

Synthesis of Bismuth Functionalized Grapheme Oxide for Radioactive Iodine Gas Removal – 16114

Sangsoo Han *, Won-Seok Kim *, Wooyong Um **

* Pohang University of Science and Technology

** Pacific Northwest National Laboratory

ABSTRACT

Released radioactive iodine from nuclear reactors and nuclear severe accidents, such as those experienced at Chernobyl and Fukushima, is one of the most hazardous materials and can affect human health. Uptake of radioactive iodine from gaseous and aqueous waste, consisting of mainly organic forms such as methyl iodide and elemental iodine after reacting with organic matter in scrubber process, is a recent concern during nuclear power plant operation. In general, Triethylenediamine (TEDA) or KI-impregnated activated carbons, silver-loaded silica aerogels, and silver-loaded zeolite are used to remove radioactive iodine compounds. However, previous research has shown TEDA and KI-impregnated activated carbons to have some limitations for use in responding to severe accidents or in pressurized-water reactors, because they are easily burned up and the iodine removal efficiency of silver-loaded sorbents is greatly decreased at high temperatures. To improve the capability of synthesized sorbent material used in iodine gas removal, highly efficient sorbents for methyl and elemental iodine removal were prepared through the functionalization of graphene oxide (GO) with bismuth. GO was synthesized from natural graphite powder (99.95%) by the modified Hummers method, and then mixed with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. After developing a sorbent for the removal of iodine, the synthesized sorbent was characterized using x-ray diffraction, a scanning electron microscope/energy dispersive spectrometer, and thermogravimetric analysis/differential scanning calorimetry, and the surface area of sorbents was determined using the BET- N_2 adsorption method. Methyl iodine batch experiments were conducted for 7 days and elemental iodine gas adsorption experiments were conducted at high temperature (190°C) using a carrier gas (air). The final concentration of iodine in batch and off-gas scrubber solutions (0.1 M NaOH) was analyzed using inductively coupled plasma mass spectrometry. The breakthrough curve and decontamination factor values were also investigated using bismuth-functionalized GO and the results were compared with Ag-zeolite, Sn-apatite, and activated carbon.

INTRODUCTION

Radioactive iodine, including isotopes I-131, I-135, I-125, and I-129, is a major constituent of fission products released into the environment from damaged containment at nuclear power plants (NPPs) during severe core melt accidents, such as those experienced at Chernobyl and Fukushima, as well as during nuclear fuel reprocessing [1]. These isotopes have significant radiological hazards that affect human health because of their high fission yield, volatility, and environmental

mobility. Among the isotopes of iodine, I-131, which has a short half-life of 8 days, is the most significant source due to its large initial inventory. Also, I-129 is one of several radioactive iodine isotopes formed as a fission product in nuclear fuel reprocessing. It has a very long half-life of 15.7×10^6 years [2]. Because of the long half-life of I-129, the U.S. Environmental Protection Agency has implemented strict regulations for the release of I-129 from reprocessing facilities that require effective capture efficiency in excess of 99% (decontamination factor [DF] >167) [3].

Usually iodine exists in gaseous phases at NPPs. Technologies for capturing I-129 in off-gas systems are divided into two categories. First, the wet scrubbing methods that use scrubbing solutions of 1 to 2M NaOH, 0.4M $\text{Hg}(\text{NO}_3)_2$, and 20 to 23M HNO_3 , also use highly concentrated scrubbing solutions to react with I-129 in the off-gas system [4-6]. The maximum DF of these technologies is reported to be approximately 10^4 for I-129. However, the removal of I-129 from the off-gas system must be followed by removal of iodine from aqueous solutions. Hence the second category—the solid sorbents method—uses sorbents such as activated carbon and silver to bind iodine. For example, the use of Triethylenediamine (TEDA) or KI-impregnated activated carbons, silver-loaded silica aerogels, or silver-loaded zeolite is based on the adsorption of gaseous I-129 onto a material that has a high surface area. But impregnated activated carbons are not usually considered an option for iodine removal in fuel reprocessing plants because they are easily burned up and iodine removal efficiency is extremely decreased at high temperature. The silver-loaded solid sorbents method is also thermally unstable at high temperature, expensive, and involves high toxicity [4]. Because of the thermal instability of silver-loaded zeolites, most captured iodine in zeolites is physisorbed and can be easily re-volatilized at elevated temperatures [7].

