Simultaneous Multifunctional Sorption of PFOS and Cr(VI) on Activated Carbon Prepared by One-Step Microwave Activation

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Abstract Multifunctional sorbents, activated carbons (AC), were prepared by one-step microwave activation utilizing peanut shells and sunflower seed husks. The influence of the original particle size of raw materials on the yield and specific surface area of AC was studied, which reached 33.5 % and 1133.27 m²/g, respectively. The repetitive and competitive uptakes of perfluorooctane sulfonate (PFOS) and chromium were applied to investigate the sorption properties of AC. The sorption mechanisms were demonstrated using sulfur K-edge X-ray absorption near edge structure analysis (XANES). In the repetitive experiment, AC made from peanut shells (AC_{P05}) still retained 70 % removal efficiency of PFOS after the fourth sorption because sorbed PFOS might form a new organic phase that supplied effective sites for the hydrophobic partition of PFOS. However, the removal efficiency of Cr(VI) decreased dramatically from 60 to 11 % after the fourth uptake because electrostatic attraction was its only removal pathway. In the binary solutes system, AC_{P05} possessed perfect sorption performance for both PFOS and Cr(VI), which were 885 and 192 mg/g, respectively. In the multivariate solutes system, the XANES spectra indicated that the thiol functional group existed in the resulting

AC and a metal chelate was formed between thiol and Zn²⁺/Cu²⁺. Hence, the presence of Zn²⁺/Cu²⁺ further promoted the removal of PFOS and Cr(VI) through the electrostatic attraction between the anions and positive metal chelate.

Keywords Activated carbon · Cr(VI) · PFOS · Sorption mechanism · XANES

1 Introduction

Perfluorooctane sulfonate (PFOS, C₈F₁₇O₃⁻) has drawn considerable scientific and public concern due to its wide applications and ubiquitous contamination in various media (Ahrens et al. 2010; Giesy and Kannan 2001; Lam et al. 2014; Pan and You 2010; Zhang et al. 2011b). Although the 3M Company has phased out PFOS, the substance is still used in some specialized fields such as the firefighting and electroplating industry. In an electroplating plant, PFOS is usually utilized as an inhibitor of chromium (Cr) fog to reduce the atmospheric pollution of Cr during the electroplating process. Eventually the high concentration of PFOS mixed with coexisted Cr(VI), Cu, and Zn is discharged into natural waterbodies via the effluent of wastewater from the electroplating plant (Wang and Xiao 1995). Various methods were developed to remove Cr(VI) (Yuan et al. 2009) and PFOS (Vecitis et al. 2009; Zhang et al. 2011a; Zhou et al. 2013a), respectively, because of the endocrine-disrupting effect of PFOS and the carcinogenic effect of Cr(VI). Sorption is effective in

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simultaneously removing PFOS and Cr(VI) from water (Zhou et al. 2013a). There is an urgent need to discover sorbents that are both economic and effective for simultaneous removal of PFOS and Cr(VI).

Activated carbon (AC) is a perfect sorbent for most contaminants from aqueous or gaseous environments due to the functionalized surface and high specific surface area. However, the higher cost of activated carbon is an important consideration because of its use of non-renewable raw materials and conventional heating methods. Recently, cost cutting in producing AC has focused on utilizing raw materials/precursors from agricultural solid waste or by-product, including cotton stalk, rice husks, orange peel, and sunflower seed oil residue (Deng et al. 2009, 2010; Foo and Hameed 2011). In addition to the precursor or raw material, the heating method also affects the properties and cost of AC. For conventional heating, the temperature gradient proceeds from the surface to the interior of the particle within several hours, which results in a relatively larger energy loss and increases the expense. In contrast, microwave activation is a promising technique for preparing AC because of its short reaction time and low energy consumption. Microwave radiation is an internal and volumetric reaction, in which a high sintering temperature causes some released components to generate additional pores, which consequently supplies effective sorption sites and space (Hesas et al. 2013).

