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Enhanced sorption of perfluorooctane sulfonate and Cr(VI) on organo montmorillonite: influence of solution pH and uptake mechanism

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Abstract An effective sorbent to remove the perfluorooctane sulfonate (PFOS) and hexavalent chromium (Cr(VI)) simultaneously from simulating plating wastewater was prepared in this study. The removal of Cr was pH-dependent. However, PFOS removal on organo-montmorillonites (Mts) was not sensitive to pH changes. The presence of micelles and hemi-micelles resulted in an enhanced PFOS sorption capacity which reached 1,000 mg/g on the hexadecyltrimethylammonium bromide (HDTMAB) modified montmorillonite. The cationic surfactants on organo-Mts were largely responsible to the hydrophobic partition. For Cr(VI), the stable coordination compounds between amido, sulfhydryl groups and $HCrO_4^-$ were beneficial to its sorption on AET–Mt and AET–HDTMAB–Mt (AET, 2-aminoethanethiol hydrochloride). The result indicated that the AET–HDTMAB–Mt was highly effective for removing both PFOS and Cr(VI) simultaneously, and their sorption capacities reached 890 and 14 mg/g respectively.

Keywords Perfluorooctane sulfonate (PFOS) · Hexavalent chromium · Hydrophobic partition · Electrostatic attraction · Sorption · Simultaneous

Abbreviations

PFOS	Perfluorooctane sulfonate
HDTMAB	Hexadecyltrimethylammonium bromide
AET	2-Aminoethanethiol hydrochloride
Mt	Montmorillonite

1 Introduction

The perfluorooctane sulfonate (PFOS) has been proved to result in toxic influences on some organisms as well as human beings (Ye et al. 2007; Li 2009) and been detected ubiquitously in various mediums including soil (Higgins and Luthy 2006), water (Yamashita et al. 2005), wildlife (Giesy and Kannan 2001) and humans (Kannan et al. 2004) in recent years. As a kind of emerging pollutant, PFOS was added in the list of persistent organic pollutants in 2009. Though the application of PFOS was restricted, it is still used in some special areas such as firefighting, electroplating fields. PFOS was used to inhibit the chromium fog in the chromium plating in order to reduce the chromium contaminant in the atmosphere. Actually, the high concentrations of hexavalent chromium mixed with PFOS still were discharged to aquatic environment through the wastewater from electroplating plants (Wang and Xiao 1995).

The complicated contaminant combined hexavalent chromium with PFOS has attracted few concerns in scientific community recently. It's urgent to remove the heavy metals and organic pollutions before being discharged into the environment due to the carcinogenic, teratogenic characteristics of Cr(VI) to living organisms (Yuan et al. 2009) and potential endocrine disrupting effect and multiple toxicities of PFOS (Giesy and Kannan 2002; 3M 2003). In current wastewater treatment, various methods had been developed to remove them respectively. For chromium removal, the common techniques include chemical precipitation, ion

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exchange, bio-sorption, reduction, etc. (Zhou et al. 1993; Tiravanti et al. 1997; Aksu et al. 2002; Ortiz et al. 2003). Whereas, most of the mentioned methods have disadvantages, for instance, incomplete metal removal, expensive equipment, etc. (Aksu et al. 2002). Among these methods, sorption is the most widely used technique. For PFOS, it's also difficult to degrade in natural environment using the common methods such as oxidation, reduction and biological degradation because of its extreme stability (Vecitis et al. 2009). Sorption has been proved effective to treat PFOS from water (Li et al. 2011; Zhang et al. 2011; Xiao et al. 2012). Some common sorbents including carbon materials, resin, clays and biosorbents have been tried (Senevirathna et al. 2010; Zhou et al. 2010; Xiao et al. 2011, 2012; Zhang et al. 2011). However, to our knowledge, less research attentions were paid to the treatment of Cr(VI) and PFOS simultaneously from point sources, e.g. electroplating wastewater, in which high concentrations of chromium and PFOS was contained. The existing of Cr or PFOS possibly interferes with the removal behavior of PFOS or Cr on the adsorbents. Herein, it is necessary to discover easily available sorbent for removing of hexavalent chromium and PFOS from the water simultaneously.

