Feasibility Study of Bismuth based Metal-Organic Framework as an Adsorbent for Radioiodine Capture

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1. Introduction

Radioiodine is released as a gaseous form from reprocessing plant. It may also be released into the environment from nuclear power plant (NPP) during a severe accident. Most important radioiodines are [129]I and [131]I. In case of [129]I, which has a very long half-life, it is released as off-gas at reprocessing plants. For ^{131}I, it decays quickly and has high radioactivity, posing short-term danger to the public if released directly into environment during severe accident. Thus in the nuclear industry, it is paramount to capture radioactive gaseous iodine and prevent it from being released into environment before treatment.

Commercially, silver-based adsorbents (silver-doped zeolite (AgX), mordenite (AgZ), etc.) are mainly used to capture radioiodine in a nuclear facility. In spite of its reliable adsorption capability due to affinity of silver in iodine, silver-based adsorbents cannot be a permanent solution for iodine capture because of several shortages: 1) economically uncompetitiveness, resulting from the pricey silver; 2) toxicity of silver; and 3) main adsorption mechanism being physical sorption, which may cause revolatilization and possible environment release after disposal.

Metal-Organic Frameworks (MOFs) is an organic-inorganic hybrid compound. Over the past two decades, MOFs have been spotlighted because of their attractive features such as ultrahigh porosity, huge surface area, and very tunable structure. With these features, the extraordinary degree of variability for both the organic and inorganic components of their structures grant powerful applicability in a variety of areas including gas storage and separation, adsorbent, catalyst.

Gas adsorption in MOFs primarily occurs via a physisorptive process with partial chemisorption. Though there are several advantages of physisorption, generally, chemisorption is preferred for adsorbents because of thermal and thermodynamic stability of adsorbate-loading absorbents, which is important in radioiodine capture.

Several MOFs have been applied to capture iodine. Among them, ZIF-8 (Zn(2-methylimidazolate)$_2$)) and Cu-BTC (Cu$_3$(benzene-1,3,5-tricarboxylate)$_2$(H$_2$O)$_3$)) showed remarkable adsorption capacities for iodine capture, 125 wt% I$_2$ (2.2 I$_2$/Zn) and 175 wt% I$_2$ (or 3 I$_2$/Cu) at 77 °C, respectively [1-2].

Both ZIF-8 and Cu-BTC do not produce chemical bond between metal and iodine. ZIF-8 captures iodine through strong iodine charge-transfer complex within the cages of the ZIF-8 [1]. This chemisorption occurring between linker of ZIF-8 and iodine molecular allows iodine to be confined in the sodalite cages of ZIF-8 up to when the framework begin collapsing at 302 °C. However, about 20% of iodine is attached on the surface, which is released around 125 °C [1]. The mechanism of iodine adsorption of Cu-BTC is physisorption due to the proper pore size of Cu-BTC for iodine capture, which acts as a pocket for iodine molecular granting iodine selectivity when water coexists with iodine. However, the captured iodine is released around 150 °C [2].

Recent studies on the use of bismuth for iodine capture indicated bismuth-based porous material as an alternative to silver-based adsorbent by providing stable chemisorption sites [3]. Considering the affinity of bismuth with iodine, there is strong possibility that bismuth based MOFs may provide a robust porous material for iodine capture. A number of bismuth based MOFs have been developed for several purposes such as gas adsorption (CO$_2$, CH$_4$) and photocatalyst. However, since many MOFs are often based on divalent late first row transition metals (Cu(II) and Zn(II)) to obtain low framework density for gravitational advantage, bismuth based MOFs have not been actively developed and applied in various area including gaseous iodine adsorption. Bismuth based MOFs (Bi-MOFs) have several interesting features resulting from unique properties of bismuth. For instance, Bi-MOFs can have diverse structures resulted from its variety of coordination numbers and the presence of the lone pair of electrons affecting the coordination angle of bismuth. They allow geometrically flexible coordination environments.

