

Preparation of Octadecyl and Amino Mixed Group Modified Titanate Nanotubes and Its Efficient Adsorption to Several Ionic or Ionizable Organic Analytes

Hongyun Niu and Yaqi Cai*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

In this study, octadecyl (C_{18}) and aminopropyl group modified titanate nanotubes (C_{18}/NH_2 -TNs) were prepared successfully with a silylation method by introducing octadecyltrimethoxysilane (ODS) and aminopropyltrimethoxysilane (APS) simultaneously to the surface of titanate nanotubes (TNs). The properties of the products were characterized in detail. The results indicated that there might be steric hindrance effects to C_{18} groups on the nanoscaled interior and exterior space of TNs. Therefore, aminopropyl groups were more ready to immobilize on the surface of TNs than C_{18} groups when the organosilanes ODS and APS coexisted in reaction solution. C_{18}/NH_2 -TNs with the obvious characteristic of C_{18} and aminopropyl groups were obtained as the ratio of ODS/APS in reaction solution was 4.0, and the corresponding proportion of the two groups (C_{18}/NH_2) on the C_{18}/NH_2 -TN surface was about 0.25. This adsorbent had good water dispersibility, overcoming the bad deficiency of reverse phase nanosized materials in water and improving its accessibility to polar analytes. Due to the cooperative effect of alkyl and aminopropyl groups coupled with the residual hydroxyl groups on the surface, C_{18}/NH_2 -TNs exhibited excellent affinity efficiency to some ionic or ionizable organic analytes under a different solution pH, including anionic (perfluorooctane sulfonate, perfluoroctanoic acid, and sodium dodecyl sulfate), cationic (cetyltrimethylammonium bromide), and amphoteric compounds (sulfamethazine). The selective binding of these anionic, amphoteric, and cationic analytes could be achieved by adjusting solution pH to acid, neutral, and alkaline conditions, respectively. Since C_{18}/NH_2 -TNs possessed relatively large surface areas and strong affinity ability to ionic analytes, especially with long alkyl chains, it showed significantly higher adsorption capacity for perfluorooctane sulfonate than activated carbon and anion-exchange resin.

* To whom correspondence should be addressed. Address: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China. E-mail: caiyiqi@rcees.ac.cn. Tel: (086) 010-62849182. Fax: (086) 010-62849239.

Sample preparation is considered as a vital step in the analysis of organic contaminants with very low concentrations in complex matrixes, regardless of the kind of detection utilized.¹ Solid-phase extraction (SPE) is widely used for the preconcentration of analytes from pharmaceutical, clinical, environmental, and food samples. However, the major disadvantage of conventional SPE adsorbents is inadequate selectivity and coextraction of matrix interference components with the target analytes. To eliminate these problems, development of affinity-based adsorbents to be selective in extracting the target analytes is of great interest. There are two main approaches: the immunosorbents and the molecularly imprinted polymers (MIPs).^{2–4} Using these adsorbents, we can selectively extract a target analyte or simultaneously extract structurally related analytes from a drug and its metabolites from biological fluids or a class of herbicide and its degradation products from environmental samples.⁴ However, the preparation of immunosorbents is labor intensive and, thus, very expensive, and the experimental conditions have to be carefully selected to guarantee their stability.¹ Compared with immunosorbents, the preparation of MIPs is easy, low-cost, and quick, and MIPs can be used under drastic conditions.⁴ Nevertheless, the design and synthesis of a successful MIP can be an issue that is far from trivial.¹

Another interesting approach is to develop the mixed-mode adsorbents, which bear two or more functional groups.^{3,4} The cooperative effect of these groups imparts a special characteristic to the adsorbents, such as combining both reversed-phase and ion-exchange mechanism interactions.^{3–5} The mixed-mode adsorbents also can selectively bind guest species with special functional groups and have shown application potential in drug delivery, biosensor, stationary phase, or catalyst.^{5–9} In the field

- (1) Chico, J.; Meca, S.; Companyo, R.; Prat, M. D.; Granados, M. *J. Chromatogr., A* 2008, 1181, 1–8.
- (2) Haginaka, J. *Trends Anal. Chem.* 2005, 24, 407–415.
- (3) Hennion, M. C. *J. Chromatogr., A* 1999, 856, 3–54.
- (4) Poole, C. F. *Trends Anal. Chem.* 2003, 22, 362–373.
- (5) Souverain, S.; Rudaz, S.; Veuthey, J. L. *J. Chromatogr., B* 2004, 801, 141–156.
- (6) Yang, S. K.; Weck, M. *Macromolecules* 2008, 41, 346–351.
- (7) Jang, J.; Ko, S.; Kim, Y. *Adv. Funct. Mater.* 2006, 16, 754–759.
- (8) Hensley, J. E.; Way, J. D. *Chem. Mater.* 2007, 19, 4576–4584.
- (9) Chen, C. C.; Cheng, S.; Jang, L. Y. *Microporous Mesoporous Mater.* 2008, 109, 258–270.
- (10) Sunding, M. F.; Jensen, I. T.; Stenstad, P. M.; Diplas, S. *Surf. Interface Anal.* 2008, 40, 751–753.

of analytical chemistry, mixed-mode adsorbents have been mainly utilized to determine basic drugs and pharmaceuticals in offline or online mode, they allow the extraction and cleanup of biological matrixes (urine, blood, or plasma) in the same sequence.³ This kind of adsorbent is usually focused on polymeric matrixes or porous silica particles. For the silica matrixes, the adsorbents can be prepared by the silylation method. With this simple reaction, the surface of silica can be modified with appropriate functional groups.^{10,11} Besides silica, other inorganic matrixes, such as titania and zirconia, have attracted extensive attention in the field of analytical chemistry and environmental science for their better alkali resistance, practically being insoluble within a wide pH range, and having outstanding resistance to dissolution at high temperature.¹² The surfaces of these metal oxides can also be functionalized by reacting with organosilanes. Recently, Ogawa and co-workers reported that a layered titanate mineral bearing interlayer hydroxyl groups and controlled amounts of alkyl groups (C_8) adsorbed *n*-alkyl alcohols selectively but not *n*-alkanes.¹³ In another study, they prepared titanate mineral with two different organic functional units, alkyl and phenyl groups, to specifically bind 4-nonylphenol.¹⁴ This adsorbent was synthesized with a three-step method: first, the titanate mineral was allowed to react with dodecyltrimethylammonium (C_{12} TMA) to get its C_{12} TMA-exchanged form as the intermediate; then, phenyltrimethoxysilane and octadecyltrimethoxysilane (ODS) were reacted subsequently with this intermediate to immobilize both alkyl and phenyl groups on titanate mineral. In recent years, TiO_2 -derived nanotubes (titanate nanotubes, TNs) have attracted much attention in many fields such as hydrogen storage,^{15,16} protein immobilization,¹⁷ or photocatalysis.^{18,19} The one-dimensional nanostructures, uniform nanochannel, large surface areas, and sufficient functional hydroxyl groups of TNs impart its great potential for the development of SPE adsorbent. Different from the traditional metal oxide adsorbents, the nanoscaled tube diameters and multilayered space of TNs may result in different distribution of organic units with diverse dimensional size inside or outside the tubular space, which might result in special properties of TNs and alter the adsorptive tendency of substances on its surface in complex matrixes. Therefore, modification of TNs with multigroups for molecular recognition is worthy to be studied. However, research works on TNs about its surface functionalization with organic units and application as adsorbents for sample pretreatment in analytical chemicals have rarely been carried out. In this study, we try to introduce octadecyl and aminopropyl groups together to TNs with a one-step method

