Calix[4]resorcinarene hosts having functional adsorptivities in preparation and their applications

(機能性吸着能を持つカリックス[4]レゾルシナレンホストの作製およびその応用)

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Abbreviation List

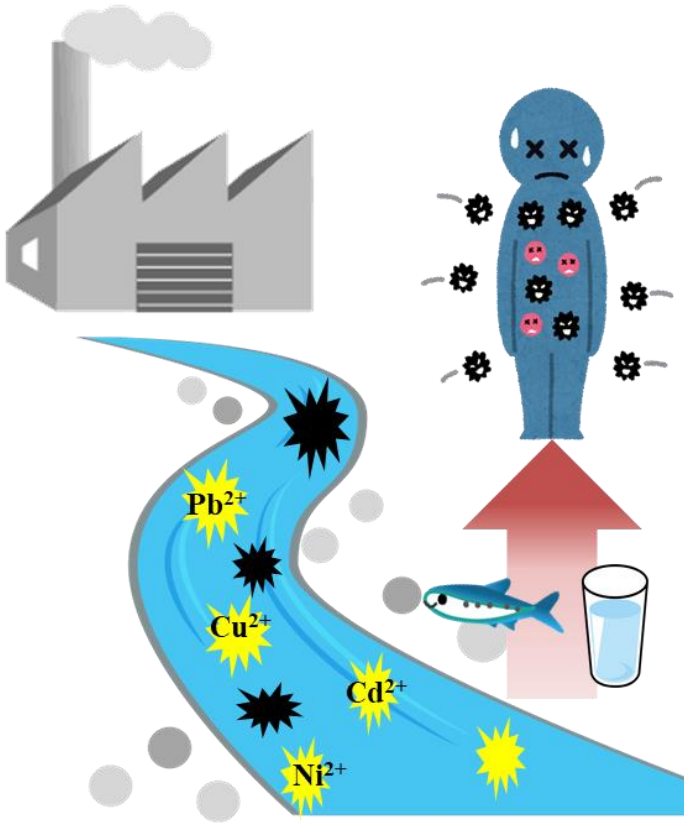
AC	Activated carbon
d_6-DMSO	Deuterated dimethyl sulfoxide
S-host	Syringaldehyde calixarene
V-host	Vanillin calixarene
PH-host	*p*-Hydroxybenzaldehyde calixarene
FT-IR	Fourier transform infra-red
NMP	*N*-methyle-2-pyrrolidone
PES	Poly(ethersulfone)
SEM	Scanning electron microscopy
NMR	Nuclear magnetic resonance
TOF-Mass	Time of Flight Mass Spectrometry
THF	Tetrahydrofuran
DMF	*N*,*N*-dimethylformamide
UV-vis	Ultraviolet-visible spectroscopy

Chapter 1

General Introduction

1.1 Water conservation with green chemical uses

Water covering over 70 % on the earth's surface and such water storage is very important resource for people life. Therefore, people pay high attention to the purification of water and its recycle. However, it is known that water pollution becomes a problem anywhere, when waste water is discharged into the earth environment in the bodies. Due to an insufficient waste water treatment in industries, the human's life faces with extremely important crisis. As accompanied by industrial growth and importance of the vital energy, the industrial discharge of heavy metal and organic solvent can pollute rivers and lakes. Among their pollutants, sometime heavy metal ions enter into the human body through feeding food, air and drinking water and also bioaccumulate ion has been seen over a period of time [1, 2]. Therefore, through the growth of the human economy, the polluted water extends in water sources of rivers, lakes and oceans by extending such industrial wastewater. As a result, the effects harm human health [3]. So, attention of wastewater treatment and their conservation technologies has been developed in several fields. In particular, heavy metal ions such as lead (Pb), nickel (Ni), cadmium (Cd) and copper (Cu) are known to accumulate in the human body and are toxic. As shown in Figure 1.1, contamination of heavy metal ions, Pb^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} into our water sources on the earth becomes serious in the



Heavy metal	Max. acceptable conc. of drinking water [5]	Adverse health effects [4]
Lead	0.01 mg/l	Vomiting, abdominal pain, diarrhea, hypotensive depression, oliguria etc.
Nikkel	0.07 mg/l	Skin diseases
Cadmium	0.003 mg/l	Abnormal fatigue, dull smell, anemia, osteomalacia
Cupper	2 mg/l	Gastrointestinal problems

Present technology

- Chemical precipitation
- Membrane adsorption
- Ion exchange
- Adsorption on activated carbon

Figure 1.1 Industrial works sometime forces problems of contaminated water.

person's body in harmful sources. For example, Pb causes vomiting, abdominal pain, diarrhea, hypotensive depression, oliguria and coma. Also, chronic intoxication, anemia, disorders of the gastrointestinal tract, disorders of the nervous system are occurring. It is known that skin diseases by contacting with Ni are caused. In the case of Cd, the contamination to people is not able to spend much exposure on the negative body waste. The exposure causes chronic intoxication, such as abnormal fatigue, slowing of smell, anemia and osteomalacia etc. Another case can find that, although Cu is less toxic to mammals, gastrointestinal disturbances are affected depending on intake amounts to the body [4]. According to the World Health Organization (WHO), the limiting values of the concentration of metal in drinking water for Pb^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} are 0.01 mg/L, 0.07 mg/L, 0.003 mg/L and 2 mg/L, respectively [5]. Therefore, because of the heavy metal pollution, purification process of such toxic ion is recognized importantly in the water treatment one [6-8]. Generally, such chemical precipitation method [9, 10], membrane adsorption method [11, 12], ion exchange method [13], etc. are used for such industrial waste treatment. In addition, it includes expensive separation technology in the physical adsorption method [14] of commercially available activated carbon (AC). It exhibits high adsorptivity, but it also has the problem of lacking selectivity in removing necessary ions. Thus, it is better to find low-cost technologies to be used for solving such problem by adsorption with selectivity. Until now some adsorbents are obtainable with low cost, e.g. natural adsorbents such as peanut pellets [15, 16], leaf powder [17], plant original lignin [18, 19] and ACs prepared from agricultural wastes. Such peanut hull [20], tea dust leaves [21], parthenium plant [22] or coconut tree sawdust [23] is known additionally so on.

Especially, in these matters lignin is the second most abundant natural (Figure 1.2). Thus, the green chemicals are in the most abundant natural aromatic polymer on earth. As a result, this is a class of complex organic polymers which are formed importantly as structural materials in vascular plants and some algae [24]. Because the average wood consists of 40-50 % of cellulose, 25-35 % of lignin and 20-25 % of hemi cellulose, through the paper manufacturing and bio ethanol production, lignin is produced as byproduct and has always been treated as waste and only used in organic source to power plants. However, if the resources are successfully converted to renewable resources or are valued for more valuable materials, their abundance has great potential to solve the problem of rapidly depleting

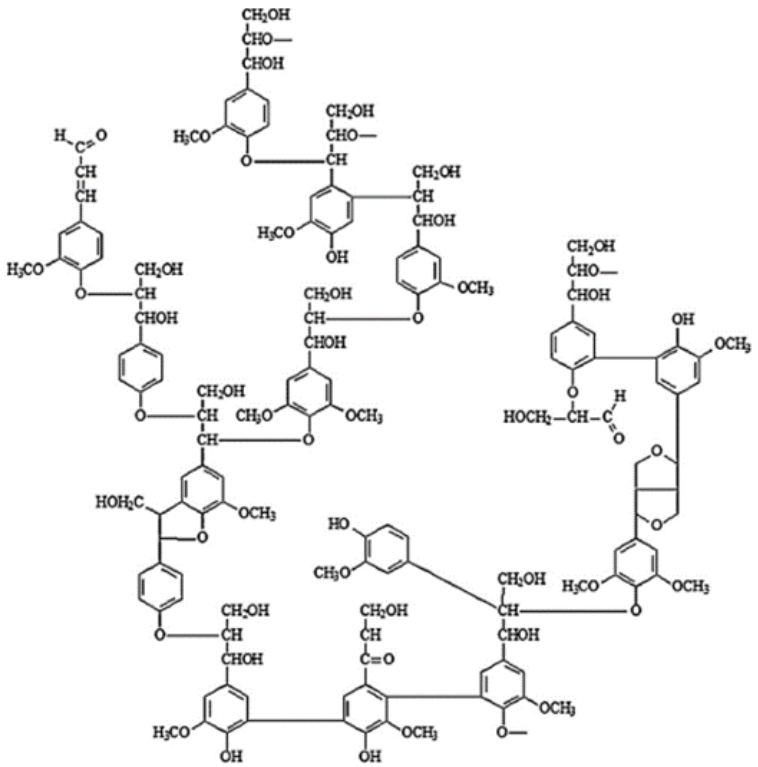


Figure 1.2 A part of chemical structure of lignin.

resources. Furthermore, as a production of lignin amounts to be more than 50 million tons/year, there has been increasing recycle interest in the development of economically viable new applications [25].

1.2 Effective utilization of biomass lignin as separation materials

In 1982, Wedekind and Garee, who studied the uptake of hydrochloric and sulfurous acids in around biomass, published first report about sorption by lignin [26]. Actually, phytoremediation is environmentally and friendly on decontamination technology in purification to land and surface water from contamination with metal ions. Plant remediation has however been performed, when phytoremediation is used with directly living green plants including such lignin. As shown in Table 1.1, many researchers reported the absorptivity of lignin for heavy metal ions [25]. It was revealed that the surface of lignin contains two main types of acid sites due to carboxyl and phenolic groups. The phenol moiety has a higher affinity for the metal ion than the carboxyl moiety. In addition, the representative results show that lignin can be good adsorbent over a wide concentration range. On the other hands, isolated lignin is also studied for their effective utilization. From 1930 to 1940, it was discovered that, when lignin was heated with nitrobenzene and NaOH under high pressure, aromatic aldehyde such as vanillin, syringaldehyde and *p*-hydroxybenzaldehyde were produced. [26-28]. Before this was investigated, there were no reports on the chemical structure of lignin. Therefore, as a result, it is recognized now that the chemical structural units of lignin are consisted of glacial type, siringil type and *p*-hydroxyphenyl type having aldehyde group. As shown in Figure 1.3, the topic mentioned

Table 1.1 Reported sorption capacities (mg/g) for lignin adsorbent [25].

Reference	Pb(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Cr(III)	Cr(VI)	
Merdy et al. (2002)		4.2						[30]
Acemioglu et al. (2003)		~1.7						[31]
Sciban and Klasnja (2004)		~3.4						[32]
Sciban and Klasnja (2004)		1.7						[32]
Sciban and Klasnja (2004)		26.4						[32]
Dizhbite et al. (1999)		26.4				11.5		[33]
Dizhbite et al. (1999)		~1.7				~0.8		[33]
Mohan et al. (2006)		137		87				[34]
Demirbas (2004)	8.2			6.7				[35]
Demirbas (2004)	9.0			7.5				[35]
Basso et al. (2004)				48.3				[36]
Lalvani et al. (2000)						6.6	5.6	[37]
Bailey et al. (1999)					150			[38]
Srivastava et al. (1994)	1865		95					[39]

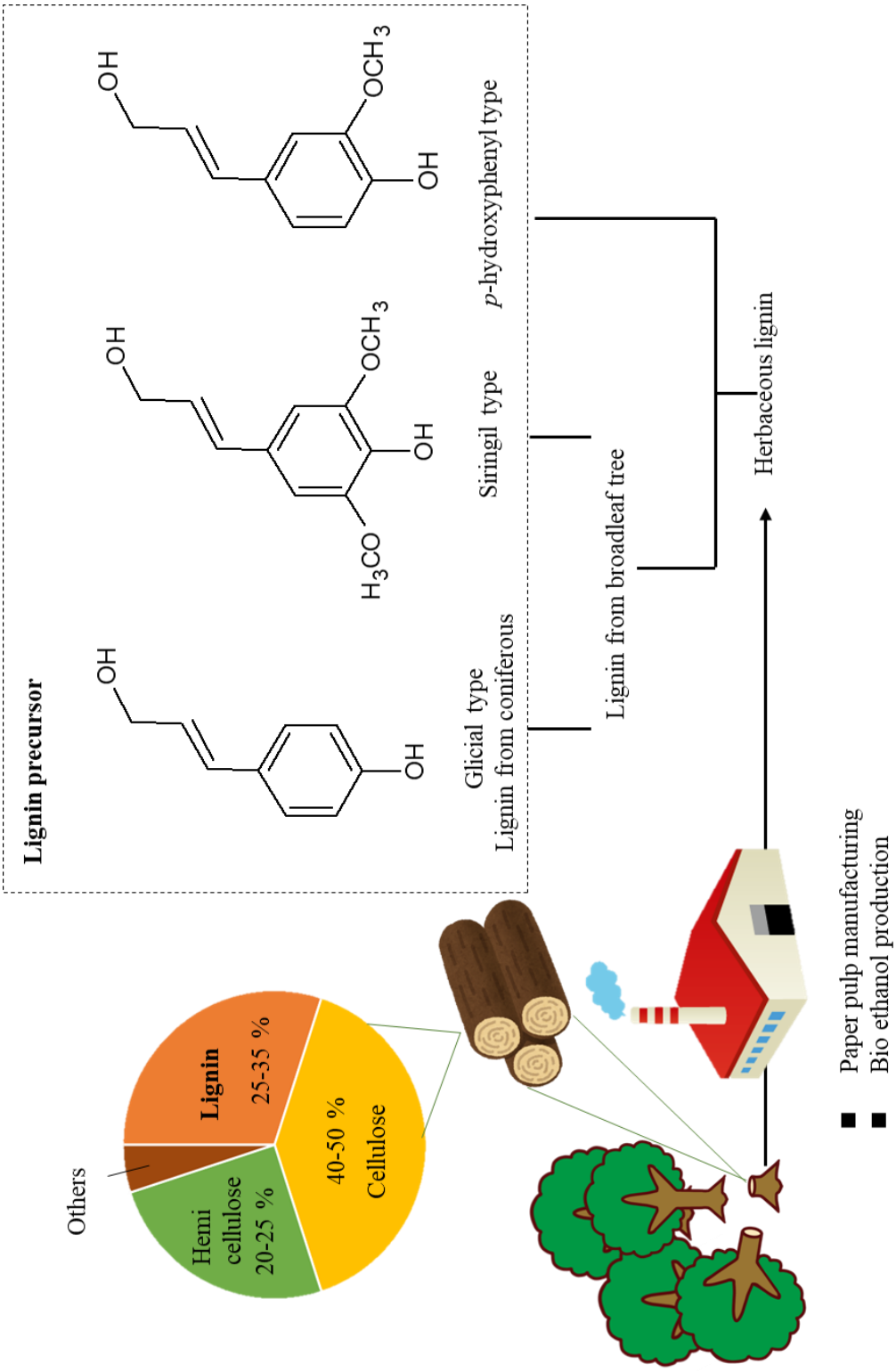


Figure 1.3 Aromatic units of lignin from coniferous, broadleaf tree and

before meant that wood contains cellulose, hemi cellulose and lignin, the lignin components and these are in broad leaf types to glacial and syringil types and another *p*-hydroxyphenyl type. Even though the skeletal structures in the classified three types are looked similarly, there are slight differences in their properties. The coniferous lignin is of the guaiacyl type and the hardwood lignin consists of syringyl type and *p*-hydroxyphenyl type. So, the chemical structure of lignin is different depending on the plant source such as coniferous tree, broadleaf tree, and herbaceous plant.

Until now, in industrial uses, these isolated lignins have been studying for two ways. Firstly, for example, phenol formaldehyde (PF) resin widely used as an adhesive for wooden materials conducted development of replacement binder [40]. Moreover, application to epoxy resin by epoxy crosslinking of isolated lignin has also been carried out in industrialization, since the 1960's year [41, 42]. Secondly, isolated lignin has as low molecules as seen in Figure 1.4, for chemical utilization like syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde), vanillin (4-hydroxy-3-methoxybenzaldehyde) and *p*-hydroxybenzaldehyde, which can be obtained as lignin-derived aldehyde. Syringaldehyde possesses worthy bioactive properties, therefore, used in pharmaceuticals, food, cosmetics,

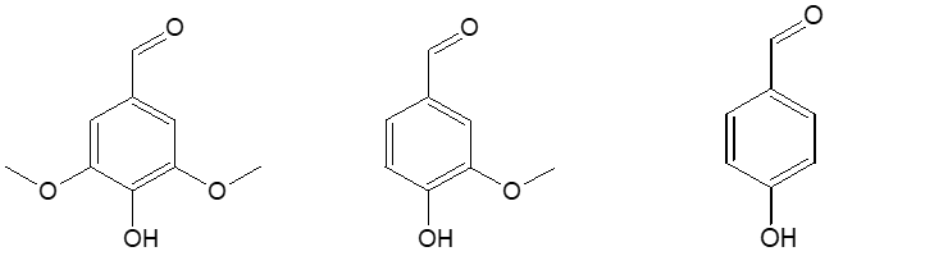


Figure 1.4 Chemical structure of syringaldehyde, vanillin and *p*-hydroxybenzaldehyde.

textiles, pulp and paper industries and even in furthermore biological control applications [43]. On the other hands, vanillin is known as one of the major compounds that contribute to the distinct flavor and aroma of vanilla. This vanillin is a unique and highly prized flavor compound used as an ingredient in food flavors in pharmaceuticals and fragrance in perfumes and odor-masking products [44, 45]. Additionally, *p*-hydroxybenzaldehyde is one of vanillin precursors. In general, it is difficult to obtain a pure low-molecular compound from lignin having a very complicated chemical structure, but vanillin is a compound that can be obtained comparatively and easily from lignin as important food chemical. For effective utilization of vanillin desired from isolated lignin, in 2009, the production process was appeared from lignin with about 15% yield in the industrial synthesis [46]. It also served as an assessment of the potential research and commercialization of naturally occurring syringaldehyde beyond the scope of the food and cosmetic industry. However, it is known that such natural adsorbents are insufficient to treat low levels of heavy metal ions in wastewater. This may be due to the complicated chemical structure of the plant, including cellulose, hemi cellulose, minerals and lignin. However, the characteristic of such lignin components becomes a great hint and idea to develop of new adsorbents having high selectivity, especially to use vanillin, syringaldehyde and *p*-hydroxybenzaldehyde. Because lignin segments have a potential ability for metal adsorption by using their phenolic site on the surface. Exploring and developing functional adsorbents from the isolated lignin chemicals through synthesis step are significantly required for the natural sourced lignin in the utilization of lignin. On the basis of this point, this approaching and studying have

started in my doctoral research to reach to highly selective adsorbents departure from such herbaceous lignin sources by applying host-guest process.

