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Simultaneous removal of U(VI) and humic acid on defective TiO_{2-x} investigated by batch and spectroscopy techniques

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HIGHLIGHTS

- Defective TiO_{2-x} with abundant oxygen vacancies were fabricated.
- TiO_{2-x} can simultaneous remove U(VI) and HA from aqueous solutions.
- The sorption capacities of U(VI) and HA on TiO_{2-x} at pH = 5.0 were 65 and 142 mg g^{-1}, respectively.
- The presence of HA enhanced U(VI) sorption on TiO_{2-x}, the surface adsorbed U(VI) also enhanced HA sorption.
- The oxygen vacancies could provide high chemical activity to trap U(VI) in the defective sites.

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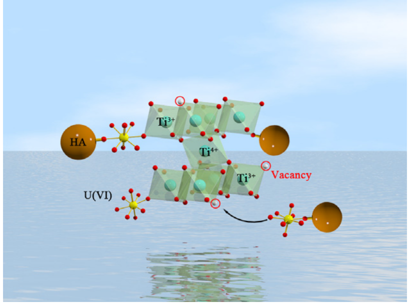
GRAPHICAL ABSTRACT



ABSTRACT

In this paper, the defective TiO_{2-x} with abundant oxygen vacancies were fabricated through a simple modified solvothermal strategy and characterized by SEM, TEM, XRD, FT-IR, EDX, Zeta-potential, and XPS techniques in detail. The prepared TiO_{2-x} was applied to remove U(VI) and humic acid (HA) from aqueous solutions to evaluate its sorption performance. The sorption of U(VI) and HA on TiO_{2-x} was examined under various environmental conditions (*e.g.*, contact time, pH, ionic strength, initial HA/U(VI) concentrations, the addition sequences of HA/U(VI) and temperature). According to the Langmuir model simulation, the maximum sorption capacities of U(VI) and HA on TiO_{2-x} at pH = 5.0 were calculated to be 65 and 142 mg g^{-1}, respectively, which were higher than most current reported materials. The kinetic results indicated that the sorption of U(VI) and HA onto TiO_{2-x} was better described by the pseudo-second-order kinetic model. The presence of HA enhanced U(VI) sorption on TiO_{2-x} at pH = 5.0, meanwhile, the surface adsorbed U(VI) on TiO_{2-x} also enhanced the sorption capacity of HA, which was mainly attributed to the formation of U(VI)-HA-TiO_{2-x} ternary complexes. Combining FT-IR and XPS analysis, the oxygen vacancies could provide high chemical activity and trap U(VI) in the defective sites of TiO_{2-x}, while the sorption of HA was dominated by surface complexation. The findings might provide an opportunity to estimate and optimize the efficient simultaneous elimination of radionuclides and natural organic substances by using defective TiO_{2-x}.

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1. Introduction

With the rapid development of economy and industry, the increase of nuclear and textile industries have inevitably caused various kinds of environmental problems [1–3]. Uranium was a toxic radioactive element that was usually discharged into the environment through various processing of nuclear fuel fabrication, manufacturing, aboveground/underground nuclear tests as well as mining operations [4–6]. Due to the long half-life, the release of U(VI) could cause serious damage of biological organization such as toxic hepatitis, skin corrosion, histopathological system damage, kidney damage and even cancers [7]. The World Health Organization (WHO) has adopted an uranium maximum contaminant level (MCL) of 15 $\mu g\ L^{-1}$, and the U.S. Environmental Protection Agency (EPA) has proposed the guideline value of 30 $\mu g\ L^{-1}$ for U(VI) concentration in drinking water [8]. Humic acid (HA) was one of humic substances originated from the decomposition of plants and animals in aquatic and terrestrial systems [9]. HA contained various kinds of functional groups like phenol, quinine, hydroxyl, carboxylic and amine groups, which can provide many available sites for the binding of metal ions and thereby greatly affect the growth of plants and microorganisms [10]. Meanwhile, HA could bind with organic chemicals that may influence the toxicity of these compounds to plants and microorganisms [11]. During the disinfection of municipal drinking water treatment, HA can react with chlorine resulting in the formation of trihalomethanes that cause cancer and seriously affect the health of human beings [12]. Generally, the concentration of HA in natural water system usually ranges from 0.1 to 200 $mg\ L^{-1}$. Hence, the knowledge about the development of advanced techniques and materials was required to reduce the risk posed by U(VI) and HA into the environment, which were harmful to human health and ecosystems. Meanwhile, the safe disposal and treatment of the wastes containing U(VI) and/or HA have become one of essential pursuits for environmental remediation [13].