by reacting ODS and aminopropyltrimethoxysilane (APS) simultaneously with TNs in toluene solvent. The former provides hydrophobic property to TNs; the latter makes the surface pH-responsive and offers electrostatic interactions to ionic analytes.²⁰ The results showed that TNs with the characteristic of the two organic units could be achieved successfully with this simple method. This material had good water wettability and strongly and efficiently adsorbed several ionic or ionizable analytes including anionic (perfluorooctane sulfonate, perfluorooctanoic acid, and sodium dodecyl sulfate), amphoteric (sulfamethazine), and cationic (cetyltrimethylammonium bromide) compounds by adjusting solution pH to acid, neutral, or alkaline conditions, respectively.

EXPERIMENTAL SECTION

Materials and Reagents. The model compounds included perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) (Sigma-Aldrich, Oakville, ON, Canada), sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB) (Beijing Chemical Reagents Company, Beijing, China), antibiotic compound sulfamethazine (Acros, Morris Plains, New Jersey), and nonionic compounds di-*n*-butyl-phthalate (DBP), bisphenol (BPA), 4-*n*-nonylphenol (4-NP), and phenanthrene (Phe) (Tokyo Kasei Kogyo Co. Ltd. Tokyo, Japan). The sodium hydroxide was supplied by Beijing Chemical Reagents Company (Beijing, China). The organosilanes APS and ODS were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Ultrapure water was prepared in the lab using a Milli-Q Advantage A10 reagent water system from Millipore (Milford, MA). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany).

Adsorbent Preparation. TNs were prepared with the hydrothermal method described in ref 22. Surface modification of TNs with octadecyl and aminopropyl groups was performed with the silylation method as follows: 100 mg of dry TNs were dispersed in 50 mL of toluene in a Teflon bottle; a suitable amount of APS and ODS were added to the mixture simultaneously and then kept in a PTFE-lined autoclave and heated at 120 °C for 24 h; the products were then filtered, washed with toluene, acetone, ethanol containing 50% 0.1 M HCl solution, and absolute ethanol, subsequently, and dried overnight at 60 °C. In order to get TNs bearing clearly the characteristic of aminopropyl and alkyl groups, the ratio of ODS/APS in the TN suspension ranged from 4 to 0.25 mL (namely ODS/APS 0.16:0.04 mL; 0.15:0.05 mL; 0.134:0.066 mL; 0.1:0.1 mL; 0.066:0.134 mL; 0.05:0.15 mL; 0.04:0.16 mL). The dual group product was abbreviated as $C_{18}/NH_2(x)$ -TNs ($x = 0.25, 0.33, 0.5, 1, 2, 3, 4$) according to the ODS/APS ratio in the reaction mixture. To show the importance of the presence of the two functionalities, the organic derivatives of TNs with one of the two silanes were also prepared using the same procedure and the products were coded as NH_2 -TNs and C_{18} -TNs, respectively.

Adsorbents Characterization. Transmission electron micrograph (TEM) images of TNs before and after modification were recorded on a JEM2010 electron microscope operating at 200 kV (Hitachi, Japan). An energy-dispersive X-ray spectroscopy (EDAX) was equipped on TEM to analyze the element composition of TNs

- (11) Heikkinen, J. J.; Heiskanen, J. P.; Hormi, O. E. O. *Polym. Adv. Technol.* **2006**, *17*, 426–429.
- (12) Xu, L.; Lee, H. K. *Anal. Chem.* **2007**, *79*, 5241–5248.
- (13) Fujita, I.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2005**, *17*, 3717–3722.
- (14) Ide, Y.; Ogawa, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8449–8451.
- (15) Bavykin, D. V.; Friedrich, J. M.; Lapkin, A. A.; Walsh, F. C. *Chem. Mater.* **2006**, *18*, 1124.
- (16) Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C. *Adv. Mater.* **2006**, *18*, 2807–2824.
- (17) Liu, H.; Wei, M. D.; Honma, I.; Zhou, H. S. *Anal. Chem.* **2005**, *77*, 8068–8074.
- (18) Geng, J. Q.; Jiang, Z. Y.; Wang, Y. B.; Yang, D. *Scr. Mater.* **2008**, *59*, 352–355.
- (19) Inagaki, M.; Kondo, N.; Nonaka, R.; Ito, E.; Toyoda, M.; Sogabe, K.; Tsumura, T. *J. Hazard. Mater.* **2009**, *161*, 1514.
- (20) Calvo, P. C.; Angelomé, V. M.; Sánchez, D. A.; Scherlis, F. J.; Williams, G. J.; Soler-Illia, A. A. *Chem. Mater.* **2008**, *20*, 4661–4668.

- (21) Niu, H. Y.; Wang, J. M.; Shi, Y. L.; Cai, Y. Q.; Wei, F. S. *Microporous Mesoporous Mater.* **2009**, *122*, 28–35.
- (22) Geng, J. Q.; Yang, D.; Zhu, J. H.; Chen, D. M.; Jiang, Z. Y. *Mater. Res. Bull.* **2008**, *44*, 146–150.

samples. An X-ray powder diffractometer (Rigaku III/B max) was used to determine the crystalline structures of adsorbents. The radiation source was Cu K α ; the applied current was 30 mA, and the voltage was 40 kV. During the analysis, the sample was scanned from 10 to 100° at a speed of 0.4°/min. The points of zero charge (pHpzc) of the materials were obtained with zetasizer 2000 apparatus (Malvern, United Kingdom). The specific surface areas of adsorbents were determined by the BET method with N₂ gas (ASAP2000 V3.01A; Micromeritics, Norcross, GA). A Nicolet Avatar 360 spectrometer was used for the FT-IR determination of samples. To check the chemical composition and chemical state of all the elements on the surface of adsorbents, TNs and its organic derivatives were freeze-dried and analyzed using X-ray photoelectron spectroscopy (XPS) collected on an ESCA-Lab-220i-XL spectrometer with monochromatic Al K α radiation (1486.6 eV). C1s peaks were used as an inner standard calibration peak at 284.7 eV. XPS data process and peak fitting was preformed using a nonlinear least-squares fitting program (XPSpeak software 4.1, Raymund W. M. Kwork).

