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Enhanced adsorption of aqueous perchlorate on quaternary ammonium chloride surfactant-modified activated carbon fibers

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ABSTRACT

Perchlorate contamination of drinking water and groundwater is a worldwide concerned issue, and technologies are needed for the treatment of aqueous perchlorate. In this study, activated carbon fibers (ACFs) and quaternary ammonium chloride surfactant-modified ACFs were tested for perchlorate removal from aqueous solution. The ACFs modified by cetyltrimethyl ammonium chloride (CTAC) exhibited the best performance on perchlorate adsorption. Batch experiments were performed to investigate the equilibrium, thermodynamics, kinetics, and mechanism of perchlorate adsorption onto CTAC-ACFs. The results showed that the spontaneous perchlorate adsorption process followed the Langmuir isotherm and the pseudo-second-order kinetic model. Perchlorate adsorption onto CTAC-ACFs was enhanced as the initial perchlorate concentration, contact time, and solution temperature increased. Alkaline pH and higher ionic strength did not favor the adsorption of perchlorate. Ion exchange between the perchlorate and carried chloride was the major adsorption mechanism, but other adsorption processes (e.g. electrostatic attraction and physical adsorption) may also play important roles for the adsorption. The CTAC-ACF adsorbent showed a relatively high adsorption capacity of 26.74 mg/g (at an initial perchlorate concentration of 20 mg/L). Moreover, its well stability and regenerability enable it as a potential adsorbent material for the decontamination of aqueous perchlorate.

Keywords: Perchlorate; Active carbon fibers; Adsorption; Quaternary ammonium chloride surfactants

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1. Introduction

Recent years, perchlorate contamination has been frequently detected in groundwater, surface water, drinking water, and soil systems in many countries such as the Unite States, Japan, China, Korea, and India [1,2]. Perchlorate salts are widely applied in industry and used for manufacturing matches, airbag inflators, rockets, safety flares, explosives, and fireworks [3,4]. Perchlorate has raised public health concerns because it can inhibit the iodide uptake in the

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thyroid gland and possibly cause mental retardation in fetuses and infants [5,6].

Although perchlorate is a strong oxidant due to the high oxidation state of chlorine, its oxidizing power is retarded because of its high activation energy (120 kJ/mol), which results in a stable existing of perchlorate contamination in the normal environment for several decades [7]. Therefore, an increased interest has been focused on the removal of perchlorate contamination from groundwater and drinking water. Various physical, chemical, and biological methods, including adsorption, ion exchange, membrane, chemical reduction, electrochemical reduction, microbial reduction, and integrated technologies have been used for the treatment of perchlorate-bearing water [3,8,9]. Among these methods, adsorption is a common removal technique for perchlorate due to low initial cost, ease of operation, simplicity of design, and insensitivity to toxic substances [8]. At present, a number of adsorbents, including powdered and granular activated carbon (GAC) [10–12], protonated cross-linked chitosan [13], acid-washed zero-valent aluminum [14], calcined layered double hydroxides [15], quaternary amine modified reed [16], and granular ferric hydroxide [17] have been already applied in the treatment of perchlorate contamination. Among these adsorbents, the GAC is the most common adsorbent due to its low cost, safety, and easy to be retrofitted to target perchlorate [8,9].

In recent years, activated carbon fibers (ACFs) have received increasing attention as an adsorbent for purifying air and water [18]. ACFs possess a number of significant advantages over the traditional powdered activated carbon and GAC, such as high adsorption capacity and fast adsorption rate in gas or liquid phase [19]. ACFs are highly microporous materials with low mesoporosity and absence of macroporosity, and their uniform micropores directly connected to the external surface [20]. Moreover, the fibrous shape of ACF allows its use in various physical forms such as felt, fabrics, and monoliths [19]. A number of researchers therefore have applied ACFs in aqueous media for the removal of trichloroethylene [20], phenolics [21,22], nitrates [23], *p*-nitrophenol [24], dyes [25], and organic compounds [26]. Based on the fact that the surface chemistry significantly impacts the adsorption property of activated carbon [19], some scholars tailored the surfaces of ACFs for selective adsorption of one molecule over others. For example, Mangun et al. obtained a high removal rate of SO_2 from flue gases using ammonia-modified ACFs due to the incorporation of the nitrogen functional groups [27]. Yi et al. increased the adsorption capacities of ACFs for VOCs by modifying the surface with $CuSO_4$ [28]. Rong et al. found that the amount of formaldehyde adsorbed by the *p*-aminobenzoic acid modified ACFs increased on the introduction of amino groups [29]. However, no work has been done regarding the use of ACFs or modified ACFs for the removal of perchlorate from aqueous solution.

The present study aims to investigate the feasibility of uptaking perchlorate using ACFs and modified ACFs. A number of quaternary ammonium chloride surfactants are used to modify the ACFs and the best one among them is selected for further study. The current work systemically investigates the mechanism, adsorption thermodynamics, and the adsorption kinetics of perchlorate onto the modified ACFs. The effect of water chemical conditions (pH, initial perchlorate concentration, and ionic strength) on perchlorate adsorption is investigated. Furthermore, the stability and regenerability of the adsorbents are studied to evaluate their safety and cost-effectiveness in the application to drinking water and groundwater treatment systems.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

