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Structure and properties of vanadium(V)-doped hexagonal turbostratic birnessite and its enhanced scavenging of Pb^{2+} from solutions

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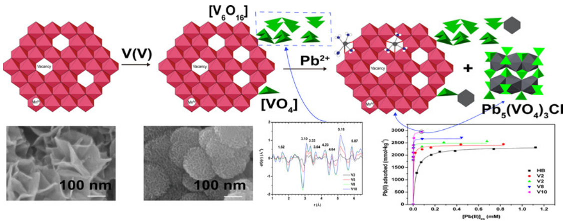
HIGHLIGHTS

- V was coprecipitated with birnessite at a series of V/Mn molar ratios.
- V-doped birnessites have greatly reduced particle sizes and increased SSAs.
- V exists as V(V) oxyanions, including $[V_6O_{16}]$ and $[VO_4]$, on birnessite surfaces.
- Scavenging of Pb^{2+} by these V-doped birnessites is greatly enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

Vanadium(V)-doped hexagonal turbostratic birnessites were synthesized and characterized by multiple techniques and were used to remove Pb^{2+} from aqueous solutions. With increasing V content, the V(V)-doped birnessites have significantly decreased crystallinity, i.e., the thickness of crystals in the *c* axis decreases from 9.8 nm to ~0.7 nm, and the amount of vacancies slightly increases from 0.063 to 0.089. The specific surface areas of these samples increase after doping while the Mn average oxidation sates are almost constant. V has a valence of +5 and tetrahedral symmetry, and exists as oxyanions, including $V_6O_{16}{}^{2-}$, and $VO_4{}^{3-}$ on birnessite edge sites by forming monodentate corning-sharing complexes. Pb L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra analysis shows that, at low V contents ($V/Mn \leq 0.07$) Pb^{2+} mainly binds with birnessite on octahedral vacancy and especially edge sites whereas at higher V contents ($V/Mn > 0.07$) more Pb^{2+} associates with V oxyanions and form vanadinite $[Pb_5(VO_4)_3Cl]$-like precipitates. With increasing V(V) content, the Pb^{2+} binding affinity on the V-doped birnessites significantly increases, ascribing to both the formation of the vanadinite precipitates and decreased particle sizes of birnessite. These results are useful to design environmentally benign materials for treatment of metal-polluted water.

1. Introduction

Heavy metal-contaminated soils and wastewater has been a serious environmental problem in the past few decades, owing

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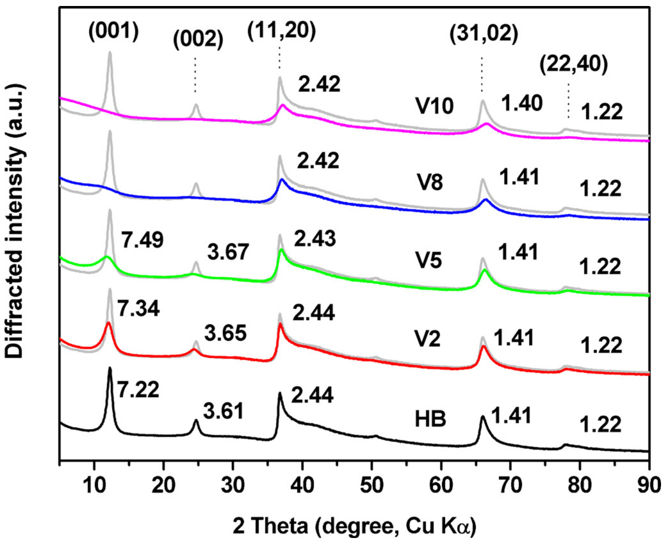

Fig. 1. Powder XRD patterns of V-doped birnessites (the high angle regions (30–90° 2θ Cu Kα) were scaled by a factor 5. The HB pattern was repeated as a light gray line with the other XRD patterns for sake of comparison).

to the increase in anthropogenic activities, e.g., mining, metal industries, incinerators, power plants, agriculture application of sewage sludge, pesticides and fertilizer and so on [1]. Pb^{2+} is among the most notorious heavy metals for its high toxicity to plants and animals and especially for its adverse neurological effects on humans [2,3]. Numerous approaches have been developed for heavy metal removal from waters, including but not limited to chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies. Among them, adsorption has been recognized as an effective approach to remove Pb^{2+} from water systems [4–9].

