

OCTADECYL AND AMINO MIXED GROUPS MODIFIED TITANATE NANOTUBES FOR SELECTIVE ADSORPTION OF CATIONIC AND ANIONIC SURFACTANTS

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Abstract

In this study, octadecyl (C₁₈) and aminopropyl groups modified titanate nanotubes (C₁₈/NH₂-TNs) were prepared successfully with silylation method by introducing octadecyltrimethoxysilane (ODS) and aminopropyltrimethoxysilane (APS) simultaneously to titanate nanotubes (TNs) surface. The results suggested that C₁₈/NH₂-TNs possessed the obvious characteristic of C₁₈ and aminopropyl groups and showed good water dispersibility. Due to the cooperative effect of alkyl and aminopropyl groups coupled with the residual hydroxyl groups on its surface, C₁₈/NH₂-TNs exhibited excellent affinity efficiency to ionic surfactants under different solution pH. The highest uptake efficiency of anionic (perfluorooctane sulfonate, perfluorooctanoic acid and sodium dodecyl sulphate), and cationic (cetyltrimethylammonium bromide) analytes on C₁₈/NH₂-TNs could be reached by adjusting solution pH to acid and alkaline conditions respectively. Since C₁₈/NH₂-TNs possessed large surface areas and strong affinity ability to ionic organic compounds with long alkyl chains, it showed significantly higher adsorption capacity for perfluorooctane sulfonate than activated carbon and anion-exchange resin. This material was expected to provide a new tool for preconcentration or removal of ionic organic contaminants from water samples.

Introduction

The development of affinity-based adsorbents to be selective in extracting the target analytes from biological and environmental samples with complex matrices is of great interest. There are two main approaches: the immunosorbents and the molecularly imprinted polymers¹. Using these adsorbents, we can selectively extract a target analytes or a family of structurally related analytes from biological fluids or environmental water samples. However, their preparation is labour intensive and expensive². Another interesting approach is to develop the mixed-mode adsorbents, which bear two or more functional groups. This kind of adsorbents can selectively bind guest species with special functional groups, and have shown application potential in drug delivery, biosensor, and stationary phase or catalyst³⁻⁷. In the field 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 the clean-up of biological matrices (urine, blood or plasma) in the same sequence⁸. These adsorbents are usually focused on polymeric matrices or porous silica particles. Besides silica, other inorganic matrices, such as titania and zirconia, have attracted extensive attention in the field of analytical chemistry and environmental science for their better alkali resistance, practically insolubility within a wide pH range, and outstanding resistance to dissolution at high temperature⁹. The surfaces of these metal oxides can also be functionalized by reacting with

organosilanes. Recently, TiO₂-derived nanotubes (titanate nanotubes, TNs) have attracted much attention in many fields such as hydrogen storage, protein immobilization or photocatalysis¹⁰. Due to their unique hollow structure, large surface areas and special surface chemistry properties, modification of TNs with multi-groups for molecular recognition is worthy to be studied. The nanoscaled tube diameters and multilayered space of TNs can result in different distribution of organic groups with diverse dimensional size inside or outside the tubular space, which might impart special properties of TNs and alter the adsorptive tendency of substances on its surface in complex matrices. However, functionalization of TNs with organic units has seldom been carried out. In this study, we try to introduce octadecyl and amino groups together to TNs surface. As a result, this product shows good water dispersibility, and strongly and efficiently adsorbed anionic and cationic analytes only by adjusting solution pH to acid and alkaline conditions respectively.

Materials and Methods

The model compounds included perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), supplied by Sigma-Aldrich (Oakville, ON, Canada), sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) (Beijing Chemical Reagents Company, Beijing, China); Ultrapure water was prepared in the lab using a Milli-Q Advantage A10 reagent water system from Millipore (Milford, MA, USA). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany).

TNs were prepared with hydrothermal method by using the method described in Ref. 11. Surface modification of TNs with octadecyl and aminopropyl groups was performed with the silylation method as follows: 100 mg dry TNs were dispersed in 50 mL toluene in a Teflon bottle, 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 TNs suspension was ranged from 4 to 0.25 (namely ODS/APS 0.16 mL: 0.04 mL; 0.15 mL:0.05 mL; 0.134 mL:0.066 mL; 0.1 mL:0.1 mL; 0.066 mL:0.134 mL; 0.05 mL:0.15 mL; 0.04 mL:0.16 mL). The dual groups product was abbreviated as C₁₈/NH₂(x)-TNs (x=0.25, 0.33, 0.5, 1, 2, 3, 4) according to the ODS/APS ratio in 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 NH₂-TNs and C₁₈-TNs respectively.

Batch experiments were carried out to examine the adsorption behaviors of model compounds on adsorbents. For PFOS and PFOA, batch experiments were performed in 250 mL of PE bottles; for other 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 performed with 1 mg of C₁₈-TNs, NH₂-TNs or C₁₈/NH₂-TNs and 1 µg mL⁻¹ of initial model compounds concentrations. The pH of the solution was adjusted with 1 M HCl and/or 1 M NaOH to designated values in the range of pH 2.0-10.5. Adsorption isotherm studies were conducted with initial PFOS and PFOA concentrations ranging in 0.05-5 mg L⁻¹ at pH 2.5 in deionized water. For SDS and CTAB the concentration changed from 0.5 to 100 mg L⁻¹. After vibrating of the solution for 24 h, the mixture was centrifuged at 6000 rpm for 10 min, and the supernatant aqueous solution was used for the analysis of model compounds. The temperature of the batch experiments was set at 20±0.5 °C.