The polyacrylonitrile-based ACF used in this study was purchased from Carbon Fiber co., LTD, Jiangsu Kejing, China. All chemicals used were of A.R. grade and obtained from Sinopharm Chemical Reagent, Shanghai, China. The ACFs were first boiled in deionized water for 30 min, then washed repeatedly with distilled water to remove the impurities, and dried at 80℃ for 24 h. Four types of quaternary ammonium chloride surfactants, tetramethylammonium chloride (TMAC), *n*-octyltrimethylammonium chloride (OTMA), cetyltrimethyl ammonium chloride (CTAC), and octadearyldimethylammonium chloride (OTAC) were used as the modifiers. The critical micelle concentrations (CMC) for OTMA, CTAC, and OTAC are 140, 1, and 0.3 mM at 25℃, respectively. The modified ACFs were prepared by mixing 0.2 g pristine ACFs with 100 ml 5 mM quaternary ammonium chloride surfactant in a 150 ml erlenmeyer flask, the mixture was shaken in a rotary shaker at room temperature for 12 h at a speed of 120 rpm. After filtered and repeatedly washed with distilled water, the modified ACF absorbent was finally oven-dried at 50℃ for 24 h in air, and used for the subsequent characterization and adsorption experiments. The total organic carbon (TOC) contents of the initial solution (before the addition of ACFs) and the final solution (after mixing for 12 h) were determined using a Multi N/C 2100 TOC analyzer (Analytik Jena, Germany) to calculate the loading amount of surfactants on the pristine ACFs.

According to the calibration curve between TOC value and the concentration of surfactants, the loading amount of surfactants (M, mmol/g) could be calculated by Eq. (1). Due to the background TOC from the deionized water, the determination limit of the method was 0.4 mg/L CTAC. The concentration of surfactants was double-checked by the Tsubouchi dye protocol using a two-phase titration [30], and a regression analysis between these two methods showed a well agreement.

$$M = \frac{V(C_{s0} - C_{sf})}{m_{ACFs}} \tag{1}$$

A fourier transform infrared spectrometer (FTIR Spectrometer, NICOLET 5700) was used to determine the surface functional groups of the pristine ACFs and the modified ACFs. The morphology was observed using a scanning electron microscopy (SEM, FEI Sirion field emission). An elemental analyzer (EA, Vario III) was used to determine the C, N, and H contents. The surface charges were determined using a zeta-potential analyzer (ELS-8000, Photal, Ostsuka Elec). The released Cl^- from the adsorbent in solution was determined by ion chromatography (IC, DX-120, DIONEX).

2.2. Adsorbate and chemicals

$NaClO_4$ was selected as the adsorbate in the present study. A stock solution of 100 mg/L ClO_4^- was prepared by dissolving 141.2 mg $NaClO_4 \cdot H_2O$ in one liter of deionized water. The working solutions with appropriate concentrations were obtained by diluting the stock solution with deionized water. The pH of solution is not adjusted if not elsewise specified. A perchlorate ion selective electrode (Model K-27502-35, Cole-Parmer, US) was used to determine the perchlorate concentration (0.7 mg/L detection limit). CH_3COONa of 1 M was used as the total ionic strength adjustment buffer for determination.

2.3. Procedure of batch adsorption experiments

Batch experiments were conducted by mixing 50 mg as-prepared adsorbents with 100 ml 20 mg/L perchlorate solution in a 150 ml erlenmeyer flask. The solution with an initial pH of ~6.7 was shaken at 120 rpm at a constant temperature of 25°C for 2 h, which was more than sufficient for reaching the adsorption equilibrium. After adsorption, the residual perchlorate was determined by centrifuging the reaction mixture and measuring the supernatant. If not otherwise specified, all batch experiments followed above conditions. The equilibrium adsorbed amount (q_e, mg/g) of perchlorate onto the pristine and modified ACFs can be calculated by Eq. (2).

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

For selecting the best modifier from the four types of surfactants, the adsorption capacities of the modified ACFs (TMAC-ACFs, OTMA-ACFs, CTAC-ACFs, and OTAC-ACFs) were determined, respectively. The one with the largest q_e was selected as the adsorbent for further study. Isotherm experiments were conducted at different initial perchlorate concentrations (5, 10, 20, 30, 40, and 50 mg/L) at different solution temperatures (25, 45, and 60°C). The obtained experimental data were also used for thermodynamics analysis. Kinetic experiments were conducted at different temperatures (15, 30, 45, and 60°C). At predetermined times, the amount of the adsorbed perchlorate at time t (q_t, mg/g) and perchlorate removal efficiency (η_r, %) was calculated by Eqs. (3) and (4), respectively. In the tests to evaluate the effect of pH and ionic strength, the solution pH was adjusted to the desired values, and ionic strength was represented by NaCl concentration (0 ~ 50 mmol/L).

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{3}$$

$$\eta_r = \frac{C_0 - C_t}{C_0} \times 100\% \tag{4}$$

2.4. Stability and regenerability experiments

The leaching amount of the surfactant in aqueous solution was measured to evaluate the stability of the adsorbent. Fifty milligram ACFs were immersed in 200 ml sterilized deionized water at room temperature for 32 d. The TOC of the solution was measured after 2, 4, 8, 16, and 32 d of immersion. The concentration of the surfactant was then determined using the TOC data as aforementioned. The percentage of leaching out at time t (η_{lt}, %) was calculated by Eq. (5).

$$\eta_{lt} = \frac{m_{lt}}{m_s} \times 100\% \tag{5}$$

The regenerability of the adsorbent was also investigated. Fifty milligram saturated absorbent was immersed in 200 ml 1 M HCl solution for 24 h at room temperature. After washed with deionized water repeatedly and dried at 50°C, the adsorbent was used to adsorb the perchlorate again and the adsorption capacity after regeneration was investigated. The regeneration efficiency ($\eta_{\rm rg}$, %) was calculated using Eq. (6).

$$\eta_{\rm rg} = \frac{q_{en}}{q_{{\rm e}(n-1)}} \times 100\% \tag{6}$$

2.5. Adsorption isotherm, thermodynamics, and kinetics

Two commonly used models, the Langmuir isotherm which assumes that adsorption takes place on homogeneous surfaces, and the Freundlich isotherm which assumes that adsorption takes place on heterogeneous surfaces, were selected to simulate the adsorption isotherm. The Langmuir model can be described as Eq. (7), and the dimensionless constant separation factor ($R_{\rm L}$), which is used to characterize the adsorption equilibrium, can be calculated by Eq. (8) [31]. The Freundlich model can be expressed by Eq. (9) [32].

$$q_{\rm e} = \frac{Q_{\rm m} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{7}$$

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_0} \tag{8}$$

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{9}$$

Thermodynamic parameters for the adsorption of perchlorate can be determined using Eqs. (10)–(12).