Peanuts and sunflower seeds are the main oil crops in China that yield more than 4500 and 200 kilotons per annum of peanut shells (PNS) and sunflower seed husks (SFSH), respectively. Most of these products are burnt as wastes, which causes environmental pollution and the loss of a precious resource. Therefore, preparing activated carbon using the shells of peanuts and sunflower seeds not only reduces the cost of waste disposal but also addresses the environmental problem. In this study, the influence of the particle size of raw materials (i.e., PNS and SFSH) on the yield and physico-chemistry of the resulting activated carbon by one-step microwave technology was evaluated. With a view to treat the wastewater from the electroplating process, the single sorption, repetitive and competitive uptakes of PFOS and Cr(VI) from aqueous solution were studied to estimate the removal performance of AC. The sorption mechanisms of PFOS and Cr(VI) on activated carbon were interpreted based on their uptake behavior and sulfur K-edge X-ray absorption near edge structure analysis (XANES) spectra analyses.

2 Materials and Methods

2.1 Materials

The peanut shell (PNS) and sunflower seed husks (SFSH) were collected from a local food bazaar. The perfluorooctane sulfonate (PFOS, 98 %) was purchased from Fluka (Milwaukee, WI, USA). The chemical reagents $K_2Cr_2O_7$, $ZnCl_2$, and $CuCl_2$ were obtained from China National Medicines Corporation Ltd. The HPLC-grade methanol was obtained from Fisher Scientific Chemical (USA). All of the other reagents used in the experiment were analytical grade.

2.2 Preparation of Activated Carbon

The PNS and SFSH were crushed using a grinder to obtain two particle sizes: 5 and 0.5 mm. The particles were washed with deionized water to remove any impurities. Then, the cracked shells were dried at 80 °C for 24 h. The activation process was modified based on the previous studies (Alslaibi et al. 2013; Hesas et al. 2013). Twenty grams of dried shells was immersed in 70 mL of $ZnCl_2$ (50 % wt) for 15 h in a quartz crucible at room temperature. The quartz crucible was placed inside the microwave oven (Galanz WD750S) at a radiation power of 750 W for 10 min. Then, the samples were cooled to room temperature. A volume of 250 mL of dilute hydrochloric acid ($V_{HCl} : V_{H_2O} = 1 : 9$) was added to the quartz crucible and allowed to boil for 30 min to remove the ash content. The products were then washed with deionized water to neutralize the pH and remove chlorine ions. The moist materials were dried at 80 °C for 24 h and then ground to obtain 200 mesh activated carbon. The resulting activated carbon products were marked as AC_{P5} , AC_{P05} , AC_{S5} , and AC_{S05} . The subscripts “P” and “S” represent peanut shell and sunflower seed husks, respectively. The numbers “5” and “05” indicate the 5 and 0.5 mm of particles, respectively. The dry activated carbon was weighed to calculate the product yield according to Eq. (1):

$$\text{yield (\%)} = W_R / W_0 \times 100\% \quad (1)$$

where W_R and W_0 are the weights (g) of the activated carbon and raw material, respectively.

2.3 Characterization of Activated Carbon

The specific surface area (Brunauer–Emmett–Teller, BET), pore size distribution, and pore volume were determined according to the BET equation and the BJH method from the adsorption–desorption isotherm of N₂ at 77 K using ASAP 2020 HD88 (Micromeritics, USA). The morphology of the activated carbon was observed using field emission scanning electron microscopy (FE-SEM, HITACHI SU8020). The Fourier transform infrared (FTIR) spectrum of the samples was obtained on an FTIR spectrophotometer (NEXUS 670, Nicolet, USA) by attenuated total reflectance (ATR) within the 400–4000 cm^{−1} range. The resolution of FTIR spectroscopy was 2.0 cm^{−1}. The zeta potential was measured as described in a previous report (Zhou et al. 2010) with a ZETASIZER 2000 instrument (Malvern, USA). Sulfur K-edge XANES spectra analyses were conducted at the Canadian Light Source (CLS) on the Soft X-ray Micro-characterization Beamline (SXRMB) and the Beijing Synchrotron Radiation Facility (BSRF) on the 4B7A-Mid-energy Spectroscopy. The process was manipulated as follows: Air-dried samples were placed on a piece of double-sided carbon adhesive tape that was then transferred into the ultra-high-vacuum (UHV) chamber. In total, scans were run from 2430 to 2520 eV. To obtain high resolution in the pre-edge and edge region, a step size of 0.2 eV was used from 2430 to 2464 eV and a step size of 0.15 eV was used from 2466 to 2485 eV. In the other regions, a step size of 1.0 eV was used. A pre-edge background was removed from all spectra by fitting a straight line to the pre-edge region and subtracting this line from the entire spectrum.