Batch Experiments. Batch experiments were carried out to examine the adsorption behaviors of the model compounds on different adsorbents. For PFOS and PFOA, the experiments were performed in 250 mL of polyethylene (PE) bottles; for SDS, CTAB, SMT, and all the nonionic organic analytes, the adsorption tests were conducted in 250 mL of glass bottles. The final aqueous volume in each of the bottle was 100 mL. The effect of solution pH was examined with initial concentration of each model compound maintained at 1 μ g mL⁻¹ at varying solution pH (pH 2.0–10.5). The pH of the solution was adjusted with 1 M HCl and/or 1 M NaOH. Adsorption isotherm studies were conducted with initial PFOS and PFOA concentrations ranging from 0.05 to 5 mg L⁻¹ at pH 2.5 in DI water; while for SDS and CTAB, the isotherms were obtained by varying their initial concentrations from 0.5 to 100 mg L⁻¹ at pH 2.5 and 8.5, respectively. The adsorption isotherms of nonionic analytes were executed at neutral solutions with the initial concentrations changing from 0.05 to 5 mg L⁻¹ (for DBP, BPA, 4-NP, and SMT) or 0.05–1.2 mg L⁻¹ (for Phe) considering their low water solubility. After mixing for 24 h at 25 °C in a shaken water bath (200 rpm), the mixture was centrifuged for the solid–liquid separation. For the polar and ionic analytes, the mixture was kept in plastic centrifuge tubes (PE) and centrifuged at 10 000 rpm for 10 min. For nonpolar analytes, the separation is performed in glass centrifuge tubes at 3500 rpm for 10 min. The supernatant aqueous solution was used for the analysis of model compounds.

LC/MS and LC Analyses. The concentrations of PFOS, PFOA, SDS, and CTAB were quantified by LC/ESI-MS/MS system (API 3200 triple quadrupole mass spectrometer configured with ESI, API). Phe, DBP, SMT, BPA, and 4-NP were detected using a Dionex SUMMIT HPLC system (Dionex, Sunnyvale, CA) with a PDA-100 photodiode array detector. The detailed information about the LC/MS and LC conditions were described in the Supporting Information.

RESULTS AND DISCUSSION

Characterization of Dual Group Modified Tianate Nanotubes. TNs before and after modification with organic units

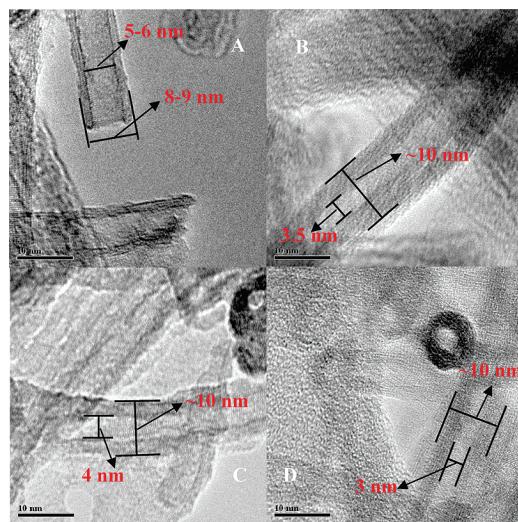


Figure 1. High-resolution transmission electron microscopy (HRTEM) images of TNs (A), C₁₈/NH₂-TNs (B), C₁₈-TNs (C), and NH₂-TNs (D).

maintained perfect tubular morphologies (Figure S1 in the Supporting Information). The outer and inner diameters of as-prepared TNs were 8 to 9 nm and 5 to 6 nm, respectively. After functionalization, the outer diameters of C₁₈, aminopropyl, and dual group modified TNs were all increased to 10 nm, while the inner diameters of these products were decreased to 4, 3, and 3.5 nm, respectively (Figure 1). Then, the thickness of the multiwall of TNs had increased by 1–1.5 times. These results might suggest that the silylation had taken place both on the external and internal surface of TNs. The difference in inner diameter of surface modified TNs might be caused by the different silylation efficiency of ODS and APS on internal space of TNs due to the possible steric hindrance effects to the C₁₈ group.

The element composition and their atom contents on the surface of all the materials were analyzed with EDAX. The results showed that, in the surface of C₁₈-TNs and NH₂-TNs, the C element content was about 50% and 20% and the C/Si ratio was 18.3 and 3.7, respectively, which was close to the theoretical value of organosilyl groups (Table S1 in the Supporting Information), implying the successful immobilization of alkyl or amino groups on TNs. For the dual group products, a slight increase of C contents was observed (20–28.5%) as the ODS/APS ratios changed from 0.25 to 4 compared with that of NH₂-TNs, while an opposite trend for N content in these materials was observed, but the difference between NH₂-TNs (5.6%) and C₁₈/NH₂(x)-TNs (4.2–5.1%) was rather small. The atom content of Si element on the surface of NH₂-TNs and C₁₈/NH₂(x)-TNs (5.2–5.4%) was higher than that of C₁₈-TNs (3.6%), reflecting different silylation efficiency on the TN surface between the two organosilanes APS and ODS. We concluded that aminopropyl groups were more ready to immobilize on the surface of TNs compared with C₁₈ groups, which was probably caused by the steric hindrance effects to the C₁₈ group existing on the interior and exterior space of TNs. This result was consistent with the TEM observation in Figure 1. According to the theoretical ratio of C, N, and Si elements of the C₁₈ and aminopropyl groups, the actual C₁₈/NH₂ ratio in the products would be in the range of 0.047–0.25. It could be expected that

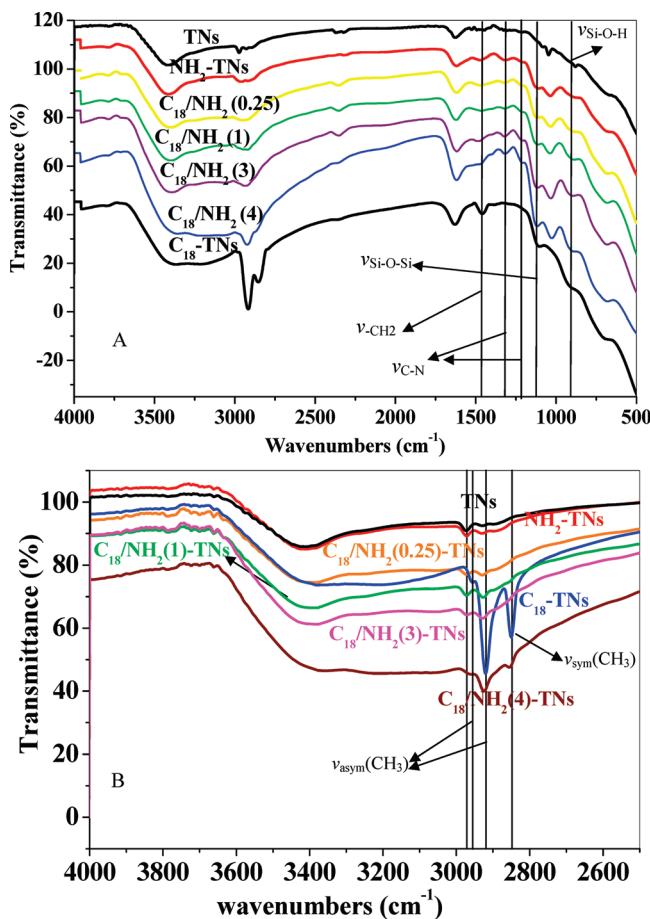


Figure 2. FT-IR patterns of TNs and C_{18} and NH_2 and dual group modified TNs in the range of 4000–400 cm^{-1} (A) and 4000–2500 cm^{-1} (B).

the alkyl group density would not increase obviously with the further increase of the ODS/APS ratio in the reaction solutions.