1.3 Host-guest molecules to candidate for highly selective adsorbents

Host-guest processes have been widely investigated because of their numerous applications such as selective separators for chemicals [47]. Host-guest chemistry describes complexes that are composed of two or more molecules or ions that are held together in host cavity by using unique structural relationships concerned with insertion driving forces. There are four commonly mentioned driving forces in types of non-covalent interactions such as hydrogen bonds, ionic bonds, van der Waals forces, and hydrophobic interactions [48]. As shown in Table 1.2, numerous organic and inorganic host molecules were designed from 1800's, e.g. cyclodextrin (by Villiers, A., in 1891) [49, 50], cucurbituril (by Behrend,

Table 1.2 Lists of research examples for host-guest molecules.

Host molecules	Reference	
Cyclodextrin	Villiers, A. "Fermentation of starch by the butyric ferment." *Compt Rend* 112 (1891): 536-8.	[50]
Cucurbiturils	Behrend, R. et al. "Ueber Condensationsproducte aus Glycoluril und Formaldehyd, " *Ann. Chem.* 339 (1905): 1-37.	[51]
Crown ether	Charles, J. P. "Cyclic polyethers and their complexes with metal salts."*J. Am. Chem. Soc. 89*.26 (1967): 7017-7036.	[52]
Calixarene	Gutsche, C. D. and Muthukrishnan, R., "Calixarenes. 1. Analysis of the product mixtures produced by the base-catalyzed condensation of formaldehyde with para-substituted phenols." *Org. Chem.* 43 (1978): 4905-4906.	[54]
Zeolite	Barrer, R. M. "Synthesis of a zeolitic mineral with chabazite-like sorptive properties. " *J. Chem. Soc.* 0 (1948): 127-132.	[56]

R., in 1905) [51], crown ether (by Charles, J., 1960's) [52, 53], calixarene (by Gutsche, C. D., in 1978) [54, 55] and zeolite (ZK-5) (by Barrer, R. M., in 1948) [56-58]. These host molecules are effectively applied functional materials used for selective adsorbents. For example, it is well known that cyclodextrin is the representative example of organic host molecule used in food areas as stabilizers of perfumes. Also, there are applications in pharmaceuticals as stabilizers and water-soluble agents for prostaglandins. The ringed molecule of diaza crown ether and their derivatives show very good calcium and magnesium selectivity and are widely used in ion selective electrodes [59]. In the case of cucurbituril, there was disadvantage that it is difficulty was to dissolve in solvents and to be the lack of processability. However, recently, papers showing the possibility of cucurbituril as a drug delivery [60], sorbent for the removal of reactive dyes [61] and fluorescence sensor [62] are reported. On the other hands, synthetic zeolite is inorganic polymer having molecular sieve site and both ion exchange site and hosting one are included. At common issue for such host molecule, when the comparison is made, it is seen that annular structure plays host-guest function with high selectivity to targeted ion or molecule.

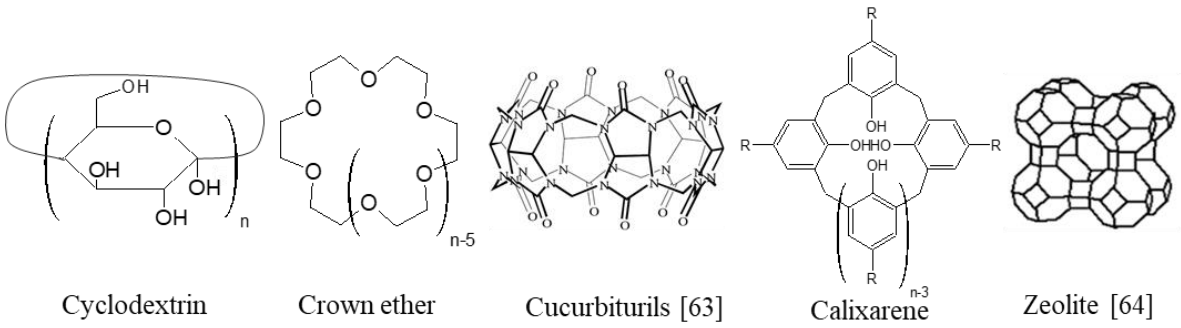


Figure 1.5 Chemical structure of representative examples of host molecules.

1.3.1 Calixarene and their resorcinarene derivatives

As host having annular structure, it was reported that calixarenes found high inclusion behavior of the macrocyclic crown ethers and cyclodextrins [65, 66]. Generally, calixarenes are simply condensed with phenol and aldehyde to a cyclic structure having phenolic hydroxyl group according to the condensation. As noted in the chemical structure, calixarene is classified depending on the number of aryl groups on their annular framework with n numbers like calix[n]arenes. There are two kinds of phenol and resorcinol derived macrocycles, calixarene and resorcinarene, respectively (Figure 1.6). Here, the n stands for the numbers of aryl groups in the macrocycle as typically ranged with n=3–20 [66]. Since the phenol or resorcinol has OH group, it is known that these groups coordinate to the metal ions tightly and the aromatically cycled rings incorporate the guest ion [67, 68]. Figure 1.7 is an illustration for the incorporation to ion. These manners provide high selectivity for hosting guest molecule or ion. Thus, calixarene and resorcinarene have received much attention in analytical chemistry and is widely used in extraction [69], in recognition [70] and ion-selective electrodes [71].

In the conformational isomers made of phenol and methylene units, it was reported that calixarenes were on two possible rotational modes of the phenol units as shown in Figure 1.8 [72]. In the mode, one is *p*-substinent-through-the-annulus rotation and another is oxygen-through-the-annulus one. The conformational isomers thus yielded and afforded a great number of unique hosting natures in the different size and the different shape of the macrocycles.

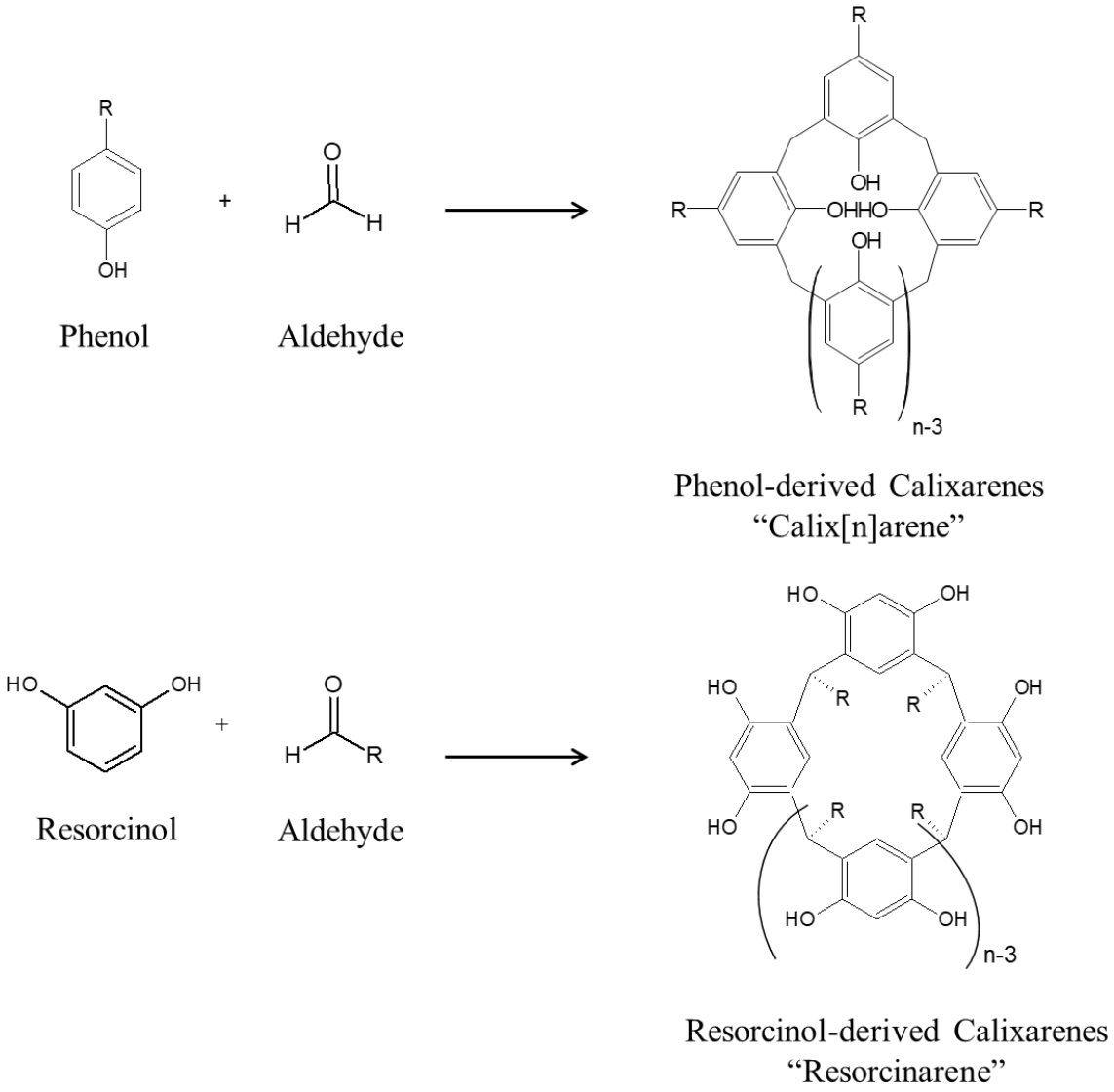


Figure 1.6 Phenol-derived and resorcinol-derived calixarenes.

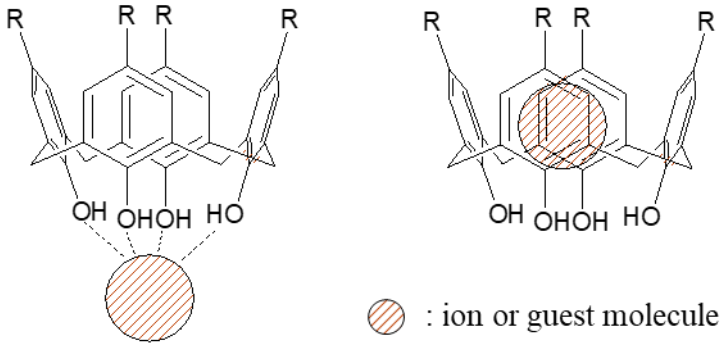


Figure 1.7 Inclusion of metal ion and molecular guest by calixarene.

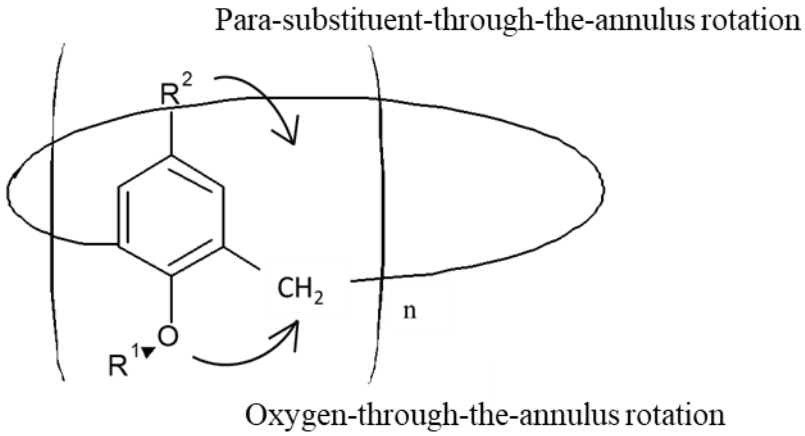


Figure 1.8 Two different modes for inversion of the phenyl unit [72].

Figure 1.9 shows stable conformation of calix[4]arene in four isomers of "cone", "partial cone", "1,2- alternate" and "1,3-althernate". While the smallest homologue, calix[4]arene is also typically represented as a flexible truncated cone or cup, the conformational variability of calixarene is much larger than that of cyclodextrins.

On the other hand, another kind of macrocycle can be easily seen in calix[4]resorcinarenes that resorcinol and various aldehydes obtained similarly the

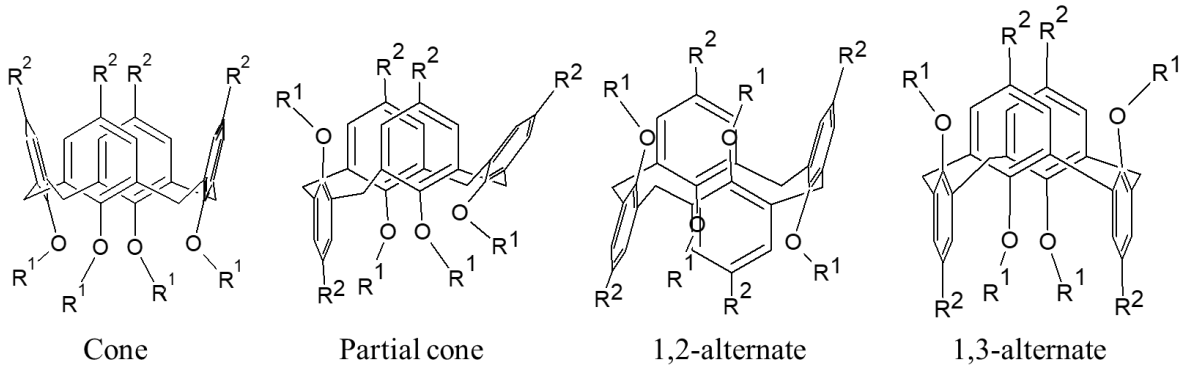


Figure 1.9 Four stable conformations of calixarene.

condensation reaction. On heating these reactants, to reflux in a mixture of ethanol in the presence of concentrated acid enhanced the reaction according to the reaction scheme in Figure 1.10. Although it is easily considered that each resorcinarene unit can rotate according to the oxygen-through-the annulus rotation mechanism actually, it is favorably adopted ion to the cone conformation as reported [72-75]. This is because of the stabilization by intramolecular hydrogen-bonding interactions among OH groups. In pioneering research, Aoyama et al reveled that the calix[4]resorcinarene has the possibility of interaction with other molecules such as organic cations, anions and molecules as host-guest complex [76]. Izatt reported that resorcinarene is available for cation transport of Li, Na and others [77, 78]. In Table 1.3, the host-guest behavior of calix[4]resorcinarene is summarized for resorcinarenes in metal ion extraction agents for heavy metal ions. For example, in the previous research by Nadiah et. al., two kinds of calix[4]resorcinarene, 2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol (N-host) [67] and 5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol (DA-host) [67] (Figures 1.11) were successfully synthesized

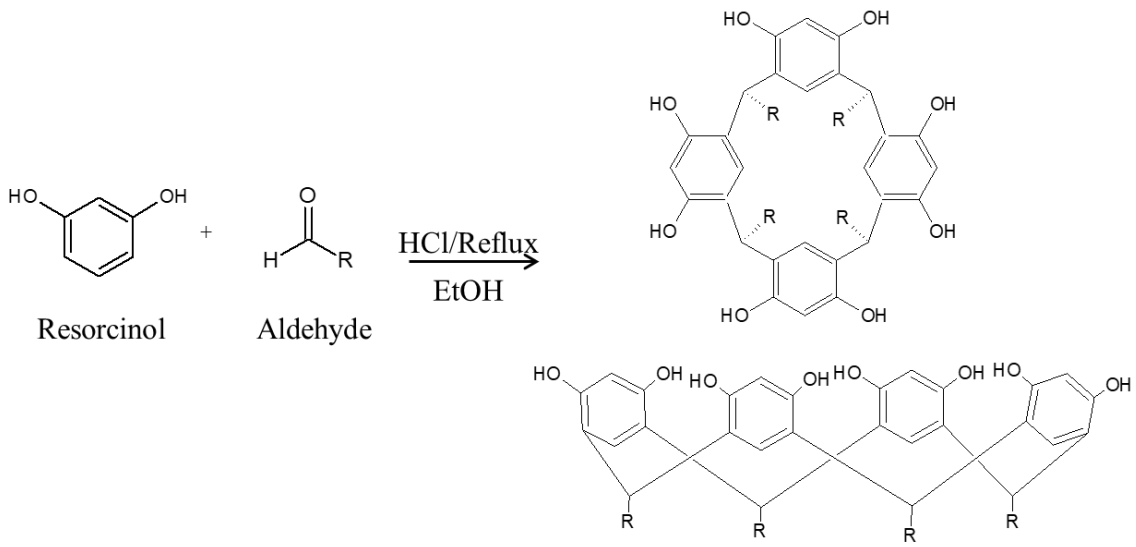
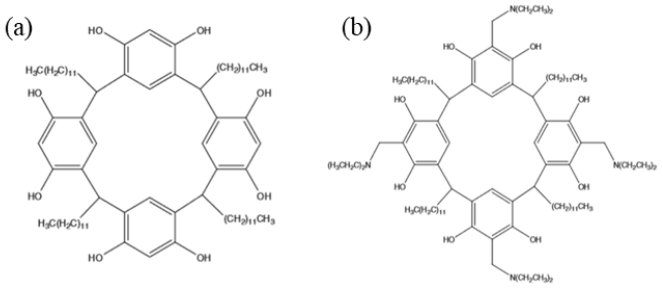


Figure 1.10 Synthesis scheme of calix[4]resorcinarene by condensation with resorcinol and aldehyde in the presence of acid in ethanol.

Table 1.3 Reported adsorption capacities (μmol/g) of calix[4]resorcinarene for heavy metal ions.

Reference	Pb(II)	Ni(II)	Cd(II)	Cu(II)	
Sardjono, R. E., et al. (2008)	5.44				[79]
Sardjono, R. E., et al. (2009)	1.99				[80]
Utomo, S. B., et al. (2012)	450		190		[81]
Al-Trawneh, S. A., et al. (2015)	0.541			1.34	[82]
MARDJAN, M. I. D., et al. (2016)	3.91		9.10		[83]
Anwar, C., et al. (2017)	2.15				[84]
N. N. M. Yusof., et al. (2014) (N-host)	575	115		379	[67]
N. N. M. Yusof., et al. (2014) (DA-host)	610	448		363	[67]

and prepared as novel calix[4]resorcinarene having imprinting polymer characters for heavy metal ion in mixture solution. However, from the viewpoint of the powdery shape, there is limited utilization for adsorbents of heavy metal ions in water medium. Therefore, little is known in the details of calix[4]resorcinarene in the fabricated adsorbents (Table 1.4), which are suitable for functional heavy metal adsorbents. Also, there are quietly less examples applied for water environment in nature. As seen, until now, some heavy metal adsorbents were only developed to calix[4]resorcinarene in modified resin [85], polymer



Figures 1.11 Previously synthesized calix[4]resorcinarenes (a)N-host (2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol) and (b) DA-host (5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol) [67].

Table 1.4 List of reports of calix[4]resorcinarene as heavy metal adsorbent.

