

Mobile Iodine Mineralization Based on Malachite Transformation

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1. Introduction

Iodine generally exists as anionic (e.g., I^-), molecular (I_2), and organic (e.g., CH_3I) forms according to specific conditions. Their forms are affected by redox conditions. For example, the anionic form of I^- would be a dominant specie in a solution, if it is dissolved under anaerobic condition. Iodide (I^-) is soluble and mobile in water, so it is very difficult to capture and precipitate it with common adsorbents.

Until now, various exchanger and getter materials have been developed to capture radioactive iodine in wastewater. The materials developed generally showed a good performance under acidic conditions. However, the adsorption amounts were not relatively large in neutral and high pH conditions. Furthermore, the capacity to capture iodine is limited by their properties, such as the specific surface area and adsorbing affinity. Recently, Ag-coated materials have attracted attention as adsorbents [1-2]. They have shown higher uptake for I^- compared to other substances, but they are costly.

Our new method that is proposed here, however, offer drastic cost cutting by using copper. Moreover, the selectivity of iodine in anion-rich water is advantage to lower the disposal cost by reducing the radioactive waste volume. Recently, we published a paper that shows a method of microbial copper reduction that was very effective to remove iodine [3]. This time we present a new way to scavenge iodine inorganically based on a self-transformation of copper compound.

2. Methods and Results

2.1 Methods

To study the selective uptake of iodide from anion-rich water, some common anions such as Cl^- , HCO_3^- , and SO_4^{2-} were previously dissolved in distilled water in serum bottles. The anions are common in natural waters, and their concentrations injected were mM levels as chemicals of NaCl, $NaHCO_3$, and Na_2SO_4 . Iodide was injected as NaI from a stock solution (100 mM).

To perform a practical radioactive test, radioiodine ^{125}I (half-life: 60 days) was prepared at 185 MBq/l from a reagent solution of 5 mCi NaI (Perkin Elmer, Inc.). From the radioactive solution, ^{125}I was provided to be 2.2 MBq/l in the test solution.

To study a potential binder for mobile iodide, copper was injected as $Cu(NO_3)_2$. The overall solution pH was around 7.3. The prepared serum bottles were put in a shaker (120 rpm) in the dark for several days. Periodically, liquid samples were removed by syringe and needle through 0.2 μm filter and were analyzed by ICP-MS or liquid scintillation counter (LSC).

2.2 Analytical Techniques

In the radioactive test, the radioactivity of ^{125}I in a liquid sample was measured by a LSC (Perkin Elmer, Tri-Carb 2910 TM). A diluted solution of the liquid sample (0.5 ml) and distilled water (4.5 ml) was mixed with 15 ml of a cocktail solution (Ultima Gold). To confirm the oxidation state of copper, solid samples were analyzed by X-ray photoelectron spectroscopy (XPS). To identify the mineral form and crystallinity, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used as mineralogical analyses tools.

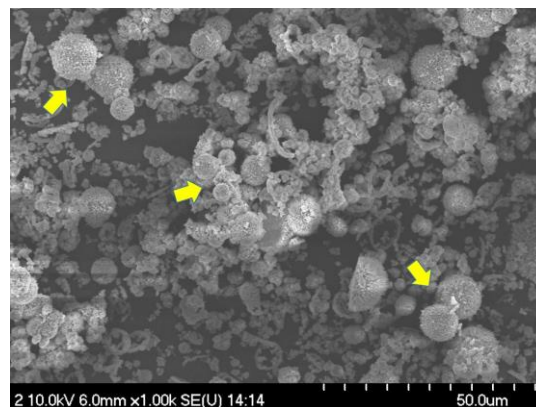


Fig. 1. SEM image of malachite particles (arrows) with a microscale spherical form.

2.3 Iodine Removal as CuI Microcrystals

Copper was precipitated as copper carbonate, malachite ($Cu_2CO_3(OH)_2$), in the early stage. Most copper that was injected in water was initially combined with carbonate species forming low-crystalline malachite with spherical forms (Fig. 1). The malachite was very interactive with iodide. In particular, when sulfate was present in the media, the malachite was gradually transformed to a cuprous form that incorporates iodide ions. The cuprous iodide (CuI) was crystallized as a halide mineral that is insoluble.

Iodide was removed along with copper in the experiment (Fig. 2). Most iodide was removed within a day and then slowly decreased from the anion-rich solution. Other anions such as Cl^- did not interfere with the iodide removal. Iodide was selective among anions by freely combining with copper.

The merit of our system is to strongly restrict the mobilization of volatile iodide by transforming the mobile phase into an immobile crystal. The crystal phase of iodide is insoluble in nature, further ensuring its long-term stability.

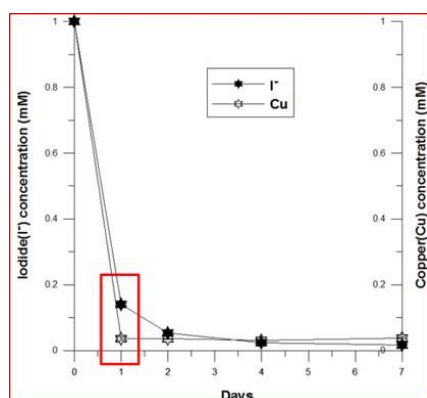


Fig. 2. Decline of aqueous iodide concentration along with copper (Cu^{2+}) in the presence of malachite precursor that was initially generated in the media.

3. Conclusions

Radioactive iodine isotopes are characterized as volatile and mobile species that are difficult to capture by adsorbents. In our study, we developed a new way to uptake and crystallize the mobile iodide as cuprous iodide (CuI). This method will be a promising way to simply stabilize iodide in a solid form with compacted volume. Furthermore, the cost that operates the system is cheaper than the previous methods.

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