Through preliminary research, several reported Bi-MOFs were investigated to select a suitable Bi-MOF as an iodine adsorbent based on chemical property and thermodynamic reactivity between adsorbent and adsorbate, which allowing chemisorption. As a result, Bi-mna, developed as a photocatalyst by Wang [4], was selected as an iodine adsorbent. In Bi-mna, one Bi forms six chemical bonds with each two sulfur atoms, nitrogen atoms, and oxygen atoms [4]. Considering the difference of electronegativity between Bi and other organic including iodine and Gibbs free energy of formation, it is expected that Bi-mna allows a direct chemical bond between Bi and I grating the thermal stability.

In this study, Bi-mna is synthesized and tested for gaseous iodine adsorption experiment. The resulting samples are investigated using x-ray diffractometer (XRD). ZIF-8 and Cu-BTC, which have been studied for iodine adsorption representative MOFs [1-2], are also examined in a similar manner for comparison with Bi-mna.

2. Experiment

Bi-mna was synthesized by a solvothermal method referring to reference [4] with some modification of the procedure. For comparison of the iodine adsorption capacity at different temperatures, ZIF-8 and Cu-BTC, are purchased from Sigma-Aldrich as same from the reference studies [1-2]. The product name is Basolite Z1200 and Basolite B300, respectively. The synthesis method for Bi-mna and experiment conditions are discussed in this section.

2.1 Synthesis of Bi-mna and characterization

The Bismuth(III) nitrate pentahydrate (3.00 g, 6.2 mmol), 2-Mercaptopyridine-3-carboxylic acid (4.63 g, 29.8 mmol), and potassium hydroxide (KOH) (0.60 g, 10.7 mmol) were mixed in 120 mL N,N-Dimethylformamide (DMF). After stirring for 30 min at room temperature, the solution was introduced into a 1000 mL PTFE bottle, heated to 100 °C and kept at this temperature for 96 hr, and then cooled to room temperature under natural circulation. The precipitate was obtained by filtration, washed with DMF, washed with deionized water, and then dried in air at 60 °C. All reagent was purchased through Sigma-Aldrich. The structure of the synthesized material is investigated using high resolution powder XRD (RIGAKU, SmartLab) and the result is compared with a published data from [4] to identify whether the synthesized final product is the same MOF.

2.2 Absorption experiment

The gaseous iodine adsorption experiments were conducted in various temperatures from 350 K to 575 K to investigate the feasibility of utilizing Bi-MOF as an adsorbent for radioiodine in nuclear industry requiring thermal stability. The temperature of 350 K represents the off-gas temperature in a reprocessing facility releasing ^{129}I. In NPP, however, iodine may be released in much severe conditions (such as higher temperature) if a severe accident occurs allowing radioactive material release. Thus, this study investigates the adsorption capacity of adsorbents up to 575 K. In general, iodine adsorption research do not deal with such high temperature [1-3, 5].

Iodine adsorption experiment in the closed environment was performed inside a furnace with an experimental configuration as shown in Figure 1, similar to how it was done in Ref [5]. Gravimetrical method was used to calculate the iodine adsorption capacity. Approximately 0.20 g of adsorbent (i.e. Bi-mna, ZIF-8, or Cu-BTC) was placed inside an alumina crucible with much larger amount of non-radioactive iodine beads (approximately 2.0 g) to ensure high gaseous iodine concentration. A microporous alumina disk (pore size: <1mm) was placed at 1/3 way up the crucible to separate the adsorbents from gaseous iodine. The alumina crucible was covered with an alumina lid, and the sample

was placed inside a furnace at 350, 425, 500, and 575 K (77, 152, 227, 302 °C) for 6 hours to allow enough time for iodine adsorption. After 6 hours, the cover was taken off and the samples were allowed to cool inside the furnace till 343 K (70 °C). This was done to prevent rapid cooling which may result in some condensation and to allow rest of non-adsorbed iodine to escape the sample. Then, the final mass of each sample was measured.

