Fig. 7. adsorption isotherms of PFOS and PFOA on the bamboo-derived GAC and modeling results using the Langmuir and Freundlich models

elemental composition of bamboo-derived GAC prepared at the KOH/C ratio of 4 and 900 °C, and the weight percents of C, H, O, and N were 94.9%, 0.4%, 2.7%, and 0%, respectively, indicating that only the oxygen-containing functional groups were present on the activated carbon. Using Boehm titration, the contents of carboxyl, lactone, phenolic hydroxyl, and carbonyl groups were measured to be 0.16, 0.06, 0.19 0.22 mmol/g, respectively. These oxygen-containing functional groups on the activated carbon are hydrophilic, but they are impossible to adsorb the anionic PFOS/PFOA [7,21], and even their approaching is also difficult due to the electrostatic repulsion mentioned above.

3.6. Sorption isotherm

The adsorption isotherms of PFOS and PFOA on the bamboo-derived GAC are shown in Fig. 7. The adsorbed amounts of PFOS and PFOA increased with the increase of their equilibrium concentrations, and the adsorbed amounts of PFOS on the activated carbon were much higher than those of PFOA, but they did not reach the adsorption capacity within the concentrations studied. Both the Langmuir and Freundlich models were used to describe the adsorption isotherms of PFOS and PFOA on the activated carbon, and the Freundlich model was found to be better than the Langmuir model according to the correlation coefficient (R^2) obtained (Fig. 7), indicating the possible multi-layer adsorption. The PFOS and PFOA anions may adsorb on the surfaces of activated carbon via the hydrophobic interaction, and they may form micelles and hemi-micelles in the pores of the activated carbon when the adsorbed PFOS/PFOA anions reach 0.01–0.001 of their critical micelle concentrations [7,27]. The obtained constants of the Langmuir and Freundlich models were listed in Table 2. According to the Langmuir fitting, the adsorption capacities of PFOS and PFOA on the activated carbon were 2.20 and 1.03 mmol/g, respectively, which were lower than the experimental data of 2.32 mmol/g for PFOS at the equilibrium concentration of 0.33 mmol/L, and 1.15 mmol/g for PFOA at the equilibrium concentration of 0.38 mmol/L. The higher adsorption of PFOS than PFOA on the bamboo-derived GAC may be related to the higher hydrophobicity of PFOS, resulting in the stronger hydrophobic interaction on the hydrophobic surfaces of activated carbon [7].

The adsorption capacities of PFOS and PFOA on different activated carbons reported in the literature are listed in Table 3. The coal-based GAC had the adsorption capacity of 0.36–0.44 mmol/g for PFOS, and 0.29–0.39 mmol/g for PFOA. In contrast, the PAC exhibited the adsorption capacity of 0.37–1.43 mmol/g for PFOS, and 0.038–1.05 mmol/g for PFOA. Evidently, the PAC had much higher adsorption capacities for PFOS and PFOA than the GAC. In addition, the char M400 had low adsorption capacity for PFOS due to the only pyrolysis of maize straw at 400 °C. Since the
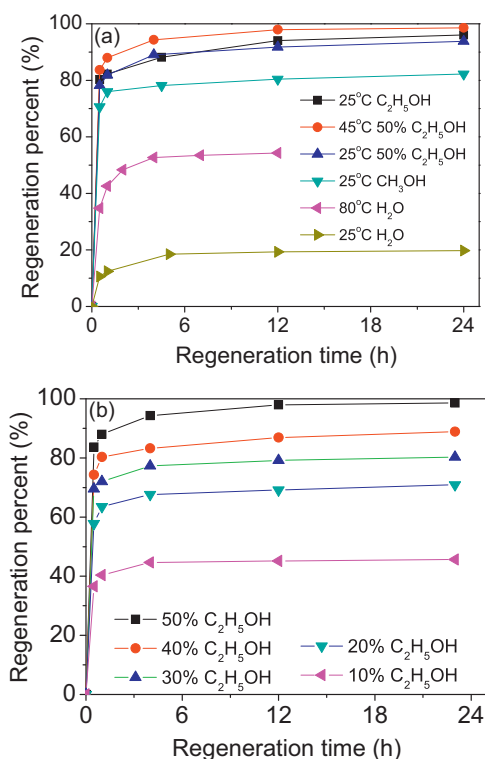

Fig. 8. Regeneration kinetics of spent bamboo-derived GAC using different regeneration agents (a) and ethanol at different concentrations (b).

activated carbons were prepared from different precursors and using different activation methods, they exhibited different adsorption capacities for PFOS and PFOA. The bamboo-derived GAC prepared in this study showed the highest adsorption capacities for PFOS and PFOA among all the activated carbons reported.

The adsorption capacity of PFOS and PFOA on activated carbons are closely related to their pore size and surface area. Since the bamboo-derived GAC had much higher surface area (Fig. 3) and more mesopores than the commercial activated carbons [6,7], it had much higher adsorption capacity than other activated carbons. For example, the pore size distribution of the commercial coal-based GAC we used before is shown in Fig. S2, and its pores in the range of 1–4 nm (especially 2–4 nm) was much less than that of the bamboo-derived GAC prepared at the KOH/C ratio of 4 and 900 °C (Fig. 2b); the mesopore volume of the commercial coal-based GAC was 0.08 cm^3/g, much less than 0.67 cm^3/g of the bamboo-derived GAC; this commercial coal-based GAC also had low specific surface area of 712 m^2/g [7].

