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Characterization of a cetyltrimethyl ammonium bromide-modified sorbent for removal of perfluorooctane sulphonate from water

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This study was carried out to develop a cost-effective and practicable sorbent for application in abrupt perfluorooctane sulphonate (PFOS) pollution accidents. The main merit of this work was that a waste material, namely construction and demolition (C&D) waste, was employed as a raw base material for the sorbent synthesis. The waste material underwent alkaline fusion-hydrothermal synthesis and a cationic surfactant cetyltrimethyl ammonium bromide (CTAB) modification process to form a CTAB-modified sorbent (CMCDSS). Experimental results showed that PFOS concentrations and solution pH had significant effect on the PFOS sorption on construction and demolition waste synthesized sorbent (CDSS) and CMCDSS (using 0.2CMCDSS as representative). PFOS could be effectively and rapidly adsorbed on CMCDSS, and sorption equilibrium was achieved within 2.5 h. The sorption amounts of PFOS on CMCDSSs enhanced along with the increase in CTAB loading amounts. Moreover, the CMCDSS can be applied effectively under acidic condition at pH 2–6 and various removal mechanisms were clarified at different sorption conditions. Accordingly, this work developed a novel and applicable material for dealing with abrupt environmental PFOS contamination accidents.

Keywords: PFOS sorption; construction and demolition waste; fusion-hydrothermal synthesis; CTAB-modified sorbent; hydrophobic partition

1. Introduction

In recent years, abrupt environmental pollution accidents, such as nitrobenzene pollution accident in Songhua River and arsenic contamination accident in Su river of Shandong province, frequently emerged. Nevertheless, less attention but not less importance, has been paid to future potential abrupt environmental pollution accidents. Because of lacking cost-effective alternative technologies in certain applications, perfluorooctane sulphonate (PFOS) and related substances are still largely manufactured and used. Once the abrupt PFOS pollution accident emerges in waters, the PFOS concentration will be high. PFOS and its derivatives have been extensively used as surfactants for industrial applications and commercial products, mainly to repel dirt, water and oils.[1] These compounds are defined as a special type of persistent organic pollutants with a strong fluorine–carbon bond that can effectively shield carbons by the highly electronegative fluorines posing high chemical and thermal stability.[2] Moreover, the oleophobic and hydrophobic properties of the fluorinated alkyl chain provide it with greater ability to lower the surface tension of water than non-fluorinated surfactants.[3]

The widespread use and mass production have resulted in an extensive release of PFOS and its derivatives into

the environment either from direct sources such as the manufacturing of PFOS and the use of products containing PFCs, or from indirect sources like reaction impurities or degradation of precursors.[4,5] PFOS is not amenable to biological treatment due to their outstanding stability against microbial attack. Thus far, various chemical treatment approaches, including reduction with zero-valent iron in subcritical water,[6] photolysis treatment,[7] advanced oxidation process,[8] electrolytic oxidation treatment,[9] sonochemical treatment,[10,11] electro-microfiltration treatment,[12] dc plasma method [13] and oxidation under alkaline condition,[14] have been employed to the decomposition of PFOS. However, these treatment technologies present various drawbacks and limitations, mainly due to their high energy demand and/or specific conditions requirement. Some technologies including coagulation and sorption were also reported to remove PFOS from aqueous solution. Conventional coagulation during drinking-water treatment removed only less than 20% of PFOS and PFOA (perfluorooctanoic acid).[15] Among these, sorption has been proved to be an effective and commercial approach for the PFOS removal in wastewater, and some adsorbents such as ion-exchange polymer,[16,17] activated carbon,[16–20]

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zeolite,[21] molecularly imprinted polymer adsorbents,[22] resins,[18,23,24] alumina,[25,26] clay,[27,28] activated sludge,[19,29] carbon nanotube [30–32] and aminated rice husk [33] have been studied for the sorption performance of PFOS from aqueous solution. Among these adsorbents, porous materials normally have high sorption capacity for PFOS, but the sorption velocity is generally slow, while non-porous materials usually possess fast sorption but low sorption capacity.