Reference		Target	
Calix [4] resorcinarene modified resin	Ghaedi, M., et al. (2009)	Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+}	[85]
Polymer inclusion membranes (PIMs) containing calix[4]resorcinarene	Benosmane, N., et al. (2009)	Zn^{2+}, Cd^{2+}, Pb^{2+}	[86]
	Ugur, A., et al. (2014)	Zn^{2+}, Cd^{2+}	[87]
	Sgarlata, C., et al. (2008)	Cd^{2+}, Pb^{2+}, Hg^{2+}	[88]
Liquid membrane of calix[4]resorcinarene	Fedorenko, S. V., et al. (2001)	Cu^{2+}, Co^{3+} complexes	[89]
	Alpaydin, S., et al. (2011)	Cr^{5+}	[90]

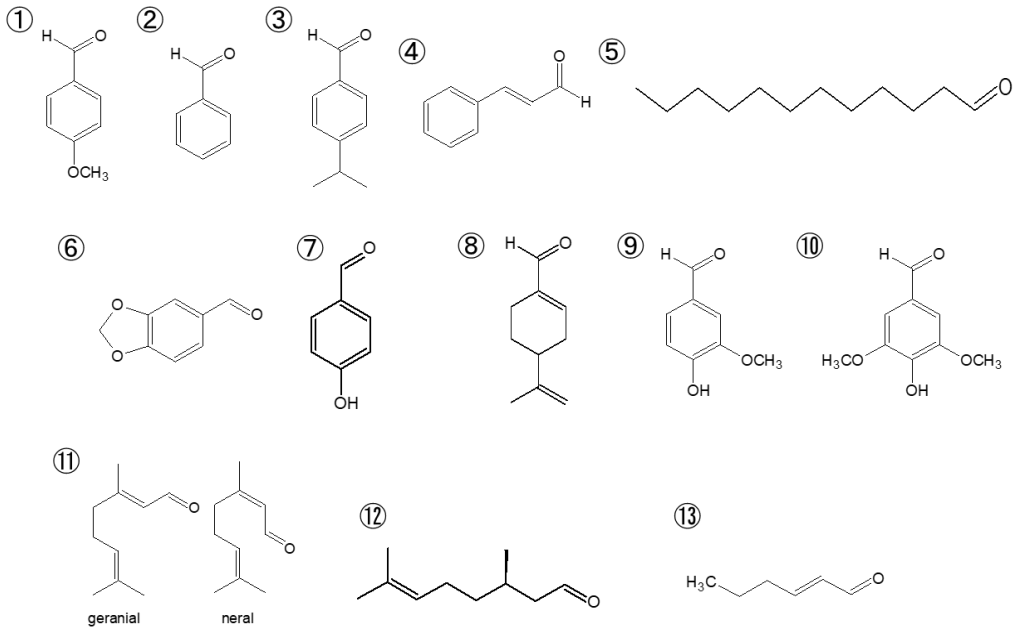
inclusion membrane (PIMs) containing calix[4]resorcinarene [86-88] and liquid membrane [89, 90] of calix[4]resorcinarene. Therefore, challenges remain studying host-guest separators of calix[4]resorcinarene for targeting to metal ions.

1.3.2 Plant-based chemicals for hosting molecules

More recently, since earth has damaged by consumption of carbon source for production and energy, carbon neutral concept is proposed. In sustainable development points, Sustainable Development Goals and targets (SDGs) concept was proposed by United Nations Educational, Scientific and Cultural Organization (UNESCO) in 2015 [91]. Therefore, plant-based chemistry is interesting in the innovative sector for energy saving and environmental conservation. From viewpoints of SDGs, this is one of the pillars of green based society to an alternative based on natural resources. When we consider about synthesis calix[4]resorcinarene from resorcinol and aliphatic or aromatic aldehyde, the plant-based aldehydes are selected from herbaceous aldehydes. As seen, there are interesting chemicals and their chemical structures for the plant based chemicals (Table 1.5). As mentioned before, such chemical is derived from lignin for aldehyde monomers, for example, in syringaldehyde, vanillin and *p*-hydroxybenzaldehyde. Typically, they also can be obtained from plant such as maple tree, vanilla seed and gastrodia for syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, respectively [44, 45, 92, 93]. In syringaldehyde, vanillin and *p*-hydroxybenzaldehyde each plant-based aldehyde has a one hydroxy group and different number of methoxy groups in their chemical structure (Figure 1.4). If it is expected that such chemical framework can be introduced to calix[4]resorcinarene ring, the condensation products may develop similar function with

Table 1.5 Plant derived aldehyde and their chemical structures.

	Aldehyde	Source	
1	Anis aldehyde	Anise	[94]
2	Benzaldehyde	Ischnoderma	[95]
3	Cumin aldehyde	Eucalyptus, cumin	[96, 97]
4	Cinnamaldehyde	Cinnamomum	[98]
5	Dodecanal	Coriander, cucumber, carrot, orange, tomato	[99-102]
6	Heliotropine	Meadowsweety, vanilla bean	[103]
7	*p*-hydroxybenzaldehyde	Gastrodia elata	[93]
8	Perillaldehyde	Shiso	[104]
9	Vanillin	Vanilla bean	[44, 45]
10	Syringaldehyde	Maple tree	[92]
11	Citral	Lemon, orange	[105, 106]
12	Citronellal	Lemon balm	[107]
13	Trans-2-hexanal	Cucumber, tomato, strawberry, banana, tea leaf	[108]



lignin for ion concentrators. Therefore, in the present study, approaching to use syringaldehyde, vanillin and *p*-hydroxybenzaldehyde is adopted of synthesis of new calix[4]resorcinarene for aldehydes extracted from the plant. Then adsorptivities of calix[4]resorcinarene are examined on behalf of the plant-derived aldehyde as low materials.

1.4 Outline of the thesis

The scope of the present thesis includes calix[4]resorcinarenes in the basis of the idea of plant-based chemistry for newly developed host molecules. Three kinds of calix[4]resorcinarenes are prepared from resorcinol and such plant-based lignin derivative of aromatic aldehydes, syringaldehyde, vanillin and *p*-hydroxybenzaldehyde in the condensation synthesis. The innovative points of the approach of the calix[4]resorcinarenes used in new functional materials are concerned with metal ion hosting (a) applied with adsorbents, (b) sensitive analysis technique and (c) separation process. In (a), the selectivity to several metal ions and ethylene gas are additionally described depending upon degree of methoxied macrocycles. The point (b) mentions a new fluorescence chemo probe of calix[4]resorcinarenes for metal ions. By compositing the calix[4]resorcinarene and polymer, the (c) point presents separator to porous membrane composites as described in my thesis. In their composite materials, properties of functional adsorbents in ions are demonstrated.

This thesis is constructed in six chapters including synthesis and preparation of calix[4]resorcinarene adsorbents and their applications. The important points are uses of

green chemicals for synthesis of the macrocyclic molecules and then those of application to elimination and detection to several ions by the calix[4]resorcinarenes. The layout of the present thesis is illustrated in Figure 1.12.

Chapter 1 presents a brief introduction to related topics to environment pollution, plant derived materials as the concerned importance of host-guest chemistry. Especially, as a highly selective separator, of calix[4]resorcinarene derivatives, the synthetic approach and their basic properties and applications are summarized in this chapter. Chapter 2 describes investigation on the facile syntheses of calix[4]resorcinarene by condensation of resorcinol and plant derived aromatic aldehyde such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde. In this chapter, the comparative investigations of adsorption behaviors of several heavy metal ions for the obtained calix[4]resorcinarenes are described. This chapter also focuses in analytical tool to heavy metal ions by sensitive fluorometric diagnostic to pollutant ions, especially in detection of Pb^{2+} ion. Chapter 3 focuses on the fabrication of composite membranes consisting of poly(ethersulfone) and calix[4]resorcinarene. The membrane morphology and the adsorption behavior for heavy metal ions of the composite membrane are studied as firstly reported porous adsorbents including calix[4]resorcinarene host. The introduction of the calix[4]resorcinarene sites having selective hosting led to the improvement separator to heavy metal separation. The calix[4]resorcinarene composited membrane shows innovative perm-rejection to Pb^{2+} ion through the permeation process. Chapter 4 describes investigation of Cs^{+} ion separation from alkali metal ion mixture such Na^{+} ion and K^{+} ion by calix[4]resorcinarenes. This chapter mentions the calix[4]resorcinarenes adsorbents that are worked well even in the co-

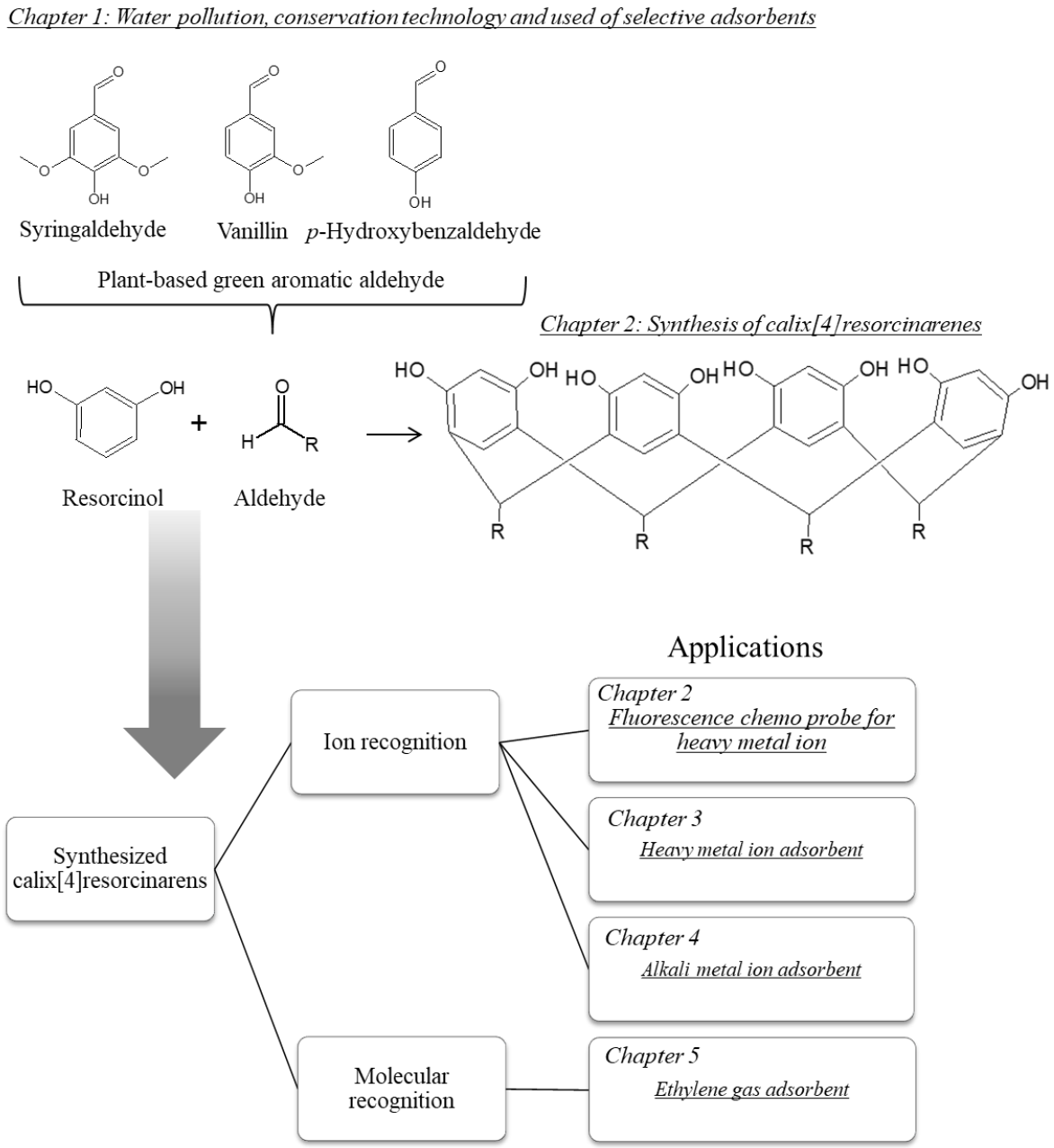


Figure 1.12 Experimental flowchart in this thesis.

presence of Na^+ and K^+ ions for Cs^+ ion with cation of clarify the high selectivity. Chapter 5 focuses on studying gas adsorptivity of calix[4]resorcinarenes as mentioned in additional application. The calix[4]resorcinarene is concerned with a first report effectively hosting C_2H_4. In accordance of biomass related adsorbents, vegetable wastes are also investigated for C_2H_4 absorbers. There is a comparison of the C_2H_4 adsorption behavior of the biomass materials and the calix[4]resorcinarene hosts. The evidence of the synthesized calix[4]resorcinarenes maintains chemical interaction with electron deficient C_2H_4 occurred with methoxy groups, leading chemisorbed binding with calix[4]resorcinarene. Finally, Chapter 6 is the summary of this thesis.

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Chapter 2

Preparation of calix[4]resorcinarene by using plant-based aldehyde and their fluorescence analysis to develop the chemo probe for Pb^{2+}

Abstract: Calix[4]resorcinarenes of syringaldehyde (S-host), vanillin host (V-host) and *p*-hydroxybenzaldehyde one (PH-host) were successfully prepared by one-step condensation of resorcinol and syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, respectively. The yields of their new hosts of S-host, V-host and PH-host were 28%, 32% and 37%, respectively. These hosts were characterized by ^{1}H-NMR, FT-IR and mass spectrum (MS), confirming that these were successfully obtained.

Then, the ability of these calix[4]resorcinarenes as the hosts for heavy metal ions (Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+}) was investigated by fluorescence studies. The results show that the fluorescence of the calix[4]resorcinarenes was effectively quenched by adding Pb^{2+}, particularly for S-host. The result of Stern-Volmer analysis showed a nonlinear relationship with the Pb^{2+} concentration. The quenching was saturated in the Pb^{2+} range 0.20-1.0 M, indicating the multiassociation of Pb^{2+} with the host. The quenching constant (K_{sv}) was estimated from the linear region in the range 0.25-2 μM of Pb^{2+} to be 1.2×10^{6} M^{-1} for the S-host and 0.22×10^{6} M^{-1} for the V-host. Moreover, Benesi Hildebrand analysis obtained the formation constant (κ) to Pb^{2+} and the host, for 1.9×10^{5} M^{-1} and 1.2×10^{6} M^{-1} at the V-

host and S-host, respectively. These results indicate that Pb^{2+} was effectively complexed with the S-host.

2.1 Introduction

Chemosensors have attracted much attention in various fields of safety, medical engineering, and industrial processes. In particular, water pollution from industrial discharge is a severe problem all over the world. Because the increasing accumulation of Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the environment is a great concern [1], technological advances in heavy metal diagnosis are required for the development of alternative techniques. Among the heavy metals, Pb^{2+} is the most abundant and surely most toxic and causes health problems such as digestive, nervous, heart and mental problems. Pb^{2+} is particularly dangerous for children who cause mental retardation. Thus, the level of this harmful ion present in tap water is a result of dissolution from the domestic plumbing system and is subject to several public standards. Currently, the amount of Pb^{2+} is measured using atomic absorption or emission spectroscopy [2]. However, the use of fluorescence offers many advantages in terms of selectivity, sensitivity and low cost. Fluorescent molecular sensors have been developed for alkali and alkaline earth cations, but there are few examples of fluoroionophores developed for heavy metal ions, especially for Pb^{2+} [3]. A chemosensor provides information about the quantity of a sample chemical species or class of chemical species. Most of the alternative chemosensing techniques were proposed in the early 1960s, for example, solid electrolyte-type sensor (1961), ion electrode sensor (1961), biosensor basic concept (1962), oxide semiconductor-type gas sensor (1962), and fluorometry (1966)

[4, 5]. The fluorescence phenomenon was first described by Brewster in 1838. Because of its high sensitivity and selectivity, fluorescence spectroscopy has been widely used, for example, epifluorescence microscopy and video intensification microscopy. Combined with a fluorescence probe, fluorescent labeled molecules have been developed [6]. Until now, fluorescence chemosensors based on small molecules, including macrocyclic compounds linking fluorophores [7, 8], organic-inorganic hybrid fluorescent materials [9], polymer-based fluorescence chemosensors [10, 11], nanoparticle luminescent chemosensors [12, 13] and fluorescence-based sensor arrays [14] have been reported.

On the other hand, host molecules have been widely studied because of their innumerable applications such as selective separators for chemicals [15]. Currently, the development of new host molecules is indispensable for the creation of advanced functional materials such as high performance catalysts, ultra-high sensitivity sensors, ultra-precision separation materials. What is required for the basic skeleton of a practical host molecule, (1) It can be synthesized in a simple and large amount and (2) Easy to modify chemically. In addition, what is important as a host molecule. There are recognizing of a guest and introducing to a function accompanying by the host. As a host molecule satisfies the above requirements, a calix[n]arene cyclic molecules obtained by crosslinking a plurality of phenols with a methylene group is known. Calix[n]arene is a compound that has attracted attention as a third host molecule next to crown ether and cyclodextrin. This is due to its structural features in addition to alternative synthesis and chemical modification.

Calix[n]arene can be synthesized by condensing phenol with an aldehyde in the presence of acid or base. By selecting conditions, it is possible to selectively obtain a

specific number of ring members [16]. Furthermore, it is now reported that the isolation of calix[20]arene with 20 phenols [17]. Therefore, the cavity size can be controlled according to the purpose. Also, since the basic skeleton is a phenol, chemical modification is easy to introduce functional groups in the cycle molecule. So, a functional group can be introduced into the phenolic hydroxyl group by etherification or esterification, and to the *p*-position by electrophilic substitution reaction [18-20]. In addition, calixarenes have conformational properties without other host molecules. From these reasons, calixarene is one of the famous hosts for organic molecules and heavy-metal guests [21, 22] Therefore, calixarene has received much attention in analytical chemistry and is widely used in extraction [23], ion recognition [24] and chemical sensor [25]. Furthermore, several studies have described the eff ectiveness of resorcinarene which can be synthesized from resorcinol and aldehyde by condensation as a metal ion extraction agent [26, 27]. Especially, the cyclic molecule can be easily synthesized as calix[4]resorcinarene by using acidic catalyst through synthesis. Both calixarene and resorcinarene such as calix[4]resorcinarene have phenolic hydroxyl groups of the aromatic rings inside the macrocycle cavity, acting as the hosting functionally and incorporate with guest [28].

On the other hand, natural chemicals such as vanillin with an aldehyde group are obtained from plants. As mentioned in Chapter 1, environmental protection and environmental cleanup are needed for sustainable development. Therefore, herein, natural chemicals used as the raw materials are provided for the synthesis of resorcinarenes with regard to green chemistry. Syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde) has an aldehyde group, a hydroxyl group, and two methoxy groups, which can be obtained from

spruce and maple trees. Also, vanillin (4-hydroxy-3-methoxybenzaldehyde) which is the primary extract of the vanilla bean has an aldehyde group similar to that of syringaldehyde as well as a methoxy groups. *p*-Hydroxybenzaldehyde having an aldehyde group, a hydroxy group and no methoxy group, can extracted from gastrodia elata.