Montmorillonites (Mts) with low costs and good sorption capacity have been widely applied to treat a series of inorganic pollutions (Fu et al. 1994; Mekhemer et al. 2009; Al-Jariri and Khalili 2010; Hamidpour et al. 2010). However, the natural Mt without modification is ineffective to remove the hydrophobic organic pollutants since the hydration of metal ions makes the surfaces of the clay hydrophilic. Therefore, it is important for Mt modification with appropriate reagents to convert the hydrophilic surface to hydrophobic one, consequently to prepare the clay-based adsorbents for hydrophobic organic contaminants (Bergaya and Lagaly 2001; He et al. 2006; Zhou et al. 2010).

In this study, we estimated the feasibility of using modified Mts as sorbents to remove Cr(VI) and PFOS simultaneously from the chromium electroplating wastewater. The hexadecyltrimethylammonium bromide signed as HDTMAB ($CH_3(CH_2)_{15}(CH_3)_3NBr$) and 2-aminoethanethiol hydrochloride (AET, $C_2H_7NS{\cdot}HCl$) were employed as modifying reagents. The resulting sorbents were applied in the batch sorption experiments to evaluate their properties, and the uptake mechanism on basis of the influence of solution pH and uptake isotherm was interpreted.

2 Experimental section

2.1 Materials

The synthetic sodium montmorillonite (Na–Mt) with cationic exchange capacity 106 mmol/100 g was obtained from Inner Mongolia without further purity. Its main components were listed in Table 1. The HDTMAB was provided by Sigma-Aldrich Co. LLC. (Shanghai, China). The AET was obtained from Beijing Sanshengtengda Technology Co., Ltd. in China. PFOS was purchased from Tokyo Kasei Kogyo in Japan. Potassium dichromate ($K_2Cr_2O_7$) is from China National Medicines Corporation Ltd. The methanol from Fisher Chemical (USA) was HPLC-grade. The other chemical reagents were of analytical grade.

2.2 Preparation of sorbents

The organo-montmorillonite (HDTMAB–Mt) was prepared according to the procedure described by the method (Zhou et al. 2008, 2010). A mass of 5.79 g HDTMAB was added into the 100 mL hot water to obtain the HDTMAB solution, and then 10 g Na–Mt was dispersed into the above solution. The suspension was stirred in order to make full use of the HDTMAB at 80 °C water bath for 2 h. Subsequently, the suspension was centrifugated at 3,000 rpm for 10 min. The moist solid was washed six times with deionized water until without Br^- ($AgNO_3$ was used as indicator), and then they were dried at 60 °C in an up-draught drying oven. The resulting product was signed as HDTMAB–Mt.

A mass of 10 g Na–Mt and 1.806 g AET were dispersed into the suspension. The mixtures were stirred slightly overnight and washed with deionized water until no Cl^- was determined. The washing and drought procedure was as same as above. The resulting product was denoted as AET–Mt.

A solution containing 1.806 g AET was dropped into the above HDTMAB–Mt suspension before washing, the mixtures were stirred slightly overnight and washed, dried with the same method above mentioned. The product marked as AET–HDTMAB–Mt.

2.3 Sorption experiments

A certain amount of sorbents were added into 50 mL polypropylene (PP) flasks containing 25 mL of different concentrations PFOS and $K_2Cr_2O_7$ solutions. The PP flasks

Table 1 The main components of Na–Mt

Components	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Ignition loss
Content (%)	55.74	15.51	0.11	2.03	5.87	3.31	5.57	0.8	8.03

were shaken at 25 °C with 150 rpm for 120 h. A series of sorption experiments including influence of solution pH and initial concentration of sorbates were conducted. The initial pH value of the solution was adjusted from 2 to 8 with 50 mg/L PFOS and 1 mmol/L $K_2Cr_2O_7$ during the pH influence experiment. The other experiments were carried out at a pH of 3.0 because the usual pH value of plating chromium wastewater was from 2.85 to 3.0 (Tang et al. 2006; Lin et al. 2009). The sorption isotherms were conducted with $K_2Cr_2O_7$ concentrations from 0.1 to 1 mmol/L and PFOS concentrations varying from 50 to 400 mg/L at a controlled constant pH of 3.0. The increased volumes were negligible because of the little volume of acid and alkali added. All the sorption experiments were carried out duplicate, and the averages were adopted. Note that the errors were obtained by the difference between detection and average.

