

Removal of Heavy Metals from Wastewater by Wine Processing Waste Sludge: Researches of Competitive Adsorption Mechanism and Organ-metallic Bonding by Using EXAFS Technique

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According to the studies of IR spectrum, the carboxylic group is the most important functional group of the wine processing waste sludge (WPWS). We supposed the Cr(VI) anion species could be bound to the protonated carboxylic groups of WPWS at low pH. In addition, partial reduction of Cr(VI)–Cr(III) might be conducted on biosorbent surfaces that contain a high content of organic carbon under extreme acidic, high Cr(VI) concentration and high temperature conditions. In last XANES studies, the results revealed that there were only Cr(III) sorbed on WPWS surface, not Cr(VI), in steady state. But it still remained obscurities about the interaction between WPWS and Cr(VI). We didn't know whether the Cr(VI) could be detected at early stage of the reaction. If the Cr(VI) ions are detected at that stage, it means the transformation of Cr(VI) to Cr(III) on WPWS is a slow reaction. The objective of this study was to determine the Cr species sorbed on WPWS at the early stage of adsorption reaction by using XANES technique. The appearance of a pre-edge peak can be taken as an indicator of the presence of Cr(VI). Nevertheless, the spectra of Cr(III) compounds do not exhibit any pre-edge peak.

In this study, four Cr-loaded WPWS samples were provided for XANES analysis. For preparing the samples, 1.2 g and 100-140 mesh of WPWS were individually added to four 100 mL of potassium dichromate solutions, with initial pH 2.0 and 100 mg L⁻¹ of Cr(VI) concentrations at 30°C. The mixtures were shaken vigorously by a mechanical shaker for 1.5, 3, 9, and 30 minutes, respectively. When the sampling time was up, the suspensions were immediately poured on Whatman No. 41 filters settling in working suction equipment and rinsed properly with deionized dilute water to clean up the surplus Cr species which were not really sorbed on WPWS surfaces. In other hands, avoiding excess removal of adsorbed Cr species from the WPWS particles, the pH of deionized dilute water should be adjusted to the values equaling that of the suspensions at sampling time. The Cr K-edges (5989 eV) spectra were recorded in fluorescence mode on beamline 17C. The experiments were achieved in the Cr K-edge, ranging from 5789 to 6989 eV, at ambient temperature.

As shown in Fig. 1, the contour shapes of all the Cr-loaded WPWS samples are similar to that of Cr(NO₃)₃;

that is, there is no noticeable pre-edge peak in the spectrum. This indicates that only the Cr(III) existing on WPWS rather than the Cr(VI), during whole reaction. This reveals that lots of Cr(VI) ions previously sorbed on the positive sites of WPWS were transformed into Cr(III) *in situ* by the oxidation of the organic constituents of WPWS, and they were then complexed with WPWS, translocated to the negative sites of WPWS or the liquid phase. Extended X-ray absorption fine structure (EXAFS) could be employed to provide further information about the coordination environment, the nearest neighboring atoms and the ligands which are involved in the binding of Cr, but there are limitations for complex materials such as sludge. In addition, the presence of Mn, originated from the WPWS, might interfere with the analysis of EXAFS data, because its K-edge energy is close to that of Cr.

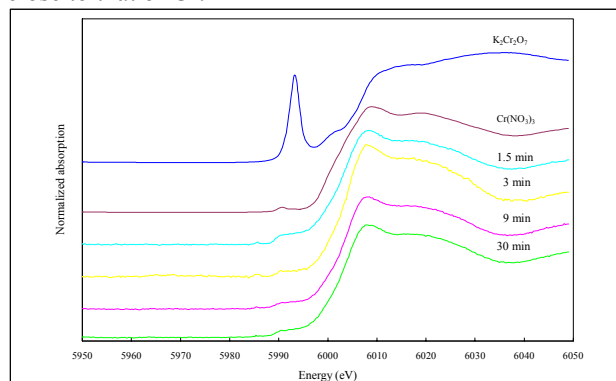


Figure 1. X-ray absorption near edge spectra (XANES) of Cr(NO₃)₃, K₂Cr₂O₇, and WPWS-sorbed Cr sampling at different reaction timer (pH 2.0, at 30°C)

We proposed two mechanisms for the WPWS acting as a biosorbent for removing Cr from Cr(VI) solution: (i) the Cr(VI) ions sorbed on the protonated carboxylic groups and then quickly transformed into Cr(III) ion *in situ*; and (ii) the Cr(III) ions translocated to the positive sites on the WPWS. We conclude that the potential of conversion from Cr(VI) to Cr(III) is the key factor affecting Cr removal in our experiments due to oxidation of the organic constituents in WPWS.