The FT-IR patterns of TNs and functionalized TNs were shown in Figure 2. The Si–O–H and Si–O–Si bands could be observed in the range of 900–1000 cm^{-1} and 1100–1220 cm^{-1} , respectively, in the spectra of surface modified TNs.^{22,23} A peak appeared in the range of 1450–1500 cm^{-1} for all TNs derivates and was caused by the bending vibration of $-CH_2$ species of aminopropyl or alkyl groups.²⁴ Two adsorption peaks at about 1200 cm^{-1} and 1320 cm^{-1} were only present in the spectra of amino-containing TNs, which should be ascribed to the C–N stretching vibration.^{25,26} The stretching vibrations of N–H in the 3280–3370 cm^{-1} region and the bending vibration in the zone of 1500–1650 cm^{-1} could not be detected in these products due to the broad peak centered at the two regions, corresponding to the adsorbed H_2O and hydroxyl groups.^{25,26} In Figure 2B, there were two sharp peaks and one weak peak in the IR peaks of C_{18} -TNs in the range of 2800–3000 cm^{-1} . The peak at

2850 cm^{-1} could be assigned to the symmetric stretching of the $-CH_3$ group; the adsorption peak at 2920 cm^{-1} and weak peak at 2956 cm^{-1} were ascribed to the asymmetric stretching bands of the $-CH_3$ group which belonged to the C_{18} group on the TNs surface.^{27,28} Among TNs and NH_2 -containing TNs samples, these peaks (except the peak at 2956 cm^{-1}) only could be observed in $C_{18}/NH_2(4)$ -TNs. In the spectra of NH_2 -TNs and other $C_{18}/NH_2(x)$ -TNs, however, the stretching band of the methyl group could not be discerned, and the peaks were located at 2973 and 2929 cm^{-1} , respectively, which could also be identified in the spectrum of TNs, and were attributed to the stretching vibration of the Ti–OH or Ti–O bond.^{22,23} These results indicated that only $C_{18}/NH_2(4)$ -TNs combined the characteristic of C_{18} -TNs and NH_2 -TNs, which could be regarded as the evidence for the simultaneous attachment of C_{18} and aminopropyl groups. Therefore, this material was regarded as the desired dual group modified TNs (abbreviated as C_{18}/NH_2 -TNs).

XPS measurements were carried out to study the chemical state of all the elements on the surface of TNs, C_{18} -TNs, NH_2 -TNs, and C_{18}/NH_2 -TNs. Compared with TNs, the peaks for Si, N, and C elements appeared, and the intensity of Ti and O decreased greatly on the surface of functionalized samples. The O1s peak deconvolution of all the adsorbents and the assigned bonds were shown in Figure 3. The O1s spectra of each adsorbent was composed of overlapped peaks of oxide oxygen (O^{2-}), hydroxyl (–OH), and sorbed water (H_2O).²⁹ All of the spectra were fitted using a 50:50 Gaussian/Lorentzian peak shape; the fitting results were listed in Figure S2 in the Supporting Information. The results indicated that O^{2-} was the most abundant (50–70%) species in all the adsorbents. –OH, which was the key factor for surface functionalization through silylation reactions, occupied 31.7% of the total oxygen species in TNs. The immobilization of C_{18} , aminopropyl, and dual groups led to an obviously decrease of the –OH species, and the residual –OH contents were 23.5%, 16%, and 7.6% of the oxygen in C_{18} -TNs, NH_2 -TNs, and C_{18}/NH_2 -TNs, respectively. These changes might also reflect the different immobilization efficiency between C_{18} and aminopropyl groups on the TN surface. Changes of water content were also observed; the sorbed water took up about 8.4% and 8% of the O species on TNs and C_{18} -TNs, respectively, and it increased to 34% and 28.5% on the surface of NH_2 -TNs and C_{18}/NH_2 -TNs, respectively, due to the presence of aminopropyl groups. On the other hand, the O1s lines of amino-containing TNs were found to shift to lower binding energies; while the opposite trend was observed for C_{18} -TNs whose binding energy for O^{2-} and OH was shifted to 530.9 and 531.9 eV, respectively. This shift indicated that, compared with TNs, the surfaces of NH_2 -TNs and C_{18}/NH_2 -TNs became more hydrated with the immobilization of amino groups, while the surface of C_{18} -TNs was more

- (23) Alba, M. D.; Luan, Z. H.; Klinowski, J. *J. Phys. Chem.* **1996**, *100*, 2178–2182.
- (24) Shi, B. F.; Wang, Y. S.; Guo, Y. L.; Wang, Y. Q.; Wang, Y.; Guo, Y.; Zhang, Z. G.; Liu, X. H.; Lu, G. Z. *Catal. Today* **2009**, *148*, 184–188.
- (25) Zhang, Y.; Yang, M.; Dou, X. M.; He, H.; Wang, D. S. *Environ. Sci. Technol.* **2005**, *39*, 7246–7253.
- (26) Tarafdar, A.; Pramanik, P. *Microporous Mesoporous Mater.* **2006**, *91*, 221–224.
- (27) Yadav, B. S.; Ali, I.; Kumar, P.; Yadav, P. *Indian J. Pure Appl. Phys.* **2007**, *45*, 979–983.

- (28) Anbia, M.; Lashgari, M. *Chem. Eng. J.* **2009**, *150*, 555–260.
- (29) Guo, G. S.; He, C. N.; Wang, Z. H.; Gu, F. B.; Han, D. M. *Talanta* **2007**, *72*, 1687–1692.
- (30) Nesbitt, H. W.; Canning, G. W.; Bancroft, G. M. *Geochim. Cosmochim. Acta* **1998**, *62*, 2097–2110.
- (31) Stakheev, A. Y.; Shapiro, E. S.; Apijok, J. *J. Phys. Chem.* **1993**, *97*, 5668–5672.