2.4 PFOS and Cr(VI) determination

After centrifugation, the supernatants were filtered with a 0.22 μm polypropylene membrane. Shimadzu HPLC (LC-10ADvp, Japan) with a CDD-6A conductivity detector was used to determine the PFOS concentrations as described in Yu et al. (2008). The HC-C18 column (4.6 × 250 mm, Agilent, USA) was taken. The mobile phase was a mixture of solvent methanol/0.02 M NaH_2PO_4 (v/v, 70/30) at a flow rate of 1.2 mL/min. The injection volume was 20 μL. The PFOS uptake capacities on all kinds of sorbents were calculated with the following equation.

$$q_e = (C_0 - C_e)V/m \qquad (1)$$

Where q_e was sorption capacity of PFOS (mg/g), C_0 was initial PFOS concentration (mg/L), C_e was equilibrium concentration (mg/L), V was solution volume (L), and m was sorbent mass (g).

An IRIS Intrepid II XSP ICP-OES (inductively coupled plasma optical emission spectrometry, USA) was used to determine the concentration of Cr. The uptake amounts of Cr were also calculated with the Eq. (1).

2.5 Characterization

The different types of Mts were analyzed by X-ray diffraction (XRD) on a D8 ADVANCE diffractometer from Bruker (Germany). The samples were carried out under CuK_α radiation ($n = 1.5418$ Å) running at 40 kV and 40 mA with 0.25° divergence slit from 1.5 to 30° (2θ) at the step size of 0.0167°.

The zeta potential instrument from Beckman Coulter (Delsa Nano C, USA) was used to analyze the isoelectric point (Zhou et al. 2010). The solution pH was from 2 to 11 by dropping of 0.1 mol/L NaOH and HCl solution. All the data were measured for five times, and the average values were obtained.

TOC (total organic carbon) was measured using an instrument from Shimadzu (TOC-VCPH, Japan) to quantify the organic matters.

3 Results and discussion

3.1 Characteristic of sorbents

The XRD patterns of different types of Mt were shown in Fig. 1. The interlamellar spacing of Na–Mt was 1.24 nm. The Mt layers expanded when the sodium was exchanged with the HDTAMB or AET, and the interlamellar spacing of modified Mts was 1.31, 3.87 and 3.62 nm respectively. The results indicated that the HDTMAB and AET had intercalated the Mts by cationic exchange, which was consisted with the previous reports (Boyd et al. 1988; He et al. 2006; Zhou et al. 2007).

The zeta potentials of all the Mts were shown in Fig. 2. The isoelectric point (pH_{zpc}) and the organic carbon

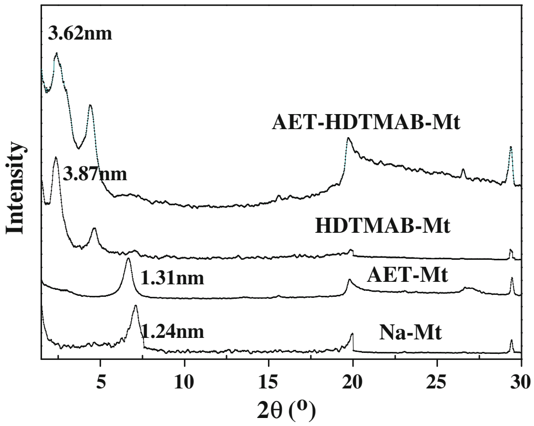

Fig. 1 XRD patterns of different types of montmorillonites

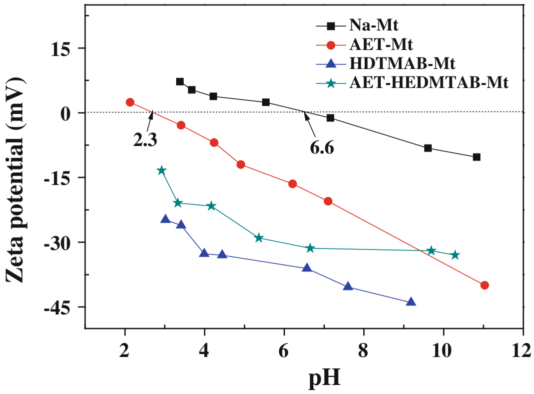

Fig. 2 The zeta potentials of different types of montmorillonites

Table 2 The pH_{zpc} and organic carbon fraction in the sorbents

Sorbents	Na–Mt	AET–Mt	HDTMAB–Mt	AET–HDTMAB–Mt
pH_{zpc}	6.6	2.3	None	None
f_{OC} (%)	0.08	1.51	21.34	19.24