In the present chapter, by using the green chemicals of syringaldehyde, vanillin and *p*-hydroxybenzaldehyde as plant based aldehyde, synthesis processes of calix[4]resorcinarene were described. Then, they were evaluated as new fluorophore calix[4]resorcinarene hosts for chemical probes for heavy metal ions.

2.2 Experimental

2.2.1 Materials

All the reagents were used as received without further purification. Vanillin was purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA). Syringaldehyde, *p*-hydroxybenzaldehyde, and resorcinol were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Methanol, ethanol, hydrochloric acid, $Pb(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $CdSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

2.2.2 Synthesis of calix[4]resorcinarenes

The calix[4]resorcinarenes were synthesized by the condensation reactions shown in Figure 2.1. The syringaldehyde, vanillin or *p*-hydroxybenzaldehyde (0.125 mol) was reacted with resorcinol (0.125 mol) and 12 M HCl (25 mL) in an ethanol solution (150 mL) at 70°C

Figure 2.1 Chemical structure of syringaldehyde calix[4]resorcinarene (S-host), vanillin calix[4]resorcinarene (V-host) and *p*-hydroxybenzaldehyde calix[4]resorcinarene (PH-host).

under nitrogen atmosphere. The reaction mixture was stirred for 12 h, affording in a pink color precipitate. Then, each precipitate was washed several times with hot water and purified by washing twice with methanol and twice with ethanol. The yields of the syringaldehyde calix[4]resorcinarene (S-host; 2,18,14,20-tetra (3-hydroxy-2,4-dimethoxybenzyl) calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol), vanillin calix[4]resorcinarene (V-host; 2,18,14,20-tetra(3-hydroxy-4-methoxybenzyl)calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol), and *p*-hydroxybenzaldehyde calix[4]resorcinarene (PH-host; 2,18,14,20-tetra(*p*-hydroxybenzyl)calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol) were approximately 32%, 28% and 37%, respectively. These calix[4]resorcinarenes were soluble in organic solvents such as acetone, ethanol, methanol, butanol, *n*-hexanol, THF, DMF, and DMSO.

2.2.3 Experimental procedures for characterization of calix[4]resorcinarenes

To confirm the chemical structure of synthesized calix[4]resorcinarenes, the ^{1}H-NMR spectra of S-host, V-host and PH-host in deuterated dimethyl sulfoxide (d_6-DMSO) were measured by using NMR equipment (JEOLAL-400; JEOL, Japan). Functional group analysis of the calix[4]resorcinarenes was carried out using Fourier transform infrared (FT-IR) spectroscopy (FT-IR 4100 series, Jasco Corp. Japan) over a frequency range 500 - 4500 cm^{-1}. Pellets were made from samples with KBr. Furthermore, the calix[4]resorcinarenes were characterized by mass spectroscopy (MS) (autoflexIII smartbeam, Bruker, U.S.A.).

2.2.4 Adsorption experiment of heavy metal ions

To observe the heavy metal adsorptivity of calix[4]resorcinarenes, adsorption experiment was carried out by using batch method. Each heavy metal ion solutions Pb^{2+},

Ni^{2+}, Cd^{2+}, and Cu^{2+} were prepared 20 ml at 20 ppm concentration in glass holder. In the single solution of each heavy metal ions, 0.03 g of calix[4]resorcinarenes, S-host, V-host and PH-host were added respectively. Then, the holder was shaken at 25 ℃ for 24 h by using TS-200 Shaking bath (Advantech, Taiwan). The concentrations of remaining heavy metal ions Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the aqueous solution were measured at a certain wavelength using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan). Optimum selectivity of the calix[4]resorcinarene for the interfering metal ion was evaluated using the following equation (2-1).

$$q_e = \frac{(C_i - C_f)V}{W} \qquad (2\text{-}1)$$

Here, C_i signifies the initial concentration of metal ion (μmol/L) and C_f denotes the final concentration of metal ion (μmol/L) after the equilibrium, V represents the volume of the metal ion solution (L), and W stands for the weight of the calix[4]resorcinarene (g) used. The unit for the adsorption capacity, q_e was μmol/g. The wavelength of the emission line for Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} was 283.3, 232.2, 228.8 and 324.8 nm, respectively.

2.2.5 Fluorescence and absorption measurements in the presence of heavy metal ions

The calix[4]resorcinarenes, S-host, V-host and PH-host, were dissolved in ethanol, and 1.0×10^{-5} M calix[4]resorcinarene-ethanol solutions were prepared. The fluorescence spectra of S-host, V-host and PH-host were measured without and with various metal ions such as Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the range from 2.5×10^{-7} M to 1.0 M. The excitation was carried out at 280 nm in each case. To measure their UV-visible absorption spectra,

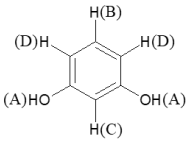
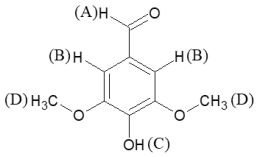
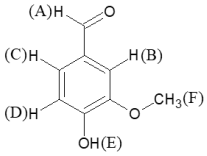
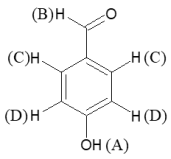
various heavy metal ions Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} in the concentration range from 2.5×10^{-7} M to 1.0 M were added into a 1.0×10^{-5} M calix[4]resorcinarene-ethanol solution.

2.3 Results and discussion

2.3.1 Characterization of calix[4]resorcinarenes

Table 2.1 shows ^{1}H-NMR (500 MHz, d_6-DMSO) assignments for row materials such as resorcinol, syringaldehyde, vanillin and *p*-hydroxybenzaldehyde. The chemical structures of the S-host, V-host and PH-host were elucidated by using ^{1}H-NMR spectra in d_6-DMSO, as follows (Figure 2.2): ^{1}H-NMR (500 MHz, d_6-DMSO) [S-host]: δ 8.43-7.64 (8H, CH, m), 6.43-6.19 (8H, CH, m), 5.95 (12H, OH, s), 5.44 (4H, CH, s), 3.40 (24H, OCH_3, s). [V-host]: δ 8.31-7.90 (12H, CH, m), 6.40-6.31 (8H, CH, m), 6.15 (12H, OH, s), 5.42 (4H, CH, s), 3.45 (12H, OCH_3, s). [PH-host]: δ 8.83-8.35 (16H, CH, m), 6.60-5.90 (8H, CH, m), 5.41 (4H, CH, s). In the ^{1}H-NMR spectra of the calix[4]resorcinarenes, the peak at δ 5.42 ppm originating from the ring current effect indicated the formation of the calix[4]resorcinarene ring. Moreover, the peak of aldehyde in the range 9-10 ppm was absent, indicating that resorcinol and each aldehyde reacted and cyclized to afford the corresponding calix[4]resorcinarenes. The FT-IR spectra (Figure 2.3) of the S-host, V-host and PH-host using the KBr method were contains for the S-host [cm^{-1}] in following peaks: 3396 (O-H), 2935 (C-H, aromatic), 1616-1510 (C-C, aromatic), 1220 (C-O-C), 1080 (C-O-C). V-host [cm^{-1}]: 3425 (O-H), 3020 (C-H, aromatic), 1618-1510 (C-C, aromatic), 1276 (C-O-C), 1076 (C-O-C). PH-host [cm^{-1}]: 3385 (-OH), 3014 (C-H, aromatic), 1602-1510 (C-C, aromatic) (Table 2.2). All of the calix[4]resorcinarene spectra revealed a broad and

Table 2.1 ^{1}H-NMR (500 MHz, d_6-DMSO) assignments for resorcinol, syringaldehyde, vanillin and p-hydroxybenzaldehyde.

Assign.	Resorcinol	Syringaldehyde	Vanillin	*p*-Hydroxybenzaldehyde
	δ (ppm)			
A	9.15	9.81	9.82	10.6
B	6.93	7.15	7.42	9.82
C	6.22	6.00	7.42	7.79
D	6.21	3.96	7.05	6.97
E	-	-	6.18	-
F	-	-	3.96	-
				

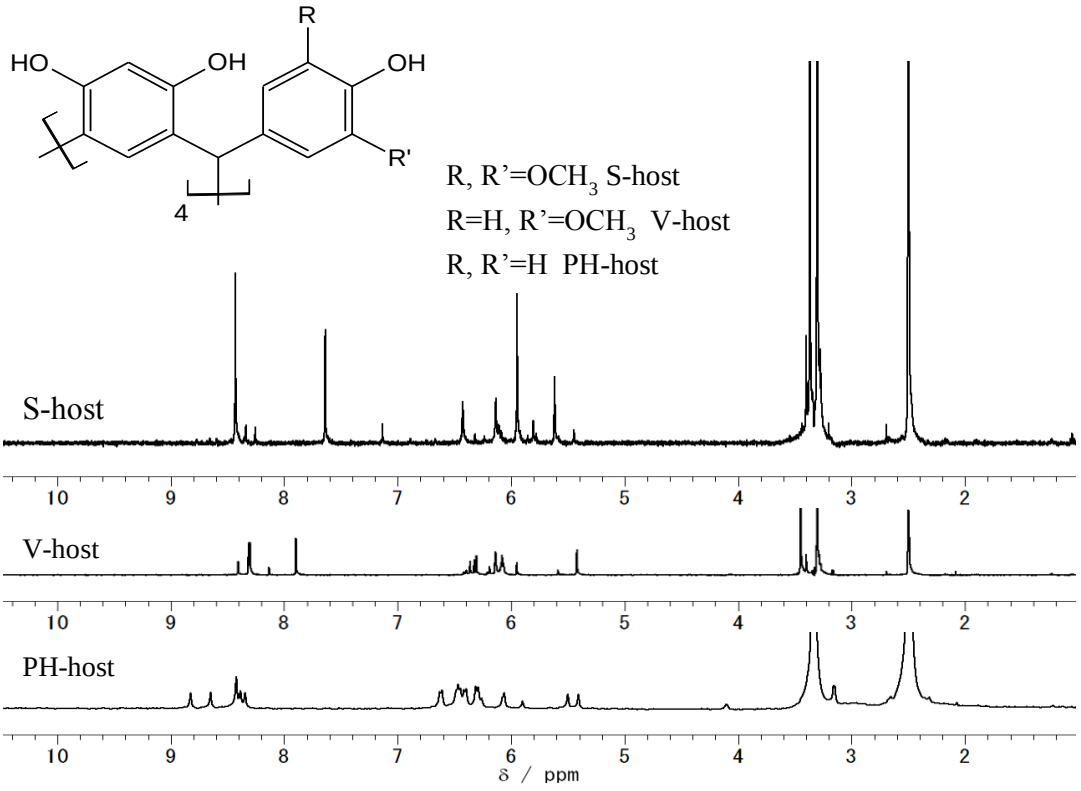


Figure 2.2 ^{1}H-NMR spectra of S-host, V-host and PH-host.

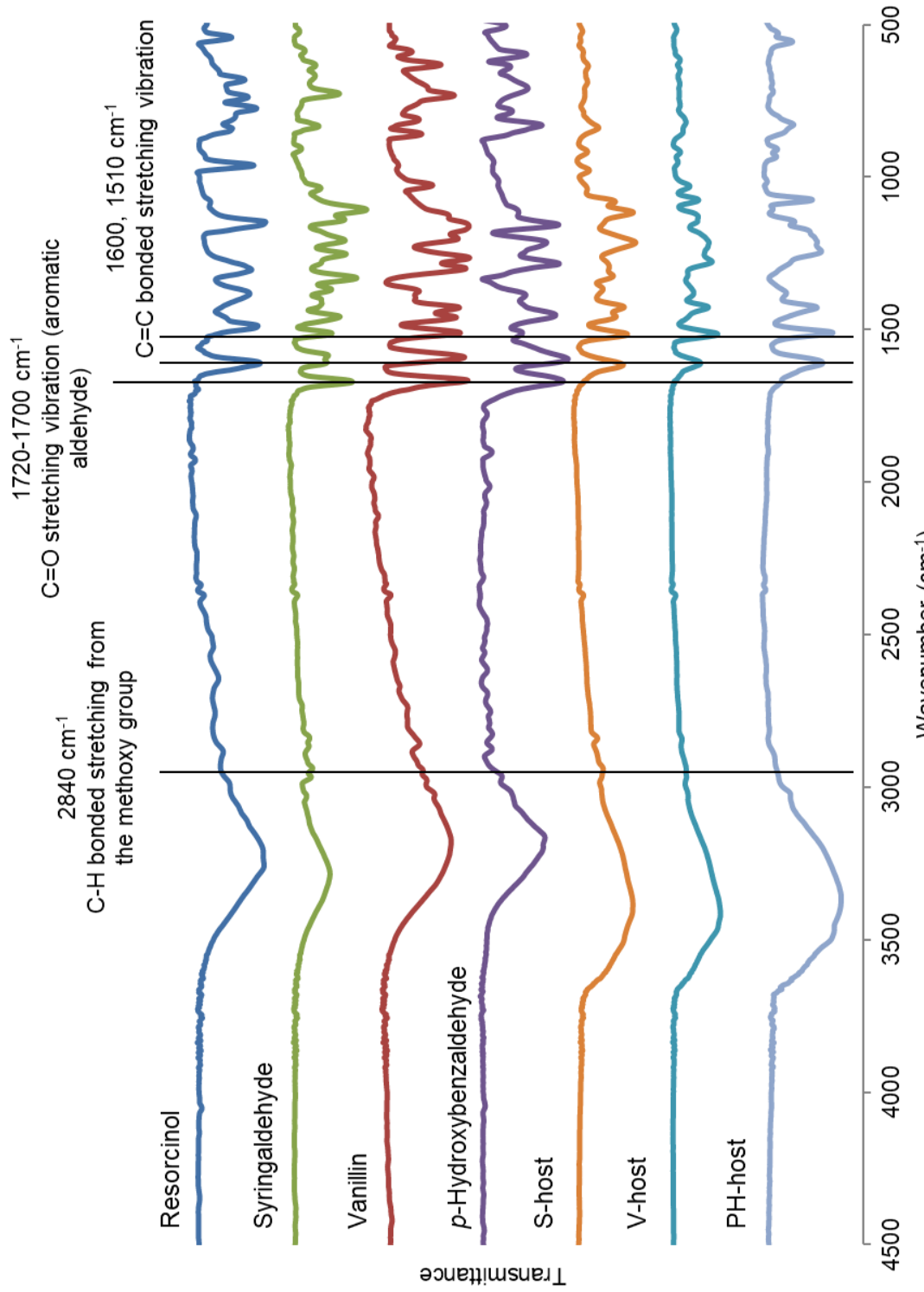


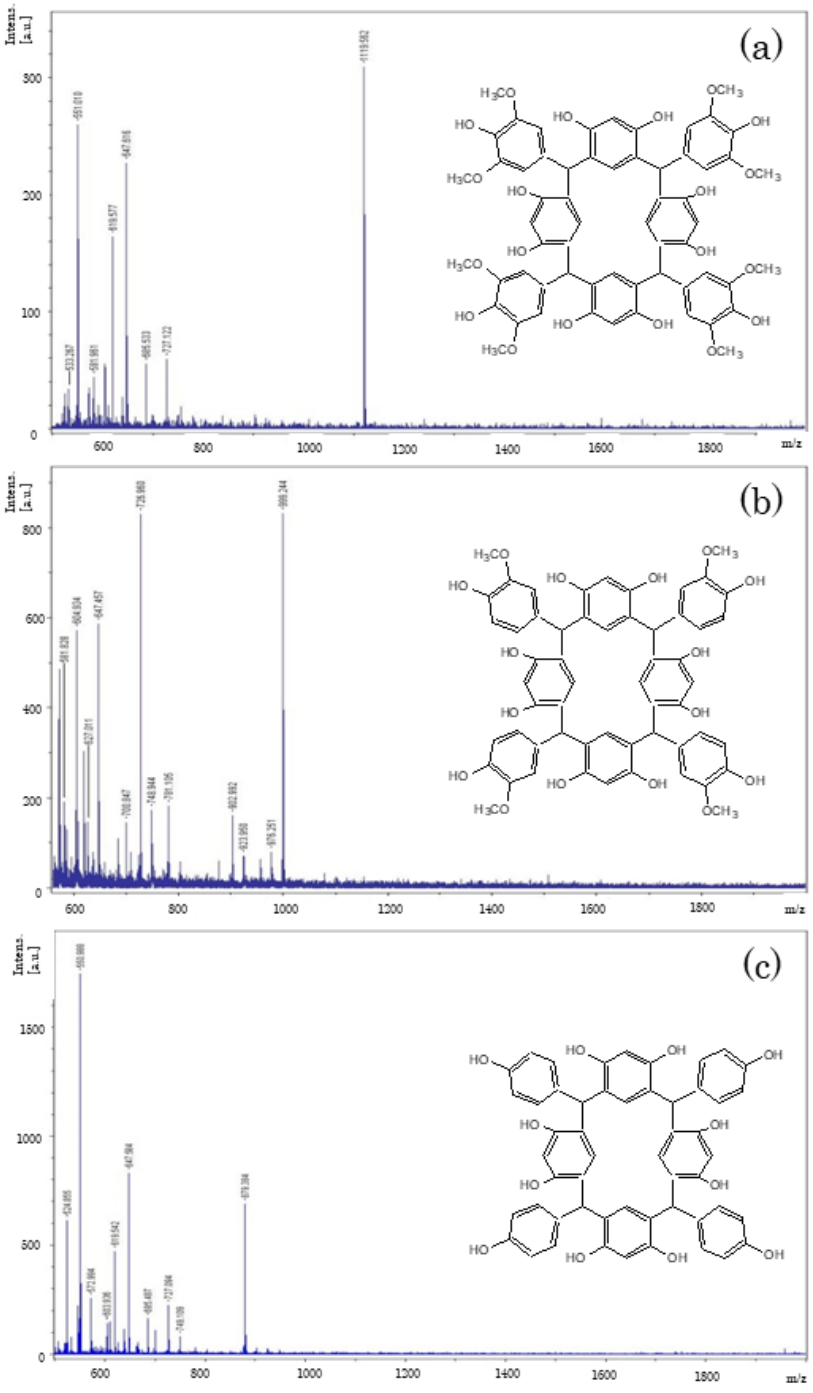
Figure 2.3 FT-IR spectra of raw materials and S-host, V-host and PH-host.

Table 2.2 The attribution list of FT-IR spectra of raw materials and S-host, V-host and PH-host.