3.7. Regeneration of spent activated carbon

The bamboo-derived GAC after PFOS adsorption was regenerated using different agents, and the regeneration kinetic data are shown in Fig. 8. When the spent activated carbon was regenerated by deionized water at 25 °C, the regeneration percent after 24 h was 19.8%. When the temperature of deionized water was increased to 80 °C, the regeneration percent after 7 h was enhanced to 53%, indicating that increasing temperature facilitated the desorption of PFOS, but only about half of the adsorbed PFOS anions were successfully desorbed from the activated carbon. The regeneration percents were less than 1% after 24 h when 0.06% NaCl and 0.06% NaOH solutions were used to regenerate the spent activated carbon (data not shown), implying that the ion exchange was hardly involved in the adsorption of PFOS on the activated carbon.

Table 2
Calculated constants of the Langmuir and Freundlich equations for the adsorption of PFOS and PFOA on the bamboo-derived GAC.

| Adsorbates	Langmuir model[a]			Freundlich model[b]		
	q_m (mmol/g)	b (L/mol)	R^2	K_f	n	R^2
PFOS	2.20	52.2	0.910	3.20	3.41	0.977
PFOA	1.03	157.1	0.869	1.34	5.28	0.971

[a] $q_e = q_m C_e / (1/b + C_e)$.
[b] $q_e = K_f C_e^{1/n}$.

Table 3
Comparison of adsorption capacities of PFOS and PFOA on different activated carbons.

Activated carbons	Size (mm)	PFCs	C_0[a] (mg/L)	pH	q_m[b] (mmol/g)	Refs
Filtrasorb 300/400 (coal)[c]	0.85–1.7	PFOS	15–150	7.2	0.36/0.44	[6]
Filtrasorb 400 (coal)[c]	0.85–1.7	PFOA	15–150	7.2	0.29	[6]
GAC (coal)	0.9–1.0	PFOS	20–250	5	0.37	[7]
		PFOA			0.39	
PAC	<0.149	PFOA	5–40	6.1	0.038	[28]
PAC	NA[d]	PFOS	30–200	NA	0.73	[15]
PAC (S-10)	0.036	PFOS	25–300	7	1.43	[16]
		PFOA			1.05	
PAC (coal)	<0.1	PFOS	20–250	5	1.04	[7]
		PFOA			0.67	
PAC	NA	PFOS	1–1000	NA	0.88	[5]
		PFOA			1.03	
Char M400[e]	<0.15	PFOS	1–500	7	0.30	[29]
GAC (bamboo)	0.60–0.85	PFOS	20–250	5	2.32	This study
		PFOA			1.15	

[a] PFOS/PFOA initial concentrations.
[b] Maximum adsorbed amount or adsorption capacity obtained by the Langmuir fitting.
[c] Coal-based activated carbon produced by Calgon Co.
[d] Not available.
[e] Maize straw pyrolyzed at 400 °C.

The organic solvents including methanol and ethanol were also tried, and their regeneration percents at 25 °C after 24 h were 83% and 96%, respectively. When 50% ethanol solution at 25 °C and 50% ethanol solution at 45 °C were used, their regeneration percents after 24 h were 93% and 98%, respectively. To further decrease the content of ethanol in water, 10%, 20%, 30%, 40%, and 50% ethanol solutions at 45 °C were used to regenerate the spent activated carbon, the regeneration percents after 23 h were 46%, 71%, 80%, 89%, and 98%, respectively (Fig. 8b). The regeneration was very fast within 1 h, and most regeneration was almost finished within 4 h. For example, the regeneration percent was 84% after 0.5 h and 94% after 4 h. Evidently, the 50% ethanol solution at 45 °C was suitable for complete regeneration of the spent activated carbon. Fig. 9 shows the removal of PFOS by the activated carbon in the five adsorption cycles. The removal percents decreased from 74.9% in the 1st adsorption to 71.0% in the 2nd adsorption, and kept stable in the following three cycles, indicating the good reusability of this activated carbon for PFOS removal.
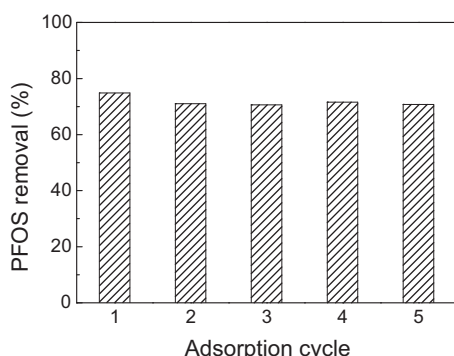
Fig. 9. PFOS removal on the activated carbon in five adsorption cycles.

4. Conclusions

The bamboo-derived GAC prepared under the severe activation condition contained the enlarged pores, which facilitated the diffusion and adsorption of PFOS and PFOA in the granular adsorbent. The adsorption equilibrium of PFOS and PFOA on the bamboo-derived GAC was achieved within 24 h, faster than other granular adsorbents reported. This GAC had the adsorbed amounts of 2.32 mmol/g for PFOS and 1.15 mmol/g for PFOA at pH 5.0, much higher than other PAC and GAC reported. Increasing the size of nano-sized pores was a feasible method to enhance the adsorption of PFOS and PFOA on the GAC. The adsorption of PFOS and PFOA decreased with increasing solution pH, and the significant decrease was observed at pH below 4.0 for PFOS and pH below 6.0 for PFOA. The spent activated carbon was successfully regenerated by methanol or ethanol solution, and the regeneration percents were 84% after 0.5 h and 98% after 23 h using 50% ethanol solution at 45 °C. This cheap bamboo-derived GAC had a promising application in wastewater treatment for the removal of high concentrations of PFOS or PFOA.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.03.045.