Recently, it was reported that cationic surfactant cetyltrimethyl ammonium bromide (CTAB)-loaded zeolite-based sorbent is much more effective for the PFOS removal.[34] In our previous study, co-combustion ash was derived to synthesize zeolite-based adsorbent for heavy metal removal,[35] and moreover, a special functional material, namely ceramsite-zeolite composite, was successfully prepared using construction and demolition (C&D) waste as raw material,[36] elucidating that C&D waste possesses the potential to be converted into zeolite-like materials.

The main objective of this research was to develop a low-cost and effective surfactant-modified sorbent using C&D waste as a base material for application in abrupt PFOS pollution accidents in which the PFOS concentration would be very high. For this purpose, the sorbent should have the properties of rapid sorption and relatively high sorption capacity, and can be subjected to mass production. High concentrations of PFOS were used in our study to simulate the abrupt PFOS polluted water. The sorption behaviours and mechanisms of PFOS on the sorbent were investigated in detail and the optimum sorption parameters were established.

2. Materials and methods

2.1. Materials

The C&D waste employed in this study was provided by a baking-free brick plant in Xianyang, Shaanxi province, China. This region disposes more than 100,000 tons of C&D waste every year. The main components of the C&D waste include brick scraps, concrete scraps, crushed stone, waste soil, waste glasses, etc. The raw material was first crushed into small scraps with the size of 1–3 cm, then pulverized by a ball grinder and sieved through an 80 mesh sieve. The main chemical composition of the raw

material analysed by X-ray fluorescence (XRF) is listed in Table 1. Perfluorooctane sulphonate (PFOS, potassium salt) was obtained from Alfa Aesar (Ward Hill, MA, USA). HPLC-grade methanol was from Fisher Chemical (USA). Ammonium acetate (NH_4OAc , chromatographically purity >99.9%) that was used to prepare the mobile phase in ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS) analysis was obtained from Anaqua Chemicals Supply (USA). Cationic surfactant CTAB ($\text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{NBr}$) was from Shanghai Reagent Corporation (Shanghai, China). Other chemicals (GR) were from Beijing Chemicals Corporation and were used as received without further purification.

2.2. CTAB-modified sorbent synthesis

The C&D waste powder was added in the diluted hydrochloric acid solution (1%, wt%) at the ratio of 1:5 (g : mL). The mixture was stirred at room temperature for 0.5 h to mainly remove the components containing carbonate in the C&D waste powder and decrease the iron components to some extent. The solids were separated by filtration, washed several times with distilled water (until the solution close to neutralization) and then dried in an oven at 105°C. Then, the alkaline fusion-hydrothermal synthesis process was performed for the preparation of the sorbent based on previous report.[35]

Five grams of the foregoing powder was mixed and ground with NaOH powder to obtain a homogeneous mixture, then heated in a nickel crucible at 500°C for 1 h with the NaOH/C&D powder ratio 1 (g:g). The fusion products were then ground and transferred into 200 mL reaction bomb with 50 mL distilled water together followed by an ageing process with vigorous shaking at room temperature for 12 h. The mixture then underwent the hydrothermal process at 90°C for 6 h. The solids were recovered by vacuum filtration, washed for several times with distilled water until the solution reached pH 10 and dried in an oven at 105°C. The construction and demolition waste synthesized sorbent was identified as CDSS and ground to an 80 mesh size for further treatment and application.

The CTAB solution was prepared by addition of different amounts (0.2, 0.4 or 0.8 g) of CTAB into 100 mL of hot Milli-Q water, and then 2 g CDSS powder was added into the prepared CTAB solution. The mixture was stirred

Table 1. Chemical composition analyses of C&D waste by XRF (% by weight).

Elements analyses										
O	Si	Ca	Al	Fe	K	Mg	Na	Ti	S	others
45.89	26.85	10.66	6.48	3.84	2.59	1.08	1.37	0.49	0.24	0.51
Components analyses										
SiO_2	CaO	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	TiO_2	Others	
57.43	14.92	12.25	5.49	3.12	2.86	1.84	0.59	0.57	0.93	

slightly to avoid the formation of spume in a water bath at 80°C for 2 h. The solids were recovered by vacuum filtration and subsequently washed with Milli-Q water until no Br⁻ could be detected. The moist solid material was dried at 60°C and ground with a mortar to an 80 mesh size. The CTAB-modified sorbents were denoted as *n*CMCDSS (*n* = 0.1, 0.2 and 0.4), where the prefix numbers represent the weight ratio of CTAB/CDSS.

