Multifunction adsorption materials: Part I—Interaction of uranium and crystalline TiO$_2$.mH$_2$O modified by amorphous SiO$_2$.nH$_2$O

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The crystalline hydrous titanium dioxide modified by amorphous hydrous silicon dioxide (CTDASD), 2SiO$_2$.3TiO$_2$.6H$_2$O has been synthesized by ageing the amorphous mixed silicon-titanium hydroxide at 80°C for 36 hours. The prepared material possesses adjustable selectivity and apparent ion exchange capacity for a certain element or even for a group of elements. XRD, TGA and pH titration have been employed to characterize the prepared material. The uptake of uranyl ions on CTDASD is independent of concentration of sodium ions under the experimental conditions investigated, suggesting the material synthesized is reliable to remove uranyl ions from the media of high salt concentration. The uptake of uranium on the CTDASD is remarkably sensitive to the solution pH and reaches the maximum at pH 4.5. Plot of log $K_D$ of uranium versus equilibrium pH generates a series of lines with the mean slope of 0.63 at pH 1$\rightarrow$4, indicating the sophisticated loading mechanisms in $\overline{H}/UO_2^{2+}$ reaction.

Hydrous oxides as inorganic ion exchange materials have been well studied because of their ease of preparation. There are comprehensive reviews available describing earlier works on their preparation, properties and characterization. Ion exchange selectivities of inorganic ion exchangers have been specially devoted by Abe. Interest in titanium oxides as ion exchange media also continues. For example, Venkataramani and Gupta had examined the water sorption and ion exchange properties of 5 different hydrated titanium oxides. Abe and his coworkers describe Pb$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ selectivity depending on the anion present and also separations of Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$ applicable to low concentrations of these ions in natural waters. New preparation of hydrous Ti$^{IV}$ and Sn$^{IV}$ oxides with good stability to alkali have been reported by Yamazaki et al. Reports of composite materials based upon titanium come from Weller and Onorin et al. A layered hydrous titanium dioxide has been tested for Rb$^+$ and Cs$^+$ uptake. It showed a complex stepwise exchange, creating three intermediate phases each having a different degree of swelling which could be related to cation hydrations.

The pH titration curves for various hydrous titanium oxides showed typical amphoteric character and the increased order of the capacities is rutile < anatase < amorphous. This order parallels our investigations which also viewed that (i) uranium, practically uranyl ions, have higher selectivity for crystalline hydrous titanium dioxide than for amorphous one, and (ii) silica-titania mixed-hydroxides possess higher loading capacity than pure silica and titania hydroxides.

Herein, we present (i) the preparation of hydrous composite dioxide of titanium and silicon in which hydrous titanium dioxide exists in crystalline form and hydrous silicon dioxide in amorphous form; (ii) characterization of inorganic ion exchange materials synthesized; and (iii) testing of its ion exchange/adsorption properties.

Materials and Methods

Preparation of CTDASD

Amorphous mixed silica-titania hydroxide prepared by means of direct precipitation was
aged in 80±2°C water bath for 36 hours to generate crystalline hydrous titanium dioxide modified by amorphous hydrous silicon dioxide (CTDASD). During the process, alliquots of samples were withdrawn at regular time intervals for monitoring the growth of the crystal. The final product was filtered on a G2-glass filter crucible, and thoroughly washed with deionized water. Then the CTDASD, dried at 110°C for 4 hours, was kept in a desiccator containing silica-gels until constant weight was reached.

X-ray powder diffraction measurements
The XRD patterns were recorded according to the step scanning procedure with Rigaku-2400 X-ray diffractometer made in Japan using Ni-filtered CuKα1 radiation under the conditions of 4 grade/min.

Thermogravimetric analysis
The TGA curve of the CTDASD as function of temperature was obtained by an automatic thermal analyzer (Dupont 1090) under the reported conditions12,13 by which the TGA curves of α-, γ-ZrP and crystalline hydrous titanium dioxide were recorded.

pH titration
The pH titration of the material14 was conducted as follows: 0.15 g samples of known moisture content were weighed into a series of separate tubes. Same quantity of water and different amounts of titrant (0.020 mol/l HCl or NaOH) were added to each tube, all of which were agitated on GUO-HUmbHY-2 variable-speed reciprocal shaker for 24 hours. Then the equilibrium pH of each solution was measured by means of pHS-3B acidimeter.