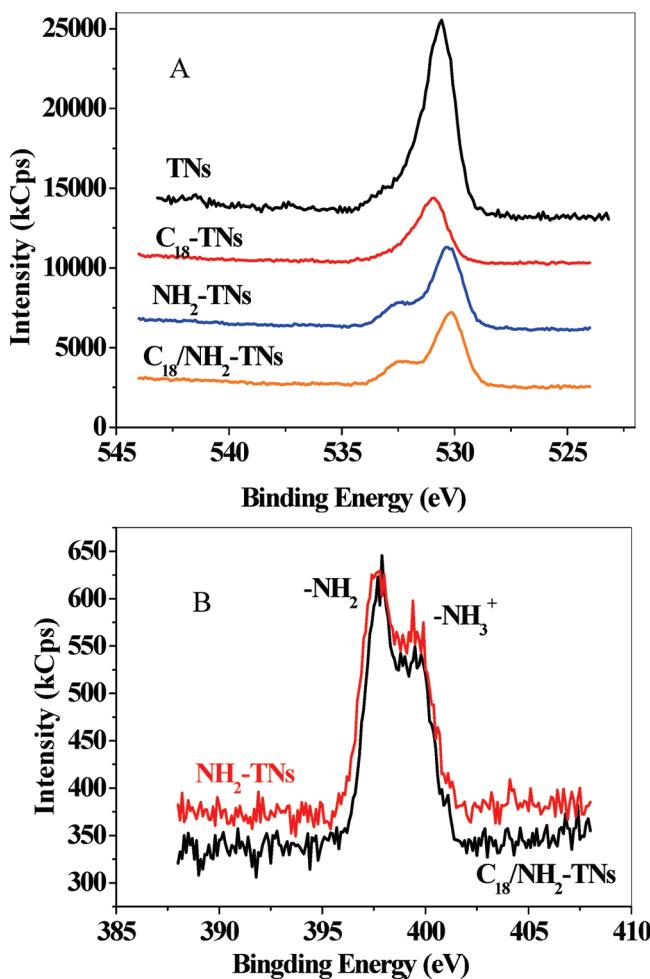


Figure 3. XPS O 1s spectra of TNs, C_{18} -TNs, NH_2 -TNs, and C_{18}/NH_2 -TNs (A) and N 1s spectra of NH_2 -TNs and C_{18}/NH_2 -TNs (B).

hydrophobic in the presence of C_{18} groups.^{20,30} In Figure 3b, the N 1s XPS signals of amino-bearing adsorbents contained two components at ~ 398 and 400 eV BE, attributing to amino ($-NH_2$) and ammonium ($-NH_3^+$) species, respectively.^{10,31} Since C_{18}/NH_2 -TNs and NH_2 -TNs were washed with water before XPS analysis, the appearance of $-NH_3^+$ at pH 7 might indicate large amino densities on their surface, which was in agreement with the high pH_{pzc} of NH_2 -TNs (pH 9.0) determined according to its zeta potentials under different solution pH.

The XRD patterns of TNs and its derivatives were shown in Figure 4. The intensity of the diffraction peaks of the surface modified TNs was higher than those of TNs, which might be caused by the heating treatment in the process of silylation. The rising of peak intensity of TNs with reaction temperature had also been reported as TNs was synthesized with the hydrothermal method.^{21,32} As shown in Figure 4, the crystal structure of TNs and its derivatives could generally be assigned to $H_2Ti_3O_7$.^{15,16} The surface area of TNs was $313\text{ m}^2\text{ g}^{-1}$ and decreased to 185 , 150 , and $114\text{ m}^2\text{ g}^{-1}$ after modification with C_{18} , NH_2 , and C_{18}/NH_2 , respectively. The changes of surface areas of TNs might also indicate the different immobilization efficiency or distribution regions of C_{18} and aminopropyl groups on the TN surface.

(32) Lee, C. K.; Lin, K. S.; Wu, C. F.; Lyu, M. D.; Lo, C. C. *J. Hazard. Mater.* **2008**, *150*, 494–503.

(33) Higgins, C. P.; Luthy, R. G. *Environ. Sci. Technol.* **2006**, *40*, 7251–7256.

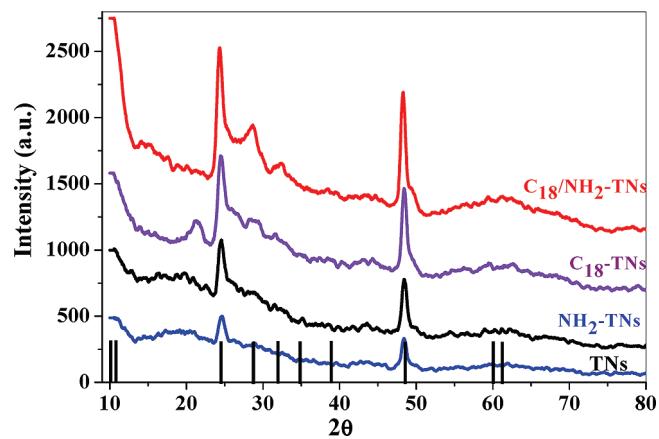


Figure 4. XRD patterns of TNs, C_{18} -TNs, NH_2 -TNs, and C_{18}/NH_2 -TNs. The pattern at the bottom is that of $H_2Ti_3O_7$ from the refs 15 and 16.

In a word, the mixed-mode adsorbents C_{18}/NH_2 -TNs combining the property of C_{18} and aminopropyl groups could be prepared just in one step with the silylation method.

Adsorption Characteristic of Several Anionic and Cationic Analytes on Dual Group Modified TNs. The adsorptions of anionic compounds PFOS, PFOA, and SDS on C_{18}/NH_2 -TNs were found to be pH dependent (Figure 5). The adsorption envelopes of the three analytes under different solution pH on C_{18}/NH_2 -TNs showed generally similar characteristics: first, a decrease began in acidic solution, kept constant in a wide pH range (pH 5–8.5), and then, the second sharp decrease existed at pH > 8.5. PFOA adsorption was more sensitive to solution pH than other compounds, as shown in Figure 5A; the first decrease was observed at pH > 2. For PFOS, the adsorption was unchanged at pH 2–4 and the first abrupt decrease happened in the range of pH 4–5. With regard to SDS, the influence of solution pH on its adsorption was negligible under acidic conditions, and the first slight decrease was discerned at pH 6.5–7.5.