Wavenumber[cm^{-1}]	Assignment		
	Syringaldehyde	S-host	
	Vanillin	V-host	
	p-Hydroxybenzaldehyde	PH-host	
3570-2970	O-H	O-H	
3020-2935	C-H (phenyl ring)	C-H (phenyl ring)	
2976-2870	C-H	C-H	
2840	C-H (aldehyde)	–	
1703	C=O (aldehyde)	-	
1613	C=C	C=C	
1600-1510	C-C (phenyl ring)	C-C (phenyl ring)	
1276-1220	C-O-C* (methoxy group)	C-O-C** (methoxy group)	
1080-1076	C-O-C* (methoxy group)	C-O-C** (methoxy group)	

*except *p*-hydroxybenzaldehyde

**except PH-host



Figures 2.4 Mass spectra of (a) S-host, (b) V-host and (c) PH-host.

intense peak at around 3400 cm^{-1} attributed to hydrogen bonded (O-H bond) stretching vibration from the resorcinol and each aldehyde such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, whereas a weak absorption peak of S-host and V-host at 2840 cm^{-1} assigned to C-H bonded stretching from the methoxy group. Moreover, they also had a weak absorption peak at 1620-1510 cm^{-1} assigned to C=C bonded stretching vibration from the aromatic rings. In addition, no peak appearance of the aromatic aldehyde was observed in the FT-IR spectra of the S-host, V-host and PH-host. With these results, it was confirmed that new calix[4]resorcinarenes, S-host, V-host and PH-host were successfully synthesized from resorcinol and syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, respectively. Furthermore, these hosts were characterized by mass spectroscopy (MS). As seen in Figure 2.4, the molecular weights of S-host, V-host and PH- host, calix[4]resorcinarenes, were 1096 g/mol, 976 g/mol, and 856 g/mol, respectively. The MS data (reflection mode, positive ion) were obtained using autoflexIII smartbeam (Bruker, U.S.A.). When NaI was used for ionization, the molecular weight of Na (=23) was added to the calculated molecular weight, resulting in the molecular weights of S-host, V-host, and PH-host as 1119.576, 999.244 and 879.384, respectively. Therefore, the exact molecular weight of S-host, V-host and PH-host calculated by resulting [molecular weight] – [weight of Na], which was well matched to their molecular weights when they have calix[4]resorcinarene structure. So, the MS data confirmed that S-host, V-host, and PH-host were calix[4]resorcinarenes, meaning no other calix[n]resorcinarenes.

2.3.2 Batch binding adsorption experiment

In studying binding ability of heavy metal ion for the calix[4]resorcinarenes of S-host, V-host and PH-host, the batch binding experiment was carried out, when 0.03 g of the calix[4]resorcinarene powder was dispersed in 20 ml of aqueous heavy metal ion (20 ppm) at pH 5 for 12 h. As shown in Table 2.3, it was noted that the S-host adsorbed Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} with adsorption amounts of 24, 0.92, 4.7 and 1.6 (μmol/g-powder), respectively. The V-host adsorbed Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} with adsorption amounts of 22, 2.4, 4.4 and 2.0 (μmol/g-powder), and the PH-host was 2.0, 0.83, 1.7 and 0.76 (μmol/g-powder), respectively. Apparently, these indicated that the S-host and V-host powder could highly bind the Pb^{2+}.

Table 2.3 Binding amounts of heavy metal ions to S-host, V-host and PH-host.

Calix[4]resorcinarene	Pb^{2+} [μmol/g]	Ni^{2+} [μmol/g]	Cu^{2+} [μmol/g]	Cd^{2+} [μmol/g]
S-host	24	0.92	4.7	1.6
V-host	22	2.4	4.4	2.0
PH-host	2.0	0.83	1.7	0.76

2.3.3 Fluorescence quenching of calix[4]resorcinarenes by heavy metal ions

The calix[4]resorcinarene moiety shows a slight fluorescence. Therefore, it is difficult to measure their fluorescence. If the host-guest complexation of these calix[4]resorcinarenes results in fluorescence, they can be used as fluorometric sensors. Because calix[4]resorcinarene has a phenyl group in the chemical structure, fluorescence is expected because of π–π* transition. Figure 2.5 shows fluorescence and excitation spectra of S-host, V-host and PH-host. Here, the concentration of each host was fixed at 1.0×10^{-5}

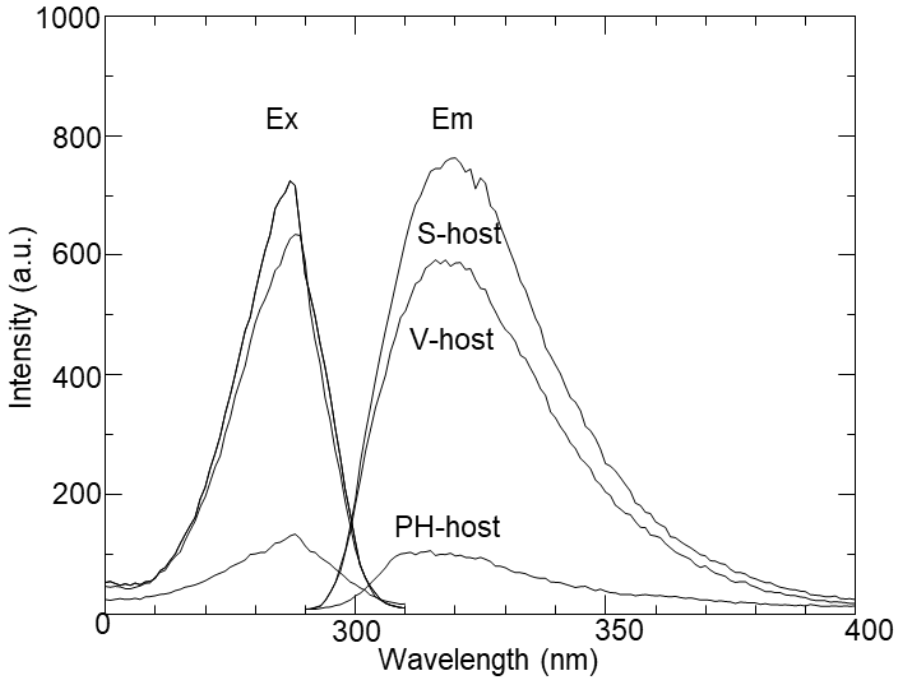
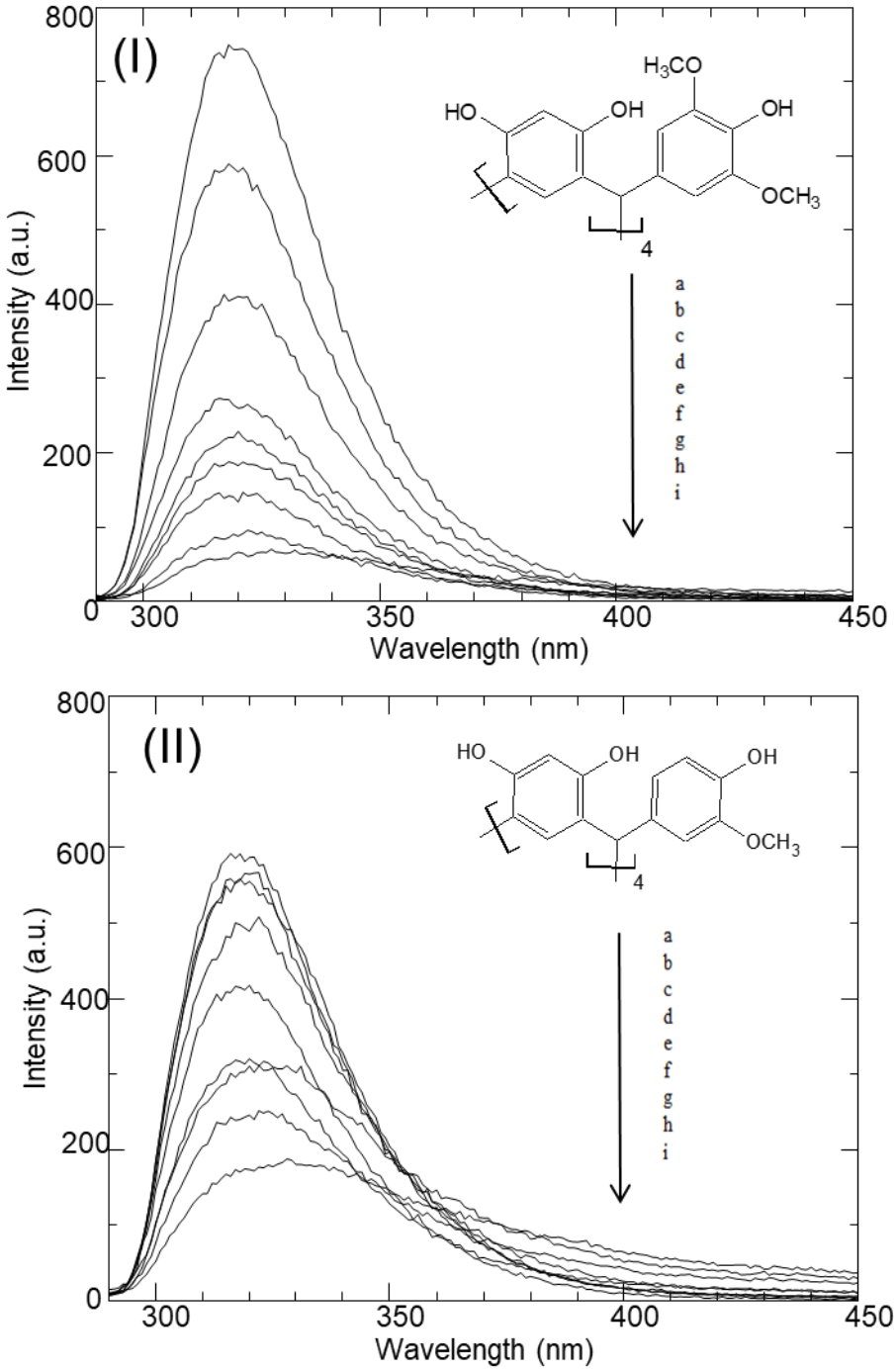


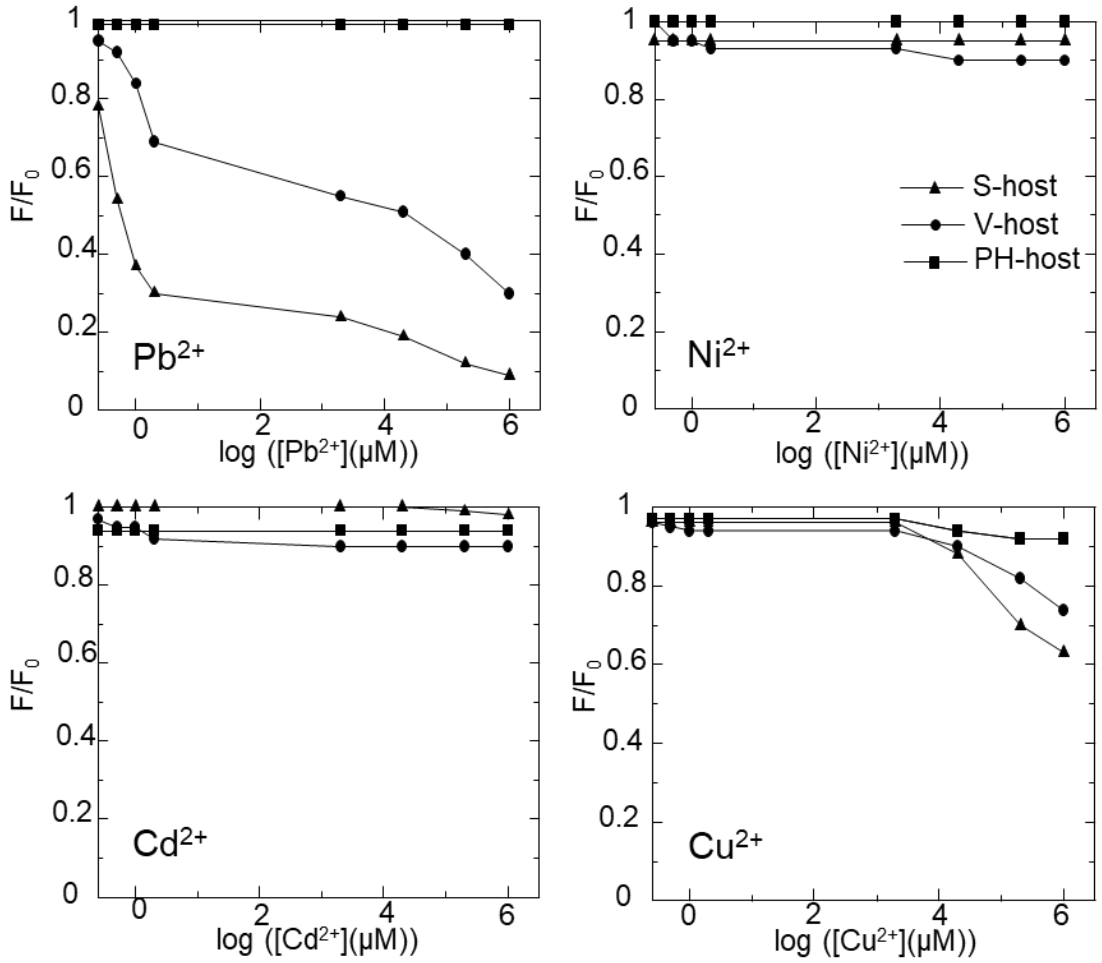
Figure 2.5 Fluorescence spectra and excitation spectra of S-host, V-host and PH-host at 1.0×10^{-5}M.

M, and the excitation wavelength was 280 nm. The spectra of the S-host and V-host had a broad peak in the range 290-400 nm with a high emission intensity at 320 nm. It was shown that the spectrum of the PH-host had a weaker peak than S-host and V-host. The excitation spectra of the calix[4]resorcinarenes are shown as term Ex, in the figure. The highest peak was observed at 285 nm in each case when 320 nm wavelength was monitored for the fluorescence maximum of the calix[4]resorcinarene. Figures 2.6 show fluorescence spectra of (I) S-host and (II) V-host in the presence of Pb^{2+} ion in the range from 2.5×10^{-7} M to 1.0 M concentration. Apparently, the fluorescence of the hosts was quenched with Pb^{2+}. The quenching was especially effective in the S-host for the Pb^{2+}. Moreover, the fluorescence



Figures 2.6 Fluorescence spectra of (I) S-host and (II) V-host at 1.0×10^{-5}M (a) without Pb^{2+} ion and with (b) 0.25 µM, (c) 0.5 µM, (d) 1 µM, (e) 2 µM, (f) 2 mM, (g) 20 mM, (h) 200 mM, and (i) 1 M Pb^{2+} ion.

intensity obtained without and with various metal ions (Pb^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+}) was measured and then the ratio of F/F_0 was calculated for each result obtained at different heavy metal concentrations. Here, F_0 and F were the intensities in the absence and presence of the heavy metal ion. Figures 2.7 show the relationship between F/F_0 and heavy metal ion concentration. Particularly, in the case of Pb^{2+}, the ratio of F/F_0 intensity changed



Figures 2.7 Fluorescent intensity ratio of calix[4]resorcinarenes in the absence and presence of various metal ions in the range from 2.5×10^{-7} M to 1.0 M. Excitation was carried out at 280 nm in each case.

significantly decreasing S-host fluorescence, but other metal ions did not quench well. Particularly, PH-host without a methoxy group (-OCH_3) showed less quenching. However, when the concentration was in the range from 2×10^{-3} M to 1.0 M, Cu^{2+} ion showed less quenching of the calix[4]resorcinarene fluorescence. This indicates that the difference between PH-host and other hosts bearing a -OCH_3 group can be attributed to the chelation effect between the -OCH_3 group and Pb^{2+}.

2.3.4 Analysis of Pb^{2+} binding to the hosts

Figure 2.8 shows the Stern-Volmer plots associated with the fluorescence titration of the calix[4]resorcinarenes with Pb^{2+} in the range from 2.5×10^{-7} M to 1.0 M. As shown in Eq. (2-2), the Stern-Volmer equation can be derived from the fluorescence intensities obtained in the absence and presence of a quencher.

$$\frac{F_0}{F} = 1 + k_q\tau_0[Q] = 1 + K_{sv}[Q] \qquad (2\text{-}2)$$

In this equation, F_0 and F are the fluorescence intensities in the absence and presence of the quencher, respectively, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of the quencher, and Q is the concentration of quencher. The Stern-Volmer quenching constant can be expressed as $K_{sv}=k_q\tau_0$ [29]. Quenching processes can be generalized as having two mechanisms, namely, they can be static or dynamic in nature [30, 31]. In static quenching, the fluorophore and quencher form complexes in the ground state. In dynamic or collision quenching, the excited state of the fluorophore is quenched by collision with the quencher. If either of these mechanisms dominates on a given system, a linear Stern-Volmer relationship will be raised [32]. The variation in the

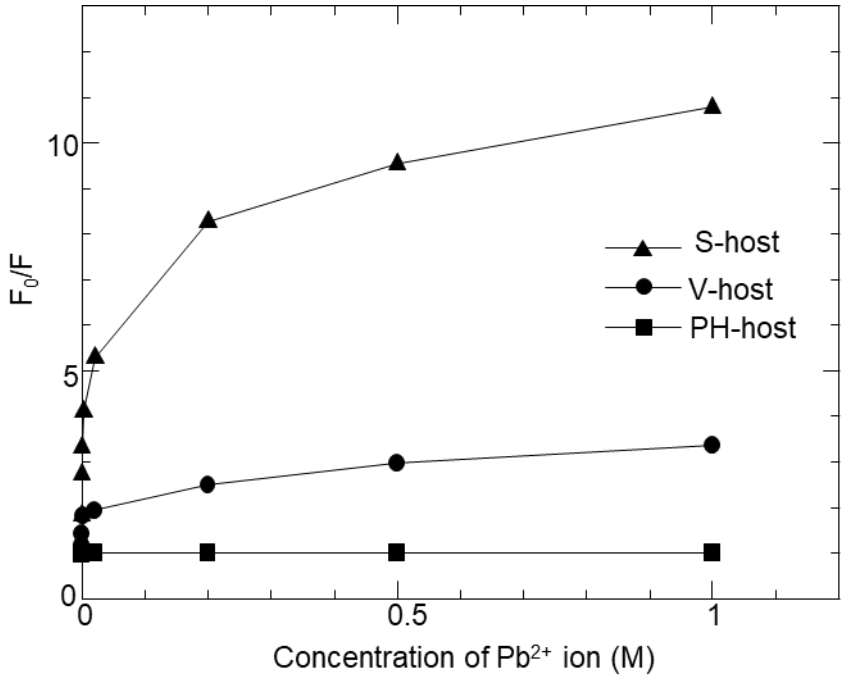


Figure 2.8 Stern-Volmer plots associated with the calix[4]resorcinarenes and Pb^{2+} ion concentration. F_0 and F are the fluorescence intensities at the maximum emission wavelength. The calix[4]resorcinarene concentration was 1.0×10^{-5} M, and the excitation wavelength was 280 nm.

fluorescence intensity with different Pb^{2+} ion concentration showed a nonlinear response. Thus, the quenching was saturated in the range 0.20-1.0 M of Pb^{2+}. In the linear region between the F_0/F and Pb^{2+} concentration, the quenching constant (K_{sv}) was estimated as 1.2×10^6 M^{-1} for S-host and 0.22×10^6 M^{-1} for V-host. Interestingly, the quenching occurred at lower Pb^{2+} concentrations in the range 0.25-2 μM. The saturated quenching behavior in the Stern-Volmer relationship indicated the multiassociation of Pb^{2+} [33-35].

