

XAFS Studies on Chromium Adsorption on Agricultural Low-cost Biowastes

Luis Federico SALA^{*1}, Cong CONG² and Masafumi HARADA^{*2}

¹Instituto de Química Rosario (IQUIR), CONICET-Universidad Nacional de Rosario,
Suipacha 531, S2002LRK, Rosario, Argentina

²Department of Clothing Environmental Science, Faculty of Human Life and Environment,
Nara Women's University, Nara 630-8506, Japan

Introduction

Chromium and its compounds are widely used in industry, with the most usual and important sources coming from the electroplating, tanning, water cooling, pulp producing, and petroleum refining processes [1]. Recently Park et al. [2] proposed a new mechanism for the biosorption of Cr(VI) on biomaterials. However, the reduction mechanism of Cr(VI) on biomaterials is still unclear because there are some complicated processes, such as adsorption of Cr(VI), reduction process of Cr(VI) to Cr(III), and chelating of Cr(III) on the surface of biomaterials [3]. In this study we have performed XAFS measurements to investigate oxidation state of chromium bound to the surface of the biomaterials during the biosorption of Cr(VI) under various conditions, as well to identify the Lewis donor atoms of the coordination sphere of Cr(VI), Cr(V) and Cr(III) complexes.

Experimental

Orange peel (OP) and rice husk (RH) were tested as agricultural biomaterials. The aqueous solutions of Cr(VI) and Cr(III) were prepared by dissolving $K_2Cr_2O_7$ and $Cr(NO_3)_3 \cdot 9H_2O$ in pure water, and OP and RH were suspended into these solutions to adsorb Cr ions with adjusting pH. The supernatants were separated, and the Cr-laden solid samples were then washed and dried under vacuum. The solid samples were finely ground with boron nitrate (BN), and pressed to afford a pellet for XAFS measurements. XAFS measurements were carried out at BL-9A in transmission mode for Cr-laden OP sample (Cr loading 4.9 wt%) and in fluorescence mode for Cr-laden RH sample (Cr loading 0.71 wt%), respectively. XAFS data were analyzed by REX2000 (Rigaku Co.). The reference samples used here were $Cr(NO_3)_3 \cdot 9H_2O$, Cr_2O_3 , $Na[Cr^V O(ehba)_2] \cdot H_2O$, and K_2CrO_4 .

Results and Discussion

Fig. 1 shows the normalized Cr K-edge XANES spectra of four reference solid compounds; oxidation state of Cr(III) as $Cr(NO_3)_3 \cdot 9H_2O$ and Cr_2O_3 , Cr(V) as $Na[Cr^V O(ehba)_2] \cdot H_2O$, and Cr(VI) as K_2CrO_4 . The XANES data for $Cr(NO_3)_3 \cdot 9H_2O$ and Cr_2O_3 show a small peak at 5990.5 eV, while those for $Na[Cr^V O(ehba)_2] \cdot H_2O$ and K_2CrO_4 show a pre-edge peak at 5993.0 and 5993.3 eV, respectively. The edge energy and the intensity of pre-edge absorbance decrease in the following order: Cr(VI) > Cr(V) > Cr(III).

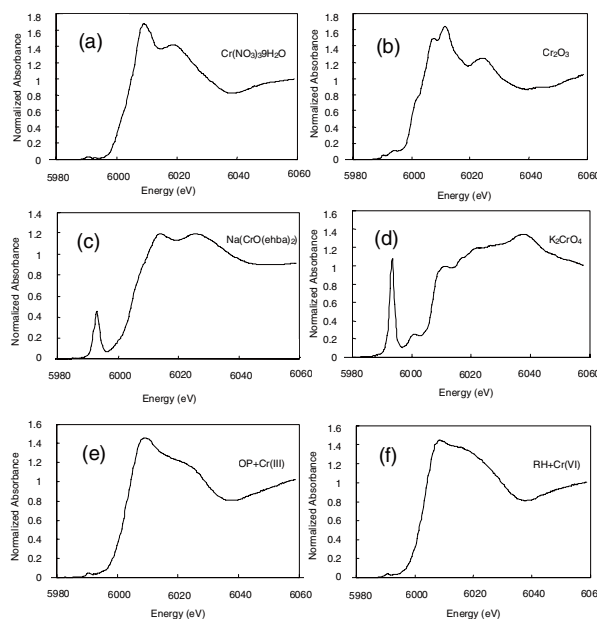


Fig. 1. Cr K-edge XANES spectra of solid samples of (a) $Cr(NO_3)_3 \cdot 9H_2O$, (b) Cr_2O_3 , (c) $Na[CrO(ehba)_2] \cdot H_2O$, (d) K_2CrO_4 , (e) Cr(III)-laden OP, and (f) Cr(VI)-laden RH biomaterial.

On the other hand, both the Cr(III)-laden OP and Cr(VI)-laden RH samples do not show a pre-edge peak between 5990 and 5997 eV, and they have a small peak at 5990.5 eV, indicating the presence of Cr(III) binding to the surface of the OP or RH biomaterials. It is also evidenced that the Cr(III) is bound to the OP surface and Cr(VI) adsorbed on the RH is completely reduced to Cr(III), which is consistent with the XPS and EPR results [4]. The process of the reduction mechanism of Cr(VI)-laden OP and RH biomaterials is now under investigation.

References

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*sala@iquir-conicet.gov.ar

*harada@cc.nara-wu.