Results and Discussion

All the surface modified TNs possessed perfect tubular morphology. The surface element composition of these adsorbents was determined by XPS. The results showed that the C/Si ratio in C₁₈-TNs and NH₂-TNs surface was 18.3 and 3.7 respectively, and close to the theoretical value of organosilyl groups, implying the successful immobilization of alkyl or amino groups on TNs. The atom content of Si element on the surface of NH₂-TNs and C₁₈/NH₂(x)-TNs (5.2-5.4 %) were higher than that of C₁₈-TNs (3.6 %). We concluded that aminopropyl groups were more readily to immobilize on the surface of TNs compared with octadecyl groups, which was probably caused by the steric hindrance effects to C₁₈ group existing on the interior and exterior space of TNs. The FTIR patterns indicated that among the dual groups modified TNs, C₁₈/NH₂(4)-TNs showed the clear characteristic of alkyl and aminopropyl groups, and exhibited good water dispersibility overcoming the deficiency of C₁₈-containing nanosized materials for accessibility to water and polar analytes. Thus this material (abbreviated as C₁₈/NH₂-TNs) was regarded as the desired adsorbent. Based on the element contents of C (30.4 %), N (4.2 %) and Si (5.2 %) on C₁₈/NH₂-TNs surface, the calculated C₁₈/NH₂ ratio was about 0.25. The N 1s XPS signals of C₁₈/NH₂-TNs and NH₂-TNs contained two components at ~398 and 400 eV BE, attributing to amino (-NH₂) and ammonium (-NH₃⁺) species respectively¹². Since these adsorbents were washed with water before XPS analysis, the appearance of -NH₃⁺ at pH 7 might indicate large amino densities on their surface, which was in agreement with the high pH_{pzc} of NH₂-TNs (pH 9.0).

The adsorption of anionic analytes PFOS, PFOA, SDS and cationic analyte CTAB to C₁₈/NH₂-TNs was found to be pH dependent. The alkyl and -NH₃⁺ on C₁₈/NH₂-TNs surface were favorable for the uptake of anionic target analytes, and deprotonation of -NH₃⁺ at high pH led to decreased adsorption of these negatively charged analytes. However, a sharp reduce of PFOS and PFOA adsorption on C₁₈/NH₂-TNs at pH 4-5 should not be caused by this reason, since there was still considerable amount of -NH₃⁺ remained at pH 7. In a comparison study, the adsorptions of PFOS and PFOA on C₁₈-TNs also underwent an abrupt decrease at pH 2-5. Thereby, there was another pH-responsive group (namely hydroxyl group) on these materials, which came from the residual Ti-OH and introduced Si-OH by silylation¹³. TNs was protonic titanate in nature¹⁰, partial ionization of the residual Ti-OH and Si-OH could occur at low solution pH. This negatively charged group would provide electrostatic repulsive interaction to PFOS and PFOA, and decrease their adsorption as pH was higher than 2.0. But for SDS the decrease delayed to pH 8.5, resulting from its higher hydrophobicity than PFOS and PFOA. The intensive decrease of anionic surfactants adsorption on all the adsorbents at pH>8.5 should ascribe to the cooperative effects of complete deprotonation of -NH₃⁺ and ionization of -OH.

Due to the electrostatic repulsive interaction between -NH₃⁺ and CTAB, C₁₈/NH₂-TNs displayed limited adsorption ability to CTAB at low pH. The adsorption efficiency enhanced with the increase of solution pH for the gradual deprotonation of -NH₃⁺. The adsorption was expected to be based on the hydrophobic interactions between C₁₈ and CTAB. However, NH₂-TNs without long alkyl chains also showed considerable adsorption ability to CTAB at high pH, which was caused by the electrostatic attraction offered by O⁻. 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.

The adsorption isotherms for these analytes were obtained with their initial concentration ranging in 0.05-5.0 mg L⁻¹ (PFOS, PFOA), 0.5-100 mg L⁻¹ (SDS and CTAB), lower than their critical micelle concentrations. 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, and obviously higher than those obtained on mono-group modified TNs. Though the densities of C₁₈ groups on C₁₈/NH₂-TNs were lower than those of C₁₈-TNs, the adsorption capacity of CTAB on the C₁₈/NH₂-TNs was still comparable with that on C₁₈-TNs at pH 8.5. These results suggested that both C₁₈ and NH₂ groups were responsible for the adsorption of the target analytes on C₁₈/NH₂-TNs. The superior or comparable adsorption abilities of these analytes on C₁₈/NH₂-TNs to mono-group modified TNs (NH₂-TNs and C₁₈-TNs) resulted from the combined effects of hydrophobic interaction and electrostatic attractions of -NH₃⁺ or O⁻. It was worth mentioning that the adsorption capacity of PFOS on C₁₈/NH₂-TNs was significantly 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)^{14,15}. This material was expected to provide a new tool for preconcentration or removal of ionic organic contaminants with long alkyl chains from water samples.

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