2.3. Characterization

XRF was utilized to determine the chemical composition of C&D waste and CDSS with a scanning rate of 8 deg/min using XRF-1800 (Schimadu, Japan). X-ray diffraction (XRD) analysis for C&D waste, CDSS and CMCDSS (using 0.2CMCDSS as representative) was performed using a Philips XRD meter (Philips PW 1700, Holland). Operating conditions were 45 kV and 250 mA using Cu-K radiation. The 2 θ scanning range was 10–80°. Fourier transform infrared (FTIR) spectroscopy of CDSS and CMCDSS was performed by the KBr method recorded on a Bruker Tensor 27 (Bruker, German), scanned from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹. N₂ adsorption–desorption isotherms of samples were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (–196°C). The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The Brunauer–Emmett–Teller method was utilized to calculate the specific surface area.

2.4. Sorption experiments

All sorption experiments were carried out in an orbital shaker at 150 rpm and 25°C for 16 h (except for sorption kinetics experiment). In all of the sorption experiments, 75 mg sorbent (CDSS or different types of CMCDSSs) was added into a 250 mL polypropylene flask (VITLAB, German) containing 150 mL PFOS solution. The sorption kinetics experiment was carried out in a 250 mL polypropylene flask (VITLAB, German) containing 150 mL of 150 mg L⁻¹ PFOS solution at pH = 5.5. The sorption isotherm experiments were carried out with PFOS initial concentrations ranging from 200 to 550 mg L⁻¹. The concentration effect experiments were carried out with initial PFOS concentrations ranging from 50 to 550 mg L⁻¹. In the sorption kinetics, concentration effect experiments and sorption isotherm experiments, all the solution pH was adjusted to 5.5 by the addition of 0.1 M HCl or 0.1 M NaOH solution; during the pH adjustment, the increased solution volume was negligible. In the pH effect experiments, the initial solution concentration was 100 mg L⁻¹, and the initial solution pH varied from 2.0 to 10.0.

2.5. PFOS determination and quality assurance

After the sorption experiments, the mixture was filtered by a filter with a 0.22 μ m nylon membrane. At least 2 mL

mixture was filtered by a filter with a 0.22 μ m nylon membrane, and the initial eluate was discharged, the residual eluate was quantitatively transferred to polypropylene volumetric flask and diluted using Milli-Q water before determination. The control experiments indicated that the adsorption of PFOS on the membrane was negligible due to the high PFOS concentration in the solution. A UPLC-MS/MS was employed to determine the PFOS concentration. The quantitative determination of PFOS was carried out with an external standard method, and the average value of all data that was determined three times was adopted. The UPLC system (Waters Corp., USA) was equipped with a C18 column (2.1 $\times$ 50 mm i.d., particle size 1.7 μ m, Waters Corp., USA) and the MS system was a Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) equipped with an electrospray ionization source. Reported analytical procedures were referred for the determination.[37] The mobile phase consisted of a binary mixture of solvent A (2 mM ammonium acetate in 100% methanol) and solvent B (2 mM ammonium acetate in water/methanol, v/v = 95/5) at a flow rate of 0.3 mL/min. The mobile phase gradient started with 25% solvent A and 75% solvent B, and linearly ramped to 85% solvent A and 15% solvent B in 5 min, then ramped down to 25% solvent A and 75% solvent B in following 2 min. The column was allowed to equilibrate for 3 min. The total running time was 10 min and 10 μ L solution was injected. The tandem MS analysis was conducted using the multiple reactions monitoring mode, and the cone voltage and collision energy were 30 and 11 V, respectively. Spike and recovery experiments were conducted to determine the precision and accuracy of the analytical procedure, the recovery of PFOS ranged from 80% to 112% for water samples. The detection limit of this instrument was 1 ng L⁻¹. The amount of PFOS sorption on the CDSS and CMCDSS was calculated according to the difference of initial and equilibrium PFOS concentrations.