The iodine adsorption capacity of each sorbent at each temperature was then determined by using the following:

$$C = \frac{m_{abs,I}}{m_{s,i}} = \frac{m_{s,f}-(m_{s,i}-m_{s,loss})}{m_{s,i}} \qquad \text{(Eq. 1)}$$

where C is the iodine adsorption capacity of the sorbent in units of milligram of iodine captured per gram of sorbent (or mg-I/g-sorbent), $m_{abs,I}$ is the mass of the iodine absorbed by the sorbent during the experiment, $m_{s,i}$ is the initial mass of the sorbent, $m_{s,f}$ is the final mass of the product, and $m_{s,loss}$ is the mass loss of the sorbent during the experiment. The mass loss of the sorbent ($m_{s,loss}$) was found using the control group experiments performed without iodine. The experimental results for the iodine adsorption capacity are shown in the next section.
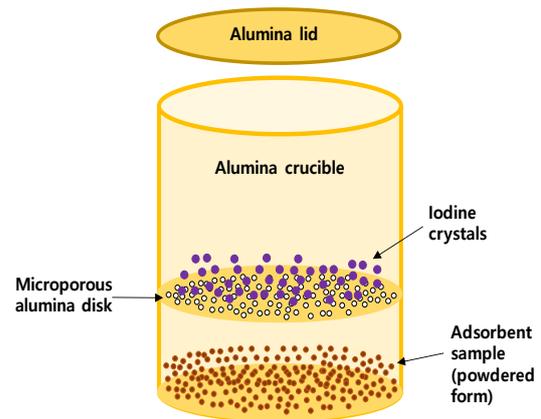
Fig. 1. Experimental setup for the closed iodine capture experiment.

3. Result and Discussion

Fig. 2 shows the results of XRD analyses. Fig. 2. (A) is the XRD pattern before adsorption experiment which has the same pattern with the published XRD pattern [4], identifying that the synthesized Bi-mna is the same with the Bi-mna in reference. XRD after the adsorption experiment at 425 K, presented in Fig. 2. (B), either analyzed to study the adsorption mechanism. The result is discussed later.
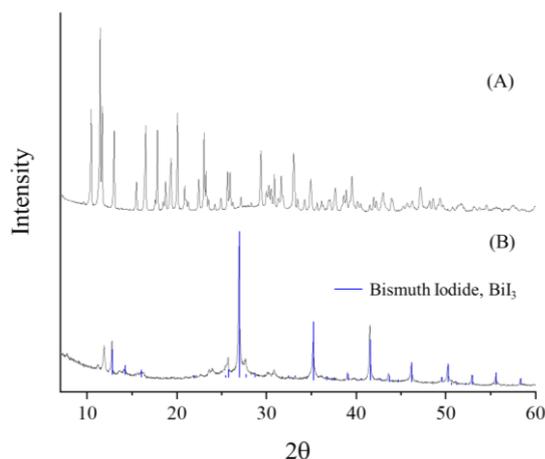
Fig. 2. XRD patterns of the synthesized Bi-mna (A) before absorption experiment and (B) after iodine absorption at 425 K.

Fig. 3 shows the results of the iodine adsorption tests for three adsorbents conducted at various temperatures.

Cu-BTC shows superior adsorption capacity among the three absorbents at 350 K. However, as temperature increases, the capacity dramatically decreases. As reported [2], Cu-BTC captures iodine by physisorption, and the captured iodine is released around 348 K. Furthermore, Cu-BTC lost about 63% of mass at 575 K from the control experiments since the framework decomposition occurs above 523 K. Therefore, Cu-BTC is not suitable to be used in situations that requires thermal stability at higher temperatures. The increase of adsorption capacity for Cu-BTC in 575 K than 500 K may come from small sample size.

