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Letter to the Editor

Mechanisms of the removal of hexavalent chromium by biomaterials or biomaterial-based activated carbons

Abstract

Three papers published during recent 2 years in *Journal of Hazardous Materials* made a mistake in analyzing chromium species in aqueous solution, resulting in incorrect elucidation of Cr(VI) biosorption; the Cr(VI) was removed from aqueous solution systems by 'anionic adsorption'. However, it has been proved that Cr(VI) is easily reduced to Cr(III) by contact with organic materials under acidic conditions because of its high redox potential value (above +1.3 V at standard condition). Therefore, it is strongly possible that the mechanism of Cr(VI) removal by biomaterials or biomaterial-based activated carbons is not "anionic adsorption" but "adsorption-coupled reduction". Thus, for researches of Cr(VI) biosorption, researchers have to analyze not only Cr(VI) but also total Cr in aqueous solution and to check the oxidation state of chromium bound on the biomaterials or activated carbons.

Keywords: Hexavalent chromium; Biosorption; Reduction; Biomaterial; Activated carbon

Recently, Bayramoğlu et al. studied about Cr(VI) biosorption onto untreated and heat-, acid- and alkali-treated fungal biomasses (white rot fungus *Lentinus sajor-caju*) [1]. The effects of pH, temperature, biosorbent dose, initial Cr(VI) concentration and contact time were investigated in a batch system. The maximum biosorption capacities of the untreated and heat-, HC1- and NaOH-treated fungal biomasses were 0.363, 0.613, 0.478 and 0.513 mmol of Cr(VI) per gram of dry biomass, respectively. It seems to readers as if the biosorption by the novel adsorbent is promising as an alternative technology for eliminating Cr(VI) from wastewaters. However, they analyzed only Cr(VI) in aqueous solution through a colorimetrical method using 1,5-dephenylcarbazide. Based upon the disappearance of Cr(VI), they concluded that Cr(VI) was removed from aqueous solution through "anionic adsorption". Thus they used a first-order equation to describe reaction pathways along times to reach equilibrium, and used Langmuir adsorption model to describe equilibrium state of Cr(VI) biosorption.

Khezami and Capart tested activated carbons produced from wood as adsorbent for Cr(VI) from aqueous solution [2]. The adsorption capacities of Cr(VI) were 315 and 186 mg/g for the KOH-activated and H_3PO_4-activated carbons, respectively. The adsorption of Cr(VI) was maximal at the lowest values of pH (pH 3) and increased with temperature for both adsorbents. However, they also analyzed only Cr(VI) in aqueous solution using the colorimetrical method. As a consequence, they used a pseudo second-order equation and Langmuir model to describe Cr(VI) biosorption. They also evaluated various thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes, on the basis of "anionic adsorption" of Cr(VI).

Karthikeyan et al. published the paper, "Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon" [3]. Activated carbon was produced by chemical activation (H_3PO_4) of rubber wood sawdust. The effects of various parameters such as contact time, initial Cr(VI) concentration, pH and temperature were considered in a batch system, and were same to that obtained by Khezami and Capart [2]. Various kinetic models and isotherm models were used to describe the adsorption kinetics and adsorption equilibrium of Cr(VI) removal by activated carbons. Finally, they suggest that the rubber wood sawdust activated carbon can be effectively used for the treatment of wastewaters containing chromium as a low cost alternative compared to commercial activated carbon and other adsorbents reported. However, they also analyzed only Cr(VI) in aqueous solution through the colorimetrical method.

It has been proved that, when Cr(VI) comes in contact with organic substances or reducing agents, especially in an acidic medium, the Cr(VI) is easily or spontaneously reduced to the Cr(III), because Cr(VI) has high redox potential value (above +1.3 V at standard condition) [4–16]. Therefore, it is very important to check the reduction of Cr(VI) by organic materials. However, the occurrence of the non-enzymatic reduction of Cr(VI) to