2.4 Sorption Experiments

The sorption experiments included three systems: PFOS or K₂Cr₂O₇ single solute, binary solute (PFOS and K₂Cr₂O₇), and multivariate solute (PFOS, K₂Cr₂O₇, ZnCl₂, and CuCl₂). Ten milligrams (10 mg) of activated carbon was added to the polypropylene (PP) centrifuge tubes containing 25 mL of different initial concentrations of the K₂Cr₂O₇ and/or PFOS solutions and 0.1 M NaH₂PO₄ as a buffer solution. In the repetitive experiment, the initial concentration of PFOS or Cr(VI) was 400 or 159 mg/L, respectively. After the first sorption equilibrium, the mixture was centrifuged at 3000 rpm for 10 min and the supernatant was collected for

determination of PFOS or Cr(VI). Then, another 25 mL of PFOS or K₂Cr₂O₇ solution and 0.1 M NaH₂PO₄ buffer solution were added into the PP tubes containing the remnant moist sorbent. After the second sorption equilibrium, the third and fourth operations were the same as the first one. It was noted that the sorbent was not regenerated in these repetitive sorption experiments.

In the competitive experiment, additional CuCl₂ and ZnCl₂ solutions with an initial concentration of 100 mg/L were added in the sorption system. It was noted that the concentrations of K₂Cr₂O₇, ZnCl₂, and CuCl₂ were relevant to the wastewater from the electroplating plant. The pH values of all experiments were adjusted to 3.0 because the actual pH of the chromium-containing electroplating wastewater was close to this value (Lin et al. 2009; Tang et al. 2006). The increased volume of alkali/acid was negligible. On the basis of our preliminary experiment, the PP tubes were shaken at 150 rpm for 120 h at room temperature to ensure equilibration. All of the sorption experiments were conducted in duplicate, and the average values were used in our analysis.

2.5 Cr(VI) and PFOS Determination

The concentration of PFOS was determined by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS), the details of which can be found in our previous study (Zhou et al. 2013b). An inductively coupled plasma optical emission spectrometry (ICP–OES, IRIS Intrepid II XSP, USA) was used to determine the concentration of chromium (Zhou et al. 2013a). The uptake amount (q_e) of Cr or PFOS was calculated with Eq. (2):

$$q_e = \mathcal{G}(C_0 - C_e) \times V_0 / M_s \quad (2)$$

where C_0 (mg/L) is the initial concentration of PFOS or Cr(VI), C_e (mg/L) is the equilibrium concentration of PFOS or Cr(VI), V_0 is the initial volume, and M_s is the mass (g) of the sorbent.

3 Results and Discussion

3.1 Effect of Raw Material and Original Particle Size

There were no obvious influences of the raw material on the production yields of activated carbon, which ranged

Table 1 Yield and structural parameters of four types of activated carbons

Samples	AC _{S5}	AC _{S05}	AC _{P5}	AC _{P05}
Yield (%)	33.5	32.8	33.3	31.14
BET (m ² /g)	3.12	700.34	744.75	1133.27
Average pore size (nm)	37.0	3.3	3.5	3.7
Pore volume (m ³ /g)	0.03	0.54	0.54	0.93

from 31.14 to 33.5 % (Table 1). The yield of AC by microwave activation was lower in comparison with that achieved by the traditional thermal method (Huang et al. 2011) because the samples reached a higher temperature rapidly in minutes and the aggressive activation caused by the microwave radiation was intense. The volatiles and tar were released very quickly from the reaction system, which resulted in mass loss of the raw materials and reduced the production yield (Huang et al. 2011).