fraction (f_{OC}) in the modified Mts were shown in Table 2. The amounts of organic carbon dramatic increased from 0.08 % in the Na–Mt to 21.34 % in HDTMAB–Mt and 19.24 % in AET–HDTMAB–Mt.

3.2 Influence of solution pH

Hexavalent chromium and PFOS removals by the four different kinds of sorbents were found to be the pH-dependent as shown in Fig. 3. The removal of PFOS had a slight change (within the errors) on the Na–Mt when solution pH below 6.2, but rapidly reduced when the pH increased from 6.2 to 7.1. Comparing with the Na–Mt, the PFOS removal on the other organo-Mts reduced gradually at the range of pH in this study. As we all know, solution pH not only affects the form of sorbates, but also influences the surface charge of sorbents. PFOS always existed as anion due to its low pK_a (Brooke et al. 2004). Hence, the PFOS removal was influenced by the surface properties of the different types of Mts. As we all know, Mt owns permanent negative plane and alterable charged edges (Zhou et al. 2012). When solution pH value was higher than pH_{zpc} (6.6) which was higher than that in the reported literature due to the different components of Mt (Table 1), Na–Mt had not only negative structural charge but also negative edges ($MOH + OH^- \rightarrow M(OH)_2^-$, M was metal cation). The electrostatic repulsion between sorbent and PFOS caused a sharp reduction of PFOS removal efficiency on the Na–Mt (Zhou et al. 2010). However, solution pH hardly influenced the PFOS removal on organo-Mts whose surfaces were always negative charge in this study range. Moreover, the PFOS removal efficiency on the organo-Mts was more or less higher than that on the Mt without modification, which implied that the surfactant of organo-Mts was the primary contribution to the sorption of PFOS.

Figure 3b showed that the HDTMAB–Mt, which had the highest sorption capacity for PFOS in this study, was almost ineffective for Cr(VI) removing. The chromium removal on the other sorbents except HDTMAB–Mt decreased when solution pH increased, declined to less than 15 % when pH >7. As we all know, hexavalent

