THESIS / DISSERTATION ABSTRACT

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Title : Preparation and Characterization of Quercetin-Imprinted Polymers For Solid Phase Extraction **Number of Pages :** 59

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Subject Acea : Materials Science/Polymers

Degree Conferred : Master of Science in Chemistry

Statement of the Problem:

The study is designed to prepare imprinted polymers that will exhibit specific affinities for quercetin and its analogues when used for solid phase extraction applications. It is further designed to investigate other modes of low-temperature polymerizations for UV-active compounds like quercetin.

Procedure:

The polymers were prepared using quercetin as template, acrylamide as functional monomer, ethylene glycol dimethacrylate (EGDMA) as crosslinker and tetrahydrofuran (THF) as porogen/solvent. In the presence of the initiator azobisisobutyronitrile (AIBN), the polymeric mixtures were subjected to the following polymerization conditions:

1. UV polymerization at 366nm for 24 hours
2. Isothermal polymerization at 60°C for 24 hours
3. Temperature-programmed polymerization at 60°C for the first hour then linearly ramping the temperature to 30°C in the next 23 hours

Resultant block polymers were ground and sieved to 45 microns. Corresponding blank polymers were also prepared using the same protocol but in the absence of the template.

Characterization of polymer selectivity was carried out using solid phase extraction method by packing the worked-up polymers in empty SPE cartridges. Quantitative analyses were done using HPLC equipped with a gradient solvent elution system and UV detector. Detection was done at 370 nm. The progress of polymerization was also monitored using FTIR, averaging 30 scans at 4 cm^{-1} resolution.

Swellability test was done by soaking the polymers in excess methanol and the volume of the swelled polymers noted after eight hours.

Hydrolyzed guava leaves extract was prepared by soxhlet extraction of dried leaves with MeOH followed by refluxing with 25% HCl_{aq}. The extract was repeatedly dried under vacuum, redissolved in MeOH and passed through C-18 SPE cartridge to remove non-polar compounds. The final solution of 100 mL with MeOH was analyzed in HPLC with and without SPE extraction.

Findings:

Results show that the MIPs demonstrated higher selectivity for quercetin compared with the blank. Complete recovery of the applied analytes was also achieved. When used directly on hydrolyzed guava leaves extract, eluent from MIPs showed apparent reduction of quercetin peak, indicating its retention on the imprinted polymer.

The time evolution study on the temperature-programmed polymerization monitored by FTIR also demonstrated an important mechanism of imprinting. The phase and physical changes of the polymers through the 24-hour process indicated that actual imprinting happens at the latter stages of polymerization, at which time, the optimum crosslink density has already been achieved. This finding was further supported by the results of swellability tests, where the swelling of polymers prepared under temperature-programmed polymerization were higher than those prepared under isothermal temperature and in effect resulted to low selectivities of the former polymers.

Conclusions:

The following conclusions were drawn in the study:

1. It is not possible to polymerize quercetin-containing polymeric mixture under UV, accounted to the ability of quercetin to screen UV radiation coupled with its free-radical scavenging activities.
2. Imprinted polymers prepared under isothermal polymerization have more pronounced affinity for quercetin compared with non-imprinted polymers. SPE analyses showed that MIPs were able to absorbed quercetin 15% higher compared with blank under conditions that have not yet been optimized.
3. Polymerization of quercetin-containing mixtures is possible under temperature-programmed conditions as evidenced by the formation of the block polymers at the end of the polymerization runs. Effective imprinting, however, was not achieved as shown by the SPE results. The lowering of temperature is believed to have slowed down the crosslinking process resulting to ineffective trapping of the template.

4. Actual imprinting happens at the latter stages of polymerization, at which time crosslinked density has already been maximized.

Recommendations:

The study has the following recommendations:

1. Modify temperature-programmed polymerization in order to maintain the rate of crosslinking formation despite lowered polymerization temperature. The following modifications may be applied:
    a. Simultaneous irradiation with UV using the same temperature programming.
    b. Step-wise decrease of temperature through time.
    c. Heating of resultant block polymers to high temperature after temperature-programming polymerization.
    d. Increase concentration of initiator.
2. Test the selectivity of MIPs against closely related analogues of quercetin, like myricetin and kaempferol.
3. Further characterizations (TGA and DSC) of polymers stability and also to gather additional information to further explain the mechanisms of quercetin imprinting.