The structures of the AC derived from the different raw materials were different. The microwave activation

failed to improve the specific surface area and pore volume of AC_{S5}, which were 3.12 m²/g and 0.03 m³/g, respectively (Table 1). Additionally, there were no abundant macro- or micro-pores in the bulk (Fig. 1a). When the original particle size of SFSH decreased from 5 to 0.5 mm, the BET surface area of the resulting AC increased dramatically from 3.12 to 700.34 m²/g. A smaller particle size of the precursor resulted in a more thorough activation with ZnCl₂ because a relatively more surface area of the precursor was exposed to the ZnCl₂ solution. For the raw material of PNS, the resulting AC_{P5} and AC_{P05} possessed much larger BET surface areas, which were 744.75 and 1133.27 m²/g, respectively. The reticulated structures and abundant pores were observed from the morphology of AC_{P5} and AC_{P05} (Fig. 1c, d). The original structure of the raw material might be a factor that affected the final morphology of the AC. Clearly, the smooth surface of SFSH results in the bulk structure of AC_{S5} and AC_{S05}. However, the fibrous texture of PNS is contributed by the reticulated structures and abundant pores of AC_{P05} and AC_{P5}.

Fig. 1 SEM images of four types of resulting activated carbons

Fig. 2 Sorption isotherms of PFOS (a) and Cr(VI) (b) on three types of AC ($C_{0\text{-PFOS}}$ 50 to 400 mg/L and $C_{0\text{-Cr(VI)}}$ 15.9 to 159 mg/L, pH 3.0)

3.2 Sorption Isotherm and Mechanism

Three types of AC with a larger BET area (AC_{S05} , AC_{P5} , AC_{P05}) were used as sorbents for PFOS and Cr(VI) (Fig. 2).

The sorption capacity of PFOS followed the order $AC_{P05} > AC_{P5} \approx AC_{S05}$, whose maximum sorption amounts (q_m) totaled 1064.61, 943.72, and 926.79 mg/g, respectively (Table 2). The q_m of PFOS on these resulting activated carbons were much higher than that on the commercial AC, in which 559 mg/g for powder AC and 199 mg/g for granular AC were measured (Yu et al. 2009). In this study, these AC had a positive potential at a pH of 3.0 (Fig. 3). We examined the infrared spectrum of AC and then found an intense absorption peak corresponding to the C=O stretching frequency in the range from 1650 to 1850 nm^{-1} (Fig. 3). An oxygen-containing functional group such as pyrone, lactones, or ketone existed on the surface of AC (Boehm 2002), where the oxygen atom from the carbonyl would be protonated under acid conditions, resulting in their

positive potentials (Dicorcia et al. 1993). PFOS exists as an anion in this experiment because of its low pK_a (Brooke et al. 2004). Hence, the electrostatic attraction between the anionic PFOS and the protonated functional groups of oxygen-containing moieties on the AC surface promoted the sorption of PFOS. The result was consistent with the previous reports (Yu et al. 2009).

Conversely, AC_{P5} , which possessed the highest zeta potential at a pH of 3.0, was not the most efficient sorbent for PFOS. Therefore, other factors might affect the sorption capability of the AC. AC_{P05} had the largest special surface area (1133.27 m^2/g), which was higher than that of AC_{P5} (744.75 m^2/g) and AC_{S05} (700.34 m^2/g). The previous studies had proved that hydrophobic partition into AC was included during the sorption process because PFOS is a type of hydrophobic surfactant (Yu et al. 2009; Zhou et al. 2013b). Though AC_{P5} possessed the higher zeta potential, AC_{P05} had a larger BET area which could supply more hydrophobic sorption sites for PFOS. Hence, the sorption capacities of PFOS followed the decreasing order of $AC_{P05} > AC_{P5} \approx AC_{S05}$ due to both the hydrophobic partition and electrostatic attraction between PFOS and AC.