Ion exchange/adsorption testing
The uptake of uranium on the crystalline hydrous titanium dioxide modified by amorphous hydrous silicon dioxide was examined with respect to batchwise operation by shaking 0.15 g CTDASD with 10.0 ml of aqueous solution including uranium for 24 hours at 25°C. The analytical concentration of uranium was determined by spectrophotometer with Arsenazo III as chromogen. The amount of uranium loaded by the CTDASD was determined by the difference between initial and equilibrium concentrations of uranium in aqueous solution.

<table>
<thead>
<tr>
<th>Table 1—XRD patterns for the CTDASD synthesized</th>
<th>Standard card of anatase</th>
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<td>1.485</td>
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Results and Discussion

Synthesis of CTDASD and its X-ray powder patterns
The CTDASD, prepared by ageing of amorphous mixed silica-titania hydroxide in 80±2°C water bath for 36 hours, was identified by means of X-ray powder diffraction, and the results are summarized in Table 1.

It can be seen from Table 1 that the crystal in CTDASD prepared is in good agreement with anatase. Presence of amorphous hydrous silicon dioxide in the anatase cannot make a great deal of difference in the crystal system but for relative intensity of diffraction peaks. This result suggests that Si-O-Ti bonds may be formed within one of the crystal faces. In other words, the formation of Si-O-Ti bonds between the crystal faces has little contribution to d/n value of the crystal. In order to verify the role of SiO2 in the generation of the crystalline hydrous titanium dioxide, a series of mixed silica-titania hydroxides with various molar ratios of Si to Ti were also aged in 80±2°C water bath for 36 hours. The relationship between crystal formation and molar ratio of Si to Ti graphically plotted in Fig. 1 indicates that, in the crystalline hydrous titania hydroxide, the silicon dioxide exists in an amorphous form. A comparison of (c) and (d) in Fig.1 also demonstrates that the presence of silicon dioxide is helpful to the formation of anatase rather than rutile.

Thermogravimetric analysis
The chemical analysis of the prepared sample (CTDASD) was in good agreement with 2:3 the molar ratio of Si to Ti within 2% of experimental error. The TGA curve of the CTDASD, together with the derivative one, was constructed in Fig. 2. As shown in Fig. 2, the loss of all water takes place in the neighbourhood of 62→200°C, generating a maximum at 105°C in derivative curve. From chemical analysis, weights of both loss and the
Fig. 1—Modification of non-crystalline SiO$_2$ for the formation of crystalline titanium hydroxide. (a) SiO$_2$, (b) molar ratio of Si to Ti is 2:3, (c) molar ratio of Si to Ti is 3:2, and (d) TiO$_2$ shows a lower pH jump with NaOH added than blank run, indicating that the CTDASD, 2SiO$_2$•3TiO$_2$•6H$_2$O, behaves as a weakly acid-type exchanger. The amount of replaceable protons responsible for ion exchange reactions can be determined by the difference between blank run and pH titration curve. The exchange capacity thus determined as function of pH is also exhibited in Fig. 3 and the maximum exchange capacity is up to 1.54 mmol H$^+$/g. In addition, the maximum apparent capacity of the CTDASD obtained with the method published$^{11,16}$ is 1.50 mmol H$^+$/g, corresponding to titration product $\text{H}_{11.3}\text{Na}_{0.7}\text{Ti}_3\text{Si}_2\text{O}_{16}$. The good agreement of two types of capacities exhibits that the uptake of the sodium ions on the CTDASD proceeded chiefly by ion exchange mechanism.

Ion exchange/adsorption properties of CTDASD

Batchwise operation was used to test the ion exchange/adsorption properties of the CTDASD prepared and some results are demonstrated as follows.

