroxyl and epoxy groups, in SC,⁵⁶ and the oxygen content of SC activated by HF was considerably reduced (from 36.7% to 15.5%), as shown in Fig. 2A, it was believed that the formation of these C–F bonds in SC_5 was possibly also *via* the addition or substitution of these oxygenated groups.

$$\begin{array}{c} OH \\ HO \end{array} + 2HF \longrightarrow \begin{array}{c} F \\ HO \end{array} + 2H_2O \qquad (2)$$

$$\overset{O}{\downarrow} + 2HF \longrightarrow \overset{F}{\searrow} F + H_2O$$
 (4)

3.2. Dependence of SC activation on CO2 adsorption

Fig. 3A presents the effect of CA activation on CO_2 adsorption of SC. It can be seen from the figure that the capture capacity firstly increased and then slightly declined with the increase of added CA. The maximum adsorption capacity was 8.0 mg g⁻¹, being 1.5 fold that of SC₁ unactivated by CA. Unfortunately, the increase ratio of the adsorption capacity was far lower than that of their BET surface (about 3.2 fold). This suggested that the activation with CA alone was not an excellent method in view of the CO_2 adsorption capacity. This was possible because CA activation mainly generated macropores, as shown in Fig. 1, and the size of the macropores did not match with that (about 0.6 nm) for suitable CO_2 adsorption.⁴³



Fig. 3 Dependence of CO₂ adsorption on activation conditions of SCs (A: effect of activator amount, B: effect of activation temperature; adsorption conditions: 25 °C, 1 bar).

Fig. 3A also displays the effect of ZnCl_2 activation on CO_2 adsorption of SC. The enhancement effect of ZnCl_2 on CO_2 adsorption was noticeably greater than that of CA. Its maximum adsorption capacity was 24.1 mg g⁻¹. The adsorption capacity was 4.6 and 3.0 fold that of the virgin SC₁ and SC₂ respectively, but still much lower than the reported adsorption capacities for many carbon materials.⁵⁴ Thus, SC₃ was further activated with KOH in order to further promote its CO₂ adsorption. Fig. 3B shows that the maximum CO₂-adsorption capacity of SC activated by KOH at 650 °C reached 87.0 mg g^{-1} , being 16.4 fold that of SC₁. The enhanced effect was consistent with the great increase of its micropore volume after KOH activation.

As mentioned before, SC generally requires demineralization by various inorganic acids,³² in which, the Si element is generally removed by HF activation.^{35,36,57} Unexpectedly, HF activation of SC₄ caused an unusual increase of its CO₂ adsorption, in addition to removing the Si element in this investigation. As indicated in Fig. 4A, the maximum capacity reached as high as 215.2 mg g⁻¹. It was about 2.5 times



Fig. 4 Dependence of CO_2 adsorption capacity of SC_5 on HF activation conditions (A–D show the effects of HF concentration, activation temperature, activation time and reuse number on the CO_2 adsorption capacity of SC, respectively. Adsorption conditions: 25 °C, 1 bar, 2 h).

that of SC₄, close to the decrease (2.4 times) of their packing densities. The similarity indicated that the increased pores were very suitable for the CO₂ adsorption. S. Jung *et al.* comprehensively summarized the recent developments of porous carbons for CO₂ capture.¹⁵ The adsorption capacity of SC₅ was very close to the maximum CO₂ adsorption capacity (220.0 mg g⁻¹ for 1 bar and 25 °C) of biochar, as shown in Table S1;¹⁵ Moreover, the adsorption selectivity of SC₅ for CO₂ and N₂ was also increased by 2.2, compared with that of SC₄. Such an enhancement further indicated that SC₅ was more suitable for CO₂ adsorption (Fig. S6[†]).

At the same time, it was observed that the increase was rather dependent on the temperature and time of HF activation (Fig. 4B and C). The optimal temperature and HF concentration were 30 °C and 9 h, respectively. Fig. 4D illustrates the changes of CO₂ adsorption capacity during the repeated use of SC₅. The CO₂ uptake retention was as high as 93.8%, after 10 adsorption–desorption cycles, indicating the high stability and reusability of SC₅. The slight decrease of CO₂ capture capacity was possibly due to a small amount of chemisorption of trace impurities for CO₂, which was not easy to desorb at 200 °C. These results showed that SC₅ was a great potential carbon material for CO₂ capture.