Therefore, the main purpose of this study was to develop a sorbent that features highly efficient removal of iodine gas during fuel reprocessing, severe accidents, and NPP operation at high temperature—all at a lower cost. To remove CH_3I and elemental iodine from the aqueous and gas phases, highly efficient sorbents were prepared using a functionalized process and graphene and bismuth.

EXPERIMENTS

Synthesis of sorbent

This research approach presented a synthesis method of developing a sorbent to uptake iodine gas using a graphene-bismuth composite material. The objective of this sorbent development effort was to enhance the sorbent's iodine removal efficiency and thermal stability.

Synthesis of graphene oxide (GO)

GO was synthesized from natural graphite powder (99.95%) using the modified Hummers method [8, 9], as follows. (1) The graphite powder (0.3 g) was put into the 4 mL H_2SO_4 , which contained 0.5 g $\text{K}_2\text{S}_2\text{O}_8$ and 0.5 g P_2O_5 . The mixture, which was dark blue in color, was stirred continuously for 4 h at 80°C . Then it was carefully washed with distilled water, and the initial product was obtained by filtering and

drying at room temperature. (2) After drying, the initial product was re-dispersed into 12 mL of concentrated H_2SO_4 , and 1.5 g KMnO_4 was added to keep the reaction temperature below 20°C . During processing, an ice bath was used to keep the temperature from increasing to over 20°C . (3) The mixture was stirred for 2 h at 35°C , and 25 mL of distilled water was added. (4) 70 mL of distilled water and 2 mL of 30% H_2O_2 solution were added, and the reaction was terminated after 15 min. The color of the mixture changed from snuff color to bright yellow. (5) Finally, the mixture was washed in a HCl solution and distilled water in turn until the pH value of rinse water became neutral. The GO product was obtained after drying.

Synthesis of bismuth functionalization

To synthesize GO-bismuth, the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ nanoparticles from Sigma Aldrich were used. 10 mg of GO and 90 mg of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were added to 100 mL of distilled water. After 1 h of sonication, the mixture was centrifuged and then dried at 30°C . Then the bismuth-functionalized graphene oxide (BFGO) was obtained and the best ratio between Bi and GO was confirmed by conducting a DF test for iodine gas removal.

Characterizations of synthesized sorbent

After developing a sorbent for the removal of iodine, the synthesized sorbent was characterized using (1) x-ray diffraction (XRD) to identify the atomic and molecular structure of a crystal, (2) a scanning electron microscope (SEM)/energy dispersive spectrometer (EDS) to determine the microstructure of the samples, (3) Brunauer-Emmett-Teller (BET) to determine the specific surface area, and (4) thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) to demonstrate the thermal stability of synthesized sorbent. These same procedures were also conducted after the iodine removal experiment.

Iodine removal experiment

The trapping capacity of $\text{I}_2(\text{g})$ is one of the most important parameters in determining the performance of the sorbent. The actual trapping of iodine-containing off-gas released from the treatment of spent nuclear fuel can be achieved using an off-gas treatment system. Figure 1 shows a schematic diagram of the developed iodine removal system. The iodine trapping test was conducted as follows. (1) The initial masses of the adsorbent (0.5 g) and the iodine crystal were measured. (2) Then, the samples were placed in a glass tube and reacted for 2 h at 190°C with a carrier gas of air. (3) After cooling, the final mass of the sample was measured again to calculate the adsorbed iodine mass using simple mass change measurements. The amount of pure iodine on the sorbent was determined by analyzing the iodine-captured sorbent. For methyl iodine, batch experiments were conducted for 7 days. The final concentration of iodine in the off-gas scrubber solution (0.1M NaOH) and batch aqueous solutions was analyzed by ICP-MS. The breakthrough curve and DF were also investigated to compare the iodine trapping performance of the newly developed sorbent with that of commercial AgZ and activated carbon sorbent powders, the latter underwent the same iodine trapping test.

