Synthesis And Characterization Of An Ion Imprinted Polymer For Cadmium Using Quinaldic Acid As Complexing Agent And Applying By Microwave

Asmawati, Abd.Wahid Wahab, Buchari, Paulina Taba

Abstract: A Cd2+ Ion Imprinted Polymer (Cd-IIP) has been synthesized by copolymerizaton of cadmium ion, quinaldic acid (complexing agent), 4-vynil pyridine (monomer), dimethyl sulfoxide (solvent), ethyleneglycoldimethacrylate, EGDMA (cross-linker) and 2,2-azobis-isobutyronitrile, AIBN (initiator). Polymerization was conducted using a microwave at a temperature of 70 oC with heating times of 45 minutes. The template (Cd2+) was removed by leaching the template with ethanol and 4 M HCl, washed by aquabidest and dried in an oven at the temperature of 60oC. The polymer particles (imprinted and nonimprinted) were characterized using fourir transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The result showed that using heating time 45 minutes at temperature 70 oC, the particle morphology is viewed like as the large homogeneous. So, the imprinted polymer had bands at 3483 cm-1 ,1726 cm-1, and 1155 cm-1 indicating the presence of OH, C=O and C-O, respectively.

Keywords: Cadmium, polymer, complexing agent, monomer, cross-linker, initiator, microwave

1 INTRODUCTION

An ion imprinting is a method to produce polymer by preparing a cavity in the form of a certain space obtained by removing a template when the polymer has been formed. The cavity will then recognize the target having identical or similar physical and chemical properties with the template used. The selectivity of ion imprinting polymer is based on geometry and coordination number, as well as charge and ion size [1,2,3,4]. Ion imprinted polymer can be synthesized by several approaches based ligand binding in the polymer matrix, among others through bifunctional crosslinking reagent with a straight chain polymer, chemical immobilization, the chemical surface and the trapping [4, 5 , 6]. There are several steps required in an ion imprinting technology . Firstly, a certain ion forms a complex with a ligand to form a template, and then the complex formed combines with a functional monomer. After the combination of the complex and the monomer, a polymerization process is performed. In this process, the choice of an initiator and a cross linker that will be used are required. Finally, the template is removed to form a cavity that is selective to the target ion [7].

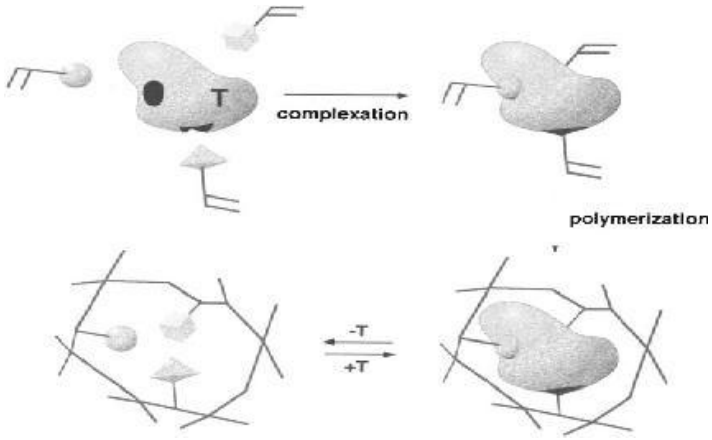

Figure 1. *Schematic showing the formation of IIPs*

Cadmium is a metal that is mainly used in an ion imprinting process by different polymerization methods. Generally, researches on metals use a trapping method [8, 9, 10]. The method is conducted by means of polymerization synthesis using a water bath at a temperature of 70 oC for 24 hours. The duration of time required by the method is quite long; therefore a method to shorten the polymerization process is required. One way to reduce the time is by using a micro wavelength called a microwave [11]. Recently, microwave heating has become a widely and it one method of synthesis used as heating. Method with microwave heating has a characteristic that is different from the usual heating (conventional). This is due to the heat generated internally, so as to target molecules and lasted continuously (simultaneously). While conventional heating, the heat generated by convection or conduction [12,13] In this research, ion imprinting was performed by using cadmium ion forming a complex with quinaldic acid with 4-vinyl pyridine as monomer and DMSO as a solvent. After the formation of a complexmonomer, an initiator of AIBN and a cross linker of EGDMA were added and polymerization was conducted using a microwave.

- *Asmawati: Departement of Chemistry, Faculty of Matematic and Natural Sciences, Tamalanrea Campus Km10, 90425, University Hasanuddin, Makassar-Indonesia Email: aas.chemuh@gmail.com*
- *Abd.Wahid Wahab and Paulina Taba: Departement of Chemistry, Faculty of Matematic and Natural Sciences, Tamalanrea Campus Km10, 90425, University Hasanuddin, Makassar-Indonesia Email: ptaba_1511@yahoo.co.id*
- *Buchari: Departemen of Chemistry, Faculty of Matematic and Natural Sciences Institute Technology Bandung, Ganesha 10,40132, Bandung-Indonesia*

METHODS

Materials Research

Materials used are Cd(NO3).4 H2O , quinaldic acid, dimethyl sulfoxide (DMSO), Ethylene glycol dimethacrylate (EGDMA purchased by Merck, and 4-vinyl pyridine purified through alumina column, 2,2'- Azobisisobutyronitrile (AIBN) purchased by Sigma- Aldrich, and other chemicals with high purity by Merck.