**pH dependence of ion exchange/adsorption behaviour**

Effect of pH on ion exchange/adsorption behaviour of the CTDASD was carried out at 25.0°C and initial uranium concentrations of 0.57×10$^{-2}$ mol/l to 3.44×10$^{-2}$ mol/l. The pH value was adjusted with HCl and/or NaOH. Figure 4 demonstrates the amount of uranium loaded by

**pH titration, exchange and apparent capacities**

It can be seen from Fig. 3 that the pH titration curve of the CTDASD using 0.023 mol/l NaOH
The uptake of uranium on the CIDASD goes through a maximum at pH~4.5. The uptake of uranium, however, begins to drop down when pH further augments chiefly because of precipitation of uranyl hydrolysis reaction cannot be described chiefly by ion exchange mechanism. In other words, uranium loaded onto the solid phase is not negligible, though a little amount of hydrogen ions are replaced into the solution.

The decrease in the uptake of uranium and log$K_D$ at pH>4.5 may be also attributed to the increased concentration of the surface hydroxyl groups of amorphous hydrous silicon dioxide, and the explanation had been well known.12

Ion exchange/adsorption isotherms

The isotherms of uranium uptake on the CIDASD, obtained by constructing a series of uranium uptake versus pH curves, together with log$K_D$, is shown in Fig. 6 which indicates that the uranyl ions are remarkably preferred by the CIDASD synthesized at pH 3.50, particularly more pronounced at low uranyl concentrations. Assuming that all uranium in the CIDASD are presented as $UO_2^{2+}$ ions at this pH value, the fraction of uranyl ions in solid phase $X_{UO_2^{2+}}$ calculated on the basis of theoretical exchange capacity of 25.64 mmol H⁺/g and standardized with monovalent ions, is up to 0.10 at the equilibrium concentration of uranium in solution of 2.0±10⁻² mol/l, corresponding to incomplete exchange product $H_{10.8}(UO_2)_{0.6}Si_2Ti_1O_{16}$.

XRD was again used to trace the progress of CIDASD structure as a function of uptake of uranyl ions, and the results are presented in Fig. 7. Rigid crystal structure of the CIDASD is found to be reliable for uptake of uranyl ions at pH 3.0.
Effect of ionic strength on the ion exchange property of the CTDASD

The ionic strength of bulk solution was conveniently characterized by the concentration of sodium chloride. The initial concentration of uranyl ions were both $1.15 \times 10^{-2}$ and $2.30 \times 10^{-2}$ mol/l, and the corresponding equilibrium pH value was $1.70 \pm 0.01$ and $1.06 \pm 0.01$, respectively. The temperature was $25.0 \pm 0.2^\circ$C. Figure 8 shows the negligible effect of sodium ions on the ion exchange/adsorption of uranyl ions on the CTDASD. This result remarkably disagrees with that published, but is excellently identical with that obtained on crystalline hydrous titanium dioxide. The material owns potential possibilities of removing uranyl ions from the media of high salt concentration.

Based on the above observations, it can be concluded that CTDASD, $2\text{SiO}_2 \cdot 3\text{TiO}_2 \cdot 6\text{H}_2\text{O}$, possesses the crystalline system of anatase. The theoretical exchange capacity of the CTDASD is 25.64 mmol H⁺/g, but its maximum apparent capacity for Na⁺ ions determined with pH titration curve is 1.50 mmol H⁺/g. The amount of replaceable protons responsible for ion exchange reactions, determined by the difference between the blank run and pH titration curve, is 1.54 mmol H⁺/g. The excellent agreement between apparent capacity and exchange capacity indicates that the uptake of Na⁺ ion on CTDASD proceeded chiefly by ion exchange mechanism. But the same cannot be said of H⁺/UO₂⁺ reaction.

The loading of uranium on the CTDASD is largely sensitive to solution pH. The uranyl ions have much more selectivity for the CTDASD than hydrogen ions and, especially than sodium ions. Thus CTDASD has the potential of being used for removing uranyl ions from the media with high salt concentrations.

References

12 Song Yinjie, Jiang Liqiang, Zhao Aimin, Jin Qixin & Song Dakang, To be submitted.