The pK_a value for PFOS and PFOA was low and about -3.27 and 2.5 , respectively.³³ Thus, the two analytes were dominantly present as anions in the whole pH range in this study. The presence of the alkyl and protonated amino groups ($-NH_3^+$) on the C_{18}/NH_2 -TNs surface was favorable for the uptake of anionic analytes, and it was reasonable that the adsorption efficiency of PFOS and PFOA decreased at high pH, resulting from the deprotonation of $-NH_3^+$. As suggested by Higgins, the pH effects on the adsorption of PFOA and PFOS on sediment were likely due to pH-dependent charges in the adsorbent rather than protonation /deprotonation of the sorbates.³³ Thereby, the sharp drops of PFOS and PFOA adsorption on C_{18}/NH_2 -TNs in acid solution should be caused by the change of surface charges on adsorbents. Since there was still a considerable amount of $-NH_3^+$ remaining at pH 7 (Figure 3b), this decrease did not result from the deprotonation of $-NH_3^+$. In a comparison study, a drastic decrease at pH 2–5 was also observed as C_{18} -TNs was used to adsorb the two analytes which should involve dominantly the hydrophobic interaction between negatively charged analytes and adsorbents. Then, there was another pH-responsive group (namely hydroxyl group) on these

(34) Van de Venne, J. L. M.; Rindt, J. P. M.; Coenen, G. J. M. M.; Cramers, C. A. M. G. *Chromatographia* **1980**, *13*, 11–17.

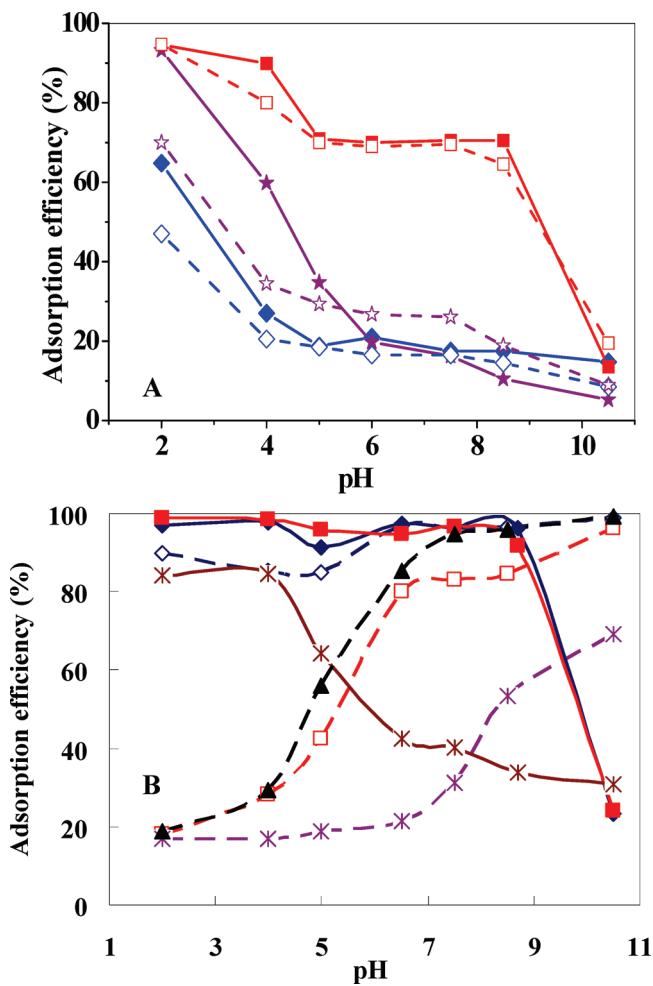
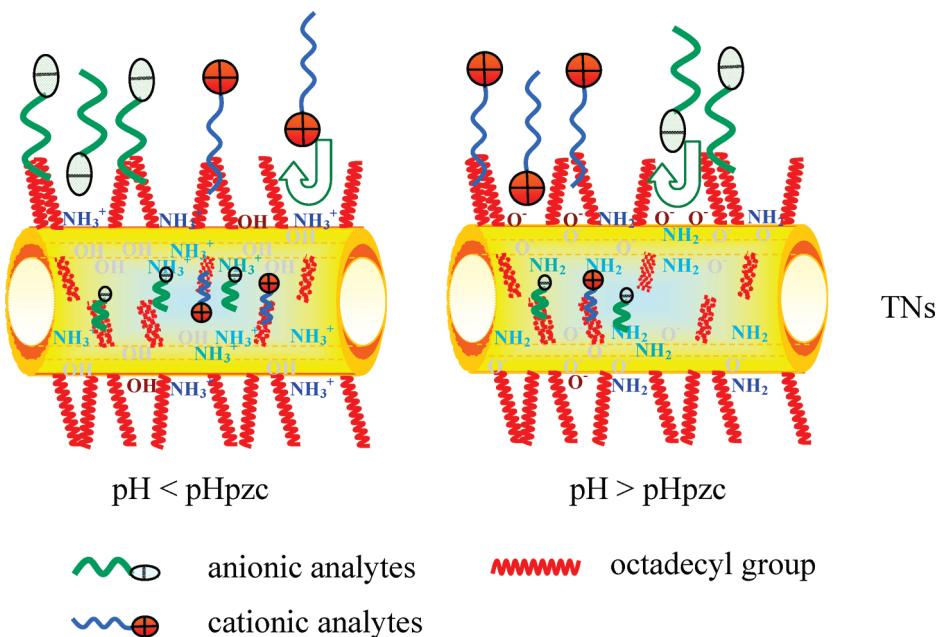


Figure 5. Effect of solution pH on the adsorption of (A) PFOS (solid line) and PFOA (dashed line) and (B) SDS (solid line) and CTAB (dashed line) to C₁₈-TNs (diamond), C₁₈/NH₂-TNs (square), NH₂-TNs (star), and TNs (triangle).

Scheme 1. Selective Adsorption of Anionic and Cationic Analytes on an Octadecyl and Amino Group Modified TN Surface under Different Solution pH



materials, resulting from the residual Ti–OH³⁴ and introduced Si–OH by silylation.¹³ TNs were protonic titanate in nature (pHpzc 4.5–4.8²¹); partial ionization of the residual Ti–OH and Si–OH could start even at low solution pH. This negatively charged group would provide electrostatic repulsive interaction to PFOS and PFOA and decreased their adsorption as pH was higher than 2.0. However, for SDS, the decrease was delayed to pH 8.5, due to its higher hydrophobicity than PFOS and PFOA. The intensive decrease of PFOS, PFOA, and SDS adsorption on all the adsorbents at pH > 8.5 should be ascribed to the cooperative effects of complete conversion of –NH₃⁺ to –NH₂ and ionization of –OH, as shown in Scheme 1. Compared with NH₂-TNs, the presence of alkyl groups made the adsorption of anionic surfactants relatively insensitive to solution pH on C₁₈/NH₂-TNs in a wider pH range.

