

Reduction of Manganese Oxide on Granulated Coal Ash through Degradation of Organic Matter in Eutrophic Marine Sediments

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Organic matter in marine sediment is mainly categorized into two fractions depending on degradability: labile, semi labile and refractory. The degradability of organic matter in coastal marine sediments depends on the properties of the organic matter contained in the sediments. Degradation of refractory organic matter in coastal marine sediments is one of strategies to remediate eutrophic coastal seas. An environmental remediation material called a granulated coal ash (GCA) was prepared to decompose organic matter in coastal marine sediments. The purpose of this study is to reveal reduction of manganese species on the GCA accompanied by degradation of organic matter in marine sediments.

The GCA was prepared by the granulation process of fly ash from thermal electric power stations with added cement as binder amounting to 13% of the final product. To obtain high-quality Mn XANES spectra, a manganese doped GCA (Mn-GCA) was prepared with immersing the GCA in saturated KMnO_4 solution for 24 hrs. and the solution was dried up at 110°C for 24 hrs. Thereafter, the GCA was calcined at 700°C for 3 hrs.

Sediment degradation experiments were carried out using a 500 mL of PP bottle. The bottle lid had two apertures, connecting the PE air pipe with an air stone at the tip of the pipe to supply air (0.2 L min^{-1}) and attached to a $0.2\text{-}\mu\text{m}$ pore size nylon membrane filter (Millex; Merck) for gas exchange. For the experiment, 10 g of the GCA or the Mn-GCA was mixed with 100 mL of homogenized wet sediment collected from Osaka Bay, Japan. The sediments were placed in the PP bottle, and 300-mL artificial seawater (MARINE ART SF-1; Osakayakken) was dispensed into the bottle. The sediments were incubated at 25°C in a constant temperature oven. The total organic carbon concentration in the sediments was measured by an elemental analyzer (JM1000CN, J-Science Lab) before and after the degradation experiments.

Manganese K-edge XAFS spectra were measured in BL3 at the Ritsumeikan SR center, Japan. The synchrotron radiation was monochromatized with a Si(220) double-crystal monochromator. The sample

XAFS spectra were measured by X-ray fluorescence yield mode using a three-elements Ge solid state detector (GUL0110S: Canberra). Vacuum packed the GCA samples were positioned at 45° to the incident beam in fluorescence mode. The manganese standards were also measured by the transmission mode using an ionization chamber filled with mixed gases: Ar 15% and N_2 85% for incident chamber (I_0) and Ar 50% and N_2 50% for transmitted chamber (I). The X-ray energy was calibrated by defining the K edge pre-edge peak of $\delta\text{-MnO}_2$ fixed at 6540eV .

The degradation percentages of organic matter in the sediments after 3 months were 15% for control without the GCA application, 22% for the GCA application and 0% for the Mn-GCA application. The high-quality Mn XANES spectra for the GCA were not obtained because the manganese content in the GCA was low (approx. 250 mg kg^{-1}). Therefore, we tried to identify the manganese species on the Mn-GCA instead of the GCA.

Mn K edge XANES of the Mn-GCA showed the manganese oxide on the material was tetravalent. After the organic matter degradation experiments, the manganese oxide on the Mn-GCA was reduced to divalent or trivalent oxide. When the GCA or the Mn-GCA were mixed with the sediments, the number of total bacteria in the sediments increased compared to control. Therefore, the manganese on the GCA was hypothesized to divalent or trivalent, and might work as electron acceptors derived from organic matter degradation by microorganism activities. However, the degradation percentage of the sediments mixed with the Mn-GCA was much lower than that of the GCA. This difference might depend on the manganese concentration of the GCA. The manganese concentration of the Mn-GCA was approx. 2.5%, which was much higher than that of the GCA (0.025%). Hence, it was considered that the high concentration of manganese on the Mn-GCA was negative impact on the degradation of organic matter in the sediments by microorganism activities. (Acknowledgements)

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