In contrast to the results obtained for PFOS, the sorption amounts of Cr(VI) on AC_{S05} , AC_{P05} , and AC_{P5} were similar, and the q_m values were 275.09, 220.8, and 229.85 mg/g, respectively. The sorption capacity of Cr(VI) on AC was more than ten times than that on organo-clay (25 mg/g) (Zhou et al. 2013a). Previously, Shi (1986) demonstrated that Cr(VI) exists as HCrO_4^- (89 %) and $\text{Cr}_2\text{O}_7^{2-}$ (11 %) at a pH of 3.0. Hence, the anionic $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ formed stable co-ordination compounds with the protonated oxygen-containing group via electrostatic attraction, which was

Table 2 Equilibrium constants using the Langmuir model for PFOS and Cr(VI)

Sorbates	Sorbents	Langmuir constants		
		K_L (L/mg)	q_m (mg/g)	R^2
PFOS	AC_{S05}	0.055	926.79	0.985
	AC_{P5}	0.058	943.72	0.984
	AC_{P05}	0.07	1064.61	0.968
Cr(VI)	AC_{S05}	0.048	275.09	0.989
	AC_{P5}	0.060	229.85	0.974
	AC_{P05}	0.059	220.8	0.917

Fig. 3 Zeta potential (a) and FTIR (b) of three types of AC

consistent with the interaction between HCrO_4^- and an amino group observed previously (Zhou et al. 2013a).

3.3 Repetitive Sorption of PFOS and Cr(VI)

To further study the performance of activated carbons, the repetitive sorption of PFOS or Cr(VI) was carried out (Fig. 4). The removal efficiency of PFOS reduced slightly approximately 10 % after the third sorption and then increased slightly after the fourth sorption. Notably, the sorption ability and removal efficiency of PFOS on AC_{P05} still reached 786 mg/g and 70 %, respectively, after the fourth sorption. As mentioned above, both hydrophobic partition and electrostatic attraction involving PFOS were the driving forces during the sorption process. Although the electrostatic sorption sites were limited, the sorbed PFOS ions/molecules on the AC after the first sorption would form a new organic phase that supplied more effective sorption sites for the hydrophobic PFOS. Therefore, all the three types of AC retained better sorption efficiencies even after the fourth sorption.

Specifically, the removal efficiency of Cr(VI) decreased dramatically from 60 to 11 % on AC_{P05}, from 48 to 15 % on AC_{P5}, and from 56 to 21 % on AC_{S05} after the repetitive fourth sorption. The distinguishing feature derived from the distinct sorption mechanisms of PFOS and Cr(VI). As mentioned above, the removal of Cr(VI) depended on the formation of stable coordination compounds via electrostatic attraction. When Cr(VI) was partially sorbed on the AC during the first sorption process, the effective electrostatic sites were occupied, which restricted the subsequent uptake of additional Cr(VI). Consequently, this resulted in a decreased removal efficiency of Cr(VI) after the repetitive sorption of Cr(VI).

3.4 Competitive Sorption of PFOS and Cr(VI)

The competitive sorption included binary solutes (i.e., PFOS and $\text{K}_2\text{Cr}_2\text{O}_7$) and multivariate solutes systems (i.e., PFOS, $\text{K}_2\text{Cr}_2\text{O}_7$, ZnCl_2 , and CuCl_2) (Fig. 5).