The pH effect on the adsorption of cationic compound CTAB on C₁₈/NH₂-TNs was just reverse to that of anionic analytes. Due to the electrostatic repulsive interaction between –NH₃⁺ and CTAB, C₁₈/NH₂-TNs displayed limited adsorption ability to CTAB at low solution pH (Figure 5B). The adsorption efficiency enhanced with the rise of pH for the gradual deprotonation of –NH₃⁺. A sharp increase was observed as the solution pH was in the range of 4–7.5, and the second gradual increase appeared at pH 8.5–10.5. As to C₁₈-TNs, the presence of long chain alkyl groups was beneficial to the adsorption of CTAB, which should be based on the hydrophobic interactions between C₁₈ and CTAB and be independent of solution pH. However, a slight increase of CTAB adsorption efficiency on C₁₈-TNs, as solution pH ranged from 5 to 7, also existed. For NH₂-TNs, the uptake of CTAB on this material was also considerable at high solution pH, and the adsorption trends were similar to that of C₁₈/NH₂-TNs, although there were no groups introduced on the NH₂-TN surface favorable to CTAB adsorption. These results indicated that the electrostatic attraction between the ionized hydroxyl group (O[−]) and CTAB molecule played an important role on the adsorption of these

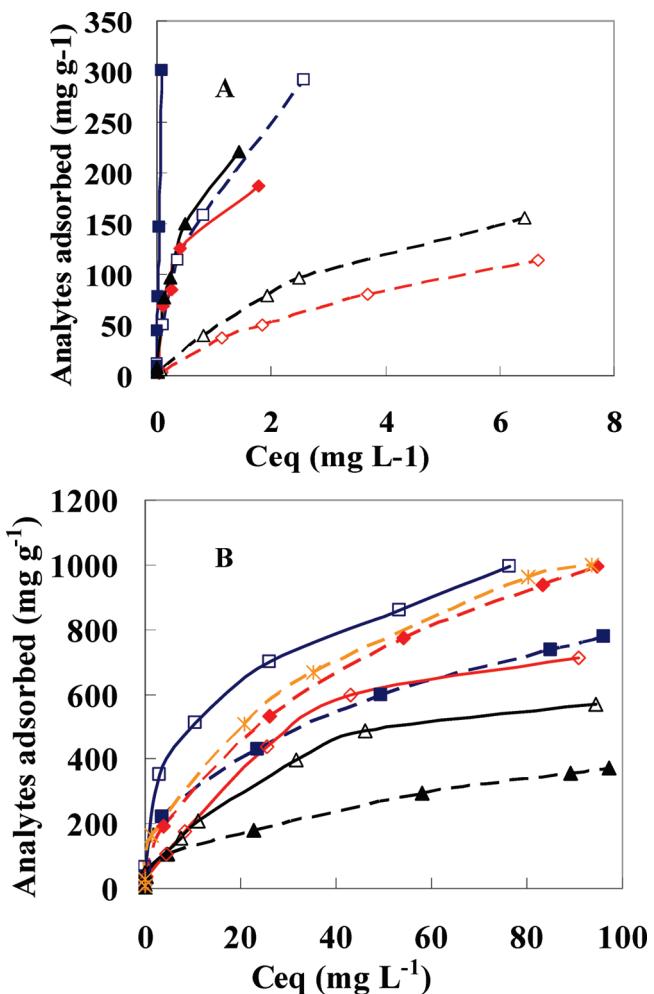


Figure 6. Adsorption isotherms for (A) PFOS (solid line) and PFOA (dashed line) and (B) SDS (solid line) and CTAB (dashed line) adsorption on C₁₈-TNs (diamond), C₁₈/NH₂-TNs (square), NH₂-TNs (triangle), and TNs (star) at optimal pH. PFOS, PFOA, and SDS, pH 2.0; CTAB, pH 10.5.

cationic analytes onto these adsorbents. The joint effect of alkyl and O⁻ group on C₁₈/NH₂-TNs led to its comparable CTAB adsorption ability to C₁₈-TNs at pH > 8.5 (Scheme 1).

The adsorption isotherms for these analytes were obtained with their initial concentration ranging from 0.05 to 5.0 mg L⁻¹ (PFOS and PFOA) and 0.5 to 100 mg L⁻¹ (SDS and CTAB), lower than their critical micelle concentrations. For anionic analytes, the calculated maximal adsorption capacities of PFOS, PFOA, and SDS at pH 2.5 on C₁₈/NH₂-TNs were 833, 333, and 1000 mg g⁻¹, respectively, which were obviously higher than those obtained on monogroup modified TNs (Figure 6 and Table S2 in the Supporting Information). As shown in Figure 6, it could be judged that the uptake capacities of these anionic analytes on C₁₈/NH₂-TNs increased with the prolonging of their alkyl chains (namely hydrophobicity), indicating the importance of the C₁₈ groups. The aminopropyl groups not only made the affinity of these ionic analytes on C₁₈/NH₂-TNs surface pH-sensitive but also contributed to their strong adsorption through electrostatic interactions at desired pH. So, it was the cooperative effect of the two groups on C₁₈/NH₂-TNs that made the adsorptions of PFOS, PFOA, and SDS significantly higher than those on C₁₈-TNs. As to cationic analyte CTAB, the aminopropyl groups on

C₁₈/NH₂-TNs were not favorable for its adsorption; however, the adsorption capacity of CTAB on this adsorbent was still comparable to that on C₁₈-TNs at pH 8.5, resulting from the joint effects of C₁₈ and residual hydroxyl groups. According to these results, we suggested that C₁₈/NH₂-TNs had great advantage for the affinity of ionic organic analytes, especially with long alkyl chains. It was worth mentioning that the adsorption capacity of PFOS on C₁₈/NH₂-TNs was remarkably higher than those obtained on activated carbon (196–520 mg g⁻¹) or anion-exchange resin (210 mg g⁻¹). With regard to PFOA, C₁₈/NH₂-TNs seemed more powerful than activated carbon (adsorption capacity 100–320 mg g⁻¹).^{35,36}

It is known that mineral oxides can be modified with ionic surfactants based on the electronic attraction between the ionic tail of the surfactant and oxide surface and the followed hydrophobic interaction between the long hydrocarbon tail-groups of surfactant. The choice of the surfactant is determined by the pH_{pzc} of mineral oxide. As a type of mineral oxide, in our previous study, we had proved that TNs also could be modified with ionic surfactants.²¹ The pH_{pzc} value of TNs ranged in pH from 4.0 to 5.0. At pH > pH_{pzc}, cationic surfactant CTAB can be used to modify TNs; while at pH < pH_{pzc}, ionic surfactant SDS can be selected. But the adsorption ability of CTAB on TNs was higher than SDS at optimal conditions. In this study, the uptake of CTAB on unmodified TNs was performed. As a result, the adsorption envelope of CTAB under different solution pH on TNs was more similar to that of C₁₈/NH₂-TNs and NH₂-TNs (Figure 5B). Since the pH_{pzc} of TNs was lower than the amino-containing TNs, the adsorption efficiency of CTAB on TNs at pH 5–7.5 was higher than those obtained on NH₂-TNs and C₁₈/NH₂-TNs. At pH 8.5, the adsorption capacity of CTAB on TNs (1100 mg g⁻¹) was even larger than that on C₁₈-TNs (Figure 6B). These results indicated that TNs without surface modification possessed strong adsorption ability to ionic analytes and proved the importance of residual hydroxyl groups on the adsorption of ionic analytes on C₁₈-TNs, C₁₈/NH₂-TNs, or NH₂-TNs.