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

$$\ln K_{\rm d} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

$$\Delta G = -RT \ln K_{\rm d} \tag{12}$$

Pseudo-first-order model and pseudo-second-order model are used to investigate the mechanism of adsorption and the transient behavior of perchlorate adsorption. The integral form of the pseudo-first-order model is generally described as Eq. (13) [33,34].

$$\log{(q_{\rm e} - q_{\rm t})} = \log\ q_{\rm e} - \frac{k_s}{2.303} t \tag{13}$$

The integral form of the pseudo-second-order model is generally described as Eq. (14) and the initial sorption rate h can be calculated by Eq. (15) [33,34].

$$\frac{t}{q_{\rm t}} = \frac{t}{q_{\rm e}} + \frac{1}{k_2 q_{\rm e}^2} \tag{14}$$

$$h = k_2 q_{\rm e}^2 \tag{15}$$

3. Results and discussion

3.1. Selection of modifier

Four types of quaternary ammonium chloride surfactants with different surfactant tail lengths were selected to modify ACFs. Fig. 1 shows the equilibrium adsorbed amount ($q_{\rm e}$) of perchlorate onto the pristine and four types of modified ACFs adsorbents. As can be seen, the $q_{\rm e}$ of the pristine ACFs is only 9.73 mg/g, which is lower than that of every modified ACF adsorbent, but higher than the commercial GAC (6.64 mg/g, determined by the same method). Among the four types of modified ACFs, CTAC-ACFs, and OTAC-ACFs exhibit larger adsorption capacity than TMAC-ACFs and OTMA-ACFs, and the CTAC-ACFs is the best one. The loading amounts of different surfactants onto ACFs were further analyzed by the TOC method (described in section 2.1) and double-checked by the Tsubouchi dye protocol. As can be observed, the loading amount of surfactant shows an order of CTAC > OTAC > OTMA > TMAC, which well explains the difference of adsorption capacities between these four surfactant-modified adsorbents. CTAC and OTAC are quaternary ammonium chloride surfactants with longer surfactant tails, which increased the hydrophobicity of the surfactant molecules, and further

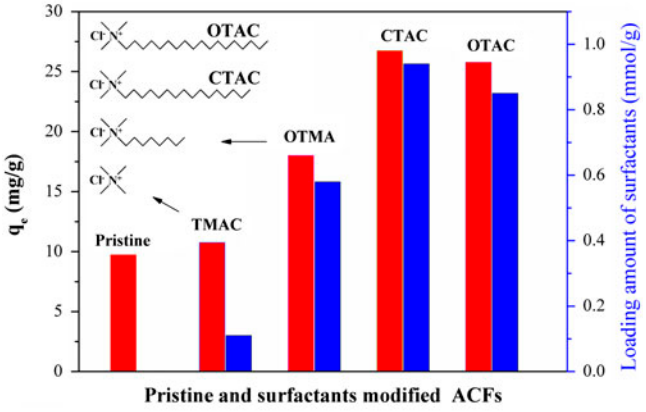

Fig. 1. Comparison of $q_{\rm e}$ and loading amount of surfactant for the pristine ACFs and four types of surfactant-modified ACFs. The red column and blue column correspond to $q_{\rm e}$ and loading amount, respectively.

enhanced the anchoring of the surfactant molecules onto the surface of ACFs through hydrophobic attraction. Thus, more surfactants were loaded and better performance was observed for CTAC-ACFs and OTAC-ACFs. On the other side, longer surfactant tail may strengthen steric effect and inhibit the further anchoring of surfactants. Therefore, the hydrophobicity and steric effect of the long chains are the two sides of the same coin, resulting in the best performance at the chain length of 16 carbons. According to analytical results, the CTAC-ACFs showed the largest q_e of 26.74 mg/g and the best removal efficiency of 67%, therefore it was selected for further study.

3.2. Characterization of pristine ACFs and CTAC-ACFs

Fig. 2(a) presents the FTIR spectra of pristine ACFs and CTAC-ACFs. Several peaks appeared on both spectra. The peak at 3,410 represents –OH and/or N–H group, and the peak at 2,920 cm^{-1} is assigned to aliphatic C–H group [35]. The peak at 1,560 cm^{-1} corresponds to the aromatic ring stretching of both C=C and C=N groups. The peak at 1,070 cm^{-1} indicates the vibrational modes of both C–H and N–H. The C=N and N–H groups are apparently derived from the ACF itself, because the ACF was made from polyacrylonitrile materials. The difference of the two FTIR spectra is from two wavenumbers, 1,487 and 708 cm^{-1}, as indicated in the figure by the red dash lines. Wavenumber 1,487 cm^{-1} is associated with the bending vibration of the $(CH_3)_4N^+$ cation (δ_{as}(C–H)), while the broad peak at 708 cm^{-1} is due to the presence of methyl group of $(CH_3)_4N^+$ [36]. The emerging peaks at CTAC-ACFs basically suggested that CTAC was successfully loaded on the surface of ACFs. It's worth noting that the loaded CTAC had little influence on the morphologies of the ACFs. As shown in the insets of Fig. 2(a), the CTAC-ACFs demonstrated a smooth surface as same as that of the pristine carbon fibers.