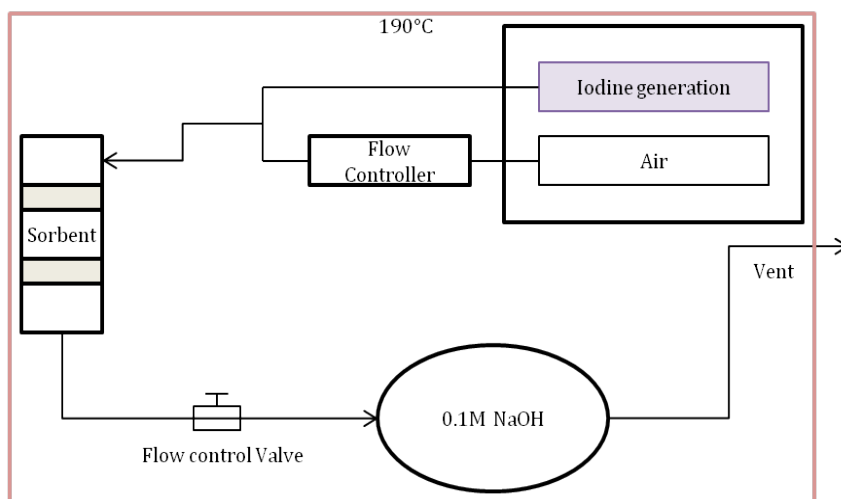


Figure 1. Schematic diagram showing the developed iodine removal system.

RESULTS

Morphology and structural characterization of sorbents

In this study, BFGO was developed; images of the samples—GO and BFGO—are shown in Figure 2. Bismuth-functionalization structures within the GO samples were confirmed by XRD peaks. The degree of mesostructural arrangement was studied using the patterns of powder X-ray scattering obtained from a Bruker D8 Advance Technical XRD system. 2θ was scanned from 5° to 80° with a 0.02° step size and 50 s dwell time.

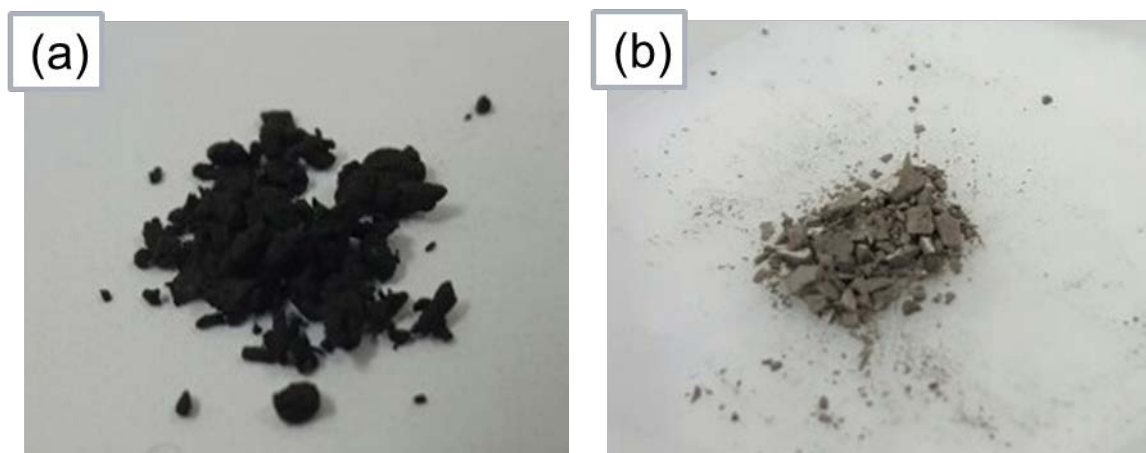


Figure 2. (a) Graphene oxide and (b) bismuth-functionalized graphene oxide.