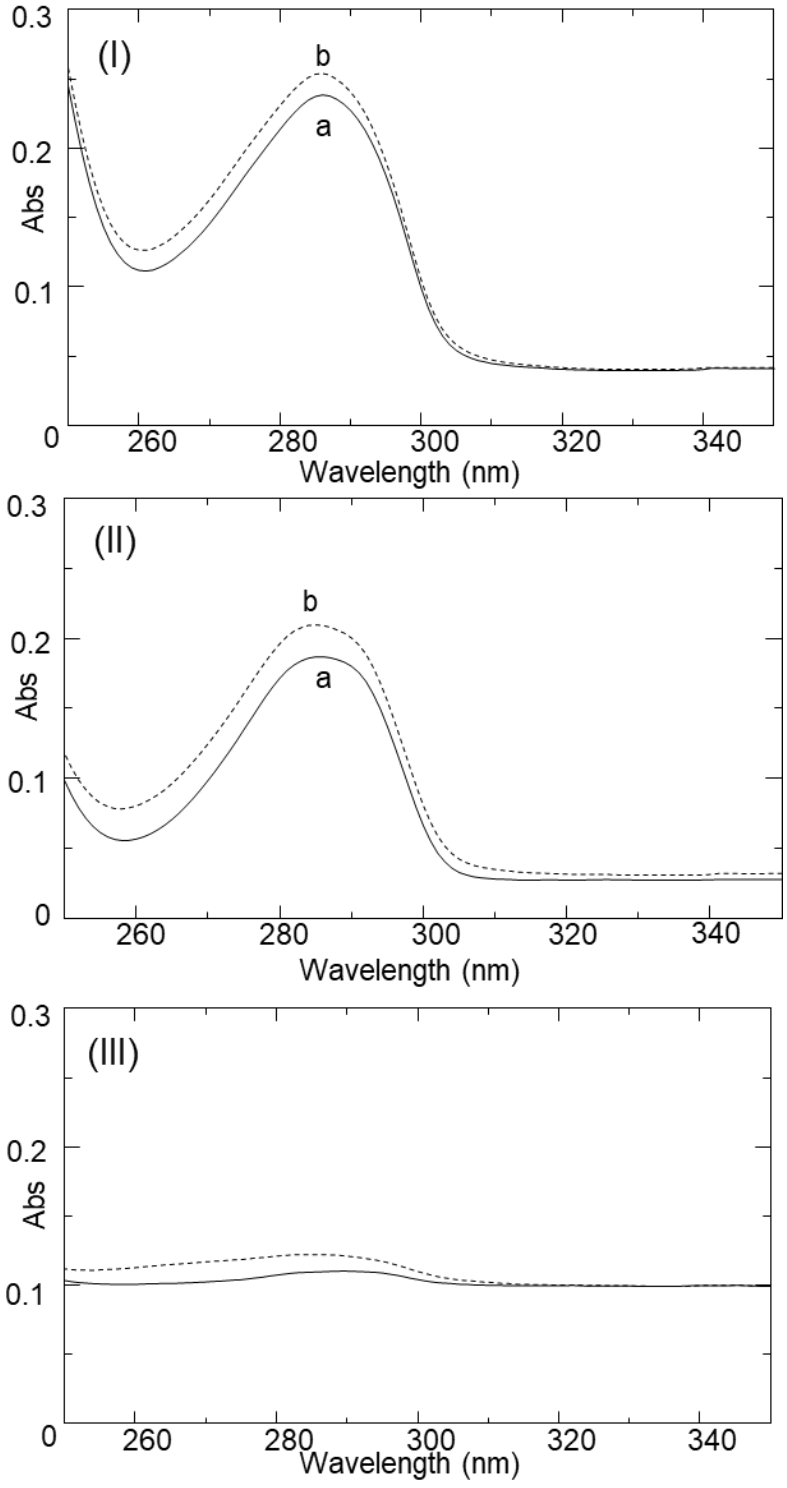
To analyze Pb^{2+} binding to the calix[4]resorcinarene hosts, the Benesi-Hildebrand method [36, 37] was applied using absorption spectroscopy. Here, the absorption spectra of the host were measured in the presence of Pb^{2+}. As shown in Figures 2.9 the absorption

spectra of S-host and V-host had an absorption maximum at 286 nm and 283 nm, respectively. When 2 μM of Pb^{2+} was added, the UV band intensity due to the phenyl group at 280 nm increased in the presence of Pb^{2+} However, in PH-host, less change was observed in the UV-visible spectra with increased concentration. Therefore, the absorption intensities of S-host and V-host measured at different Pb^{2+} concentrations were analyzed for the Benesi-Hildebrand plots (Figure 2.10). The formation constant κ between calix[4]resorcinarene and Pb^{2+} was calculated using Eq. (2-3),

$$\frac{[A]_0 l}{d_A - d_{A0}} = \frac{1}{\kappa_{\varepsilon c}} \times \frac{1}{[D]_0} + \frac{1}{\varepsilon_0} \qquad (2\text{-}3)$$

where d_A is absorbance of calix[4]resorcinarene with Pb^{2+}, d_{A0} is the absorbance of calix[4]resorcinarene, l is the path length, $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor (calix[4]resorcinarene) and donor (Pb^{2+}), and ε_c is the molar coefficient of the complex (calix[4]resorcinarene-Pb^{2+}). Using the UV-visible spectra obtained after the Pb^{2+} addition, $1/(d_A - d_{A0})$ and $1/[D]_0$ were plotted. Here, the slope and intercept of the line were used to evaluate the formation constant κ and molar coefficient ε of the complex, respectively. In S-host, the slope was 3.0×10^{-5}, and the intercept was 35.0. In V-host, the slope was 6.0×10^{-5}, and the intercept was 11.6. The values of κ for Pb^{2+} ion were 1.2×10^{6} M^{-1} and 1.9×10^{5} M^{-1} for S-host and V-host, respectively.

These results indicated that Pb^{2+} could be effectively coordinated to complex with calix[4]resorcinarenes, especially for S-host. From the results of fluorescence measurement, the calix[4]resorcinarene were well quenched by adding Pb^{2+} in the range of 0.25-2 μM and



Figures 2.9 Absorption spectra of (I) S-host, (II) V-host and (III) PH-host.

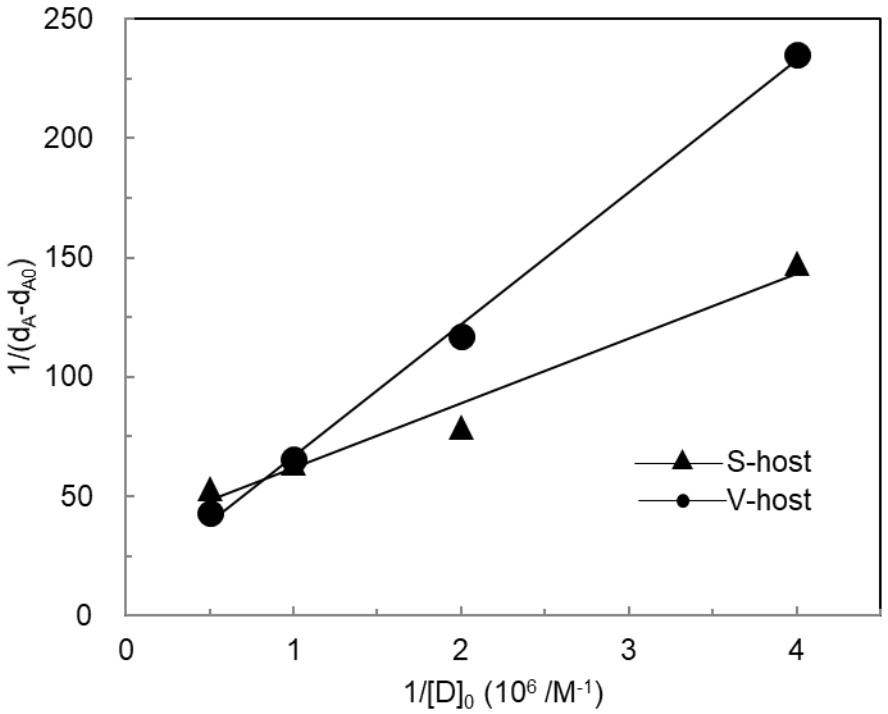


Figure 2.10 Benesi-Hildebrand plots of S-host and V-host.

then fluorescence intensity was saturated in the range of 0.2-1.0 M. Moreover, the change in the absorption spectra in the range of 0.25-2 µM confirmed that the quenching was efficient at the lower concentration range. However, a significant spectral change was not observed in these cases in the concentration range. This indicated that the change in the absorption spectra in the range of 0.25-2 µM was caused by the interaction of Pb^{2+} with the phenyl ring without or with $-OCH_3$ groups. The comparison indicated that the quenching was not due to the Pb^{2+}-calix[4]resorcinarene interaction through the $-OCH_3$ groups in the low concentration region of Pb^{2+}. Thus, the quenching occurring in the lower concentration range might be attributed to Pb^{2+} interaction with phenyl groups in calix[4]resorcinarene. Then, in the range of 0.2-1.0 M concentration of Pb^{2+}, there was one possibility which was

due to the multiassociation of Pb^{2+} occurred by interacting with the -OCH_3 groups of the calix[4]resorcinarene. Normally, fluorescent sensors for heavy metal ions, particularly ratiometric receptors for Pb^{2+} were known that heavy metal ions quench fluorescence emission via enhanced spin-orbital coupling [38], energy, or electron transfer [39]. In addition, clearly, a comparison among calix[4]resorcinarenes having different number of methoxy groups showed that the quenching behavior of Pb^{2+} by S-host was highly caused by interactions of -OCH_3 groups for the multi association. Notably, Cu^{2+} ions exhibited quenching only in the range of 0.20-1.0 M. This might be because that high concentration could be responsible for the interactions between -OCH_3 groups and Cu^{2+} in the range of 0.20-1.0 M.

2.4 Conclusion

S-host, V-host and PH-host were successfully synthesized from natural sources, syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, and used to study the chemical interactions with Pb^{2+} by fluorometry. The UV absorption intensity of the phenyl ring of the calix[4]resorcinarene varied, when the concentration of each heavy metal ion was increased, particularly for Pb^{2+}. The results indicated that the fluorescence behavior showed the multiassociation of Pb^{2+} in the calix[4]resorcinarene hosts prepared from plant sources through complex of Pb^{2+} and the -OCH_3 groups.

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Chapter 3

Heavy metal adsorptivity of poly(ethersulfone) and calix[4]resorcinarene composited membranes prepared by phase inversion process

Abstract: Calix[4]resorcinarene host-guest membranes were prepared with hybridization of calix[4]resorcinarene and poly(ethersulfone) (PES) by a phase inversion process. Herein, three calix[4]resorcinarenes, S-host, V-host and PH-host, synthesized from resorcinol and syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, respectively were composited in PES membrane. The phase inversion process was carried out in phase change of the solution of *N*-methyl-2-pyrrolidone containing both PES and the calix[4]resorcinarene to solid membrane in water coagulation. The composited membranes having different loading amounts of the calix[4]resorcinarene were prepared with 10, 25, 50 and 60 wt% loading. The observation of SEM pictures indicated porous morphology in the PES scaffold. The porous morphology in the cross section of the membrane caused high water content over 100 %, meaning easy accessibility of aqueous solution in the membrane. The adsorption behavior of aqueous heavy metal ions: Pb^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+}, was examined for the composited membranes containing 10, 25, 50 and 60 wt% of the calix[4]resorcinarene composited membranes. It was evidenced that each composited membrane adsorbed effectively Pb^{2+} ion, as the solution was permeated at 4.0×10^4 Pa applied pressure. When

the S-host was loaded at 50 and 60 wt% in the membranes, the Pb^{2+} capacity was 17 and 18 μmol/g-membrane, respectively, for the batch experiment. In addition, when the quarterly mixture of the aqueous heavy metal ions was permeated through the membrane, the composited membrane having 50 and 60 wt% of the S-host loading maintained high retention of the Pb^{2+} ion.

3.1 Introduction

As mentioned in Chapter 1, because of the rapid industrialization in recent years, the pollution of the environment by heavy metals such as Pb, Ni, Cd and Cu becomes serious problem. According to the World Health Organization (WHO), it is reported that 70-80 % of all illnesses in developing countries are related to water contamination, particularly for women and children [1]. Since Pb is one of the most harmful heavy metal ions, most of its uses by humans are strictly regulated e.g. it is banned in petrol, paint and pipes. However, it is widely used in metal products, cables, pipelines, paints and pesticides. Moreover, the Pb exists in the metal part of bag, wallet accessories, clothing for metal buttons, zippers and plastic buttons, stationery, sport and leisure goods in both metallic parts and holmers, including coating. When a large amount of Pb and its compounds are ingested, it has a big effect on the human body like anemia, insomnia, headache, dizziness, irritability, weakness of muscle, hallucination and renal damages [2-4]. Due to the heavy metal ions exist in industrial wastewater and other aqueous solutions, selective separation and enrichment of heavy metal ions becomes necessary. Until now, many methods including physical and chemical adsorption have been used for treatment of heavy metal ions. Especially for Pb^{2+},

although chemical precipitation [5, 6], membrane adsorption [7, 8], ion exchange [9, 10] and physical adsorption by such clay minerals, activated carbon [11, 12] and zeolite [13, 14] were reported as efficient way, they have their inherent advantages and limitations in application. In particular, these methods generally have the disadvantage of lacking selectivity in separation.

Calix[4]resorcinarene is a versatile supra molecule because of its synthetic feasibility and extensive analytical applications [15]. The molecules generally have a high melting point, high chemical and thermal stability, low solubility and low toxicity. These attributes make them attractive materials for exploring their use as molecular receptors for separation and sensing applications [16]. Since problems are remarked influencing amounts of water treatment like a membrane process, host guesting in separation membrane having calix[4]resorcinarene loading is interesting. The membrane includes an interface between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. Especially, the membrane separations have a less requirement to support with additives. So, this process can be performed isothermally at low temperatures and at low energy consumption in comparison with other thermal separation process [17]. The membrane technologies have been industrially established in impressively large scale and the most important industrial market segments are medical devices and water treatment [17, 18]. However, there has been very little research reported on host-guest membranes with calix[4]resorcinarene, although the liquid membrane process [19, 20] and polymer inclusion membrane [21, 22] of the calix[4]resorcinarene has been reported in extraction using organic solvents. Liquid membrane and polymer inclusion

membrane of calix[4]resorcinarene showed high selectively for heavy metal and cation ion, however, for use as an industrial separation process, the supported liquid membrane should be improved to be stable under a transmembrane pressure condition. In the present study, we aimed to prepare novel calix[4]resorcinarene composited membrane and properties of calix[4]resorcinarene-composited membranes for effective adsorption of heavy metal ion.

3.2 Experimental

3.2.1 Materials

Poly(ethersulfone) (PES: MW = 50,000) was produced from BASF (Lud-wigshafen, Germany). *N*-methyl-2-pyrrolidone (NMP), $Pb(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $CdSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Calix[4]resorcinarenes of S-host, V-host and PH-host were synthesized and purified according to procedures in Chapter 2.

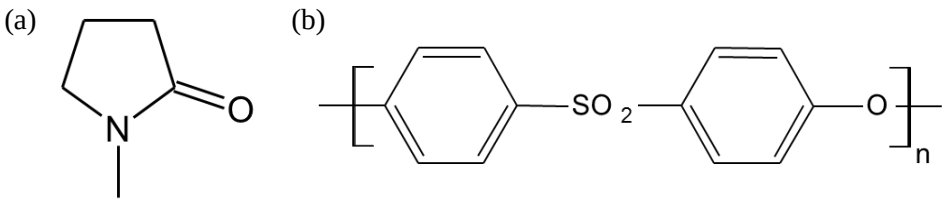


Figure 3.1 Chemical structures of *N*-methyl-2-pyrrolidone (NMP) and (b) poly(ethersulfone) (PES).

3.2.2 Preparation of the calix[4]resorcinarene-composited membranes

To prepare solid membranes consisting of the S-host, V-host and PH-host, a phase inversion membrane scaffold was adopted as in our previous method [23]. Kobayashi et al. reported membrane scaffold for molecularly imprint membranes [24]. In the present study, calix[4]resorcinarene composited membranes were reported as new functional membrane adsorbents. As shown in Figure 3.2, for the preparation of membrane containing the calix[4]resorcinarene, the S-host, V-host and PH-host were dissolved at 50 ℃ for 1 hour in

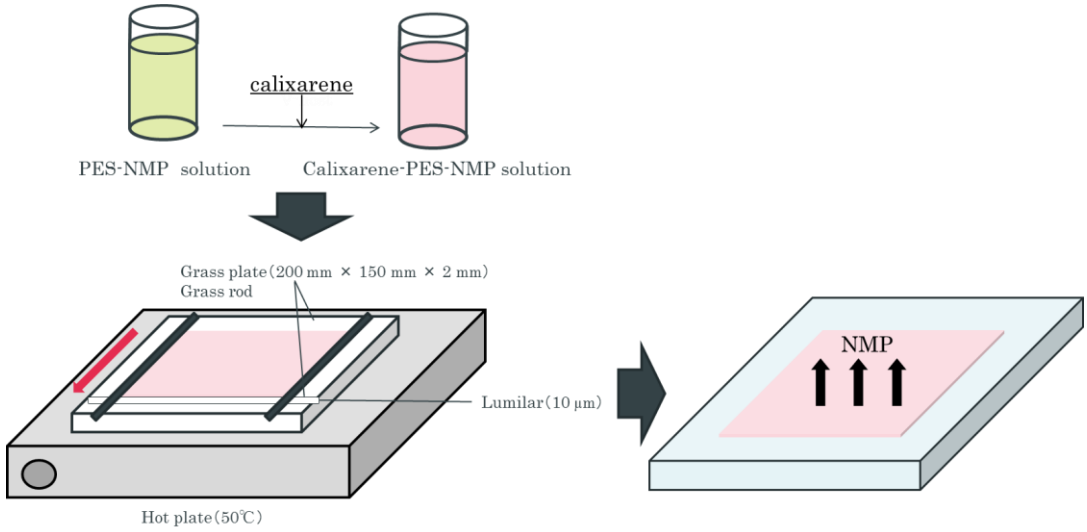


Figure 3.2. Production process of the calix[4]resorcinarene composited membranes.

Table 3.1 Components of the calix[4]resorcinarene composited membranes.

