



Extraction of copper species from the nanoporous sorbent with an ionic liquid

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ABSTRACT

The extraction of copper species from the nanoporous sorbent into an ionic liquid ([C₄mim][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate) was studied herein by means of X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (EXAFS) spectroscopies. The nanoporous sorbent is composed of adsorbed humic acid (HA) on nanoporous SiO₂ to simulate copper-contaminated nanoporous soils. During extraction with [C₄mim][PF₆] at 298, 323 and 393 K, approximately 20, 40 and 54%, respectively, of the copper species on the nanoporous sorbent were extracted into [C₄mim][PF₆]. Using the least-square fitted XANES spectra, the major copper species on the nanoporous sorbent was determined to be Cu(II)-HA (Cu(II) adsorbed on HA) (86%). At 298, 323 and 393 K, the copper dissociated from the extracted Cu(II)-HA and immediately formed Cu(mim)₂²⁺ (mim = 1-methylimidazole) in [C₄mim][PF₆]. At 323 and 393 K, Cu(mim)₂²⁺ was oxidized with oxygen in [C₄mim][PF₆] to form nanosized CuO. In this study, it was found that at least three reaction paths for the extracted copper to take from the nanoporous sorbent to [C₄mim][PF₆] at 298–393 K: (1) extraction of Cu(II)-HA from the nanoporous sorbent to [C₄mim][PF₆]; (2) dissociation of copper from extracted Cu(II)-HA to form Cu(mim)₂²⁺ in [C₄mim][PF₆]; and (3) oxidation of Cu(mim)₂²⁺ to form nanosized CuO in [C₄mim][PF₆]. Combining ¹H and ³¹P NMR spectra, nanosized CuO interacted with [C₄mim][PF₆] at 393 K. The fitted EXAFS spectra show the Cu(mim)₂²⁺ in [C₄mim][PF₆] possessed a Cu–N bond distance of 1.82 Å at 298 and 323 K. It is also found that the Cu–O bond distance was 1.93 Å at 393 K. This work demonstrates that the XANES technique can reveal structural changes of the copper species from the nanoporous sorbent into [C₄mim][PF₆] during extraction.

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1. Introduction

Heavy metals, such as copper, cadmium, lead, mercury and zinc, which are discarded or emitted in mining, transportation and smelting operations and pesticide use, result in contaminated soils [1–4]. In Europe, millions of hectares of heavy metal-polluted soils have been found in farmland [5]. Moreover, it is estimated that heavy metals are present at 77% of the Superfund sites in the United States [6]. The sorption of metals in soils can be influenced by physical and chemical conditions and bioavailability, such as the pore sizes of soils, soil pH, organic matter and living organisms [7]. The nanosized pore volume of soils raised the adsorbent concentrations of metals [8–10]. Because of the physical aging process in nature, nanosized pores in soils could be increased [11]. Therefore, high concentrations of metals could be found due to the continued formation of nanosized pores in soils. Humic substances (HSs), including humin, humic acids (HAs) and fulvic acids, are abundant in natural organic soils and water. During biological and chemical processes in soils, HSs play an important role in

cycling elements in the ecosystem. Metals can be captured with functional groups and form complexes in soils by interacting with the carboxyl, phenols, alcohol, carbonyl, lactone and ether of the HSs [12]. Metal ions are favored to form complexes with functional groups of HA [13]. The bioavailability and mobility of metals are diminished by interacting with HA in soils. Because of the low solubility of metal-HA complexes, metals gather in soils [14]. In Hong Kong, copper accumulates on organic matters in urban soils [15]. Living organisms are impacted negatively by heavy metals which have leaked into the soil. For instance, a high concentration of copper binding to organic matter, such as HA, when accumulated in soils, produces a health hazard for cattle [16]. Copper in soils can also negatively impact the human food chain. Copper, which is suspected of being carcinogenic, has also been implicated as a cause of breast and lung cancers [17]. Therefore, it would be beneficial for land utilization if the concentrations of copper in the nanosized pores of soils are reduced.

