

Sorption Behavior of Radionuclide Iodine on Organic and Inorganic sorbents

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1. Introduction

Radioactive iodine (^{125/129/131}I) has been released into the environment as a result of nuclear testing, nuclear fuel processing, and nuclear accidents such as Chernobyl and Fukushima [1]. The released iodine radioisotopes are harmful to human and ecological system due to their high toxicity. In particular, long half-life of ¹²⁹I ($t_{1/2} = 1.6 \times 10^7$ years) leads to contamination of soils, sediments, and groundwater surrounding nuclear facilities.

Prior studies have suggested that the transport behavior of iodine in environment depends on the iodine speciation, based on different chemical reaction for individual iodine species [1]. Iodate (IO₃⁻) and certain organo-iodine (OI) species are strongly affected by sorption processes, while iodide (I⁻) is not [2]. The sorption characteristics of iodine species are also differentiated by the properties and composition of soils and sediments [3]. However, contribution of mineral and organic matter types in soils/sediments on the sorption behavior was not properly evaluated. As the first step of systematical research, the objective of this study is to investigate the sorption behavior of iodine species, especially, IO₃⁻, on different types of natural inorganic and organic sorbents in soils/sediments.

2. Methods and Results

2.1 Sorbents

Two different types of organic matters such as wood char and humic acid were used for iodate sorption batch experiments. Synthetic wood char was produced in the laboratory. Pine tree xylem (heartwood) was cut to approximately 1 cm³ blocks and dried at 105 °C for 24 hours. Small batches of xylem blocks were treated in a tube furnace with a constant nitrogen flow rate of 0.1 L min⁻¹. The xylem blocks were pyrolyzed at 600 °C as a final temperature for 30 min following a temperature ramp of 10 °C min⁻¹. The char sample was pulverized with a pestle and mortar, and sieved to isolate the 75 – 150 μm size fraction (100 to 200 meshes). Commercial humic acid was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further treatment.

Iron oxides and clay mineral were used as inorganic sorbents. Goethite (α-FeOOH) was produced by a mixing of NaOH and Fe(NO₃)₃·9H₂O solutions (36.8 g in 180 mL, and 40.4 g in 100 mL Milli-Q water,

respectively) in a 2 L jar. Red-brown ferrihydrite was rapidly precipitated during mixing procedures, and goethite was produced in the jar filled by 2 L of additional water after oven-drying at 80 °C for 3 days.

The produced yellow brownish goethite was rinsed with Milli-Q water couple of times, filtered, and air-dried before use. For the production of magnetite, two solutions were prepared by adding 80 g of FeSO₄·7H₂O in 560 mL previously N₂-flushed Milli-Q water, and 44.9 g of KOH in 240 mL of an oxygen-free solution, respectively [4]. The former solution was placed in a water bath at 90 °C with N₂ purging, and then two dropwise of the latter solution was added over 5 min [5]. After additional 30 – 60 minutes reaction and overnight cooling procedures, black-colored magnetite was precipitated. Impurities were removed through rinse using DI water, centrifugation, and filtration. Bentonite was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2 Sorption Experiment

The batch sorption experiments were conducted in 10 mL crimp-top amber glass vials sealed with Teflon-lined septa at room temperature (20 °C). The ratio of sorbent:water was adjusted to achieve > 30 % sorptive uptake in each batch. The sorbents were mixed with ~10 mL of I = 0.001 M NaNO₃ aqueous solution for 24 hours prior to sorbate addition. A working solution was prepared by adding 33.5 mg of potassium iodate (KIO₃) into Milli-Q water as surrogate for ¹²⁹I. Added sorbate was ranged from 0.1 – 0.15 μg to reach equilibrium aqueous concentration at $C_w \approx 5 \mu\text{g L}^{-1}$. After the addition of sorbate working solution, the sample vials were continuously mixed at 130 rpm, using orbital shaker, over 168 hours. Approximately 5 mL of aqueous phase was subsampled, and filtered using 0.45 μm nylon membrane. The aqueous concentration was analyzed by Inductively Coupled Plasma (ICP) with mass spectrometer at KIST Gangneung.

The sorbed concentration, q (μg kg⁻¹) was determined by a mass balance approach, as follows:

$$q = (M_0 - C_w V_w) / m_s \quad (1)$$

where M_0 (μg) denotes total added mass of iodine. V_w (mL) and m_s (kg) are solution volume and sorbent mass, respectively. The sorption distribution coefficient (K_d , L

kg^{-1}) was determined by the ratio of sorbed and aqueous phase concentrations at equilibrium.

2.3 Sorption Results

Final measured pHs ranged from ~6 – 8 for wood char, goethite, magnetite, and bentonite. In contrast, the commercial humic acid exhibited more acidic condition at pH ~4.

Sorption of iodate on iron oxides was relatively comparable ranging from $K_d = 7.7 \text{ L kg}^{-1}$ and 12.1 L kg^{-1} for goethite and magnetite, respectively (Fig. 1). However, iodate sorption on bentonite was negligible. In the case of organic matter, the commercial humic acid exhibited the greatest sorption for iodate. The iodate K_d of humic acid was approximately 30 times greater than the K_d values for iron oxide samples at $C_w \approx 5 \mu\text{g L}^{-1}$. The K_d value for wood char was about 0 L kg^{-1} . The measured surface area indicated that humic acid has the smallest surface area ($\text{SA} = 0.09 \text{ m}^2 \text{ g}^{-1}$) among the used mineral and organic sorbent (Fig. 1). These observations suggested that the surface area does not dominantly control the iodate sorption processes.

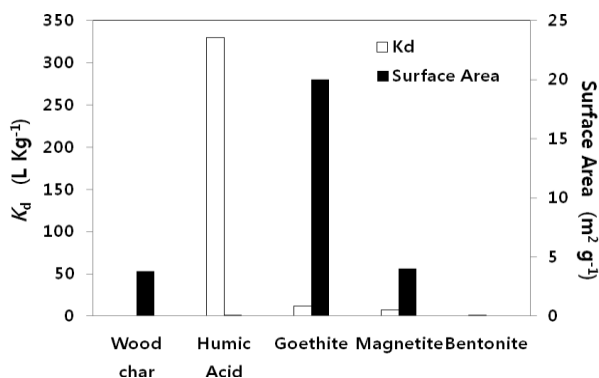


Fig. 1. Measured sorption distribution coefficients (K_d , L kg^{-1}) and surface area (SA , $\text{m}^2 \text{ g}^{-1}$) for organic and inorganic sorbents. The BET surface area of bentonite was not analyzed.

3. Conclusions

Humic acid contributes dominantly the sorption of iodate rather than other organic (wood char) and inorganic (iron oxides and bentonite) sorbents. The humic acid is ubiquitous organic substance among various types of organic matters found in natural soils and sediments. Even though amount of organic matter is relatively small in sediments, iodate mobility can be significantly retarded by humic acid in environments.

Additional studies for iodine sorption mechanism and enhanced iodine uptake by modified bentonite are still in process.

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