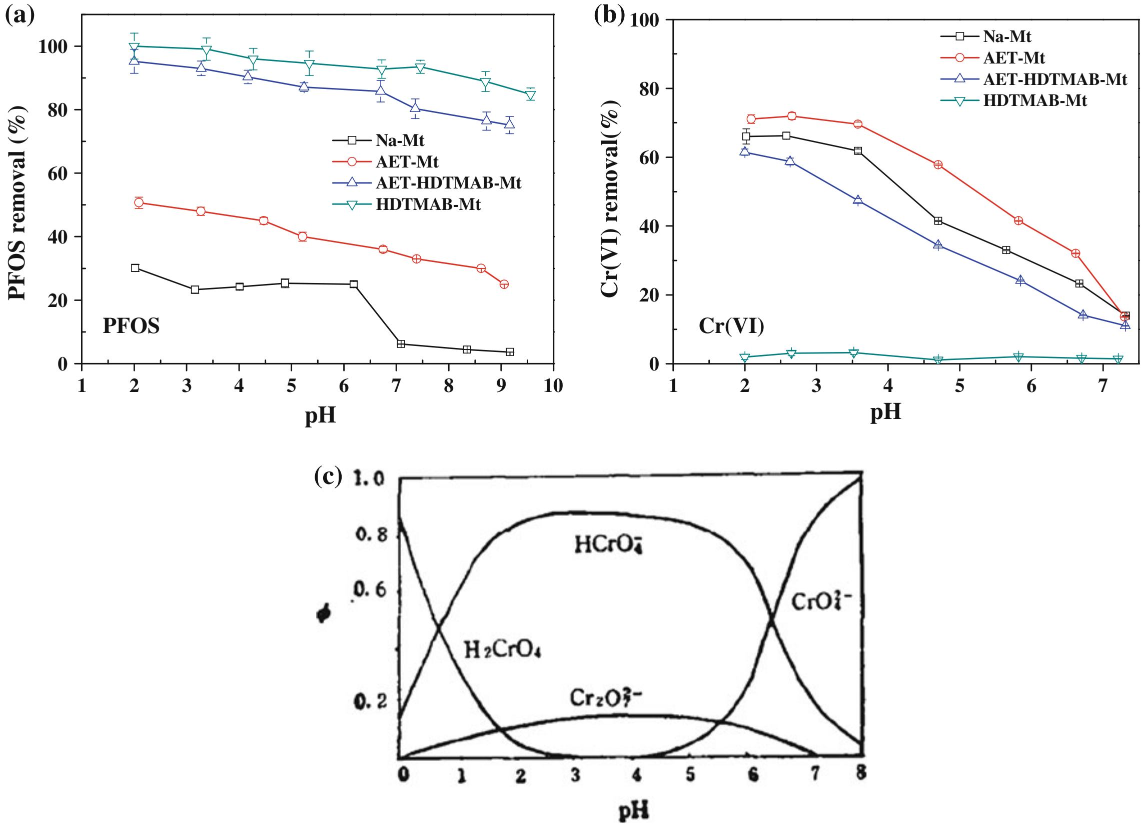

Fig. 3 Influence of solution pH on PFOS (**a**) and hexavalent chromium (**b**) ($C_{0,PFOS}$ = 50 mg/L, $C_{0,Cr}$ = 2 mmol/L, reaction time = 120 h, sorbent dose = 4 g/L), and relationship between pH and existing form of Cr^{6+} (**c**)

chromium usually exists in the form of $HCrO_4^-$ and $Cr_2O_7^{2-}$ in optimum solution pH (Shi 1986; Bansal et al. 2009). $HCrO_4^-$ as the predominant existing of Cr(VI) at acidic condition derived from the hydrolysis of $Cr_2O_7^{2-}$. $HCrO_4^-$ would be shifted to $Cr_2O_7^{2-}$ or CrO_4^{2-} with an increase of pH. The relationship between solution pH and the existing form of Cr^{6+} was shown in Fig. 3c according to the reported literature (Shi 1986). At a pH of 2.0, the sorbents surfaces were protonated, which was advantaged to the sorption of the dominant form as $HCrO_4^-$. With the increasing of pH, the competition between OH^- and $Cr_2O_7^{2-}/CrO_4^{2-}$ would decrease the sorption of anionic Cr(VI). Considering the waste solution from chromium electroplating plants usually contained strong acids (pH 2.85–3.0), a pH of 3 was adopted for the further sorption experiments.

3.3 Sorption isotherm and uptake mechanism

The uptake amounts of PFOS and Cr(VI) on different sorbents in simple and mixed system were investigated (Fig. 4). Since the experiment was carried out at a pH of 3.0, in which Cr(VI) existed as the major species $HCrO_4^-$ (89 %) (Zhang et al. 2011), there was a competitive sorption between anionic PFOS and $HCrO_4^-$ on the protonated sorbent surfaces. However, the presence of Cr(VI) had few effects on the uptake ability of PFOS on all the sorbents. The little reduction of PFOS uptake amounts implied that the importance of hydrophobic interaction during PFOS uptake process. On the contrary, anion PFOS interfered with the uptake process and decreased the Cr(VI) uptake amounts on the sorbents. The result implied the electrostatic attraction between anionic $HCrO_4^-$ and protonated amino and sulfhydryl groups in AET–Mt, AET–HDTMAB–Mt and Lewis acid in the Na–Mt surface.

