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Communications

Porous Morphology and Selective Metal-Adsorption of Burned Human Hairs

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Formation and application of unique micro morphology are emerging as an important field of micro functional materials.[1-4] In particular, porous morphological materials have been utilized in the fabrication of task-specific materials for catalysts, electronic devices, drug-delivery medicines, ceramics, pigments, molecular recognizers, desiccants, and cosmetics.[5-7] Thus, micro morphological-mimic of natural materials is one of green technological fields.[1,2] Hair is one of natural keratin materials containing protein structure.[8,9] Furthermore, US Environmental Protection Agency reported that hair analysis is a significant tool to measure the quantity of metal ions in human body.[10] Conversely, to the best of our knowledge, research on the morphology and adsorption-ability of burned human hairs (BHH) is an important issue. In this communication, preliminary results on the morphology and metal-adsorption of BHH have been reported. Some common metal ions such as Hg^{2+}, Ag^{+}, Pb^{2+}, Co^{2+}, Cu^{2+}, and Fe^{3+} were employed in the adsorption experiment. BHH selectively adsorbs mercury (Hg^{2+}) and silver (Ag^{+}) ions, as will be discussed in detail.

The present hair sample was collected from Koreans who were between 20 ~ 30 years old. The hairs were burned in a furnace at 300 °C for 1 h in the presence of air atmosphere. BHH was immersed in water, and the solution was analyzed for metals content. The mixture was stirred for 1 h at room temperature. Then, the solution was filtered off, and the solution was analyzed for metal concentrations and the amount of metal adsorbed was estimated. BHH was characterized by EDX, IR, TGA, and SEM. BHH is a brittle stable solid under air and moisture. SEM images show that BHH has a main channel with diameters in the range of 20 ~ 40 μm and satellite channels with diameters in the range of 1 ~ 2 μm as shown in Figure 1 and Supporting Information. The formation of channels indicates that the surface of hairs is different from the bulk of hairs in chemical properties. The human hairs take a weight-loss of 23% at 300 °C, and then a weight-loss of 76% at 600 °C (Figure S2). According to EDX results (Supporting Information), BHH [C (66%), O (30%), S (4%)] shows increase in oxygen, and decrease in sulfur, relative to non-burned human hairs [C (64%), O (21%), S (15%)]. Such a porous morphology has wide surface area, and thus may be a driving force for metal-adsorption. Of course, the formation and preservation of porous morphology may be indebted to the part burning rather than the complete burning of the human hairs.

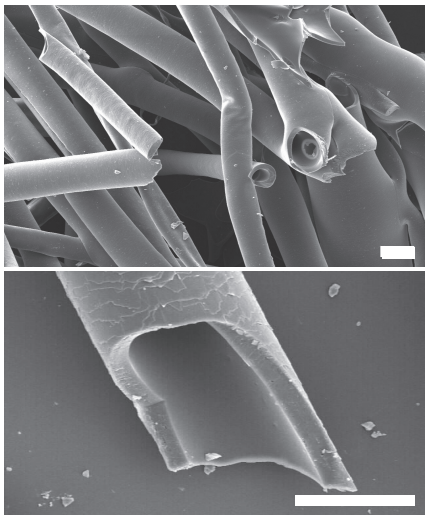

Figure 1. SEM images of BHH. Down figure shows the satellite microphores. Bar: 50 μm.

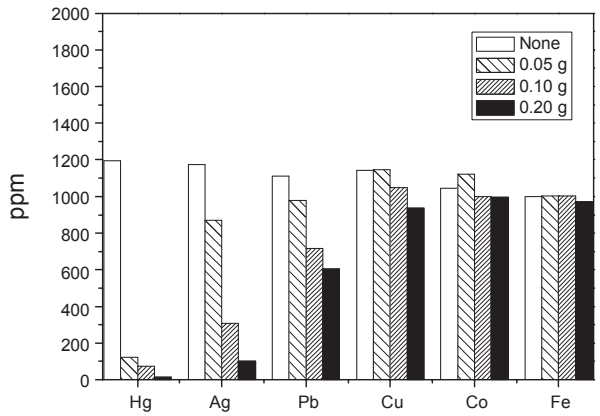

Figure 2. The metal ion concentrations after adsorption *via* BHH in solution of each metal ion.

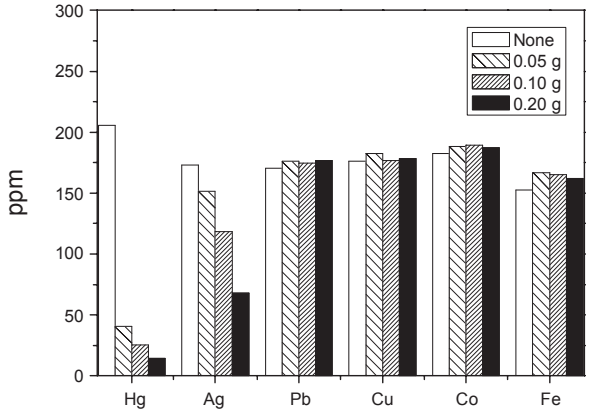

Figure 3. The metal ion concentration after adsorption *via* BHH in a mixture solution of metal ions.