The XRD patterns of graphite, GO, and BFGO are shown in Figure 3. Graphite showed a very strong 002 peak at 26.03° , GO a 001 peak at 9.21° and a 002 peak at 25.05° . The GO peak shift is due to the formation of hydroxyl, epoxy, and carboxyl groups. After functionalization with bismuth ions, some of the oxygen-containing functional

groups were removed from the GO, and this caused the graphite peak to be removed at 26.03° . Bismuth ion peaks occurred at 27.71° , 49.11° , and 60.93° . This suggests bismuth-graphene oxide (Bi-GO) is reestablished during the functionalization process, which will have a high removal reaction rate.

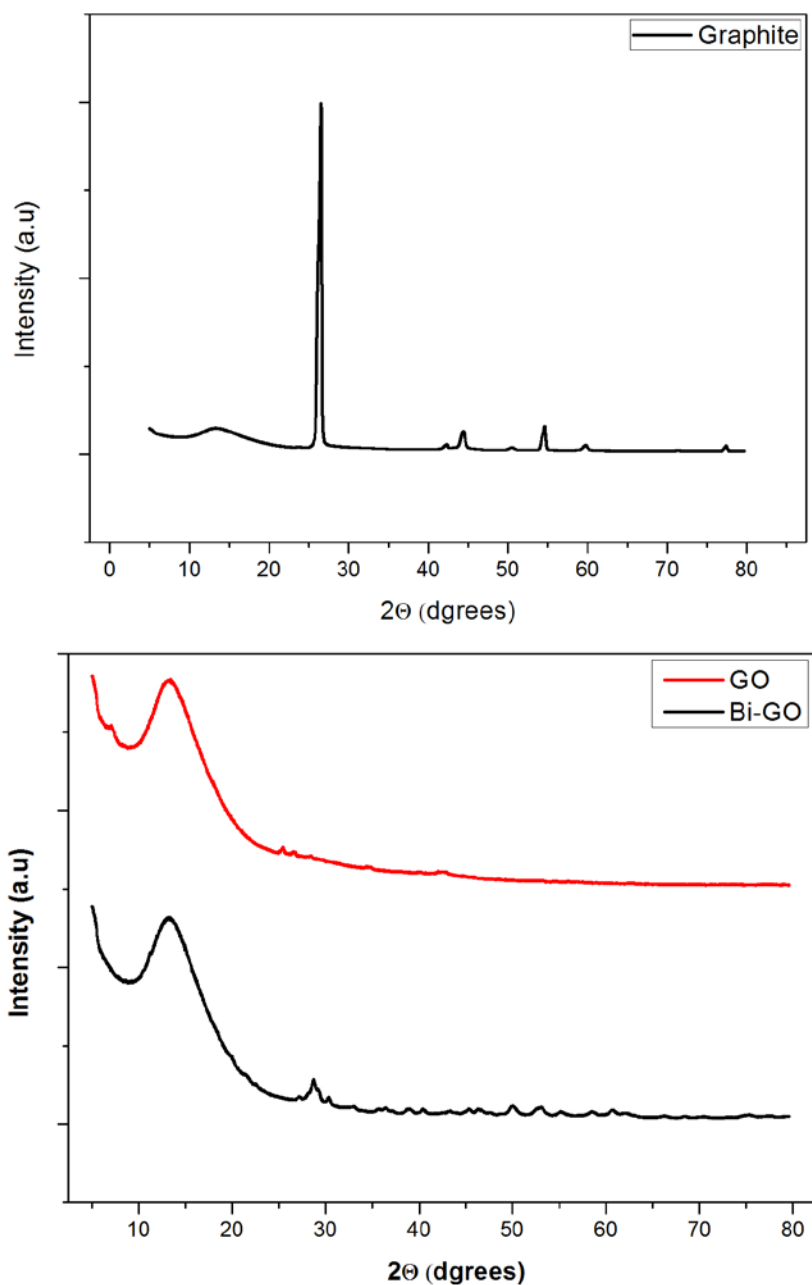


Figure 3. XRD patterns of graphite, graphene oxide, and bismuth-functionalized graphene oxide.