Ionic liquids (ILs) have special chemical and physical properties, such as low vapor pressure, low melting point, non-flammability, high thermal stability and high ionic conductivity [18]. ILs have been applied in electrochemistry, solar cells, synthesis, catalysis and sensors [19–22]. Organic contaminants in soils, such as dichlorodiphenyltrichloroethane

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(DDT), dieldrin, hexachlorobenzene, pentachlorophenol and naphthalene, have been extracted with ILs [23]. Metal ions in water have also been extracted effectively with modified ILs [24]. Crown ethers in ILs can enhance the extraction of metal ions from aqueous solutions [25]. ILs extract not only organic matters, but also metal ions. Hence, ILs could be applied in the extraction of copper species on a nanoporous sorbent.

Elements in a complex matrix, such as bond distance, coordination number (CN) and chemical identity, can be determined by EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) spectroscopies. X-ray absorption data can reveal the chemical structures of contaminants and the extracted reaction paths. Thus, the main objective of this work was to study the speciation of extracted copper from the nanoporous sorbent (adsorbing HA on nanoporous SiO₂ to simulate copper-contaminated microporous soils) into [C₄mim][PF₆] at 298–393 K using EXAFS and XANES spectroscopies.

2. Experiment

The experimental procedure is depicted in Fig. 1. The [C₄mim][PF₆] synthesis process has been described previously [26]. In the nanoporous sorbent synthesis procedure, 0.75 g of HA (sodium salt, Aldrich) was

blended with 0.4 g of SiO₂ (2 μm particle size with an ~2 nm pore opening, 99.9%, Aldrich) and 0.4 g of SiO₂ (2 μm particle size with a 4 nm pore opening, 99.9%, Aldrich) in 50 mL of deionized water and left for one day. The solution was then filtered, dried at 343 K and ground. The nanoporous sorbent was incubated with 10 mL of 0.003 M CuCl₂·2H₂O (99%, Riedel-de Haën) for 1 h and then dried at 343 K. Copper species on the nanoporous sorbent were extracted with 2 g of [C₄mim][PF₆] at 298, 323 and 393 K for 19 min. The copper species in [C₄mim][PF₆] at different temperature were analyzed using different analytic approaches to understand its extraction mechanism.

The copper adsorbed in the nanoporous sorbent and extracted in [C₄mim][PF₆] at 298, 323 and 393 K were each digested by an acid digestion procedure [27]. The Cu concentrations of digested solutions were analyzed by an atomic absorption spectrometer (Hitachi Z-5000). The Cu concentrations of the calibration curves were 0.1–5.0 ppm with the correlation coefficient > 0.9995.

¹H and ³¹P NMR (nuclear magnetic resonance) spectra of the [C₄mim][PF₆] and copper-extracted [C₄mim][PF₆] at 298, 323 and 393 K were determined on a Bruker Advance 300 spectrometer with tetramethyl silane (TSM) as an internal standard (acquisition time = 1.373 s, actual pulse repetition time = 2 s, number of scans = 32 and excitation pulse-angle = 30°).

The EXAFS and XANES spectra of the copper adsorbed in the nanoporous sorbent and extracted in [C₄mim][PF₆] at 298, 323 and 393 K were recorded using a Wiggler BL17C at the Taiwan National Synchrotron Radiation Research Center. The storage ring was operated at an energy level of 1.5 GeV and a current of 300 mA. An Si(111) double-crystal monochromator was used for the energy selection with an energy resolution ($\Delta E/E$) of 2×10^{-4} (eV/eV). The photon energy was calibrated using a copper foil absorption edge at 8979 eV. The absorption spectra were recorded using ion chambers that were filled with helium gas. The standard deviation calculated from the averaged spectra was used as estimate of the statistical noise and error associated with each structural parameter.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 simulation programs [28]. The EXAFS data were normalized to the edge jump, converted to the wavenumber scale and Fourier transform. The absorption edge was determined at the first derivative maximum point of jump absorption coefficient (μ) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of relative concentrations of Cu species [29]. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. Model compounds, such as nanosized CuO (99.3%, Kanto Chemical Co. Inc.), Cu(mim)₂⁺ (mim = 1-methylimidazole) and Cu(II)-HA (Cu(II) adsorbed on HA), were also collected on the Wiggler beam line. The model sample of Cu(mim)₂⁺ was prepared by the dissolution of 1 g of Cu(CH₃COO)₂·H₂O (99%, Hanawa Guaranteed Reagent) in 5 mL of 1-methylimidazole (99%, Fluka). The HA solution was prepared by mixing 4 g of HA and 10 mL of 0.1 M NaOH (99%, J.T. Baker) at 298 K for 30 min and adjusting the pH of the solution at 6 by 1 M HNO₃ (60–70%, J.T. Baker). An intermixture of the HA solution and 15 mL of 2% Cu(II) from CuCl₂·2H₂O were prepared for the Cu(II)-HA.