From the point view of human health and environmental safety, the development of advanced techniques and materials to remove these pollutants from aqueous solutions was of great significance. In the last decade, many technologies have been developed to eliminate pollutants from wastewater. Among these methods (*i.e.*, membrane filtration, solidification, solvent extraction, sorption, photocatalytic degradation/oxidation, ion exchange and precipitation, etc.), sorption technology has attracted more attention in fundamental studies and industrial applications because of its easy operation, high efficiency, and large scale in practical applications [14,15]. A variety of adsorbents, such as clay minerals, metal oxides, and carbon-based materials have been studied intensively to eliminate environmental pollutants from wastewater [16–21]. However, the low sorption capacities and efficiency of these materials have hindered their real applications in large scale. Herein, we fabricated a well-defined (001) facet TiO_{2-x}, which has low cost and toxicity, high stability, and unique chemical activities, to explore its application in efficient elimination pollutants in environmental pollution cleanup. Defective TiO_{2-x} has become one of the most studied photocatalysts for environmental purification, which was only applied to photo sensitivity in ultra-violet light region and photo-induced electron-hole pairs recombination [22–24]. To the best of our knowledge, the application of TiO_{2-x} for efficient removal of contaminants from aqueous solutions is still in the early stages. Thus, the incorporating of TiO_{2-x} served as adsorbent to eliminate organic and inorganic pollutants is an attractive and promising idea.

The purposes of this paper were: (1) to synthesize TiO_{2-x} and apply it as adsorbent for the elimination of U(VI) and HA from aqueous solutions; (2) to investigate the influencing factors, such as ionic strength, contact time, pH, initial concentration of U(VI) and HA, temperature on HA and U(VI) removal; (3) to study the possible sorption mechanism of U(VI) and HA on TiO_{2-x} via powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transformed infrared (FT-IR) spectroscopy, energy-dispersive X-ray spectroscopy (EDX) elemental mapping analyses, and X-ray photoelectron spectroscopy (XPS); (4) to investigate the desorption isotherms and reusability of TiO_{2-x}. The results were essential to understand the interaction mechanism of U(VI) and HA with TiO_{2-x} and to functionalize TiO_{2-x} for the practical application in environmental radioactive and organic pollution cleanup. The knowledge of the sorption of HA and U(VI) at water-solid interface was also a key role to evaluate their fate and transport in the geochemical environment.

2. Experiments and methods

2.1. Materials

The commercial-grade P25 was purchased from Degussa AG (the average particle size of ca. 21 nm) with a crystalline structure of ca.70% anatase and 30% rutile. The U(VI) stock solution (100 $mg\ L^{-1}$) was prepared from $UO_2(NO_3)_2{\cdot}6H_2O$ (99.99% purity) after dissolution and dilution with Milli-Q water. Humid acid (HA) was purchased from Sigma Chemical Co. (St Louwas, MO). All chemicals of analytic reagents including $NaNO_3$, NaOH, and 68% HNO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd and used directly without further purification. Milli-Q water (Millipore, Billerica, MA, USA) was used in all the experiments.

2.2. Preparation of TiO_{2-x}

The defective TiO_{2-x} engineered by the high-index (001) facet was synthesized according to the previous report [25]. Typically, under vigorous stirring, 4 mL of $TiCl_4$ solution was added into the absolute ethanol (80 mL) at room temperature (10–15 °C) until it formed a homogeneous suspension, followed by adding an appropriate amount of metallic zinc powders with Ti/Zn molar ratio of 4:1 into the above suspension. The reaction was magnetically stirred for 1.5 h, resulting in the formation of blue suspension. The mixture was then added into a 100 mL Teflon-lined stainless steel autoclave, maintained at 200 °C for 24 h, and then cooled to room temperature naturally. The resulting solid was collected and rinsed with ethanol and Milli-Q water thoroughly, and dried in a vacuum oven at 60 °C overnight.

2.3. Characterization of TiO_{2-x}

The physicochemical properties of the samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were obtained with a JSM 6320F FE-SEM (JEOL), and TEM images were achieved using a JEOL-2010 microscope TEM at the operation voltage of 100 kV. The crystalline structure of TiO_{2-x} was characterized by the X-ray diffraction (XRD) technique on a Rigaku/Max-3A X-ray diffractometer with a Cu-Kα as the radiation source (λ = 1.54178 Å). Fourier transformed infrared (FT-IR) spectra were obtained on a Nicolet Magana-IR 750 spectrometer with KBr pellets technology at room temperature with a range of 400–4000 cm^{-1}. Energy-dispersive X-ray spectroscopy (EDX) elemental mapping analyses were carried out using a JEOL JEMARF200F atomic resolution analytical microscope with a spherical aberration corrector. Zeta-potential values were measured by a ZETASIZER 3000HSA system. The X-ray photoelectron spectroscopy