Fig. 5A presents the effect of HF activation on the adsorption kinetic curves of the SCs. They could be well fitted with the linear driving force model: $\ln[Q_m/(Q_m - Q_t)] =$ kt, where Q_t is the amount of the adsorbed CO₂ with time t, $Q_{\rm m}$ is the maximum adsorption capacity, t is the adsorption time and k is the adsorption rate constant.⁵⁸ The adsorption rate constant k of SC₅ was fitted as 1.22 min⁻¹, as shown in Fig. 5B, which was 1.47 times the adsorption rate constant of SC_4 (0.83 min⁻¹). The fitted result indicated that HF activation could still significantly accelerate the adsorption speed of CO₂, in addition to increasing the adsorption capacity. The adsorption rate constant exceeded those of many reported activated carbons, such as a commercial activated carbon (0.93 min⁻¹),⁵⁹ wheat flour biochar (0.198 min⁻¹), and waste ion-exchange resin-based activated carbons (0.35 min⁻¹),⁶⁰ but was less than the adsorption rate constant (1.87 min⁻¹) of nitrogen enriched activated

resin.61 urea-formaldehvde carbon derived from Additionally, it was also observed that their adsorption capacities in the first 2 minutes accounted for 95.5% and 83.9% of their overall adsorption capacity, exceeding the ideal adsorption ratio (80%) required for practical application.^{62,63} Thus, it could be expected that SC₄ and SC₅ both possessed desirable practicability in view of adsorption kinetics. For comparison, Fig. 5B also shows the adsorption kinetic curve of SC activated only by ZnCl₂-KOH, but not by CA. Its adsorption capacity in the first 2.5 minutes accounted for 77.4% of the overall adsorption capacity, which was less than the ideal adsorption ratio for practical application.⁶³ The results indicated that CA activation is also important to prepare SCs with potential for actual carbon capture and storage in view of adsorption kinetics, although it does not have a great contribution to adsorption capacity. This was possibly because CA activation could increase the macropores of SCs, which could provide more transport channels for CO₂ adsorption.^{27,28}

3.3. Enhancement mechanism of HF activation

Considering that the activation mechanisms of CA, $ZnCl_2$ and KOH have been reported by others, this section focused on investigating the enhancement mechanism of HF activation. As seen from above discussions, the enhancement effect of HF activation mainly included the remarkable increases of specific surface area and CO_2 adsorption capacity of SC.

To understand the origin of the significant increase of specific surface area, several experiments were conducted. Firstly, microstructural changes of the SCs were investigated with the G and D band ratio of their Raman spectra. The I_D/I_G value can be used as an indicator of the disorder degree of carbon material structure, including defects in the chemical and crystal structures, *etc.*^{64–67} Fig. 6A presents the Raman spectra of the SCs before and after HF activation. The well-defined peaks of the D and G bands for all SCs were observed at about 1346 cm⁻¹ and 1610 cm⁻¹, respectively, but their area ratios (I_D/I_G) were different. For the SC derived from the



Fig. 5 Adsorption kinetic curves (A) and fitted curves (B) of CO₂ on three SCs (adsorption conditions: 25 °C, 1 bar).

Si-free sludge, the I_D/I_G values before and after HF activation were 1.9 and 3.2, respectively. The significant increase of the $I_{\rm D}/I_{\rm G}$ value suggested that HF activation could result in a considerable increase in the disorder degree of Si-free SC. This increase possibly originated from the etching action of the chemical reactions (2)-(4).⁵⁶ For the SC containing 4.9% Si, the I_D/I_G values before and after HF activation were 2.0 and 3.9, respectively. The increase of the I_D/I_G value before and after HF activation was greater than that of the $I_{\rm D}/I_{\rm G}$ value of Si-free SC. Moreover, the higher the Si content of SC, the higher the I_D/I_G values after HF activation, as shown in Fig. 6B. Evidently, the great increase of the I_D/I_G value was also highly dependent on the existence of Si-containing substances. According to reaction (1), the main difference of HF activation for SCs with and without Si was whether there was the generation of SiF₄ gas (Fig. S7[†]).^{35,36} Therefore, the great increase of $I_{\rm D}/I_{\rm G}$ was inferred to possibly be related to the expansion action of SiF4 gas from the inside reaction of HF and SiO₂, which led to the microstructural variation of SC, in addition to the chemical etching effect of HF.

