

ADSORPTION CHARACTERISTICS OF HAZARDOUS OXOANIONS ON HDPy-MODIFIED MONTMORILLONITE

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Introduction

Adsorption of individual anions on organo-montmorillonite (OMt) has been well investigated in previous studies (Bagherifam et al., 2014; Choung et al., 2014). In those studies different amounts of organic modifier with variable structures were applied, resulting in no criterion for comparing the selectivity of anions to OMt. A systematic study in terms of adsorption of six anions on three surfactant-modified bentonites has been conducted (Behnsen and Riebe, 2008). Their results showed the relationship between affinity and hydration energy of the anions. Besides, the amount of released organic modifier may be associated with the species of target anions. Compared with poorly hydrated anions of smaller size, a fully hydrated anion of larger size would be less able to penetrate into the head group region of a cationic surfactant for effective neutralization of the bilayer (Leontidis et al., 2002). As a result, the original counter ion would be readily replaced with those poorly hydrated anions to form tight binding and to minimize the repulsive force, inhibiting the dissociation of adsorbed surfactant back into the bulk aqueous solution (Li et al., 1997). It is of great significance to evaluate the adsorption characteristic of different oxoanions, which include hazardous heavy metals and are often mobile in environments, on OMt.

Methods

10 g of Mt with a cation exchange capacity (CEC) of 111.4 meq/100g was dispersed in 500 mL deionized water at room temperature for 2 h. Separately, 44.56 mmol of hexadecyl pyridinium chloride (HDPy-Cl), corresponding to four times the CEC of Mt, was dissolved in 500 mL deionized water. The HDPy-Cl solution was then slowly added into the Mt suspension and the mixture was vigorously stirred for 24 h. The obtained solid was separated by centrifugation, freeze-dried, ground, and sieved. 1.0 mmol/L Na₂MoO₄, Na₂SO₄, NaClO₄, NaReO₄, NaI, KIO₃, NaBrO₃, NaNO₃, Na₂SeO₃, Na₂SeO₄, Na₂CrO₄, Na₂WO₄, NaVO₃, and KH₂AsO₄ were separately prepared, without pH adjustment. 40 mg HDPy/Mt was dispersed in 50 mL target anion-bearing solution and then shaken at 25 °C for 24 h. The pH and Eh of solutions before and after adsorption were measured. After the mixture was filtered through a 0.45-μm filter, the obtained solution was provided to determine the residual anion concentration in equilibrium using ion chromatography (Dionex ICS-2100, Sunnyvale, CA, USA), and inductively coupled plasma atomic emission spectroscopy (ICP-AES, Seiko Instruments, Chiba, Japan). The amount of released HDPy was determined by UV-vis

spectroscopy (UV-2450, Shimadzu, Tokyo, Japan) at 258 nm. The solid was dried and supplied for X-ray diffraction (XRD) measurement to investigate changes in interlayer space.

Results and discussion

Based on pH and Eh values before and after adsorption, chemical speciation of all anions was not expected to change during adsorption on HDPy/Mt. Among the selected anions, with the exception of IO_3^- , H_2AsO_4^- , and CrO_4^{2-} , monovalent anions showed higher adsorption capacities and selectivities on HDPy/Mt than divalent anions. Besides, higher adsorption capacities normally corresponded to the lower amounts of HDPy release as support by the negligible HDPy release after adsorption of monovalent anions. Release of HDPy led to the decrease of interlayer distance as proved by XRD patterns. The released HDPy presented in different forms in solution, which depends on anion species. After adsorption of the anions showing high affinity to HDPy/Mt, HDPy were slightly released in form of HDPy-target anion such as HDPy- NO_3^- , whereas significantly released in form of HDPy-Cl for poorly selective anions which are mainly highly hydrated divalent anions. Hydration of counter ion (Cl^-) was the driving force of ion exchange, which accounted for the adsorption of inorganic anions on HDPy/Mt. Desorption-adsorption made partial contribution to adsorption of several anions. Dehydration of anions with stronger hydration shells consumed more energy to intercalate into HDPy/Mt and resulted in the decrease of selectivity. Moreover, the increase of dielectric constant of organic-like interlayer phase derived from HDPy release was another key factor influencing adsorption of anions on HDPy/Mt.

Conclusions

Monovalent anions normally showed higher adsorption capacities and selectivities and led to lower HDPy release on HDPy/Mt than divalent anions, because of the higher energy consumption for dehydration of divalent anions. Hydration of counter ion (Cl^-) was the driving force of anions adsorption on HDPy/Mt. Selectivity of HDPy/Mt to anions depended not only on the change in anionic size in different phases (from r_1 in aqueous solution to r_2 in the organic solvent-like OMT), but also variation of dielectric constant after HDPy release.

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