Adsorption Characteristic of Nonionic or Amphoteric Compounds on Surface Modified TNs. The affinity of nonionic organic analytes Phe, 4-NP, BPA, and DBP to C₁₈/NH₂-TNs, C₁₈-TNs, and NH₂-TNs were investigated at different solution pH. It was found that these compounds were hardly adsorbed on NH₂-TNs, and their adsorption on C₁₈/NH₂-TNs and C₁₈-TNs were generally not pH sensitive. The low affinity efficiency of DBP, BPA, and 4-NP on the two adsorbents at pH 10.5 should be caused by the degradation or ionization of these compounds. Since the adsorption of Phe, DBP, BPA, and 4-NP was based on the hydrophobic interactions between analytes and C₁₈ groups of adsorbents, the adsorption capacities of these nonionic compounds on C₁₈/NH₂-TNs were much lower than those on C₁₈-TNs (Figure 7 and Table S2 in the Supporting Information). Sulfamethazine (SMT) was highly water-soluble, and generally functioned as weak acid at a physiologic pH range although it was amphoteric. In the molecule of SMT ($pK_{a1} = 2.79$, $pK_{a2} = 7.45$), the –NH₂ group attached to the aromatic cycle

(35) Yu, Q.; Zhang, R. Q.; Deng, S. B.; Huang, J.; Yu, G. *Water Res.* **2009**, *43*, 1150–1158.

(36) Valeria, O. H.; Reyes, S. A. *Chemosphere* **2008**, *72*, 1588–1593.

(37) Sarmah, A. K.; Meyer, M. T.; Boxall, A. B. A. *Chemosphere* **2006**, *65*, 725–729.

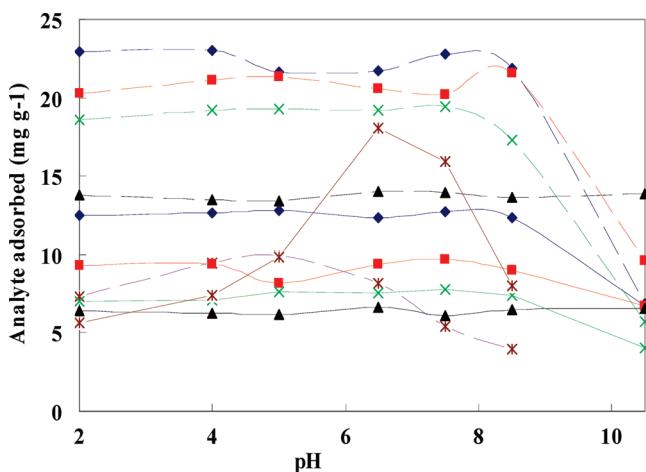


Figure 7. Effect of solution pH on the adsorption of nonionic and amphoteric analytes to surface modified TNs. Solid line, C₁₈/NH₂-TNs; dashed line, C₁₈-TNs. 4-NP, square; DBP, diamond; BPA, cross; Phe, triangle; SMT, star.

protonated at pH < 3, and the amine ($-\text{NH}-$) group attached to sulfur began to deprotonate at about pH > 5.^{37,38} Hence, SMT in neutral form only occurred as the solution pH ranged from pH 3 to 6. As a result, the affinity efficiency of SMT on the two adsorbents was less efficient in acid and alkaline solution, which might result from high water solubility of charged SMT or repulsion interaction between a positively charged SMT and $-\text{NH}_3^+$ group on C₁₈/NH₂-TNs (pH < 5) or between a negatively charged SMT and ionized hydroxyl group remaining on the C₁₈-TNs and C₁₈/NH₂-TNs surface (pH > 7.5). For C₁₈-TNs, the highest adsorption of SMT was observed at pH 5. In the case of C₁₈/NH₂-TNs, the optimal solution pH range for SMT adsorption was pH 6–7.5, at which there should be attraction interaction between an aminopropyl group and partly deprotonated SMT besides hydrophobic interaction. Accordingly, the maximal adsorption capacity of SMT on C₁₈/NH₂-TNs in neutral solution was twice that of C₁₈-TNs (Table S2 in the Supporting Information). In general, the cooperative effects of C₁₈ and aminopropyl or $-\text{OH}$ groups on C₁₈/NH₂-TNs were beneficial to efficiently adsorb ionic or ionizable organic analytes. Since TNs had the property of acid and alkali resistance, selective uptake of the ionic analytes under extreme conditions could be achieved on this material. C₁₈/NH₂-TNs were expected to provide new tools for preconcentration or removal of ionic organic contaminants from water samples.

(38) Yang, S.; Carlson, K. *Water Res.* 2003, 37, 4645–4656.

CONCLUSIONS

The product using ODS and APS to react simultaneously with 0.1 g of TNs displayed the clear characteristic of dual groups (alkyl and amino) and showed good water dispersibility, overcoming the deficiency of the reverse phase nanosized adsorbents in water and improving accessibility to polar analytes. This material (C₁₈/NH₂-TNs) was found to bind efficiently several ionic analytes from solution under different solution pH due to the cooperative effects of octadecyl and aminopropyl groups coupled with the residual hydroxyl groups on its surface. The highest affinity efficiency of anionic, amphoteric, and cationic analytes on C₁₈/NH₂-TNs could be reached by adjusting solution pH to acid, neutral, or alkaline conditions, respectively. Possessing large surface areas and strong affinity efficiency to ionic organic analytes, especially bearing long alkyl chains, C₁₈/NH₂-TNs showed significantly higher adsorption capacity for PFOS than activated carbon and anion-exchange resin. In summary, multigroup modified TNs could be prepared using a one-step method, and the new material exhibited special adsorption properties compared with one organic unit modified TNs. Due to the unique tubular morphology and nanoscaled diameters of titanate nanotubes, molecules with large dimensional size were difficult to enter the tube space of TNs. Therefore, TNs with total different chemical properties between their inner and outer surfaces were possibly prepared by adjusting the size of the functional modifiers, which was under progress in our group.

ACKNOWLEDGMENT

This work was jointly supported by National High Technology Research and Development Program of China (2007AA06Z405, 2009AA061603) and the National Natural Science Foundation of China (20837003, 20877079, 20907061).

SUPPORTING INFORMATION AVAILABLE

Tables for element composition on the surface of all the adsorbents determined by EDAX and calculated Langmuir adsorption constants for analytes on adsorbents; TEM images of adsorbents; peak fitting of O1s spectra of each adsorbent and the corresponding content of each oxygen species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Received for review July 10, 2009. Accepted November 2, 2009.

AC901531K