This inference was confirmed by the heterogeneity change of interplanar spaces of the SCs after HF activation. As shown in Fig. 2A, the XRD diffraction peaks of the 002 crystal faces of SC₄ and SC₅ were both broad peaks, indicating that they possessed various interlayer distances. These distances could be calculated with the Bragg equation and various 2θ data of the XRD diffraction peaks. As seen in Fig. 6C, before HF activation, these interlayer distances were located mainly in the range of 0.2–0.4 nm, which were near the *d*002 (0.34 nm) of typical graphite carbon.⁶⁸ After HF activation, the interplanar spacing of 0.2–0.4 nm was reduced while the interplanar spacing of 0.4-0.6 nm was increased (15% to 30.5%). Particularly, graphite-like carbons with an expanded interlayer spacing of about 0.60-0.75 nm were clearly observed in the HRTEM image of SC₅ (Fig. 7). Thus, combined with the Raman spectra, it was reasonable to infer that the significant increase of the specific surface area of the SCs after HF activation was mainly attributed to the formation of rich expanded interlayer space-type pores (slittype pores) that mainly originated from the expansion action of SiF₄ gas escaping. However, it was also observed that the change of surface area was strongly dependent on the concentration of HF, as shown in Fig. S8.† After adding different concentrations of HF, the specific surface area of the SCs increased obviously because the expansion action of SiF₄ gas increased the space between SC layers, generating more slit-shaped micropores. However, when the concentration of added HF was too high, the specific surface area of the SCs decreased. It was possibly because the expansion action of the generated SiF₄ gas was so great that the interlayer slits of the SCs excessively expanded, leading to the increase of macropores. The BET specific surface area (808 m² g⁻¹) and CO₂ adsorption capacity (112.6 mg g⁻¹) of SC desilicated with HF before pyrolysis were much lower than those of SC₅, further confirming the pore-forming role of SiF₄ in the activation process.

The N_2 adsorption-desorption isotherm (the inset of Fig. 1) of SC₄ and SC₅ exhibited the characteristics of type I with H4 hysteresis.⁶⁹ In other words, they both possessed slit-shaped pores, but the slit-shaped pores of SC₅ were much more than those of SC₄ according to the relative height of their adsorption isotherms. And, there is also a high nitrogen



Fig. 6 Effect of Si content on the properties of SC (A: Raman spectra of Si-containing and Si-free SCs before and after HF activation; B: I_D/I_G of desilicated SC vs. Si content in the original SC; C: distribution of the interplanar spacing of d002 in SC₄ and SC₅ and D: CO₂ adsorption capacity of SCs vs. Si content of SCs before and after HF activation).



Fig. 7 HRTEM images with various interplanar spacings in SC_5 .

adsorption at low relative pressure which indicated that SC_5 possessed more micropores.⁷⁰ Thus, this result indicated that HF activation of SC could form rich interlayer slit-shaped pores with the expansion action of SiF₄ gas.

Fig. 8A presents the CO_2 adsorption-desorption isotherms of SC_4 and SC_5 by the pressure swing method. It could be observed that the CO_2 adsorption amount of SC_5 at low pressure was much higher than that of SC_4 , which indicated that SC_5 possessed more micropores compared with SC_4 . This result was also consistent with the N_2 adsorption-desorption curve of SC_5 in Fig. 1, which showed that SC_5 had a high N_2 adsorption capacity at low pressure with no hysteresis, indicating that SC_5 is microporous.⁷¹