Instrumentation

MARS (Microwave Accelerated Reaction System) is subjected to rapid heating and elevated pressures, causing the sample to digest or dissolves in a short time and microwave energy at a frequency of 2450 MHz, approximately 1200 watts. FTIR (Shimadzu Prestige-21) used 300 scans over the range of 4500 – 340 cm-1 with a resolution of 4 cm-1 at room temperature, SEM-EDS (Tescan Vega3SB) for image and surface morphology, oven and sonicator

Synthesis of NIP and IIP

A cadmium source, Cd(NO3)2 .4H2O, as many as 1 mmol, 1 mmol of quinaldic acid and 4 mmol 4-vinil pyridine were weighed and then dissolved in 20 mL of DMSO. The solution was allowed for 1 hour to achieve equilibrium and 4 mL of AIBN as well as 20 mmol of EGDMA were added. The solution was then sonicated for 45 min and N2 gas was passed into the solution for 10 min. Polymerization was conducted by using a microwave oven at a temperature of 70oC for 45 minutes, The result of polymerization was dried at a temperature of 60 oC. The template was removed by using ethanol, 4 M HCl and aquabidest followed, filtering, washing, drying at a temperature of 60oC, and grinding. The same procedure was used to prepare Non–imprinted polymer (NIP) except for the addition of Cd(II) ion.

RESULTS AND DISCUSSION

Characterization by SEM

The preview of reseach, Cd(II) Imprint polimer was synthesized using materials mentioned above. For it has been obtained by using microwave heating takes 45 minutes at a temperature of 70 ° C [14]. Physical data of polymer like white colour (NIP), yellow colour (IIP unleached),and yellowish (Cd-IIP leached). The polimer particles, imprinted (leached and unleached) and non imprinted was characterized for identification of surface morphology (SEM-EDS). The surface morphology observed for NIP, IIP and Cd- IIP is not significantly different at magnification of 500 x the surface of Cd-IIP is evenly distributed with smother surface compared to IIP.

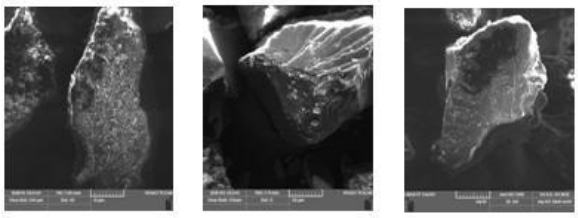

Figure 2. *SEM images 50 µm for NIP (left), IIP (middle) and Cd-IIP (right) at magnification of 500x*

Characterization by EDS

The result obtained from surface images can be identified by EDS showing the removal of the template of Cd ion from the polymer matrix.

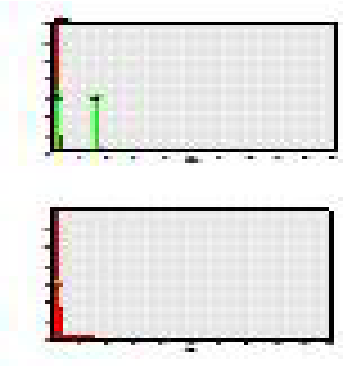

Figure 3. *EDS image of IIP and Cd-IIP*

Characterization by FTIR

Functional groups found in the polymer can be identified by FTIR. The FTIR spectra performed on NIP, IIP and Cd-IIP were recorded by using KBr pellet method except for vynil pyridine. NIP, IIP, and Cd-IIP spectra are similar because materials has similar component, such as the template, the monomer along with the cross linker.

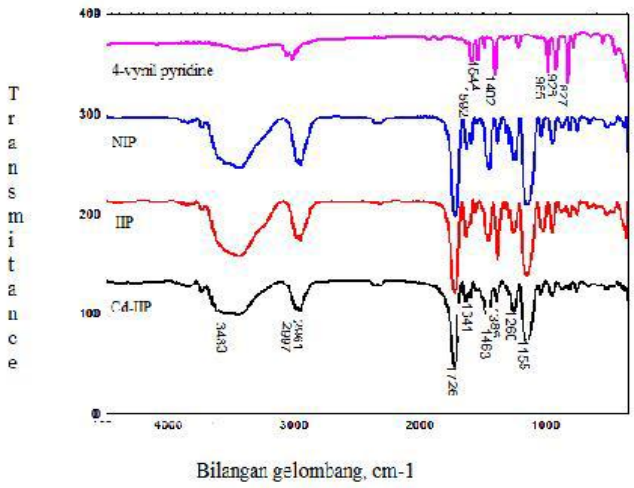

Figure 4. *FTIR spectra of 4-vynil pyridine, NIP, IIP and Cd-IIP*

The broad peak at 3483 cm-1 indicates the presence of O-H stretching vibration in materials, except for vinyl pyridine, which is given by the carboxylic group of quinaldic acid. Two typical regions for C-H stretching are observed at 2997 and 2861 cm-1. The presence of peaks at 1726 and 1155 cm-1 indicate the presence of C=O and C-O groups. A Peak at 1641-1770 cm-1 shows the presence of interaction between Cd2+ ion with quinaldic acid, observed at polymers before and after the removal of the template.

CONCLUSION

Cadmium ion imprinted polymer has been successfully synthesized by the formation of a complex with quinaldic acid combining with a monomer of vinyl pyridine and polymerizing with AIBN as an initiator and EGDMA as a cross linker. Polymerization process using microwave determined at 45

minutes and temperature70 oC. Characterization of Polymers with FTIR showed the presence of OH, C=O and C-O and the removal of the template after leaching IIP with ethanol, 4M HCl, and aquabidest. Meanwhile, SEM and EDS shows the surface morphology and ions imprinted that particle morphology the is viewed like as the large homogeneous plate and smooth for leached if compare to unleached particle.

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