2.6. Zeta potential measurement

The zeta potentials of CDSS and CMCDSS at room temperature were measured using Zetasizer 2000 (Malvern, Worcestershire, UK). The suspension for zeta potentials was prepared by adding CDSS or CMCDSS (0.5 g) into 1 L Milli-Q water. The injection volume for measurement was about 10 mL. Solution pH values were adjusted in the range of 2.0–10.0 by the addition of 0.1 M HCl or NaOH solution. The average value of all data that was determined five times was adopted.

3. Results and discussion

3.1. Characterization of CDSS and CMCDSS

As showed in Tables 1 and 2, C&D waste and CDSS mainly comprised silicon oxide (SiO₂), calcium oxide (CaO), aluminium oxide (Al₂O₃), iron oxide (Fe₂O₃), potassium oxide

Table 2. Chemical composition analyses of CDSS waste by XRF (% by weight).

Elements analyses										
O	Si	Al	Ca	Fe	K	Mg	Na	Cl	Ti	others
49.47	26.30	7.82	5.76	3.73	2.82	1.53	1.08	0.49	0.42	0.58
Components analyses										
SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂	Others		
58.37	15.23	8.52	5.70	3.58	2.61	1.49	0.74	3.76

Figure 1. XRD analysis of the C&D waste, CDSS and CMCDSS.

(K₂O), magnesium oxide (MgO) and sodium oxide (Na₂O). Figure 1 shows that the main phases in the C&D waste are quartz, calcite, microcline, albite and pirssonite. After the alkaline fusion-hydrothermal synthesis process, the main phase in the CDSS was sodium aluminium silicate (Na_{1.84}Al₂Si_{2.88}O_{9.68}) and the minor phase was calcium silicate hydrate (Ca_{1.5}SiO_{3.5}·xH₂O). The disappearance of calcite and pirssonite and reduction of calcium oxide (CaO) were attributed to the dissolution of carbonate in the diluted hydrochloric acid solution. After the CTAB modification, the diffraction peak of sodium aluminium silicate (Na_{1.84}Al₂Si_{2.88}O_{9.68}) disappeared, a new crystalline phase (symbol N in Figure 1) generated, indicating that successful CTAB modification occurred via the reaction between CTAB and Na_{1.84}Al₂Si_{2.88}O_{9.68}. FTIR spectra between 4000 and 600 cm⁻¹ for CDSS and CMCDSS are illustrated in Figure 2. The range from 3100 to 3700 cm⁻¹ corresponded to the -OH stretching.[38] The band at around 1645 cm⁻¹ corresponded to bending vibration of water. The bands at around 1480, 2850 and 2920 cm⁻¹ were

assigned to symmetric and asymmetric stretching vibration of C-N, CH₂ and CH₃, indicating the successful CTAB modification.[39] The band of CDSS at around 1168 cm⁻¹ may be assigned to the antisymmetric stretching vibration of Si-O-Si,[40] after CTAB modification, the band at 1168 cm⁻¹ showed a slight shift to lower frequency (1160 cm⁻¹). The specific surface area and the total pore volume of CMCDSS were calculated at 308.2 m² g⁻¹ and 0.29 cm³ g⁻¹; the specific surface area and the total pore volume of CDSS were 251.4 m² g⁻¹ and 0.19 cm³ g⁻¹, respectively.

3.2. PFOS sorption behaviours on CDSS and CMCDSS

3.2.1. Effect of the solution pH on sorption properties

PFOS, with a negative pK_a value (-3.27),[41] existed in an anionic form within the pH range (2.0–10.0) tested in this study. The sorption of PFOS at different pH was affected by the characteristics of the sorbent surface. In

Figure 2. FTIR spectra of CDSS and CMCDSS.

general, lowering solution pH makes the sorbent surface more positively charged, which promotes PFOS sorption (enhanced PFOS-surface interaction).