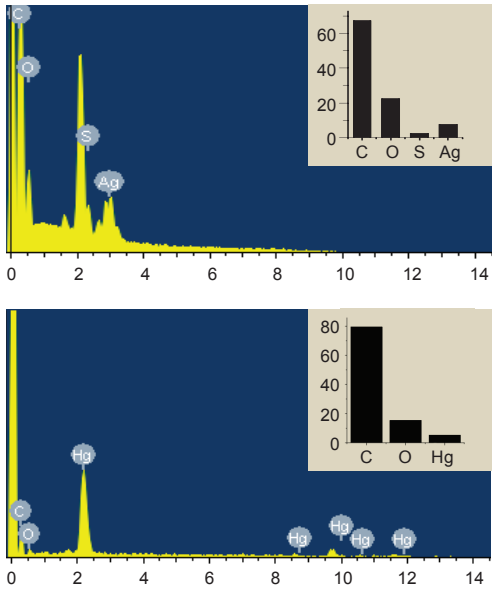

Figure 4. EDX analysis of Ag^{+} and Hg^{2+} ion on adsorbed BHH.

Inductively coupled plasma (ICP) ($AgNO_3$, $Pb(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$) and atomic absorption spectroscopy (AA) ($Hg(NO_3)_2{\cdot}H_2O$) methods were applied in the analysis. Each aqueous solution (1000 ~ 1200 ppm) of Hg^{2+}, Ag^{+}, Pb^{2+}, Co^{2+}, Cu^{2+}, and Fe^{3+} were prepared. Hg^{2+} ion was effectively adsorbed into BHH. That is, the concentration of Hg^{2+} ion drastically decreased from 1189 ppm (none BHH), to 121 ppm for (0.05 g BHH), 73 ppm (0.1 g BHH), 14 ppm (0.2 g BHH) as depicted in Figure 2. The concentration of Ag^{+} ion was significantly adsorbed. Thus, adsorption of Hg^{2+} ion is proportional to the quantity of BHH. Furthermore, for the mixture solution of Hg^{2+}, Ag^{+}, Pb^{2+}, Co^{2+}, Cu^{2+}, and Fe^{3+} ions (152 ~ 205 ppm), the similar trend was observed. Hg^{2+} and Ag^{+} ions were selectively adsorbed: 14 ppm (Hg) and 34 ppm (Ag) were remained in water containing 0.2 g BHH (Figure 3). In the case of Pb^{2+} ion, the analytical values of each solution are different from those of the mixture solution, indicating that Hg^{2+} and Ag^{+}-adsorption is more selective than Pb^{2+} ion. That is, Pb^{2+} ion was scarcely adsorbed in the mixture solution. The remaining Co^{2+}, Cu^{2+}, and Fe^{3+} ions were not adsorbed in both each and mixture solution in the all range of concentration.

For adsorption of Ag^{+} ion, EDX results [C (67%), O (22%), S (3%), Ag (7%)] were consistent with ICP analysis (Figure 4). Of course, non-adsorption Co^{2+} and Cu^{2+} ions were scarcely detected (EDX: C (70%), O (25%), S (5%), Cu (0%)). According to EDX, the similar Hg^{2+} quantity was observed for the inside and outside of main channel of BHH (Supporting Information), indicating that the inside and outside surface have similar surface properties. A combination of porous morphology and chemical composition of BHH effectively seems to adsorb Hg^{2+} and Ag^{+} ions. The channel structures are partly responsible for the adsorption of Hg^{2+} and Ag^{+} with remarkable selectivity in solution. That is the sulfur donors of non-burned hairs easily do not coordinate to soft metal ions, Ag^{+} and Hg^{2+}. However, part-oxidized sulfur donors of BHH coordinate to the soft metal ions even though the sulfur contents of BHH decrease. Charge, solvent, temperature, counteranion, generation, sex, and race effects on the adsorption of metal ions are underway.

In conclusion, BHH has both main and satellite channels, and is proved to be an effective natural material for the adsorption of heavy metal ions. We believe that BHH is useful natural materials for elimination of heavy metal ions. Further experiment on adsorption and desorption will contribute to the development of more detailed micro-based functional materials such as adsorption, transport, and sensing materials.

Supporting Information. SEM images of human hair, TGA of non-burned human hairs, ICP-AA data of the metal ion concentrations in each solution and in mixed solution, EDX of BHH, non-burned human hairs and metal-adsorbed BHH. EDX results on outside and inside of BHH (main channel) after adsorption of Hg^{2+}.

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