

## Abstract of Dissertation

Name Lisa Nakajima

Host-guest molecule is well known as a selective separator for chemical mixtures. Especially, calixarenes and its analog are representative for organic host molecules to selectively separate heavy-metal ion guests or chemicals. As condensed from phenol and formyl chemical for the cyclic cavity, therefore, such host-guest behavior of calixarene has received much attention in analytical chemistry and is widely used in extraction, ion recognition and ion-selective electrodes. In the present work, hosting molecules of calix[4]resorcinarenes were synthesized from resorcinol and plant parts of formyl chemicals such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, which are sourced from maple tree, vanilla bean and gastrodia elata, respectively. It is noted that these aldehydes also obtained from lignin which is most abundant natural aromatic polymer as useful for selective concentration of ions and ethylene hormone. Therefore, lignin and their related chemicals drawing attention as a renewable resource. The present research has an effective utilization of lignin segments derived as aromatic aldehydes to synthesize calix[4]resorcinarene.

The calix[4]resorcinarenes prepared by condensation with resorcinol and plant derived aldehyde such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, respectively, were characterized by  $^1\text{H-NMR}$ , FT-IR and MS (mass spectroscopy) and used to apply for metal ions and ethylene gas ( $\text{C}_2\text{H}_4$ ) adsorbents. Firstly, the analytical ability of these calixarenes obtained from syringaldehyde (S-host), vanillin (V-host) and *p*-hydroxybenzaldehyde (PH-host) as the hosts for heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ) was investigated by fluorescence studies. The results showed that the fluorescence of the calixarenes was effectively quenched by adding  $\text{Pb}^{2+}$ , particularly for the S-host. So, it was suggested that the S-host could be the candidate of fluorescent chemo-probe for  $\text{Pb}^{2+}$  in new fluorescence diagnosis. Additionally, application was extended to fabricate composite porous membranes of poly(ethersulfone) and calix[4]resorcinarenes for membrane separator. The heavy metal adsorption experiments were conducted by using S-, V- and PH-hosts of the calix[4]resorcinarene to the composited membranes. Then, especially the S-host composited membrane showed high absorptivity and selectivity for  $\text{Pb}^{2+}$  binding. In addition, the selectivity of  $\text{Cs}^+$  from a mixture of alkali metal ions ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ) was observed by batch binding experiments. This confirmed that the S-host was worked well even in the  $\text{Cs}^+$  adsorption in the co-presence of  $\text{Na}^+$  and  $\text{K}^+$ .

Furthermore,  $\text{C}_2\text{H}_4$  gas absorptivity of calix[4]resorcinarene was evaluated. Higher  $\text{C}_2\text{H}_4$  capacity was observed in the S- and V-hosts rather than zeolite and activated carbon having a high surface area. The comparison was made that the calix[4]resorcinarene could be used generally  $\text{C}_2\text{H}_4$  adsorbent. Chemical shift before and after  $\text{C}_2\text{H}_4$  adsorption was confirmed by NMR analysis as revealed to the chemical interaction between the calix[4]resorcinarene and  $\text{C}_2\text{H}_4$ , particularly in the S-host.

In conclusion, presence study could successfully synthesize calix[4]resorcinarene from resorcinol and plant derived aldehyde and apply for functional adsorbents to Pb(II) and Cs (I) in addition of ethylene molecule. The evidence suggested that the methoxy groups in calix[4]resorcinarenes gave effective interaction to the guest ions and molecule.