The effect of varying solution pH on the sorption of PFOS by CDSS and CMCDSS is shown in Figure 3(a). It can be seen that pH values of solution had significant effect on PFOS sorption, the variation tendency of PFOS removal by CMCDSS and CDSS in the studied pH range was approximate. The lowest PFOS removal percentage by CMCDSS and CDSS appeared at pH 6.0, simultaneously. In this study, the sorption amount of PFOS by CMCDSS was highest at pH 2.0. The sorption amounts of PFOS by CMCDSS decreased gradually with the increase in the solution pH at pH ranging from 2.0 to 6.0, increased gradually at pH ranging from 6.0 to 9.0, then decreased. The value of pH 6.0 was the first inflection point of the variation tendency curve of PFOS removal by CMCDSS, and the value of pH 9.0 was the second inflection point. Similarly, the sorption amounts of PFOS by CDSS presented downtrend with the increase in the solution pH ranging from 2.0 to 6.0. There were three inflection points of the variation tendency curve of PFOS removal by CDSS in the studied pH range, the three points were pH 3.0, 6.0 and 8.0, respectively. At the same condition of pH, the removal of PFOS by CMCDSS was much higher than that by CDSS, indicating that the hydrophobic partition to the CTAB was responsible for the enhanced removal.

Solid/solution distribution coefficients, K_d , were utilized and calculated from the sorption experiments data to

compare the relative sorption by CDSS and CMCDSS, the K_d can be expressed as follows [28]:

$$K_d = \frac{\text{mg of PFOS/kg of solid}}{\text{mg of PFOS/L of water}} = \frac{L}{\text{kg}}. \quad (1)$$

Figure 3(b) depicts the effect of increasing the solution pH on the PFOS distribution coefficients. The K_d values of CDSS were all smaller than those of CMCDSS at the same solution pH. The smallest K_d values of CDSS and CMCDSS all appeared at pH 6.0. The K_d values' variation tendency of PFOS on CMCDSS and CDSS were consistent with the variation tendency of PFOS removal by CMCDSS and CDSS at the same pH range, and the K_d value of CMCDSS increased significantly at pH 3.0.

Figure 4 depicts the zeta potentials of CMCDSS and CDSS at different pH values. Since the pH at point of zero charge (pHpzc) of CDSS is about 4.4, the CDSS has a positive edge below pH 4.4, and a negative edge and basal surfaces above pH 4.4. Contrasted with the previous research,[34] the zeta potentials of the CMCDSS were all positive in the pH range studied. The zeta potentials of the CMCDSS increased gradually at a pH ranging from 6.0 to 9.0. The zeta potentials of the CDSS increased at a pH ranging from 2.0 to 3.0, then decreased gradually with the increase in the solution pH. From Figure 4, it can be seen that electrostatic attraction contributed to the sorption to a certain extent. Electrostatic

Figure 3. Effect of solution pH on: (a) PFOS sorption on CDSS and CMCDSS and (b) distribution coefficient K_d values for PFOS (initial PFOS concentration = 100 mg L^{-1} , equilibrium concentrations ranges of PFOS were $0.32\text{--}34.85 \text{ mg L}^{-1}$ and $31.32\text{--}68.68 \text{ mg L}^{-1}$ for CMCDSS and CDSS, respectively).

attraction could not well elucidate the underlying sorption mechanism, besides hydrophobic partition and electrostatic attraction (or repulsion), hydrogen-bond interaction and ligand exchange partly participated in the sorption of PFOS and the combined interaction was responsible for the sorption.

3.2.2. Effect of PFOS concentrations on sorption properties

Figure 5 depicts the effect of initial concentrations on the sorption of PFOS by CDSS and CMCDSS. It can be seen that the PFOS removal percentage by CDSS increased gradually in the initial PFOS concentrations ranging from 50

Figure 4. Effect of solution pH on zeta potentials of CDSS and CMCDSS.

Figure 5. Effect of initial PFOS concentrations on PFOS sorption on CDSS and CMCDSS (solution pH = 5.5).

to 550 mg L⁻¹. In contrast, the PFOS removal percentage by CMCDSS decreased rapidly with the increase in initial PFOS concentrations at the concentrations range of 50–200 mg L⁻¹, then the removal percentage of PFOS kept

relatively stable at the initial PFOS concentrations range of 200–550 mg L⁻¹.