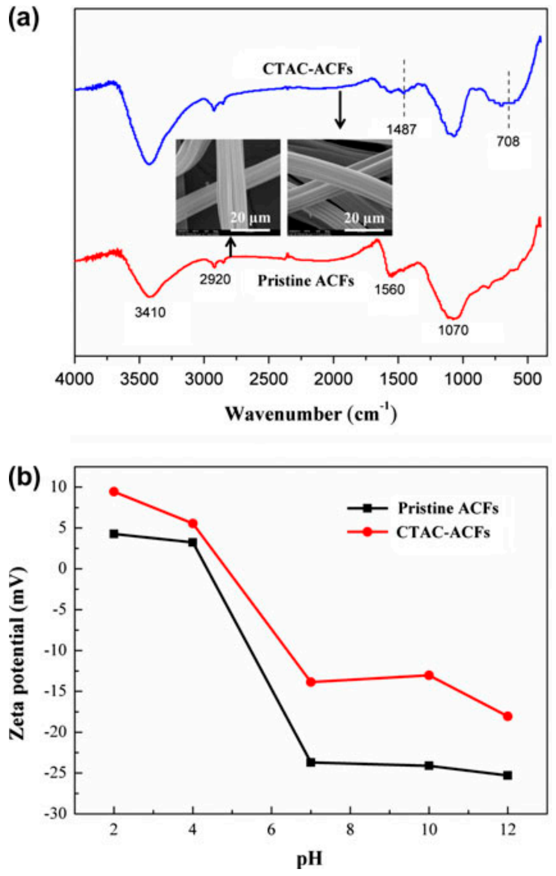

Fig. 2. (a) FTIR of the pristine ACFs and CTAC-ACFs (insets are the SEM graphs). (b) Zeta potentials of pristine ACFs and CTAC-ACFs solutions at different pHs. 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH.

Elemental analysis on the adsorbents was also carried out. The results revealed that the load of CTAC significantly increased the nitrogen and hydrogen contents of ACFs and slightly decreased the carbon content of ACFs. Specifically, hydrogen content increased from 1.66% of pristine ACFs to 3.08% of CTAC-ACFs, and nitrogen content increased from 2.65% of pristine ACFs to 4.65% of CTAC-ACFs. Meanwhile, carbon content decreased from 67.38% of pristine ACFs to 62.25% of CTAC-ACFs. The rising of N and H contents is apparently due to the presence of the quaternary ammonium group. The elemental analysis further confirms the loading of CTAC molecules onto ACFs. It should be pointed out that we also conducted XPS analysis on the pristine ACFs and CTAC-modified ACFs, however, the presence of the N1s broad peak in the pristine ACFs, did not allow us to confirm the loading of CTAC surfactant using XPS analysis.

The Zeta potentials of the pristine ACFs and CTAC-ACFs were studied in the aqueous solution as a function of pH. The results, as shown in Fig. 2(b), reveal that the Zeta potentials of both adsorbents negatively shift as the pH increased from 2 to 7, but become relatively stable in the pH range of 7 to 12. The pHs of the point of zero charge (pH_{pzc}) for pristine ACFs and CTAC-ACFs are 4.3 and 4.9, respectively. Over the entire pH range from 2 to 12, the Zeta potentials of pristine ACFs are always lower than these of CTAC-ACFs. That is to say, the modified ACFs are more positively charged in the aqueous solution. The reason for this phenomenon was primarily attributed to electropositive quaternary ammonium functional groups, which were anchored onto the surface of ACF and increased the surface potential.

3.3. Adsorption isotherms, kinetics, and thermodynamics

3.3.1. Adsorption equilibrium isotherm

The adsorption isotherm can be used to describe how the adsorbate interacts with the adsorbent and give an idea about the adsorption capacity of the adsorbent. The adsorbent surface phase is generally considered as a monolayer or multilayer [35]. The Langmuir isotherm and Freundlich isotherm are valid for monolayer and multilayer adsorption, respectively. Fig. 3(a) shows the comparison of the Langmuir isotherm (Eq. (7)) and the Freundlich isotherm (Eq. (9)) fittings for CTAC-ACFs at three different temperatures (25, 45, and 60℃). Isotherm parameters obtained by the fitting are listed in Table 1. From Table 1, the correlation coefficients (R^2) for both isotherms suggest that the Langmuir isotherm shows a better fit to the adsorption data than the Freundlich isotherm at all temperatures, indicating that the adsorption of perchlorate on CTAC-ACFs is a monolayer adsorption process. When the C_e is around 22.5 mg/g, the maximum adsorption capacity (Q_m) increases from 35.49 to 55.26 mg/g with the increasing of temperature from 25 to 60℃. The dimensionless constant separation factor R_L, which expresses the essential features of the Langmuir isotherm, is used to predict if the adsorption process is "favorable" or "unfavorable" [37]. The R_L calculated by Eq. (8) are shown in Fig. 3(b). Apparently, R_L is always in the range from 0 to 1, which implies that the perchlorate adsorption onto CTAC-ACFs is "favorable" for all the cases. Moreover, the value of R_L decreases with the increasing of the initial perchlorate concentration and solution temperature, indicating that higher perchlorate concentrations and higher temperatures are more conducive to the perchlorate adsorption onto CTAC-ACFs.