The results of adsorption tests confirm the conclusion of Sava et al [1], showing that ZIF-8 maintains its adsorption capacity in high temperature region up to 575 K, since sodalite cages of ZIF-8 up to when the framework is expected to begin collapsing at 573 K.

In case of Bi-mna, it shows the lowest adsorption capacity among the tested adsorbents at 350 K. This may have resulted from low specific surface area and porosity However, as shown Fig.2.(B), the adsorption mechanism is chemisorption. According to the XRD result of Bi-MOF after adsorption experiment in 425 K, the crystal structure of Bi-mna becomes amorphous after iodine adsorption since Bi in Bi-mna forms chemical bond with atomic iodine producing BiI_3. Though the capacity decreases in high temperature region, it is expected that captured iodine remains stable considering the thermal stability of bismuth iodide. As an evidence, after the adsorption experiment, the used Bi-mna becomes black firm solid from a brown powder, as expected for a bismuth iodide (BiI_3).

For both ZIF-8 and Bi-mna, the adsorption capacity is optimized at 425 K, and the capacity gradually decreased as experimental temperature increased. Moreover, the capability is much higher than other adsorbents having weak thermal stability. In Reference [5], Ag-X and Bi-

SBA-15 showed calculated adsorption capacity of 300 and 150 mg-I/g-adsorbent at 523 K, respectively.

Both ZIF-8 and Cu-BTC do not produce chemical bond between metal and iodine. To build ZIF-8 structure, one Zn combines four linkers (2-methylimidazolate) by Zn-N bonding. In terms of electronegativity, Zn-N bonding provides stronger polar covalent bond than Zn-I boding. Therefore, the Zn-I bonding is not favorably formed. Similarly, Cu-BTC is not able to form Cu-I bonding since Cu in Cu-BTC and linkers (benzene-1,3,5-tricarboxylate) are connected by forming Cu-O bonding which is very stable (metal oxide).
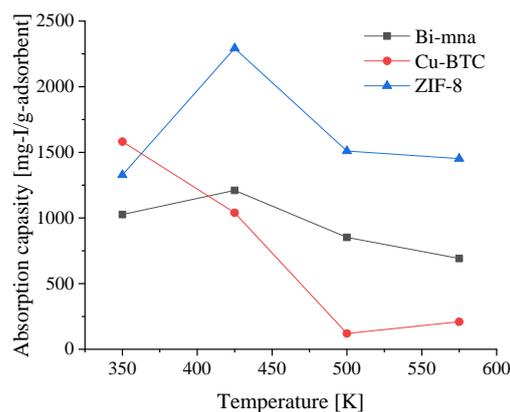
Fig. 3. Experimental results for iodine adsorption capacity of ZIF-8, Cu-BTC, and Bi-mna.

According to the results of this study, Bi-MOF is expected to have thermal stability after iodine capture by solid chemisorption (formation of Bi-I bond). This feature is essential in disposal stage in the nuclear industry. Based on the results of this study, the adsorption mechanism of Bi-mna will be investigated in detail through further analyses including thermogravimetric analysis of the used adsorbents and extra XRD analyses. Furthermore, adsorption experiments in higher temperature will be conducted to investigate whether Bi-mna can adsorb higher amount of iodine once ZIF-8 breaks down.

The fundamental goal of this research is to develop new Bi-MOF having better adsorption capacity for iodine even in low temperature via better accessibility to active site (porosity). Considering the defined requirements for linkers, new type of Bi-MOF will be developed by researching proper organics.

4. Conclusions

In this research, the feasibility of bismuth based metal organic frameworks to capture gaseous radioiodine is studied using Bi-mna. For comparison, ZIF-8 and Cu-BTC, which have been used in research of iodine capture, are also used. Bi-mna is synthesized and the results were analyzed through XRD analysis to identity the MOF. The adsorption experiments are conducted in various temperatures between 350 K to 575 K. The results show

that Bi-mna allows strong chemisorption of iodine which has thermal stability even in high temperature according to the result of XRD analysis. Based on this results, further research directions are suggested.

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