Isotope fractionation as an evidence of Cr(VI) reduction during biosorption process

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Alternative adsorbents for treatment of Cr(VI)-contaminated waters are usually desciribed in terms of their sorption capacity [1]. However, it is essential to reduce Cr(VI) to Cr(III) during the remediation and therefore knowing the reductive potential of the adsorbent is of great importance. A novel approach to study the reduction of Cr(VI) during biosorption process was tested based on a fact that lighter isotopes react preferentially during Cr(VI) reduction and the $^{53}Cr/^{52}Cr$ shifts in water indicates the extent of the reduction [2].

Three biomaterials were studied: (i) brewers draff, (ii) grape waste and (iii) technical grade humic acids. Batch experiments were performed using synthetic solution prepared by dissolving $K_2Cr_2O_7$ in 0.01 M $NaNO_3$. Three different pH of the synthetic solution (3, 4.5, 6) were tested. Both the aqueous and solid phase were used for Cr isotope analysis. The dried biomass was decomposed in HNO_3 by pressurized microwave digestion using the microwave oven (CEM Discover, USA). Chromium isotope analysis was performed on a doublefocusing multicollector inductively coupled plasma mass spectrometer (Neptune, Thermo, Germany). The $\delta^{53}Cr$ values of remaining Cr(VI) were modeled using the Rayleigh kinetic fractionation model [3].

The Cr(VI) biosorption process was accompanied with heavier Cr isotopes enrichment in the remaining Cr(VI) fraction. A significant fractionation of Cr stable isotopes was observed with no significant pH effect; $\delta^{53}Cr$ of the remaining fraction ranged from 0.2‰ to 1.9‰ while $\delta^{53}Cr$ of the product (sorbed Cr) ranged from -1.2‰ to -2.8‰. The Rayleigh fractionation model fitted well the measured data and Cr isotope analysis provides thus an efficient tool to quantify Cr(VI) reduction by the biomaterials. In general, the sorption/reduction potential of the three studied biomaterials decreased in the following order: grape waste > humic acids > brewers draff.

[1] *Levankumar et al.* (2009) *J. Hazard. Mater.* **161**, 709-713. [2] *Ellis et al.* (2002) *Science* **295**, 2060–2062. [3] *Basu et al.*(2012) *Environ. Sci. Technol.* **46**, 5353-5360.