In our study, the initial PFOS concentrations affected the PFOS sorption on CMCDSS to a certain extent. At

Figure 6. Distribution coefficient K_d values for PFOS vs. equilibrium concentrations of PFOS, C_e . (initial PFOS concentrations were 50, 100, 150, 200, 250, 300, 350, 400, 450, 500 and 550 mg L^{-1} , respectively)

the condition of same pH and different initial PFOS concentrations, reduction of sorption sites and positive charge could mainly elucidate the decrease in PFOS removal by CMCDSS at initial PFOS concentrations ranging 50–200 mg L^{-1} . Besides, hydrophobic interaction between the perfluoroalkyl tails and the hydrophobic moieties on the CDSS/CMCDSS surface could explicate the PFOS sorption enhancement on CDSS and relatively stable PFOS removal percentage by CMCDSS. The initial PFOS concentrations ranging from 200 to 550 mg L^{-1} were applied in the following sorption isotherm experiments for the sorption on CMCDSSs and CDSS, respectively.

Correction analysis between calculated K_d and PFOS equilibrium concentrations (C_e , mg L^{-1}) was conducted. The results in Figure 6 show that there is a significant correlation between K_d and C_e . The K_d values of CMCDSS decreased with the increase in PFOS equilibrium concentrations, indicating that the sorption of PFOS on CMCDSS became weaker with the increase in PFOS equilibrium concentrations, although the PFOS sorption amounts on CMCDSS kept increasing. On the contrary, the K_d values of CDSS increased with the increase in PFOS equilibrium concentrations, meaning that the sorption of PFOS and PFOS sorption amounts on CDSS kept increasing, simultaneously.

3.2.3. Sorption kinetics

Figure 7 shows the sorption kinetics of PFOS on CMCDSS and CDSS. The PFOS sorption on the CDSS was instable,

sorption and desorption dynamically varied, about 12 h were required to reach the sorption equilibrium for PFOS on CDSS. Compared with the sorption stability on CMCDSS and CDSS, it can be concluded that CTAB can enhance the PFOS sorption stability and CMCDSS can be efficiently and stably utilized for the PFOS sorption. Besides, the sorption of PFOS on CMCDSS was very rapid; after 5 min, about 75% of the maximum sorption amount of PFOS on CMCDSS at pH = 5.5 was achieved, and sorption equilibrium was achieved after about 2.5 h sorption. The CMCDSS and CDSS used in this study were all ground into powder below 180 μm and the sorbents were all porous materials, the sorption mainly occurred on the surface resulting in the fast sorption; the CTAB load enhanced the sorption amount and shortened the time required to reach sorption equilibrium.

To further understand the sorption kinetics of PFOS sorption on CMCDSS, the pseudo-second-order model, which assumes that the sorption rate is controlled by chemical sorption, was selected to fit the kinetics data. The model can be expressed as follows.[18,34,42]

$$t/q_t = 1/(kq_e^2) + t/q_e = 1/v_0 + t/q_e, \quad (2)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of PFOS adsorbed on the sorbent at equilibrium and at time t (h), respectively, and k ($\text{g mg}^{-1} \text{h}^{-1}$) is the pseudo-second-order sorption rate constant. v_0 ($\text{mg g}^{-1} \text{h}^{-1}$) represents the initial sorption rate.

As can be seen in Table 3, the pseudo-second-order model fitted the sorption data on CMCDSS well

Figure 7. Sorption kinetics of PFOS on CDSS and CMCDSS (solution pH = 5.5, temperature = 25°C).

Table 3. Kinetic parameters of the pseudo-second-order for PFOS sorption on CMCDSS.

Aqueous medium	pH	Pseudo-second-order parameter			R^2
		k ($\text{g mg}^{-1} \text{h}^{-1}$)	q_e (mg g^{-1})	v_0 ($\text{mg g}^{-1} \text{h}^{-1}$)	
Mili-Q water	5.5	0.085	146.12	1.825×10^3	0.998

according to the high correlation coefficient ($R^2 = 0.998$). The CMCDSS possessed faster PFOS sorption than granular active carbon ($4.73\text{--}45.1 \text{ mg g}^{-1} \text{h}^{-1}$) listed in the literature,[18,20] implying that CMCDSSs can be well utilized for abrupt PFOS pollution accidents.