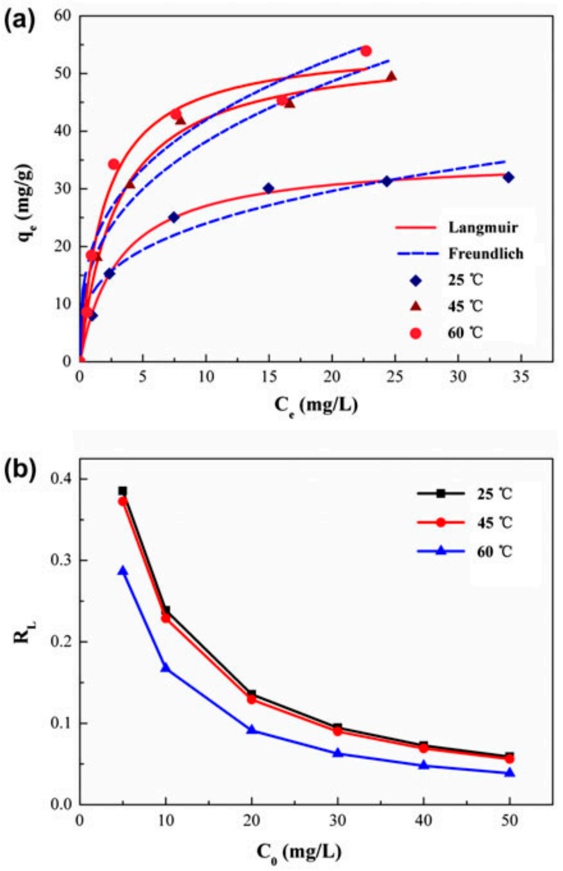

Fig. 3. (a) Adsorption isotherms of perchlorate adsorption onto CTAC-ACFs (at 25, 45, and 60℃), and the fitting curves by the Langmuir model and the Freundlich model. (b) The changes of dimensionless constant separation factor R_L. Initial perchlorate concentrations were 5, 10, 20, 30, 40, and 50 mg/L, respectively.

3.3.2. Adsorption thermodynamics

The Gibb's free energy, entropy, and enthalpy changes (ΔG, ΔS, and ΔH) for the perchlorate adsorption, determined by Eqs. (10)–(12), are tabulated in Table 2 for the further analysis on the nature of adsorption. As can be seen, the positive values of ΔH confirm the endothermic nature of adsorption when the adsorption was progressing. The ΔG value is minus and decreasing at elevated temperatures, suggesting that the spontaneous adsorption process was enhanced at higher temperatures. Meanwhile, the positive value of entropy change (ΔS) implies that increased randomness at the solid/solution interface occurred in the internal structure of the adsorbents [35].

3.3.3. Adsorption kinetics

Kinetics experiments were conducted to determine the uptake rate and equilibrium time of the perchlo-

Table 1
Parameters for the Langmuir and Freundlich isotherm models

Model	Parameter	Temperature 25℃	45℃	60℃
Langmuir isotherm	R^2	0.998	0.994	0.979
	Q_m (mg/g)	35.49	54.68	55.26
	K_L (L/mg)	0.32	0.34	0.50
Freundlich isotherm	R^2	0.949	0.945	0.931

Table 2
Thermodynamic parameters for adsorption of perchlorate at different temperatures

T (K)	ΔH (J/mol K)	ΔG (J/mol K)	ΔS (J/mol K)
298	4,065	−2,715	22.75
318	4,136	−3,098	
333	4,051	−3,525	

rate adsorption onto CTAC-ACFs [16]. Fig. 4 presents the kinetics of perchlorate adsorption onto CTAC-ACFs at different temperatures. As can be observed, the amount of adsorbed perchlorate (q_t) increases with time and eventually reaches equilibrium (q_e) within 30 min in which two distinct adsorption stages are observed. The first stage was signified by a steep slope, reflecting the rapid adsorption rate during the first 15 min of contact. In this stage, around 90% of the total perchlorate was removed. The rapid adsorption rate was mainly due to instantaneous monolayer adsorption of perchlorate at the surface of CTAC-ACFs. The second stage, which took place between 15 and 30 min, characterized a gentle slope and a gradually decreasing adsorption rate. The reduced adsorption rate was probably attributed to the rearrangement of perchlorate adsorbed on the CTAC-ACFs surface and a more thorough utilization of adsorption sites on the CTAC-ACFs. After 30 min of contact, the adsorption of perchlorate basically reached equilibrium.

The applicability of the pseudo-first-order kinetic model and pseudo-second-order kinetic model was tested for the adsorption of perchlorate onto CTAC-ACFs. Fig. 5 shows the fitting results for different temperatures and Table 3 presents the obtained parameters including linear correlation coefficients (R^2). As can be seen, the linear correlation coefficients for the pseudo-second-order model (R^2 from 0.995 to 0.999) are greater than those of the pseudo-first-order model (R^2 from 0.986 to 0.931). Furthermore, the equilibrium adsorption capacities (q_e) predicted by the pseudo-first-order kinetic model (Eq. (13)) apparently deviate from the experimental values, while the theoretical q_e predicted by the pseudo-second-order model (Eq. (14)) is very close to the experimental values. The results indicate the better applicability of the pseudo-second-order kinetic model for the adsorption of perchlorate onto CTAC-ACFs. Moreover, the values of rate constant (k_2) and initial adsorption rate (h) were also determined from the pseudo-second-order model (Eqs. (14) and (15)). The k_2 and h basically increase as the temperature goes up, being in accord with the results of the adsorption isotherm.

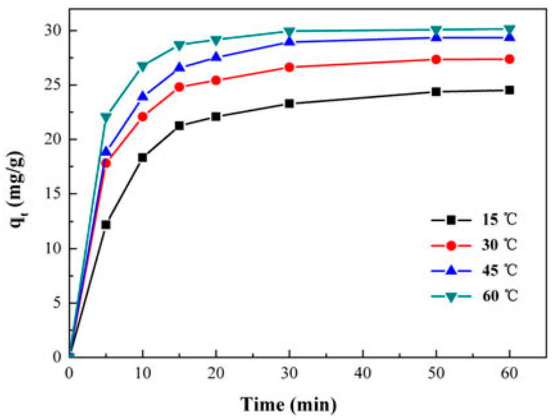

Fig. 4. Kinetics of perchlorate adsorption onto CTAC-ACFs at 15, 30, 45, and 60℃.