Among various metal scavengers, poorly-crystalline hexagonal turbostratic birnessites are highly reactive natural mineral adsorbents for metal adsorption owing to their high specific surface areas, enrichment in vacancy defects, and negatively charged surfaces [10–14]. They display extremely high Pb^{2+} adsorption affinity and have a great potential for fabrication of high-performance adsorbents for metal removal [15]. A number of studies have investigated the Pb^{2+} adsorption mechanisms on hexagonal birnessites using batch macroscopic adsorption and spectroscopic experiments [11,16,17] as well as computational chemistry [18]. At a low surface Pb^{2+} loading, Pb^{2+} forms triple corner-sharing (TC) surface complexes above or below vacancies [11,17]. At a high Pb^{2+} loading, birnessite edge sites become increasingly important for Pb^{2+} adsorption, and Pb^{2+} can further form triple edge-sharing (TE) complexes near vacancies, and double corner-sharing (DC) and double edge-sharing (DE) surface complexes on edges [11,16,17,19]. During adsorption of heavy metal cations on metal oxides, the presence of oxyanions can greatly promote the metal retention. The underlying mechanisms include that oxyanion adsorption on the surface decreases the amount of positive surface charge of the oxides, favoring metal cation adsorption, or that oxyanions and metals form metal–oxyanion ternary surface complexes or even metal–oxyanion surface precipitates [20–23]. Such synergistic effect has been observed for the adsorption of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} on Fe and Al oxides in the presence of phosphate and sulfate [23–25]. A few studies were also conducted on the adsorption of metal cations on Mn oxides in the presence of anions. Hettiarachchi et al. [26] and Zaman et al. [27] found that adding phosphate increased Pb^{2+} and Cd^{2+} immobilization on cryptomelane and pyrolusite, respectively.

In our previous studies several transition metals (TMs), Co(III), Ni(II) and Fe(III), were incorporated into the structure of hexagonal birnessites, and caused certain changes in the birnessite structures and physicochemical properties, such as, crystallinity, vacancy content, Mn average oxidation sate (AOS), specific surface area (SSA), and also Pb^{2+}/Zn^{2+} adsorption and As(III) oxidation [28–30]. However unlike these TMs V usually exists as oxyanion species [31]. Coprecipitation of V with birnessite may have totally different effects on the heavy metal adsorption behaviors of birnessite. In the present study, V(V) was co-precipitated with hexagonal birnessite to form V-doped birnessites with a series of V/Mn molar ratios, in which V(V) existed as oxyanions on the birnessite surfaces. The obtained samples were thoroughly characterized by powder X-ray diffraction (XRD), chemical analysis, field emission scanning electron spectroscopy (FESEM), N_2 physical adsorption, atomic pair distribution function (PDF) analysis and X-ray absorption fine structure (XAFS) spectroscopy. The scavenging of Pb^{2+} on these materials was further investigated by batch isotherm adsorption experiments at pH 5 and Pb L_{III}-edge EXAFS analysis. Results show that these V-doped birnessites exhibit extraordinary Pb^{2+} retention performance and can be quite a promising material for treatment of heavy metals-polluted water systems.

2. Materials and methods

2.1. Sample preparation

The synthesis of V-doped birnessites was similar to that used for Co-, Ni- and Fe-doped birnessites [28–30]. Initially 1.6005 g, 4.0007 g, 6.4014 g or 8.0018 g $Na_3VO_4{\cdot}12H_2O$ were dissolved in 45 mL of 6 M hydrochloric acid. After the solution was stirred to become yellow and transparent, it was added dropwise at a flow rate of 0.7 mL min^{-1} into a boiling solution of 300 mL 0.667 M $KMnO_4$ under vigorous stirring. The finally obtained materials were named as V2, V5, V8 and V10, correspondingly. A pristine hexagonal birnessite (HB) was synthesized in a similar way, but without V, and used as a control sample. All the samples were ground in an agate mortar to particle sizes below 100 mesh and stored in closed polyethylene plastic tubes at room temperature.

Reference compounds for V K-edge XAFS analysis including V_2O_3, V_2O_4, V_2O_5, NH_4VO_3 and Na_3VO_4 were purchased from Sigma–Aldrich. Barnesite ($Na_2V_6O_{16}$) was synthesized by hydrothermal processing of Na_3VO_4 solution at pH ~ 3.0–6.0 [32]. The XRD pattern of the obtained orange solid indicated that it was a pure barnesite phase (JCPDS 16-0601, Supplementary Information SI-1). Further a part of barnesite (0.0149 g) was added into a 45 mL of 1.67 g L^{-1} birnessite suspension (I_c = 0.1 M $NaNO_3$) with pH 5 ± 0.05 to equilibrate at 25 °C while rotation for 24 h. Then the suspension was centrifuged and the wet solid was washed with 0.1 M $NaNO_3$ solution and then stored for XAFS analysis.

2.2. The physicochemical properties of V-doped birnessites

The powder XRD analyses of the V-doped birnessites were carried out on a Bruker D8 advance diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with 10 s counting time per 0.04° 2θ step. Sample compositions were determined by flame atomic absorption spectroscopy (FAAS, Varian AAS 240FS) for Mn, graphite furnace atomic absorption spectroscopy (GFAAS) for V, and flame spectrometry (Sherwood Model 410) for K^+ and Na^+, after dissolution of the solids with the mixture of $NH_2OH{\cdot}HCl$ and H_2SO_4 solutions. The powder XRD analysis, element composition, crystallite morphologies and specific surface areas (SSAs) of