A study of I-TEDA solubility in a supercritical carbon dioxide using QCM

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1. Introduction

Nuclear power is an intrinsically clean energy source due to its high energy density and low generation of waste. However, as the nuclear industry has grown, the variety of radioactive wastes has gradually increased. The radioactive waste forms are solid, liquid or gas. The gas form of radioactive waste can be absorbed by a high efficiency particulate air (HEPA) filter or activated carbon. In particular, the radioactive organic iodide and methyl Iodine are absorbed by activated carbon; 5 wt% of TEDA (Trietylenediamine; 1,4-diazania-bicyclo[2.2.2]octane) impregnated on the activated carbon surface. In the atmosphere, the methyl Iodine (CH_3I) was combined chemically with TEDA; the final product of the chemical bond is I-TEDA. For recycling radioactive activated carbon, the I-TEDA must be removed from the activated carbon. Currently, a wet recycling method for impregnated active carbon is used to remove radioactive organic iodide in a nuclear power plant by extracting impregnated TEDA and radioactive organic iodide from the used impregnated active carbon with an acetonitrile solution. However, the wet recycling method produces a lot of secondary wastes. We need more environmentally-friendly processes for recycling. Carbon dioxide has been one alternative green solvent, because it is non-toxic, non-flammable, inexpensive and easy to handle [1]. Additionally, the tunable property of carbon dioxide through pressure and temperature control is very useful for its diverse uses in extracting many organic materials [2]. Before removing the I-TEDA from the activated carbon surface, however, the solubility was very low. Consequently, we needed a co-solvent to dissolve the I-TEDA in supercritical carbon dioxide. Based on the solubility test, methanol is the optimum solvent to remove the I-TEDA. In this experiment, we used QCM (Quartz Crystal Microbalance) for measuring the removal rate of the I-TEDA. When a change of mass occurs by either adsorption or desorption on the electrode surface of the quartz oscillator, the oscillation frequency changes. By measuring this change, information for adsorption or desorption of material on the electrode surface can be obtained directly [3-6].

In this study, we measured the removal rate of I-TEDA using QCM in supercritical carbon dioxide, and discuss its possible uses in removing the I-TEDA from radioactive activated carbon.

2. Methods and Results

2.1 Apparatus

The experimental apparatus includes a liquid syringe pump, and a QCM high-pressure vessel. The design pressure and temperature range up to 300 bar and 200 ℃ (Fig 1). The volume of the QCM high-pressure vessel is 33 ml, which is manufactured by HANWOUL ENGINEERING CO. The liquid pump inserted the co-solvent (acetonitrile or methanol) constantly. In the high-pressure vessel, two terminals were included so that there two separate QCMs. A bare QCM was installed in ch1, and a plated QCM in ch2 (Fig. 1). After a determined amount of I-TEDA deposition on the QCM surface, the experimental conditions (temperatures, pressures and solvent flow rates) were changed and then the removal efficiency was measured.
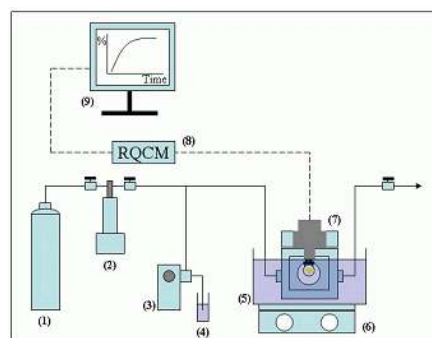

Fig. 1. QCM apparatus (1) CO_2 tank (2) Syringe pump (3) Liquid pump (4) Extraction solvent (5) Water bath (6) Stirrer (7) QCM high pressure vessel (8) RQCM (9) Monitor

2.2 Experimental conditions

The removal rates of I-TEDA were compared with acetonitrile and methanol as co-solvents. The experimental conditions were same (temperature: 60 ℃, pressure: 200 bar, CO_2 flow rate: 3~5 ml/min). As a result, methanol was the optimum co-solvent for removing the I-TEDA from the QCM surface. When using methanol, the acceleration period was around 6 minutes and then saturation period were over 17 minutes; the removal rate was over 95%. When the acetonirtile was used for the co-solvent, the saturation period was over 52 minutes. This is three times longer than when using methanol.

Following the experiment, we changed the pressures then compared with the I-TEDA removal rate. The experimental conditions were same as 60 ℃, 3~5 ml/min of CO_2. These results also had saturation period, especially, at 200 bar, the removal rate was faster than at 150 bar(Fig. 2). Following the temperature change, the highest removal rate was at 60 ℃(Fig. 3). This is because the higher temperature helped the I-TEDA dissolve into the co-solvent and supercritical carbon dioxide. Depending on the flow rate of the co-solvent, the greater the co-solvent flow rate the faster the removal rate was. However, at 3 ml/min and 2 ml/min they are similar to each other (Fig. 4). This means that over 2 ml/min of co-solvent flow rate is not the dominant factor of removal rate. From these results, we can determine the optimum experimental conditions; temperature- 60 ℃, pressure- 200bar, solvent flow rate- 2 ml/min.
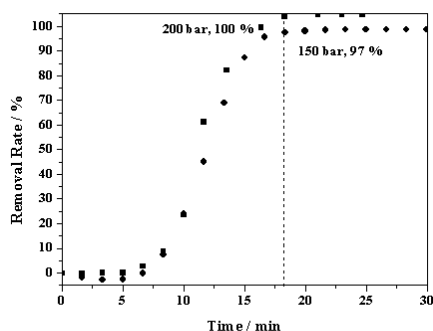

Fig. 2. Comparison of I-TEDA removal rate depends on the pressures (●=150bar, ■=200bar); 60 ℃, methanol flow rate = 2 ml/min, CO_2 flow rate – 3~5 ml/min, margin of error = ±5 %.
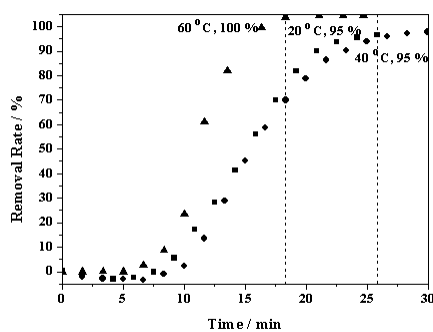

Fig. 3. Comparison of I-TEDA removal rate depends on the temperatures (▲=60℃, ■=40℃, ●=20℃); 200 bar, methanol flow rate = 2 ml/min, CO_2 flow rate = 3~5 ml/min, margin of error = ±5.
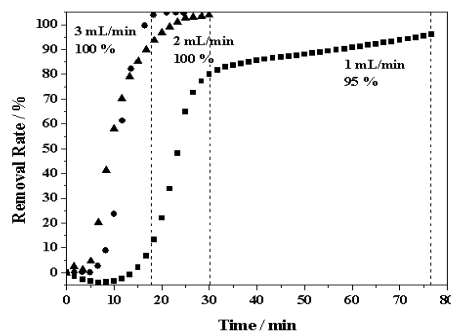

Fig. 4. Comparison of I-TEDA removal rate depends on the extraction solvents); 200 bar, 60℃, CO_2 flow rate = 3~5 ml/min, margin of error = ±5.

3. Conclusions

In this study, I-TEDA was removed from the QCM surface to determine the experimental conditions of radioactive activated carbon decontamination. The I-TEDA removal rate graphs have acceleration and saturation sections. This means that when applying it to a real specimen using methanol as a co-solvent, higher temperature, pressure, and enough time to dissolve the I-TEDA are needed.

Acknowledgements

References

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