The sorption isotherm both Cr(VI) and PFOS on the four kinds of sorbents with their different equilibrium concentrations were shown in Fig. 5. It can be observed that Cr(VI) sorption amounts decreased in the following order as AET–Mt > Na–Mt > AET–HDTMAB–Mt > HDTMAB–Mt. The electrostatic attraction between anionic $HCrO_4^-$ and protonated amino and sulfhydryl groups in sorbents resulted in the formation of coordination compounds between amido and sulfhydryl from AET and anionic form

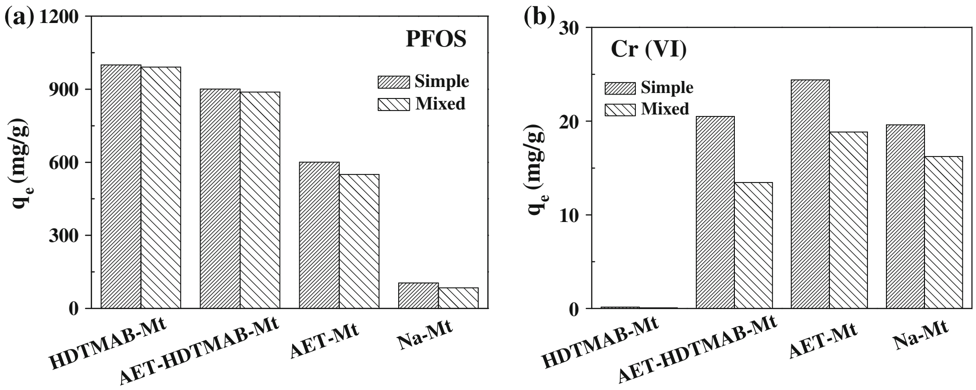

Fig. 4 Comparative sorption of PFOS and Cr(VI) in simple and mixed system ($C_{0,PFOS}$ = 400 mg/L, $C_{0,Cr}$ = 2 mmol/L, reaction time = 120 h, pH = 3.0 ± 0.05, sorbent dose = 4 g/L)

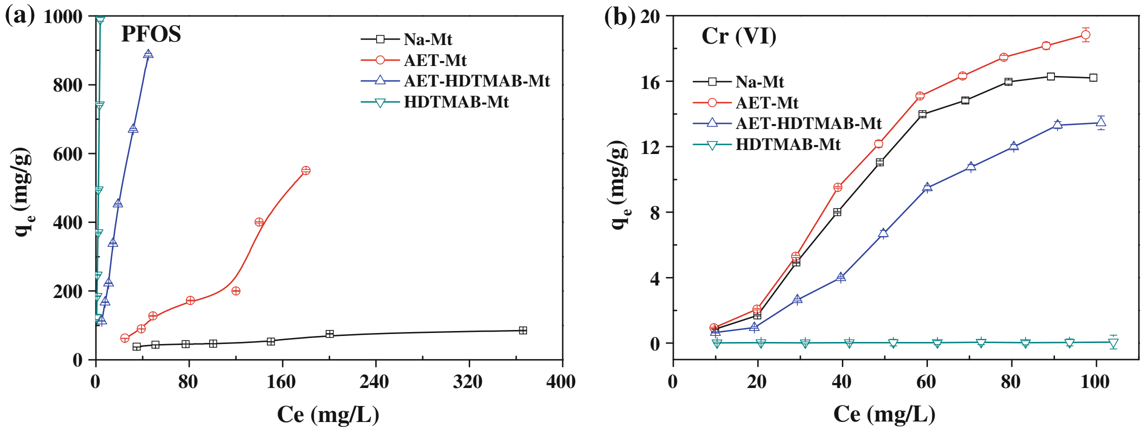

Fig. 5 Sorption isotherm both PFOS and Cr(VI) by the sorbents (**a** $C_{0,PFOS}$ = 50–400 mg/L, $C_{0,Cr}$ = 0.5 mmol/L, **b** $C_{0,Cr}$ = 0.2–2 mmol/L, $C_{0,PFOS}$ = 50 mg/L; pH = 3.0 ± 0.05; sorbent dose = 4 g/L)