3.2.4. Sorption isotherm

After fitting the isotherm data to typical isotherm models (Langmuir equation, Freundlich equation and Dubinin–Ashtakhov equation), it was found that the Freundlich equation could well describe the experimental data. The Freundlich equation is defined by

$$q_e = K_F C_e^{1/n}, \quad (3)$$

or

$$\ln q_e = 1/n \ln C_e + \ln K_F, \quad (4)$$

where q_e (mg g^{-1}) is the equilibrium sorption amount, C_e (mg L^{-1}) is the equilibrium concentration of PFOS in solution, K_F (mg g^{-1}) (mg L^{-1}) is the Freundlich adsorption constant or capacity factor and $1/n$ is the Freundlich exponent, an indicator of non-linearity, for $n = 1$ the partition between the two phases is independent of the concentration and the isotherm becomes linear. The goodness of fit of this model is judged based on the linear regression correlation coefficient, R^2 .

Sorption isotherms of PFOS on CDSS and CMCDSSs are shown in Figure 8 and the determined Freundlich constants are listed in Table 4. It was found that sorption isotherms of PFOS on CDSS and CMCDSS were nicely fitted with the Freundlich isotherm ($R^2 = 0.955\text{--}0.996$), their sorption capacities were of the following order as $\text{CDSS} < 0.1\text{CMCDSS} < 0.2\text{CMCDSS}$ (CMCDSS) $< 0.4\text{CMCDSS}$, the maximum PFOS sorption amounts on the 0.1CMCDSS, 0.2CMCDSS (CMCDSS) and 0.4CMCDSS were 289, 326 and 345 mg g^{-1} , respectively. PFOS sorption amounts enhanced with the increase in CTAB loading amounts.

3.3. Sorption mechanisms

The sorption of PFOS on CDSS and CMCDSS was complex; electrostatic attraction, hydrophobic partition, hydrophobic interaction, ligand exchange reaction and hydrogen-bond interaction were involved in the PFOS sorption at different conditions.

Figure 8. Freundlich sorption isotherms of PFOS on CDSS and CMCDSSs.

Table 4. Freundlich model parameters and sorption coefficients of PFOS on CDSS and CMCDSSs.

Sorbent	Freundlich constants			
	K_F (mg g^{-1}) (mg L^{-1}) ⁻ⁿ	n	R^2	N
CDSS	0.039	1.457	0.996	8
0.1CMCDSS	5.766	0.646	0.969	8
0.2CMCDSS	2.284	0.816	0.955	8
0.4CMCDSS	1.143	0.945	0.956	8

As can be seen from Figures 3(a), 3(b) and 5, compared with the remarkable difference of PFOS removal percentages by CDSS and CMCDSS, it can be concluded that hydrophobic partition to the CTAB was the dominant factor, responsible for the enhanced PFOS sorption amount at the same pH and initial PFOS concentration (100 mg L^{-1}). The hydrophobic moieties (the tails) of CTAB formed a hydrophobic sink for hydrophobic chemicals, thereby enhancing the PFOS sorption amounts. The result was consistent with the previous observation where the presence of the cationic surfactant of CTAB remarkably enhanced the sorption of PFOS.[43]

Previous reports [25,26] have shown that $\text{C}_8\text{F}_{17}\text{SO}_3^-$ could replace the surface hydroxyl groups by ligand exchange. The ligand exchange reaction can be expressed as follows:

In this study, the broad FTIR spectra band at $3100\text{--}3700 \text{ cm}^{-1}$ range indicated that abundant hydroxyl groups existing on the surface of CDSS can facilitate the ligand exchange reaction. Previous researches [25,26] also reported the ligand exchange reaction increased within the pH range (4.0–7.5) with the increase in the solution pH. Considering the specific observation in our experiment, we supposed that the ligand exchange reaction continued to increase with the pH increased within the pH range 2.0–10.0 in our experiment, and ligand exchange played a significant role in PFOS sorption under neutral and alkaline conditions for PFOS sorption on CDSS.

It has been reported that F and $-\text{SO}_3^-$ in PFOS molecule could easily facilitate the generation of hydrogen-bond under acidic condition, and the hydrogen-bond interaction increases along with the decrease in pH values.[44] Meanwhile abundant hydroxyl groups existing on the surface of CDSS/CMCDSS could also facilitate the generation of hydrogen-bond. In this study, the increasing generation of hydrogen-bond on the surface of PFOS molecule and CDSS/CMCDSS corresponding to the increasing H^+ concentration in the solution can enhance the PFOS sorption via hydrogen-bond interaction.