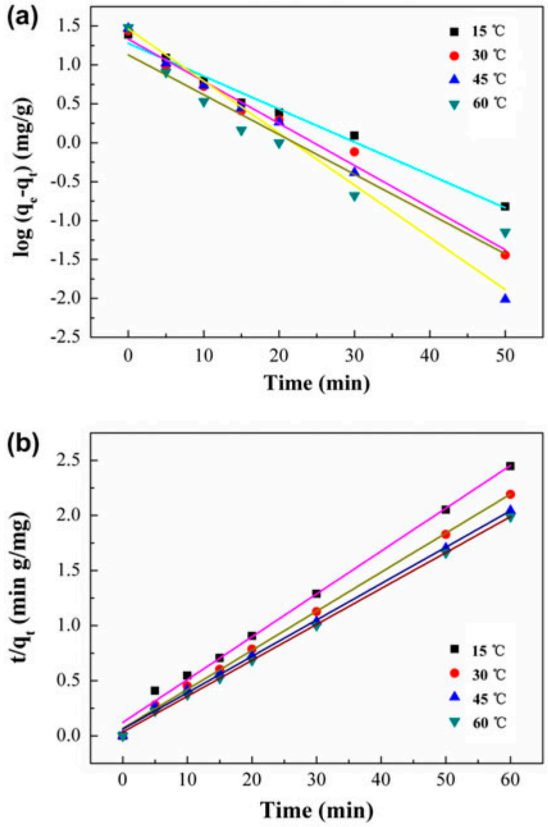

Fig. 5. (a) Pseudo-first-order kinetic model and (b) Pseudo-second-order kinetic model for perchlorate adsorption at different temperatures.

3.4. Effect of pH and ionic strength

The effect of pH on perchlorate adsorption onto pristine ACFs and CTAC-ACFs was studied in the pH

Table 3
Pseudo-first-order and Pseudo-second-order kinetic parameters

Temperature (°C)	Experimental q_e (mg/g)	Pseudo-first-order			Pseudo-second-order			
		k_s (g/mg min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	h (mg/g min)	R^2
15	24.52	0.0974	19.05	0.986	0.01248	25.71	8.25	0.995
30	27.38	0.1246	21.38	0.986	0.01861	28.26	14.86	0.998
45	29.36	0.1543	28.84	0.990	0.01784	30.34	16.42	0.998
60	30.16	0.1177	13.48	0.931	0.03119	30.73	29.50	0.999

range of 3–11 (Fig. 6(a)). As can be seen, the perchlorate adsorption capacity of pristine ACFs is almost not affected by the pH, only showing slight decrease at higher pH. In contrast, the amount of perchlorate adsorbed by CTAC-ACFs rapidly decreases from 27.21 to 10.58 mg/g due to the variation of pH from 3 to 11. As presented earlier, the loading of CTAC molecules increased the Zeta potentials of ACFs. When the pH was lower than the pH_{pzc}, the CTAC-ACFs, presenting a positive surface charge, could readily adsorb the negative perchlorate ions by the effect of electrostatic attraction. Increased pH is therefore not favorable for the perchlorate adsorption. Moreover, it is observed that excess OH^- ($pH > 9$ in Fig. 6(a)) results in a dramatical decrease in adsorption capacity, which is probably due to the competitive adsorption from OH^- and the breakdown of CTAC-ACFs. Over a wide range of pH (2–9), the adsorption capacity of CTAC-ACFs is always superior to that of pristine ACFs.

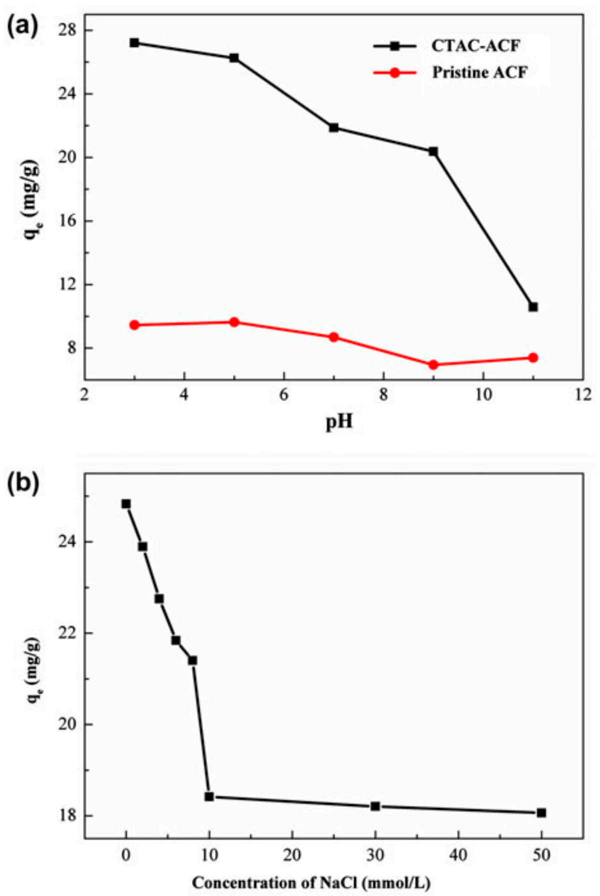

Fig. 6. (a) Effect of pH on the perchlorate adsorption onto pristine ACFs and CTAC-ACFs. (b) Effect of ionic strength on the perchlorate adsorption onto CTAC-ACFs. 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH of the solutions. NaCl was used to adjust the ionic strength.

The effect of ionic strength (NaCl) on the perchlorate adsorption onto CTAC-ACFs is presented in Fig. 6(b). As can be observed, the amount of perchlorate adsorbtion sharply decreases from 24.83 to 18.42 mg/g as the concentration of NaCl increased from 0 to 10 mmol/L. When the concentration of NaCl further increases to 50 mmol/L, the decrease becomes much more unconspicuous (from 18.42 to 18.06 mg/g). The significant inhibition on perchlorate adsorption in the initial stage may be attributed to two possible reasons: (1) competitive adsorption of Cl^- from the supporting electrolyte [38]; (2) decrease of electrostatic interaction between absorbent and adsorbate [39]. We speculate that the first reason accounts for a small part of the decrease of perchlorate adsorption, because the CTAC-ACFs already have Cl^- carrier anions. Therefore, the decrease of electrostatic interaction at higher ionic strength condition should be the main reason. We did not observe a continuous decrease of perchlorate adsorption after 10 mmol/L NaCl. This means that nonelectrostatic interactions also existed between the absorbent and adsorbate, leading to the adsorption of perchlorate. The nonelectrostatic interactions were less influenced by the ionic strength changes [39], thus a plateau of q_e (~18 mg/g) was observed after 10 mmol/L NaCl.