To further uncover the mechanism of the CO₂-uptake enhancement from HF activation, the pressure swing adsorption isotherms of CO₂ on SC₄ and SC₅ at different temperatures were also determined (Fig. S9†). Based on these isotherms, the isosteric adsorption heat (ΔH) of SC₄ and SC₅ between 0 and 10 °C and 0 and 25 °C were calculated using the Clausius–Clapeyron equation. As indicated in Fig. 8B and C, the maximum ΔH values of SC₄ and SC₅ were both lower than 50 kJ mol⁻¹, and were located in the range of physical adsorption energy.⁶⁷ Such low ΔH values denoted a low regeneration cost for both SC₄ and SC₅, compared to amine solutions.⁷²

In addition, it was observed that, for the approaching zero-loading, the ΔH of SC₄ was 29.2 kJ mol⁻¹ while the ΔH of SC₅ reached as high as 44.8 kJ mol⁻¹. The latter was 1.5 times the former. The great increase of the approaching zero-loading ΔH denoted that SC₅ possessed many stronger adsorption sites than SC₄ since the isosteric adsorption heat at zero-loading can be commonly used as a measure of the intrinsic affinity of adsorbate molecules to adsorption sites.⁷³ According to the main difference in the chemical composition and microstructure between SC₅ and SC₄, it was inferred that these strong adsorption sites were the micropores from the expansion of the *d*002 interlayer space and/or the C–F functional groups.

In order to confirm this inference, the CO₂ adsorption energy (E_a) of various adsorption sites (micropores with different sizes and/or typical functional groups) were calculated by the DFT method and simplified adsorption models (Fig. S1[†]) according to the fluorination reactions (2)-(4). $E_{a(3.4)}$, $E_{a(5.5)}$, $E_{a(6.5)}$ and $E_{a(7.5)}$ of pores with a fixed d002 interlayer size of 0.34 nm, 0.55 nm, 0.65 nm and 0.75 nm were 6.6 eV, 0.033 eV, -0.325 eV and -0.272 eV, respectively. But, the E_a values of micropores with the expandable d002interlayer size of 0.34 nm, 0.55 nm, 0.65 nm and 0.75 nm were 6.6 eV, -0.869 eV, -0.297 eV and -0.380 eV, respectively. Considering that there were potentially both expandable and fixed d002 interlayer spaces in the SCs for CO2 adsorption, it was concluded from the E_a values that the micropores of about 0.55-0.65 nm were the most suitable for CO_2 adsorption. The range of the suitable pore sizes was related to that of the increased micropores after HF activation in Fig. 6C and consistent with the reported results by X. Hu et al. and A. Rehman et al.^{40,43} $E_{a(hydroxyl)}$, $E_{a(epoxy)}$ and $E_{a(C-F)}$ of hydroxyl, epoxy and C-F groups were calculated to be -0.074 eV, -0.057 eV and -0.133 eV, respectively. These results



Fig. 8 Adsorption isotherms and isosteric adsorption heat ΔH of CO₂ on SC₄ and SC₅ at different temperatures.

indicated that the C–F groups were more CO_2 -philic, compared with the hydroxyl and epoxy groups. The DFT calculation results were consistent with the reported electrical action (C–F $\delta^- \cdots \delta^+ CO_2$) between strong polar C–F groups and high quadrupole CO_2 , respectively.^{74–77}

It was noticed that the increase in CO_2 adsorption of SC_5 was not as obvious as the increase of its BET specific surface area. This was possibly because the size of many newly formed pores after HF activation was not very suitable for CO_2 adsorption. Thus, how to generate more ultra-micropores in the size range of 0.55–0.65 nm needs further research.

4. Conclusion

It was found that simple HF-treatment of SC could result in multiple and pronounced improvements on its performance, in addition to the intended desilication, in this investigation. These included a remarkable increase of BET specific surface area and CO₂ adsorption capacity, and formation of C-F bonds. The significant increase of the BET surface area was due to the combined activation effect of the physical action of SiF₄ gas escaping and the chemical etching of HF on SC. And, the formation of C-F bonds was dependent on the epoxy addition, carbonyl addition or hydroxyl substitution. The ultrahigh capacity could be due to the formation of abundant CO₂-philic expanded interlayer space-type ultramicropores and C-F functional groups in the SCs after HF treatment. These findings provided a facile way to upgrade the performance of sludge carbons for capturing greenhouse gases and will be beneficial to understanding the interaction of biochar and CO₂ in the environment.

Conflicts of interest

The authors declare no competing financial interest.

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