Hydrogen-bond interaction between F and $-\text{SO}_3^-$ in PFOS molecule and ligand exchange reaction were the dominant factors in the PFOS sorption on CDSS and CMCDSS under acidic condition (pH range 2.0–6.0 in this study). The observed increase in PFOS sorption on CDSS and CMCDSS following the decrease in the solution pH was

attributed to the increase in hydrogen-bond interaction counteracted by the reduced ligand exchange reaction (and electrostatic repulsion for PFOS sorption on CDSS at pH range 4.4–6.0). The highest electrostatic attraction at pH 3.0 contributed to the enhanced PFOS sorption on CDSS. Ligand exchange reaction and electrostatic attraction were the dominant factors in the PFOS sorption on CMCDSS within the solution pH range (6.0–10.0). Within the solution pH range 6.0–9.0, the increasing PFOS sorption amounts on CMCDSS were mainly attributed to the electrostatic attraction due to the moderate enhancement of zeta potentials and the increasing ligand exchange reaction between PFOS and hydroxyl groups. Within the solution pH range 9.0–10.0, the decreasing PFOS sorption amounts on CMCDSS were mainly attributed to the decrease in zeta potentials and the gradual decrease in hydroxyl groups.

Ligand exchange reaction and electrostatic repulsion were the dominant factors in the PFOS sorption on CDSS within the solution pH range (6.0–10.0). The increase in sorption amounts on CDSS at the solution pH range 6.0–8.0 was attributed to the enhanced ligand exchange reaction counteracted by the increasing electrostatic repulsion. Increasing electrostatic repulsion contributed to the reduction of PFOS sorption amounts on CDSS. Besides, the gradual decrease of hydroxyl groups inhibited the ligand exchange reaction and the replacement of hydroxyl groups from CDSS by PFOS. Inhibited ligand exchange combined with increasing electrostatic repulsion led to the reduction of PFOS sorption amounts on CDSS at pH range 8.0–10.0.

As can be seen from Figures 5 and 8, the PFOS sorption amounts on CDSS and CMCDSS enhanced corresponding to the increasing initial PFOS concentrations. The hydrophobic interaction between PFOS molecule and adsorbed PFOS was responsible for the phenomenon, which was consistent with previous research.[45] When all the sorption sites were completely covered by PFOS molecule, other PFOS molecules in the solution could adsorb on the adsorbed PFOS via hydrophobic interaction.

During the PFOS sorption on CMCDSS at different initial PFOS concentrations, hydrophobic partition to CTAB was prior to other hydrophobic interaction. The reduction of sorption site provided by CTAB and positive charge could be responsible for the decrease in the PFOS removal percentage at the initial PFOS concentrations range of 50–200 mg L⁻¹. With further increase in PFOS concentrations, the sorption sites provided by CTAB were completely covered, PFOS molecules had the chance to adsorb on the adsorbed PFOS via hydrophobic interaction, which explicated the enhanced sorption amounts of PFOS on CMCDSS. Hydrophobic interaction between PFOS molecules and adsorbed PFOS was also the dominant factor for the increasing PFOS sorption amounts on CDSS with the increase in PFOS concentrations depicted in Figures 5 and 6.

4. Conclusions

A low-cost and effective sorbent (CMCDSS) was successfully synthesized from C&D waste undergoing for application in abrupt PFOS pollution accidents in the present study. Solution pH PFOS concentrations had significant effect on the PFOS sorption on CDSS and CMCDSS. The sorption of PFOS on CMCDSS was rapid and sorption equilibrium was achieved within 2.5 h. The PFOS sorption amounts of CMCDSSs enhanced with the increase in CTAB loading amounts, and the CTAB-modified sorbent (CMCDSS) could be effectively applied in acidic condition at pH 2–6, more effectively and efficiently in the low pH solution.

In the PFOS sorption process under different solution systems, the dominant factors affecting PFOS sorption were different; electrostatic attraction, hydrophobic partition, hydrophobic interaction, hydrogen-bond interaction and ligand exchange reaction were involved in the PFOS sorption.

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