3.5. Adsorption mechanism

It has been reported that the specific chemical interactions between perchlorate and surface functional groups in combination with electrostatic interaction were the major mechanism for perchlorate adsorption on activated carbon [10]. However, according to the significant difference between the adsorption capacities of the pristine ACFs and CTAC-ACFs, electrostatic interaction appears not capable of accounting for the dominating adsorption mechanism of perchlorate onto CTAC-ACFs adsorbents. Considering that ion exchange interaction between perchlorate and the carrier chloride of quaternary ammonium chloride surfactants (depicted by Eq. (16)) has been revealed by some scholars [12], a quantitative analysis on the aqueous chloride favors an in-depth investigation on the adsorption mechanism. Based on Eq. (16), an index, proportion of ion exchange (η_{i}, %), is proposed to describe the proportion of $\mathrm{ClO_4^-}$ adsorbed via the way of ion exchange, as can be calculated using Eq. (17).

$$\mathrm{CTA-Cl + ClO_4^- \rightarrow CTA-ClO_4 + Cl^-} \tag{16}$$

$$\eta_{\mathrm{i}} = \frac{\Delta n_{\mathrm{Cl^-}}}{\Delta n_{\mathrm{ClO_4^-}}} \times 100\% \tag{17}$$

In Fig. 7, the increment of aqueous $\mathrm{Cl^-}$ and the amount of adsorbed perchlorate were simultaneously measured at different initial perchlorate concentrations (0.1–0.4 mmol/L). As can be seen, more chloride ions released in the solution when the amount of absorbed perchlorate increased, and values of η_{i} are in the range from 66 to 92%. That is to say, the major adsorption mechanism for perchlorate adsorption on CTAC-ACFs was ion exchange since the values of η_{i} are all over 50%. On the other hand, we believe that other adsorption process, such as electrostatic attraction, physical absorption, and surface complexation, may also play important roles for perchlorate removal, although these processes are dependent on the solution chemistry and the surface characteristics of ACFs.

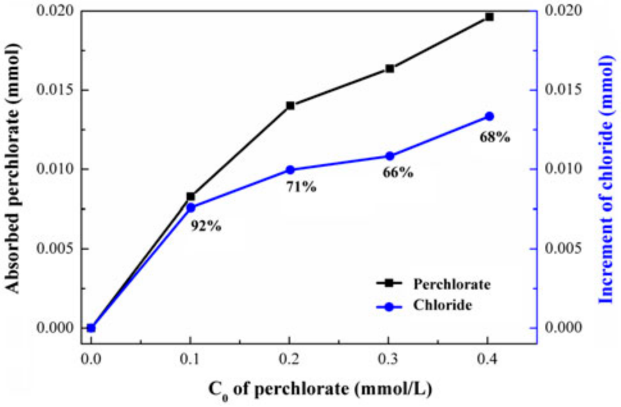

Fig. 7. Amount of the absorbed perchlorate, the increment of chloride and the proportion of ion exchange (η_{i}, %) at different initial perchlorate concentrations (0.1–0.4 mmol/L).

3.6. Stability and regenerability of CTAC-ACFs

The absorbent with good stability not only ensures the effluent quality but also avoids additional contamination. The leaching amount of the CTAC from 50 mg CTAC-ACFs in deionized water was measured to evaluate the stability of adsorbents, and the results are shown in Fig. 8(a). As can be seen, the leaching amount of CTAC increases to 4.31×10^{-3} mmol/L after 2 d immersion, accounting for 1.83% of the total loading amount (0.047 mmol) (calculated by Eq. (5)). As the immersing time prolonged to 32 d, the leaching amount of the CTAC does not show notable change, and maintains at a low leaching level (1.98%). The

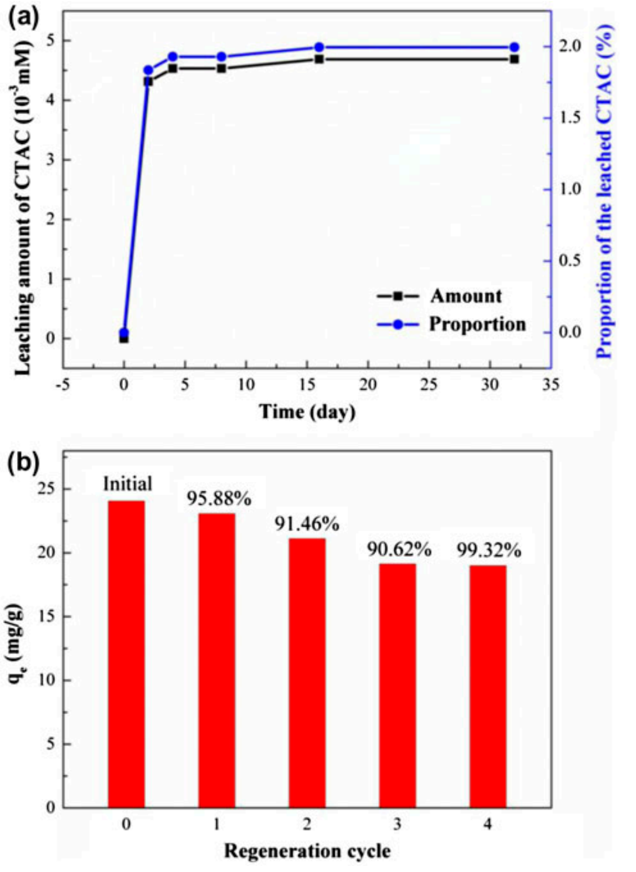

Fig. 8. (a) Amount and proportion of the CTAC leaching from CTAC-ACFs in sterilized deionized water at room temperature. (b) The perchlorate adsorption capacities of the fresh prepared and regenerated CTAC-ACFs (the numbers on the top of columns are the regeneration efficiencies).

results suggest that the CTAC-ACFs adsorbents had excellent stability in water. The stability not only avoids the additional contamination from adsorbent itself, but also ensures the adsorption capacity of the adsorbent when it is applied to a long period treatment.