Fig. 4 Repetitious sorption of PFOS (a) and Cr(VI) (b) on three types of AC ($C_{0\text{-PFOS}}$ 400 mg/L and $C_{0\text{-Cr(VI)}}$ 159 mg/L, pH 3.0)

Fig. 5 Comparative sorption of PFOS (a) and Cr(VI) (b) on three types of AC in single solute, binary solutes, and multivariate solutes systems ($C_{0\text{-PFOS}}$ 400 mg/L, $C_{0\text{-Cr(VI)}}$ 159 mg/L, $C_{0\text{-Cu}}$ 37.5 mg/L, and $C_{0\text{-Zn}}$ 47.7 mg/L, pH 3.0)

In the binary solutes system, there should be a competitive sorption between anionic $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ and PFOS on the protonated AC surface. However, PFOS and Cr(VI) displayed different behaviors. The presence of anionic $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ did not obviously affect the sorption capacity of PFOS on the AC because Cr(VI) only occupied the electrostatic sites, whereas PFOS could still be removed by hydrophobic partition (Fig. 5a). These results further indicated that the hydrophobic partition was included in the sorption process involving PFOS.

Figure 4b shows that the presence of PFOS degraded the Cr(VI) sorption ability on these AC. The previous report indicated that the formation of a stable coordination via electrostatic attraction between the anionic $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ and the protonated surface of sorbent was the only mechanism to remove the Cr(VI) (Zhou et al. 2013a). In the binary solutes system, the anionic PFOS occupied the partial electrostatic sorption sites, which resulted in a competition between Cr(VI) and

PFOS and a subsequent decrease in the removal of Cr(VI). The decrease of Cr(VI) removal efficiency on AC_{P05} in the repetitive sorption (from 60 to 11 %) and binary solutes system (from 60 to 48 %) indicated that the competition between HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ was stronger than that involving HCrO_4^- and PFOS. That is, PFOS preferred hydrophobic partition rather than electrostatic attraction when competition between PFOS and HCrO_4^- occurred. In general, AC_{P05} still possessed superior sorption capacity for both PFOS and Cr(VI) even in the competitive binary solutes system, which were 885 mg/g (79 % removal percentage) and 192 mg/g (48 % removal percentage), respectively. Surprisingly, the sorption capacity of both PFOS and Cr(VI) on the sorbents increased in the multivariate solutes system (Fig. 5). To interpret this phenomenon, sulfur K-edge XANES spectra for the samples containing AC_{P05}, PFOS, Cr(VI), Zn^{2+} , and Cu^{2+} were conducted (Fig. 6).

For AC_{P05}, the intense peaks at energies of 2473.8 and 2482.2 eV represented the thiol and sulfate on the basis of

Fig. 6 Normalized sulfur K-edge XANES spectra of models and samples

model samples and a previous report (Hashimoto and Yamaguchi 2013). The peak at 2481 eV was attributed to the sulfonate moiety of the PFOS sample. For the AC_{P05} with sorbed PFOS in single, binary, and multivariate solutes systems, the characteristic absorption peak of PFOS (at 2481 eV) became stronger gradually and shifted from 2481 to 2480.4 eV. This result implied that the presence of Cu and Zn cations promoted the sorption of PFOS on AC_{P05}, which was consistent with the sorption experiment of PFOS (Fig. 5a). However, the thiol peak weakened from 2473.8 to 2472.9 eV until it disappeared when the Cu and Zn cations were introduced into the sorption system. The cationic metals Cu and Zn can bond to the sulfur of PFOS and thiol to form a metal chelate compound, which resulted in the disappearance of the XANES signal attributed to the thiol. Because the metal chelate compound possessed a positive charge, it promoted the removal of the anionic PFOS and $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ via electrostatic attraction in the multivariate solutes system.

4 Conclusions

The activated carbon prepared by one-step microwave activation displayed multifunctional sorption performance for PFOS and Cr(VI). The analysis of the sulfur K-edge X-ray absorption near edge structure indicated that Cr(VI) did not interfere with the sorption of PFOS on AC because the hydrophobic partition became the main driving force to support sorption instead of a mechanism involving electrostatic attraction. The coexistence of Zn and Cu cations promoted the removal of PFOS due to the formation of the metal chelate compound.

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