Iodine removal experiments

To remove the iodine gas, uptake systems were developed and optimized. Figure 4 shows the iodine uptake system to remove iodine gas. In this experiment, surrogate stable iodine gas (I-127) was generated using elemental solid iodine at high temperature (190°C) with iodine at a sorbent ratio of 0.5 g/1 g, and the final concentration of iodine in off-gas scrubber solution was analyzed by ICP-MS. At first, DF values were also investigated for AgZ and Sn-apatite sorbents to optimize the iodine removal experimental conditions, which are flow rate, mass, and reaction time. Table 1 shows the iodine DF values after the uptake experiment.

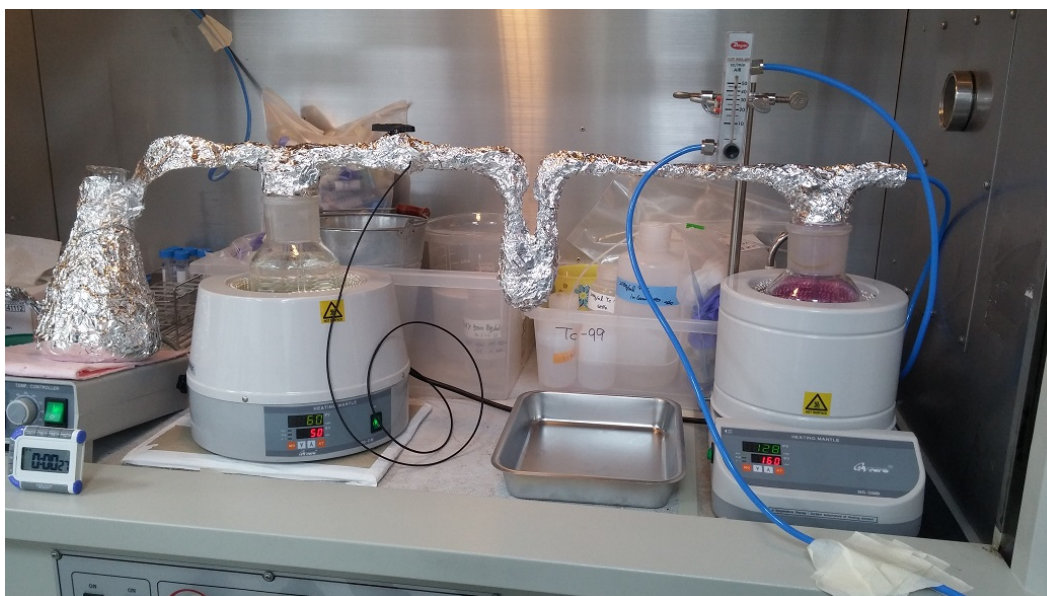


Figure 4. Uptake system for iodine gas.

Table 1. Iodine decontamination factor using AgZ and Sn-Apatite sorbents.

Nuclide	Sorbent	Initial concentration (ppm)	Total time (Min)	DF	
Iodine-127	Ag-Zeolite	2434	108	4622.455	103.665
Iodine-127	Sn-Apatite	2434	122	119.548	102.078

Comparing the results, AgZ had larger DF values than Sn-apatite. Based on preliminary testing, an uptake system was developed and tested, and the experimental conditions, including temperature, flow rate, and sorbent to iodine mass ratio, were optimized with no leakage. In addition, we compared the iodine removal efficiency with commercial sorbent and the new synthesized sorbent using BFGO.

CONCLUSIONS

The iodine removal technology was developed and applied to the decontamination of iodine gas resulting from nuclear power plant operation, fuel reprocessing, and severe accidents. This unique removal and decontamination technology is expected to lead the field of radioactive waste management and remediation. After synthesis, XRD peaks showed a functionalization state with bismuth. A trapping test was conducted using an iodine gas removal system with optimized conditions and batch testing for methyl iodine. This experiment investigated iodine uptake capacity, the DF, and removal mechanism as well as iodine bonding in an oxidation state.

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