20 wt% PES-NMP solution (g)	Calix[4]resorcinarene (g)	Calix[4]resorcinarene composited membrane (wt%)
20	0	0
	0.4	10
	1.0	25
	2.0	50
	2.4	60

PES 20 g and NMP 80 g, respectively. Each component of the calix[4]resorcinarene composited membranes was shown in Table 3.1. Then, the solution was spread on glass plate (200 mm×150 mm×2 mm) at 50 ℃and soaked with water at 25 ℃. Since liquid-solid transformation was occurred in the water medium to remove the NMP solution, the calix[4]resorcinarene was added in the membrane. The pink color polymer membrane (15 cm×10 cm) was washed by water 3 times. Finally, the obtained membrane, S-host composited membrane, V-host composited membrane and PH-host composited membrane were dried at 0.2 mmHg for 24 h in a vacuum. The morphology of the composited membranes was observed by using a scanning electron microscope (SEM, JSM-5300 LV; JEOL, Japan) after gold coating using a quick cool coater (Sanyu Denshi K.K, Japan). Analysis of the calix[4]resorcinarenes in PES membrane was carried out using Fourier transform infrared (FT-IR) spectroscopy (FT-IR 4100 series, Jasco Corp. Japan) over a frequency range 700–4000 cm^{-1}. The tensile strength of the obtained membrane 3.0 cm×2.0 cm was measured by using PCH-500N-0.12 (Minebea, Japan). Single-point BET surface areas of the membrane were measured using a Micromeritics Tristar II (Shimadzu, Japan). The membranes were cut to 1 cm×1 cm for measurement of BET surface area.

3.2.3 Binding experiments for single and quarterly mixture of heavy metal ions through the host-guest membranes

The batch binding experiment was carried out in the presence of the S-host, V-host and PH-host composited membranes (diameter 45 mm, thickness 70-90 μm) in 20 ml of aqueous solution containing each 20 ppm of Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+}, respectively. Firstly,

the effect of the pH was investigated by running a different pH values in the range of 3.0 to 9.0. A 0.05 g calix[4]resorcinarene powder such as S-host, V-host and PH-host was added to a 20 mL of each heavy metal ion solution with initial concentration of 20 ppm in glass holder. Then, the holder was shaken at 25 ℃ for 12h by using TS-200 Shaking bath (Advantech, Taiwan). The calix[4]resorcinarene was filtered and the aqueous solution of the filtrate was measured by using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan) to determine the final heavy metal ion concentration. Adsorptivity of the calix[4]resorcinarene powder at different pH value for the interfering metal ion was evaluated using the equation (2-1). After determining the optimum pH condition of adsorption experiment, similar batch binding experiment was carried out for each calix[4]resorcinarene composited membranes. Adsorptivity of the calix[4]resorcinarene composited membranes for the interfering metal ion was also evaluated using the equation (2-1). Here, the weight of the calix[4]resorcinarene composited membrane (g) was used as W in the Eq.(2-1). The unit for the adsorption capacity, q_e was similarly μmol/g. The wavelength of the emission line for Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} was 283.3, 232.2, 324.8 and 228.8 nm, respectively.

3.2.4 Permeation binding experiments for single and quarterly mixture of heavy metal ions through the host-guest membranes

A membrane permeation experiment was carried out according to our previous reports [25]. Single or quarterly mixture of aqueous heavy metal ions was permeated through the S-host composited membrane, V-host composited membrane and PH-host composited membrane, respectively. The standard aqueous solutions of Pb^{2+}, Ni^{2+}, Cu^{2+}

and Cd^{2+} were used in the 20 ppm concentration for each permeation. The perm-selective experiments were performed, when 0.05 g of the membrane was set into Amicon cell folder MA01730, Millipore Corp., USA, operated under 4.0×10^4 Pa applied pressure (Figure 3.3). In the present work, it was convenient to adjust the volume flux of a flowing aqueous solution to 1.0 ml/min the permeation through the membrane. The concentrations of remaining heavy metal ions Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} were measured for a permanent solution, after the permeation was finished in 20 minutes. Then, the atomic adsorption spectrophotometer was used for each heavy metal ions detection.

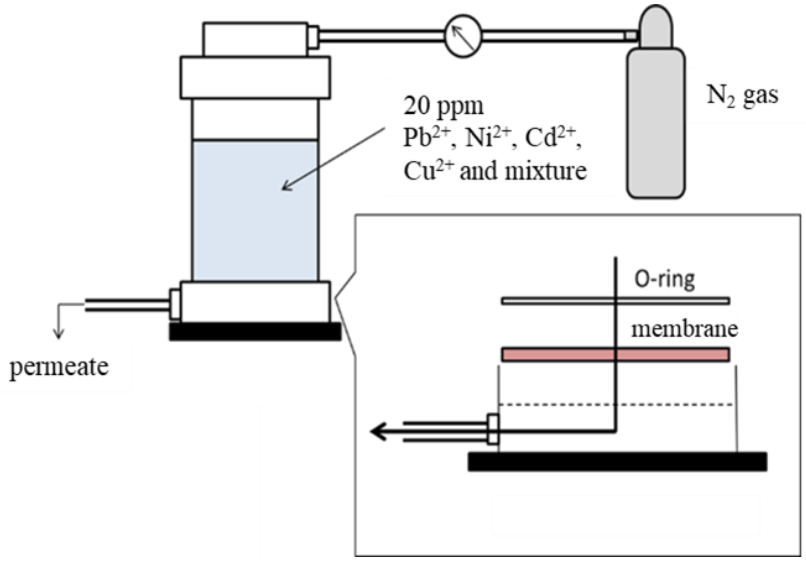
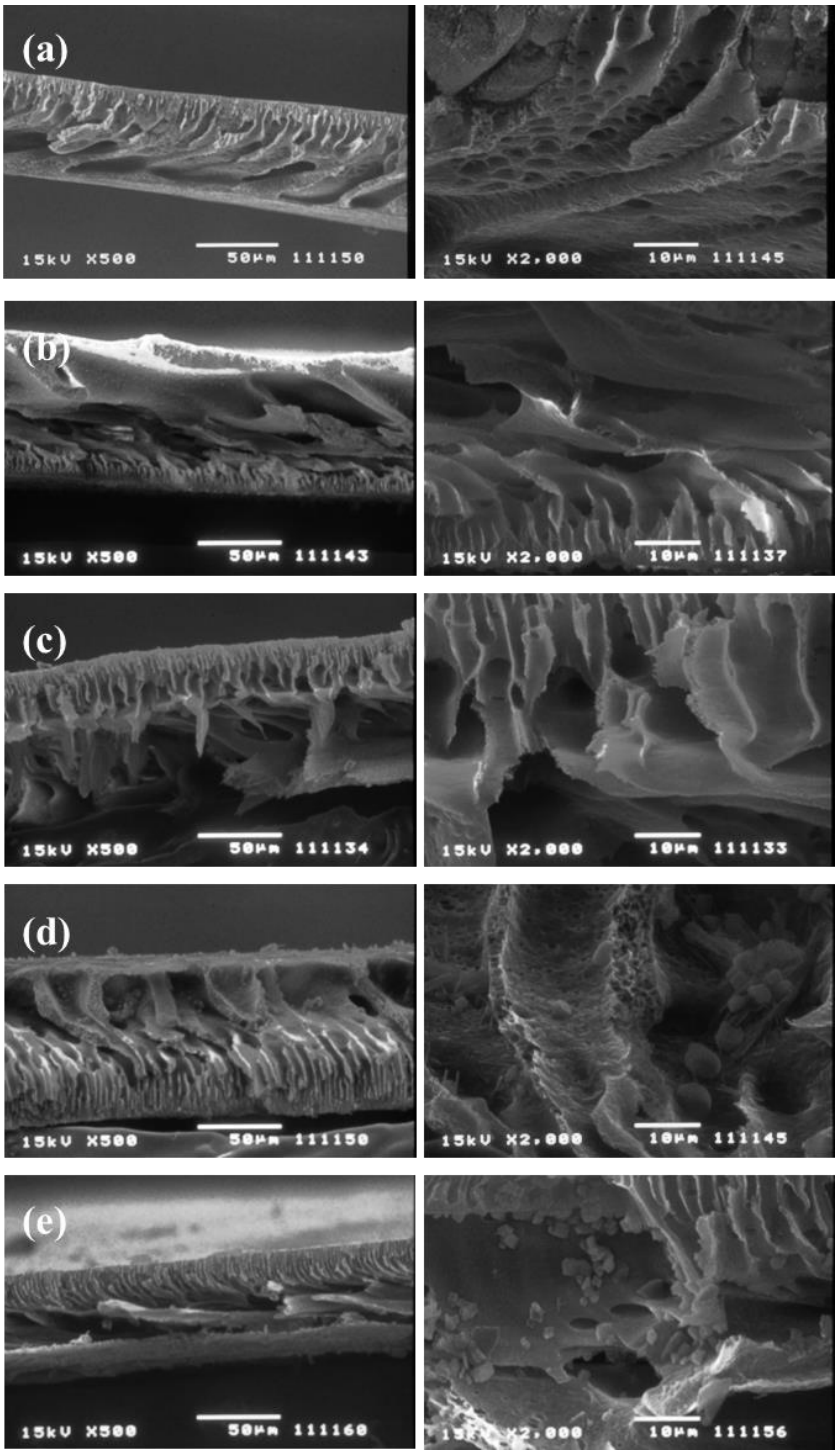


Figure 3.3 Drawing experimental apparatus of perm-selective binding by using dead end filter.

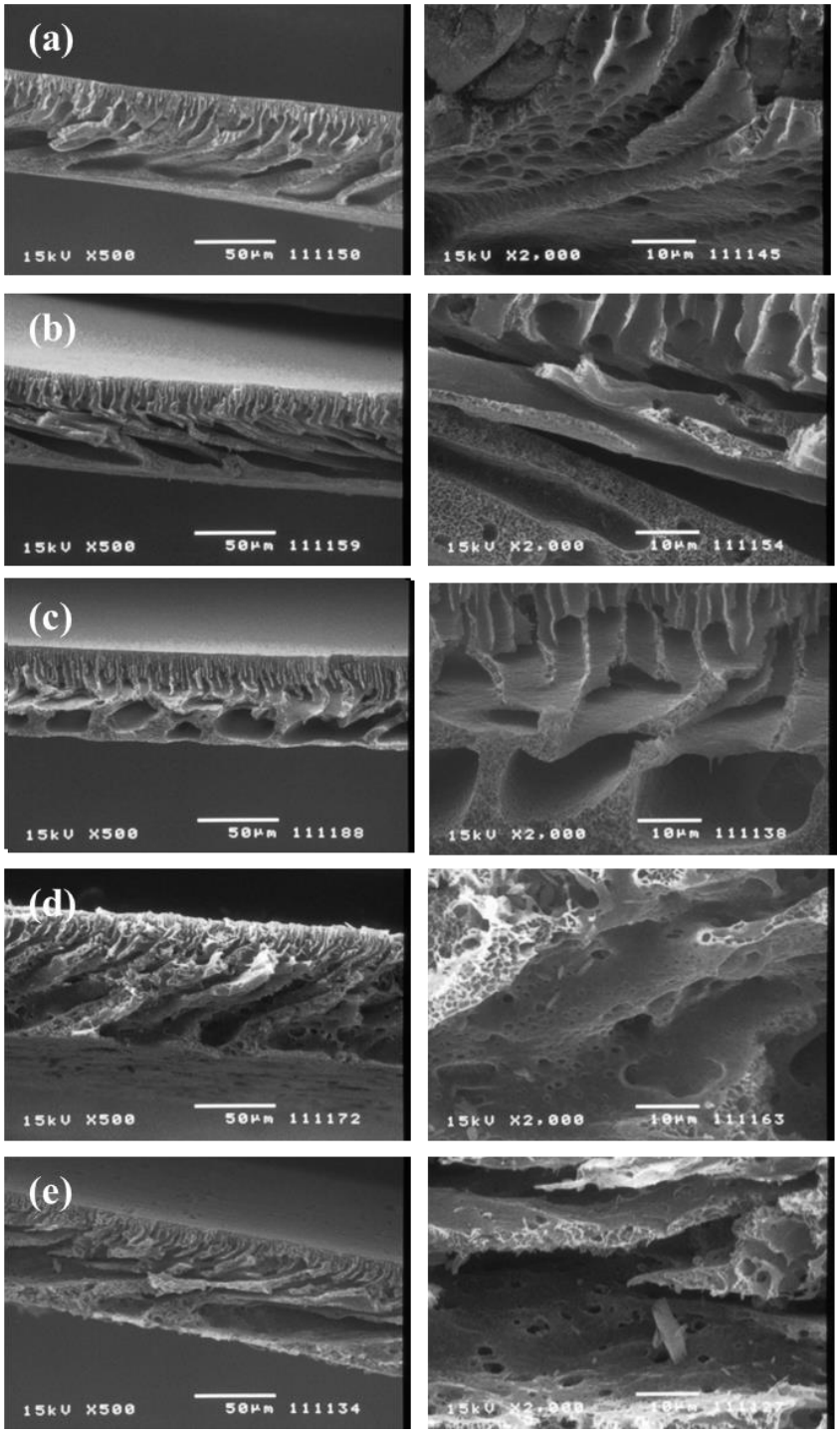
3.3 Results and discussion

3.3.4 Characterization of calix[4]resorcinarene composited membranes

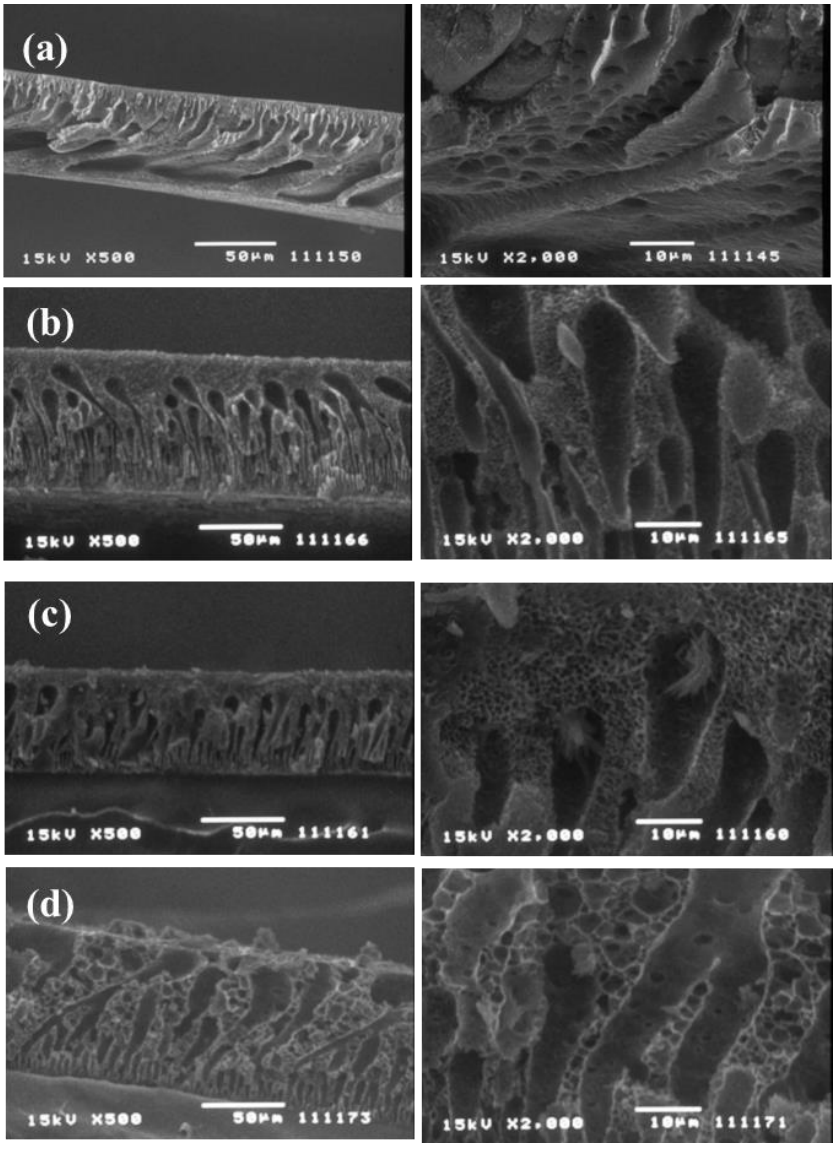
In the phase inversion process, the 20 wt% PES-NMP solution containing various concentrations (0, 10, 25, 50 and 60 wt%) calix[4]resorcinarenes, S-host and V-host as the host were used in the membranes. However, in the case of the PH-host, we could not prepare 60 wt% PH-host composited membrane. This is because the PH-host showed less solubility for NMP, therefore, 60 wt% PH-host-PES-NMP solution could not prepared. So, in 0, 10, 25 and 50 wt% PH-host concentration, the composited membranes were prepared except for 60 wt%. Figures 3.4, 3.5 and 3.6 show the morphology images of PES and the obtained S-host composited membrane, V-host composited membrane and PH-host composited membrane. It was shown that the membrane morphology of PES without the calix[4]resorcinarene was porous and had a finger-like structure. It was supported that the phase inversion and the solidification were initiated by a transition of the grown liquid condition of the NMP polymer solution to two liquid phases of the solution and coagulation solution. Therefore, the picture presented that the liquid–liquid demixing was quickly occurred by first solution exchange [26]. In contrast, the calix[4]resorcinarene composited membranes containing (b) 10 wt%, (c) 25 wt%, (d) 50 wt% and (e) 60 wt% loading of the calixarene had almost similar SEM images in the porous structure with the thickness about 90 μm. In addition, with increasing loading of the calix[4]resorcinarene, the membrane morphology was changed like a sponge in the PES scaffold portion. But the finger portion looked like less change in the cross section. Thus, the higher calix[4]resorcinarene contents in the NMP solution created sponge-like structure of the membrane, meaning that the



Figures 3.4 SEM images of (a) PES membrane and S-host composited membranes with (b) 10 wt%, (c) 25 wt%, (d) 50 wt% and (e) 60 wt% loading.



Figures 3.5 SEM images of (a) PES membrane and V-host composited membranes with (b) 10 wt%, (c) 25 wt%, (d) 50 wt% and (e) 60 wt% loading.