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Cr(III) by biomaterials or biomaterial-based activated carbons under acidic conditions studied were not considered in these papers published recently in the *Journal of Hazardous Materials* [1–3]. The adsorption capacity was simply evaluated by the difference between the initial and final concentrations of Cr(VI) in aqueous solution. Unfortunately, many papers published in 2004 and 2005 made the same mistake in researching the Cr(VI) biosorption [17–47]. In most papers, only Cr(VI) in aqueous solution was analyzed by colorimetrical method; the pink colored complex, formed from 1,5-diphenycarbazide and Cr(VI) in acidic solution, can be spectrophotometrically analyzed at 540 nm [17–40]. In the rest papers, only total Cr in aqueous solution was analyzed by atomic absorption spectrophotometer (AAS) [41–44] or inductively coupled plasma-atomic emission spectrometer (ICP-AES) [45–47]. Accidentally, several researchers analyzed both Cr(VI) and total Cr in aqueous solution, and reported that the removal of Cr(VI) was partly through reduction, as well as anionic adsorption, and the reduction could be taken place only under strongly acidic conditions (pH < 2.5) [10–13]. However, because they did not check the oxidation state of chromium bound on the biomaterials, they believed with limited information that it might be hexavalent form. Fortunately, there have been a few previous studies on the Cr species bound on the biomaterials. X-ray absorption spectroscopy (XAS) or X-ray photoelectron spectroscopy (XPS) has been used for it [14–16]. Lytle et al. reported that Cr(VI) taken from the fine lateral roots of wetland plants was rapidly reduced to Cr(III) [14]. Gardea-Torresdey et al. reported that Cr(VI) could be bound to an oat byproduct, but easily reduced to Cr(III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups [15]. Dambies et al. used glutaraldehyde cross-linked chitosan beads and native beads as a sorbent for Cr(VI) [16]. Their XPS data revealed that on cross-linked beads, Cr(VI) is entirely reduced to Cr(III), while on raw beads only 60% of the Cr(VI) is found in its reduced form.

Recently, the removal mechanism of Cr(VI) from aqueous solution by nonliving brown seaweed and fungal biomasses was clarified by Park et al. [4–9]. They showed that the Cr(VI) can be reduced to Cr(III) by contact with brown seaweed *Ecklonia* biomass [4]. The converted Cr(III) appeared in the solution and was partly bound to the biomass. An XPS analysis revealed that the bound Cr was in the trivalent form. During the Cr(VI) reduction, some of the organic carbons of the biomass were completely oxidized into inorganic carbon (HCO_3^- and CO_2). The reduction rate of Cr(VI) increased with decreasing solution pH as the protons were consumed during Cr(VI) reduction. However, Cr(VI) could be completely removed from aqueous solution, even at pH 5, if sufficient contact time is given. Since a reduction reaction of Cr(VI) to Cr(III) is endothermic, the reduction rate of Cr(VI) increased with increasing temperature. These results were also obtained in the case of fungal biomasses such as *Aspergillus niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae* and *Phenicillium chrysogenum* [6,7]. Effects of various parameters such as background electrolyte, ionic strength, other heavy metals and redox-active species on the Cr(VI) reduction were examined in detail [9]. In particular, a novel kinetic equation on the basis of the "Cr(VI) reduction" fitted well with the experimental data obtained at various conditions [7,9], which also supports that the Cr(VI) removal mechanism is "reduction".

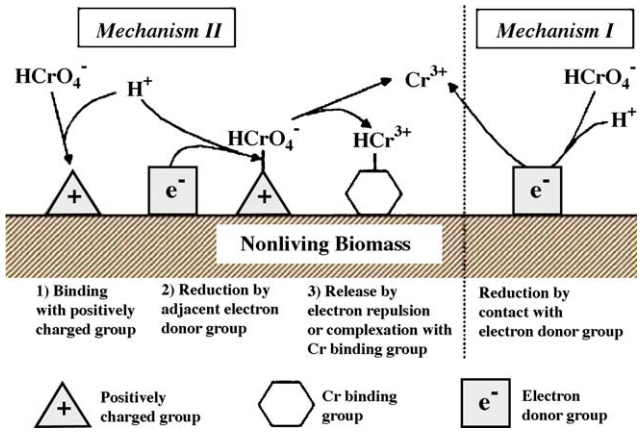

Fig. 1. Proposed mechanism of Cr(VI) biosorption by nonliving biomaterials [8].

Considering the extensive data in publications cited in this communication, Cr(VI) can be removed from the aqueous solution by nonliving biomass through following two mechanisms as depicted in Fig. 1 [8]. In mechanism I (direct reduction), Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with the electron-donor groups of the biomass, i.e. groups having lower reduction potential values than that of Cr(VI) (+1.3 V). Mechanism II (indirect reduction); however, consists of three steps: (1) the binding of anionic Cr(VI) ion species to the positively charged groups present on the biomass surface; (2) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups; (3) the release of the Cr(III) ions into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr(III) ions, or the complexation of the Cr(III) with adjacent groups capable of Cr-binding. If there are a small number of electron-donor groups in the biomass or protons in the aqueous phase, the chromium bound on the biomass can remain in the hexavalent state. Therefore, a portion of mechanisms I and II depends on the biosorption system such as solution pH, temperature, species on the biomass, and biomass and Cr(VI) concentrations.

In conclusion, we believe it is strongly possible that the mechanism of Cr(VI) removal by biomaterials or biomaterial-based activated carbons is not "anionic adsorption" but "adsorption-coupled reduction". In order to research the Cr(VI) biosorption, therefore, researchers have to analyze not only Cr(VI) but also total Cr in aqueous solution and to check the oxidation state of chromium bound on the biomaterials or activated carbons.

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