3. Results and discussion

Approximately 20, 40 and 54% of the copper species from the nanoporous sorbent were extracted into [C₄mim][PF₆] at 298, 323 and 393 K, respectively. As shown in Fig. 2, the pre-edge XANES copper spectra on the nanoporous sorbent and in [C₄mim][PF₆] exhibited a weak absorbance peak for the 1 s-to-3d transition at 8977 eV that is dipole-forbidden in the perfect octahedral symmetry by selection rules. A shoulder at 8985–8988 eV and an intensity at 8994–9002 eV are characteristic features of Cu(II), associated with the 1s-to-4p_z and 1s-to-4p_{x,y}

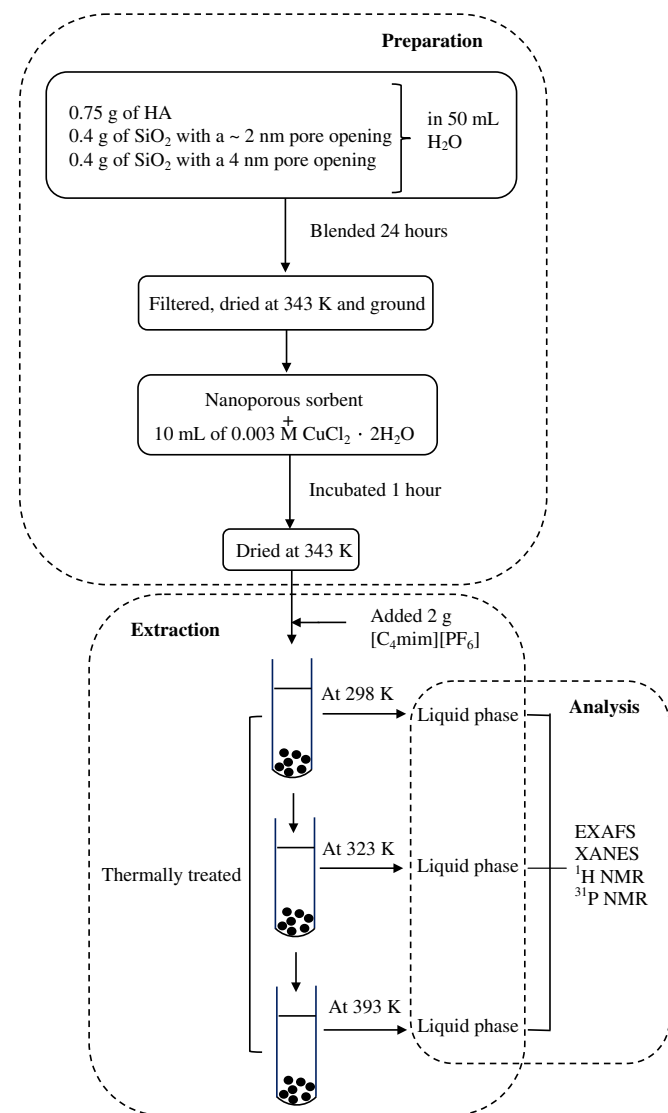


Fig. 1. Experimental flowchart for extraction of copper species from the nanoporous sorbent with [C₄mim][PF₆].

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