To determine the regenerability of CTAC-ACFs, 1 M HCl was used to treat the fresh and saturated CTAC-ACFs. The regeneration results are depicted in Fig. 8(b). It can be observed that the perchlorate adsorption capacities of the CTAC-ACFs decreased with the regeneration cycles. The as-prepared CTAC-ACFs have an adsorption capacity of 24.06 mg/L. After successive cycles of adsorption/regeneration, the adsorption capacities, respectively, decreased to 23.07, 21.10, 19.12, and 18.99 mg/g, and the regeneration efficiencies (calculated by Eq. (6)) were 95.88, 91.46, 90.62, and 99.32%, respectively. The recovered adsorption capacity after four regeneration cycles still remained 78.93% of the initial adsorption capacity. Based on our observation, HCl treatment caused less than 1.5% decrease in the adsorption capacity of fresh CTAC-ACFs. Therefore, the decrease of the adsorption capacity is most likely due to the irreversible desorption of some ions and the loss of loaded surfactants in the adsorption/regeneration process.

In comparison with other reported adsorbents, such as modified GAC ($q_e = \sim 6$ mg/g) prepared by Xu et al. [40], quaternary amine modified reed ($q_e = \sim 10$ mg/g) prepared by Baidas et al. [16] and granular ferric hydroxide ($q_e = \sim 4$ mg/g) prepared by Kumar et al. [41], the prepared CTAC-ACFs constantly exhibited better perchlorate adsorption capacity at the same initial concentration of 20 mg/L. Considering that ACFs are cost-effective materials extensively used in water treatment, the prepared CTAC-ACFs may be engineered for the removal of aqueous perchlorate.

4. Conclusion

In the present study, a new adsorbent, CTAC modified ACF (CTAC-ACF), was prepared and its perchlorate adsorption behaviors, including equilibrium, thermodynamics, kinetics, mechanism were systematically investigated. FTIR, elemental analysis, and Zeta potential characterization showed that quaternary ammonium chloride surfactant CTAC was successfully loaded onto the surface of ACFs. The CTAC-ACFs featured a fast adsorption for ppm level aqueous perchlorate, and the adsorption capacity reached 26.74 mg/g at an initial concentration of 20 mg/L. The Langmuir isotherm model gave better fittings with the experimental data than the Freundlich model. The values of the dimensionless constant separation factor R_L in the range from 0 to 1 and ΔG (<0) implied a "favorable" and spontaneous adsorption of perchlorate onto the CTAC-ACFs. The adsorption kinetic data were better described by the pseudo-second-order equation than by the pseudo-first-order equation. The perchlorate adsorption capacity of the CTAC-ACFs increased with initial perchlorate concentration, contact time, and temperature, but decreased with solution pH and ionic strength. The major adsorption mechanism of perchlorate is ion exchange, but other process such as electrostatic attraction and physical absorption, may also play an important role. Tests also demonstrated that the CTAC-ACFs absorbent showed well stability and regenerability in aqueous solution. Considering that ACFs have intrinsic affinity to organic molecules, the CTAC-ACFs adsorbents may be also applied to treat complex contamination including both organic micropollution and perchlorate.

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Symbols

C_0 — initial concentration of perchlorate in solution (mg/L)
C_e — equilibrium (final) concentration of perchlorate in solution (mg/L)
C_{s0} — initial concentration of the surfactant in solution (mmol/L)
C_{sf} — final concentration of the surfactant in solution (mmol/L)
C_t — perchlorate concentration in solution at contact time t (mg/L)
ΔG — Gibb's free energy change (kJ/mol)
h — initial sorption rate (mg/g min)
ΔH — enthalpy change (kJ/mol)
k_s — adsorption first-order rate constant (min^{-1})
k_2 — pseudo-second-order rate constant (g/mg min)
K_d — variation of the thermodynamic equilibrium constant
K_L — Langmuir equilibrium constant (L/mg)
K_f — Freundlich constant indicative of the relative sorption capacity of the sorbent (mg/g)
m_{ACFs} — mass of the treated active carbon fibers (g)
m — mass of absorbent (g)
m_{lt} — amount of the surfactant leacheate on a certain day (mmol)

m_s — amount of the surfactant loaded on ACFs (mmol)

M — loading amount of surfactants (mmol/g)

n — Freundlich constant indicative of the intensity of sorption

Δn_{Cl^-} — increment of Cl^- ions in the solution (mmol)

$\Delta n_{ClO_4^-}$ — decrement of perchlorates in the solution (mmol)

q_e — equilibrium adsorption capacity (mg/g)

q_{en} — adsorption capacity of the regenerated adsorbents after n cycles (mg/g)

q_t — amount of the perchlorate adsorbed onto adsorbents at time t (mg/g)

Q_m — maximum adsorption capacity (mg/g)

R — universal gas constant (kJ/mol)

R_L — dimensionless constant separation factor for the Langmuir isotherm model (mg/g)

ΔS — entropy change (kJ/mol K)

t — time

T — absolute temperature (K)

V — solution volume (L)

η_i — proportion of ion exchange (%)

η_r — perchlorate removal efficiency (%)

η_{lt} — percentage of leaching out of surfactant at time t (%)

η_{rg} — regeneration efficiency of adsorbent (%)

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