

Influence of humic acids on pyrene sorption by carbon nanotubes

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Understanding the interactions between organic contaminants and carbon nanotubes (CNTs) is essential for evaluating the materials' potential environmental impact and their application as sorbent. Although a great deal of work has been published in the past years, data are still limited in terms of compounds, concentrations, and conditions investigated. This can be mainly explained by limitations associated with the generally-applied batch sorption test set ups. The present study focuses on the effects of humic acids (HA) on the sorption of organic contaminants onto CNTs. The presence of HA may have two opposite effects on sorption. On one hand, competition between HA and organic contaminants can result in a decrease in sorption to CNTs. On the other hand, HA are known to disperse CNTs and we showed in a previous study that sorption capacity is directly related to surface area. The presence of HA may thus increase sorption of organic contaminants through an increase in the available surface area. The balance between these phenomena remains unclear as classical separation techniques (e.g. centrifugation or filtration) are not adequate to efficiently separate the CNTs and liquid phase under conditions where CNTs are partially dispersed. We previously validated a passive-sampling method to study sorption of PAHs. The method is applicable to dispersed CNTs and we here use it to investigate the influence of HA on the sorption of pyrene. Sorption isotherms were determined over a wide concentration range. Changes in isotherm shapes were interpreted in terms of sorption mechanisms for a range of HA concentrations (0-200 mg/L).

Changes in the sorbent properties as a function of HA concentration are essential to understand and distinguish the various processes involved. CNTs settling behaviour, size distribution in suspension and particle diameter in the supernatant were determined by UV-vis spectrometer, particle size analyzer (CIS-100) and dynamic light scattering, respectively. Preliminary results confirmed the strong dispersing effect of HA on CNTs. The size range of CNTs decreased from 0-60 μm down to 0-8 μm in suspensions containing 0 and 200 mg/L HA, respectively. The speed of settling also decreased dramatically with increasing HA concentration, but after 2 d, particles remaining in the supernatant had similar diameters for all HA concentrations (200 nm), as compared to the control without HA (650 nm). Together with the isotherm analysis, these results will allow a better understanding of the interactions between organic contaminants and CNTs in complex environmental matrices.

Chemical sensors based on Zr/ZrO₂ electrode for measurement of pH in a subcritical to supercritical aqueous water

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A Zr/ZrO₂ oxidation electrode was fabricated for in situ measurement of pH values in aqueous solutions at elevated temperatures. Combined with an Ag/AgCl reference electrode, the Zr/ZrO₂ sensor responded rapidly and precisely to the pH of the solutions over a wide range of temperatures. The Zr/ZrO₂ electrode was made by oxidizing Zr metal wire with a Na₂CO₃ melt to produce a thin film of ZrO₂ on the Zr wire surface. The nanostructure of the ZrO₂ thin film was characterized using high-resolution transmission electron microscopy (HRTEM) observations. The nature of the nanostructured ZrO₂ thin film on the Zr of the Zr/ZrO₂ electrode plays a vital role in the construction of Zr/ZrO₂ chemical sensors, particularly when the electrode is utilized for in-situ measurement of the electrochemical parameters of aqueous solutions at high temperatures and pressures.

Electric probe analyses of the ZrO₂ thin films revealed that the Zr/ZrO₂ interface is divided into 5 zones from the outermost zone to the center: 1) prismatic and oxygen-rich ZrO₂ zone; 2) ZrO₂; 3) oxygen-rich Zr; 4) oxygen-bearing Zr; 5) Zr metal. Especially, the outermost oxygen-rich ZrO₂ zone of the films is composed of nanometer-sized monoclinic crystals.

The experimental measurements of the Zr/ZrO₂ sensor potential against an Ag/AgCl reference electrode indicate that the sensor potential responds linearly with the pH of NaCl-HCl-H₂O (and NaCl-NaOH-H₂O) over the temperature range from 20 to 200°C. The slope of the potential versus pH plot at 200°C is close to the theoretical value of the Nernstian slope for the test solution at electrochemical equilibrium. The Zr/ZrO₂ sensor is expected to find use for in situ measurement of pH in aqueous fluids in natural processes over a wide temperature range, especially for hydrothermal vent fluids at mid-ocean ridges.

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