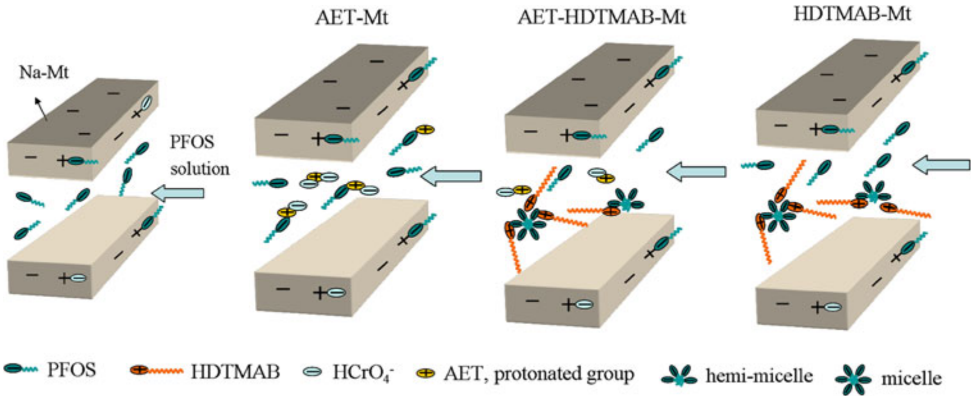

Fig. 6 Schematic sorption of PFOS and Cr(VI) on different sorbents (Color figure online)

of hexavalent chromium, which was beneficial to the Cr(VI) sorption on AET–Mt and AET–HDTMAB–Mt.

The PFOS sorption amount by the HDTMAB–Mt was approximately several times as higher as that by Na–Mt with the same initial concentrations. It was observed that the PFOS sorption isotherms on HDTMAB–Mt and AET–HDTMAB–Mt nearly were linear within the range of concentration studied. The linear isotherm for PFOS implied that the hydrophobic partition was the main uptake mechanism (Ochoa-Herrera and Sierra-Alvarez 2008). The result was consistent with as discussed above, that is, hydrophobic interaction was the important role during the PFOS sorption process. Organic carbon had been proved to be the main factor which affected PFOS sorption, implying the significance of hydrophobic partition (Higgins and Luthy 2006; Pan et al. 2009). In this study, organic carbon fraction (f_{oc}, %) of Na–Mt, AET–Mt, AET–HDTMAB–Mt and HDTMAB–Mt were 0.08, 1.51, 19.24 and 21.34 % respectively. The f_{oc} increasing of organo-Mts resulted from the surfactants in the interlayer of the sorbents. Hence, the most effective sorbent for PFOS was HDTMAB–Mt, AET–HDTMAB–Mt the second, AET–Mt the third, finally Na–Mt. Integrating the discussed above, the resulting sorbent named AET–HDTMAB–Mt was the most efficient for the sorption of both Cr(VI) and PFOS from simulating plating wastewater.

Considering the PFOS speciation such as anion, hemi-micelles and micelles formation, the uptake mechanism was much more complicated. The schematic drawing of the sorption process of PFOS and Cr(VI) by the different sorbents was illustrated in Fig. 6.

The edge of Na–Mt was positive charge when solution pH was 3.0. The electrostatic attraction between anionic PFOS, $HCrO_4^-$ and positive edges of sorbent contributed to the sorption of pollutants on the Mt without modification during the sorption process. For AET–Mt, the interlayer AET with protonated amino and sulfhydryl groups attracted the anionic PFOS and $HCrO_4^-$ to format the stable coordination by electrostatic attraction. Meanwhile, the long C–F chains of PFOS were sorbed on the HDTMAB on the AET–HDTMAB–Mt and HDTMAB–Mt by hydrophobic partition. When more and more PFOS were sorbed, some micelles or hemi-micelles of PFOS occurred in the interlayer of the AET–HDTMAB–Mt and HDTMAB–Mt where hydrophobic phase was formed from HDTMAB. The presence of PFOS micelles and hemi-micelles resulted in a high sorption capacity on the HDTMAB modified Mt. The result was consistent with the previous report where HDTMAB contributed to the high uptake amounts of PFOS (Zhou et al. 2010).

4 Conclusions

The sorption of Cr(VI) on the Na–Mt, AET–Mt and AET–HDTMAB–Mt was pH-dependent, indicating that the electrostatic attraction was the main role. The comparative sorption of Cr(VI) and PFOS in simple and mixed system verified that the importance of hydrophobic interaction for PFOS and electrostatic attraction for Cr(VI) during the sorption process. The presence of PFOS hemi-micelle and micelle contributed to a high sorption capacity on the HDTMAB modified Mt. In general, AET–HDTMAB–Mt was the most effective among all the sorbents for removing both PFOS and Cr(VI) simultaneously, and their sorption capacity reached 890 and 14 mg/g respectively.

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