Figures 3.6 SEM images of (a) PES membrane and PH-host composited membranes with (b) 10 wt%, (c) 25 wt% and (d) 50 wt% loading.

aggregation of PES in water medium was retarded in the presence of the calix[4]resorcinarene. To confirm the interaction of PES and the calix[4]resorcinarene in the composited membrane, FT-IR spectra of their composited membranes were measured. As shown in Figures 3.7, 3.8 and 3.9, the bands appearing from 1100 to 1238 cm^{-1} and from 1103 to 1149 cm^{-1} were attributed to $>S(=O)_2$ stretching vibration of PES and it could be seen in the spectrum of calix[4]resorcinarene composited membranes. In addition, in the case of S-host, for the 1650-1700cm^{-1} region, the peak of A of PES (b) with composited membranes shifted toward shorter wavenumber side for B at 1674 cm^{-1} and C at 1658 cm^{-1} in 10 and 60 wt% loading of the S-host, respectively. Both of the V-host and PH-host composited membranes, each peak of A of PES shifted toward shorter wavenumber side in loading of the V-host or PH-host in the composited membrane. It was revealed that the S=O groups of the PES were interacted with the calix[4]resorcinarenes in the composite membrane. In addition, the appearance of 1510 cm^{-1} and 1600 cm^{-1} band of C=C stretching vibration in all calix[4]resorcinarene composited membrane represented the presence of the calix[4]resorcinarene in the membrane. These indicated that the S-host, V-host and PH-host were properly composited in PES membrane, respectively. Table 3.2 include the data of tensile strength, water content and BET surface area of each calix[4]resorcinarene composited membrane. The tensile strength of the composited membrane was decreased, when the loading of the calix[4]resorcinarene was increased. The water content (WC) was evaluated by the following equation (3-1):

$$WC = (([W]_{after} - [W]_{before})/[W]_{before}) \times 100 \qquad (3\text{-}1)$$

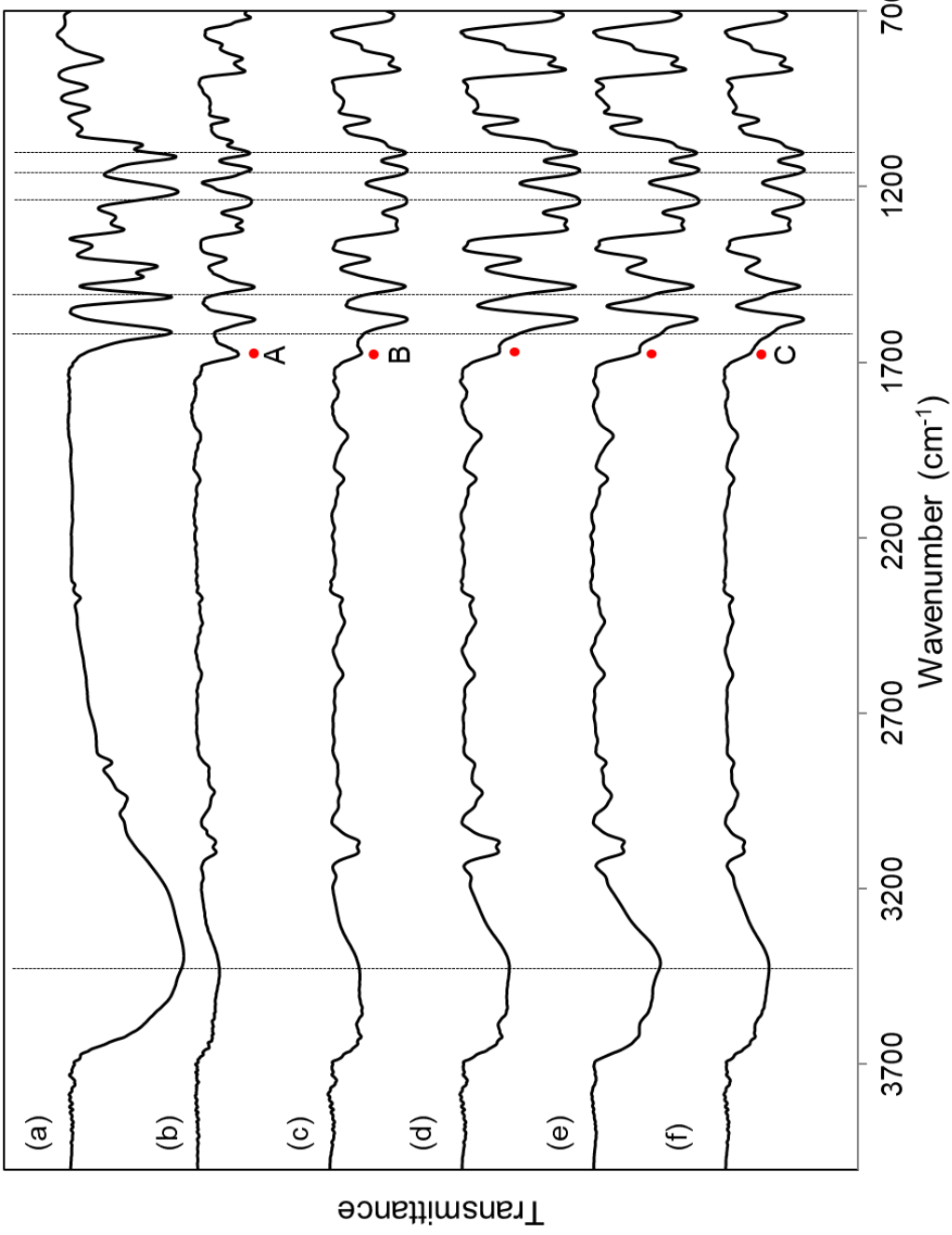


Figure 3.7 FT-IR spectra of (a) S-host, (b) PES and S-host composited membranes with (c) 10 wt%, (d) 25 wt%, (e) 50 wt% and (f) 60 wt% loading.

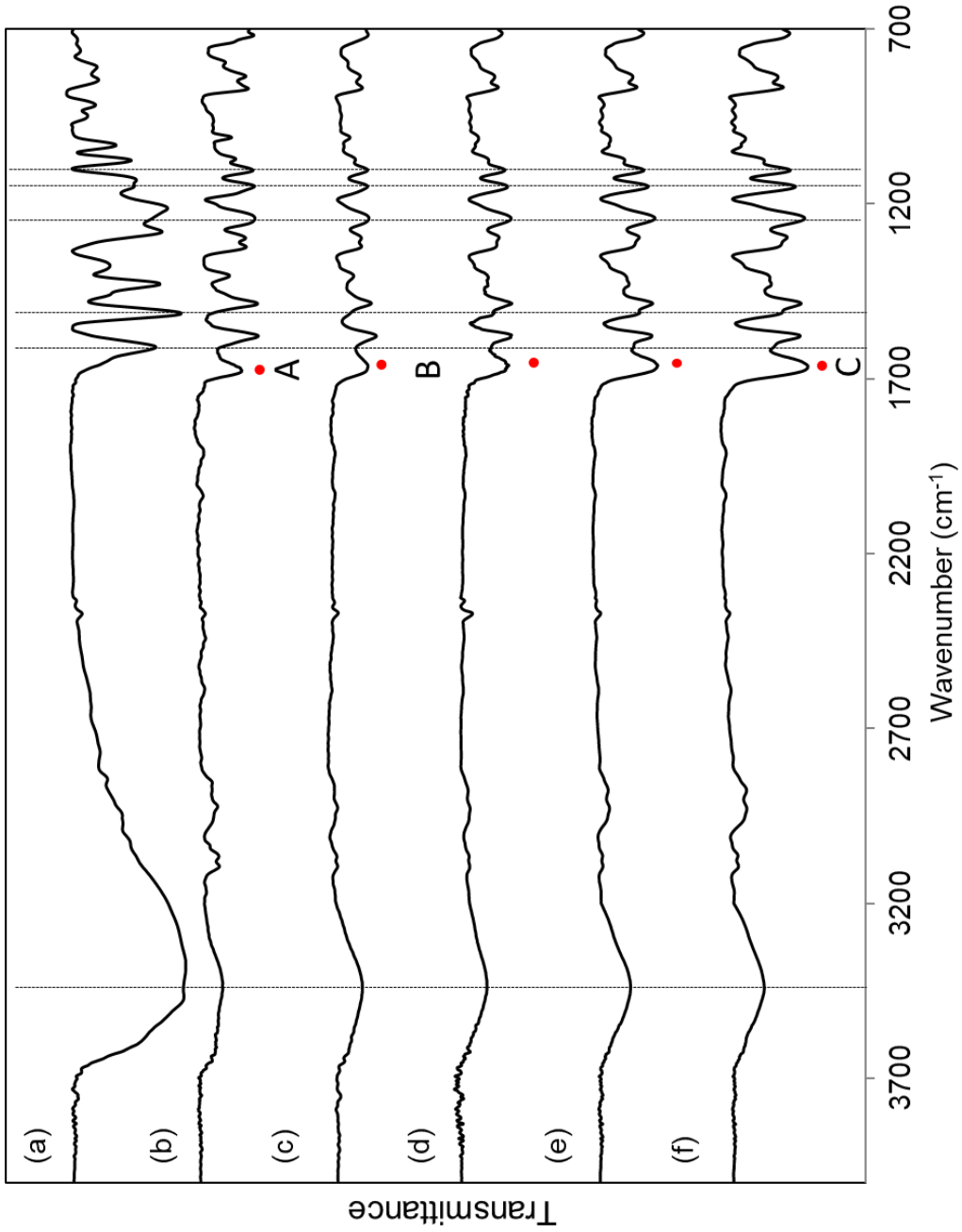


Figure 3.8 FT-IR spectra of (a) V-host, (b) PES and V-host composited membranes with (c) 10 wt%, (d) 25 wt%, (e) 50 wt% and (f) 60 wt% loading.

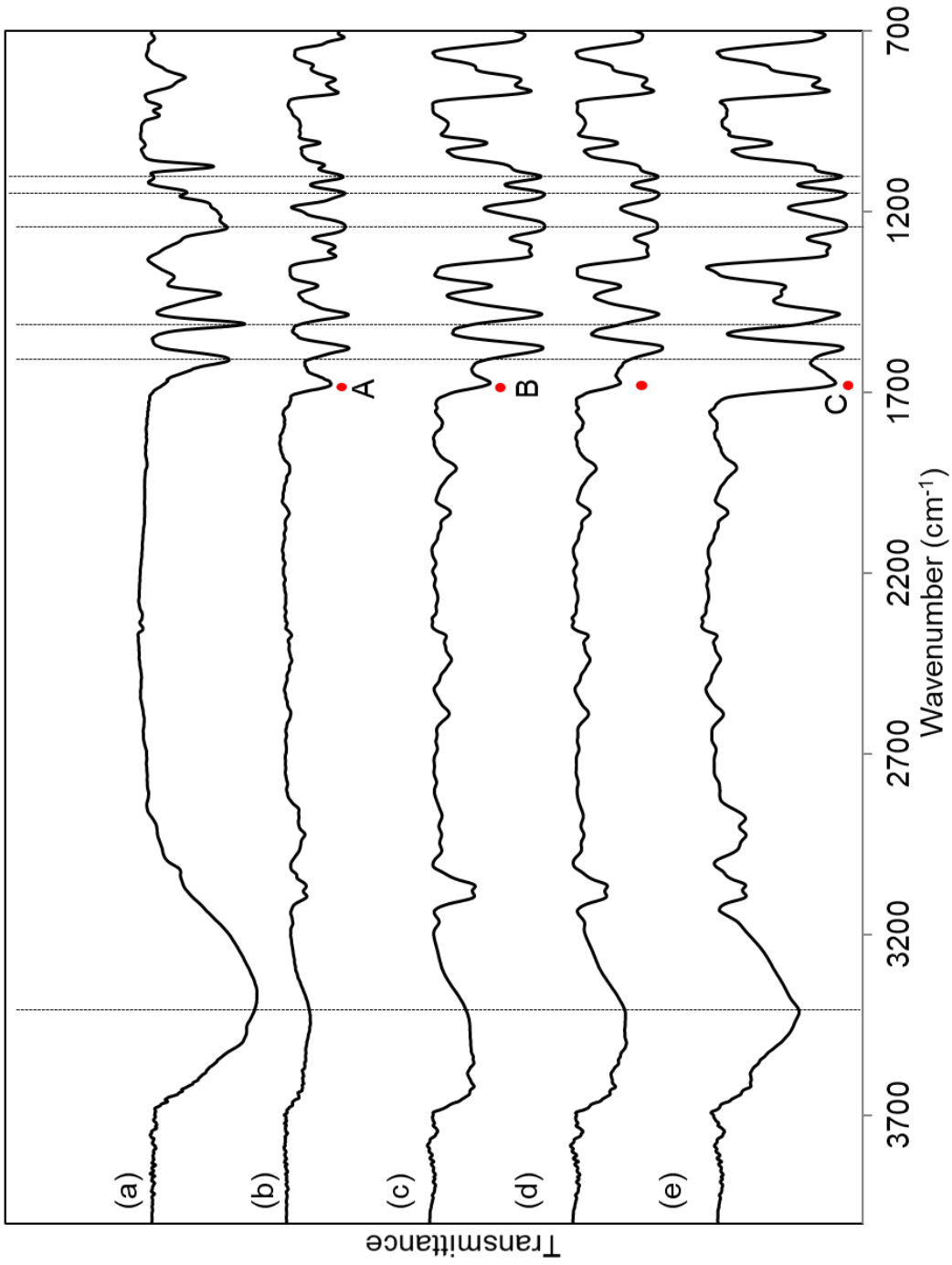


Figure 3.9 FT-IR spectra of (a) PH-host, (b) PES and PH-host composited membranes with (c) 10 wt%, (d) 25 wt% and (e) 50 wt% loading.

Table 3.2 Tensile strength, water content and BET surface area of calix[4]resorcinarene composited membranes with 10 wt%, 25 wt%, 50 wt% and 60 wt% loading of each calix[4]resorcinarene.

Host	Loading (wt%)	0	10	25	50	60
S-host	Tensile strength (MPa)	3.32 ± 0.38	2.57 ± 0.21	2.32 ± 0.11	2.02 ± 0.22	1.67 ± 0.16
	Water content (%)	42	214	301	358	337
	BET surface area (m^2/g)	12.3	16.3	17.6	13.9	13.5
V-host	Tensile strength (MPa)	3.32 ± 0.38	3.25 ± 0.47	2.36 ± 0.13	2.02 ± 0.11	1.95 ± 0.05
	Water content (%)	42	244	375	372	371
	BET surface area (m^2/g)	12.3	17.6	18.5	16.6	15.4
PH-host	Tensile strength (MPa)	3.32 ± 0.38	2.47 ± 0.59	2.38 ± 0.29	1.84 ± 0.41	-
	Water content (%)	42	79.0	129	204	-
	BET surface area (m^2/g)	12.3	16.3	16.4	15.9	-

where $[W]_{before}$ and $[W]_{after}$ represents the weight of the calix[4]resorcinarene composited membrane before and after soaking in water. Before we weigh the calix[4]resorcinarene composited membrane, it was wiped off moisture on surface of membrane. It was noted that the value of water content became high, when the 50-60 wt% of each calix[4]resorcinarene was loaded in the membrane. The values were higher than that of 100 % for the loading membranes. This meant that the porous volume in their membranes easily took water. This also suggested that the introduction of the calix[4]resorcinarene consisting of OH groups led to the improvement in water access. Thus, the calix[4]resorcinarene loading in the membrane changed the hydrophilic city of the composited membrane, even though the scaffold PES had hydrophobic nature. In order to analyze porous properties of the calix[4]resorcinarene composited membranes, the BET surface area was evaluated by nitrogen adsorption to the dried membranes. As the calix[4]resorcinarene loading was increased about 25 wt% in the membrane, the surface area was gradually increased. For example, the maximum BET surface area of S-host, V-host and PH-host composited membranes are 17.6, 18.5 and 16.4 m^2/g, respectively, when each calix[4]resorcinarene was loaded 25 wt% in the membrane. When the calix[4]resorcinarene loading was changed from 25 to 60 wt%, the values of BET surface area were decreased. This might be changed in the sponge-like structure of the membrane as seen from SEM images, for 50 and 60 wt% of the calix[4]resorcinarene loading. Figures 3.10, 3.11 and 3.12 show nitrogen adsorption isotherm of the PES membrane and each calix[4]resorcinarene composited membrane. According to their adsorption behavior, the PES membrane and S-host, V-host and PH-host composited membranes belonged to type II

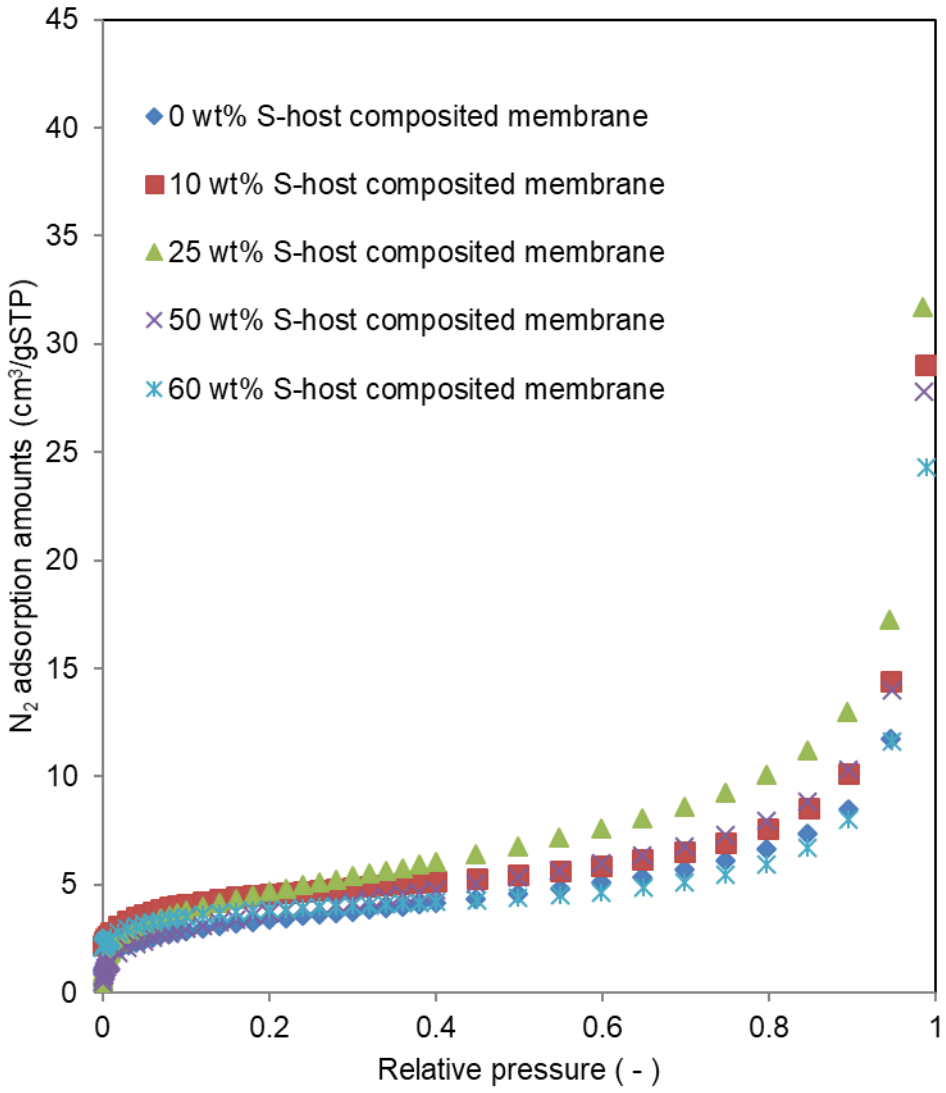


Figure 3.10 Nitrogen adsorption isotherm of PES membrane and the composited membranes having 10 wt%, 25 wt%, 50 wt% and 60 wt% loading of the S-host.

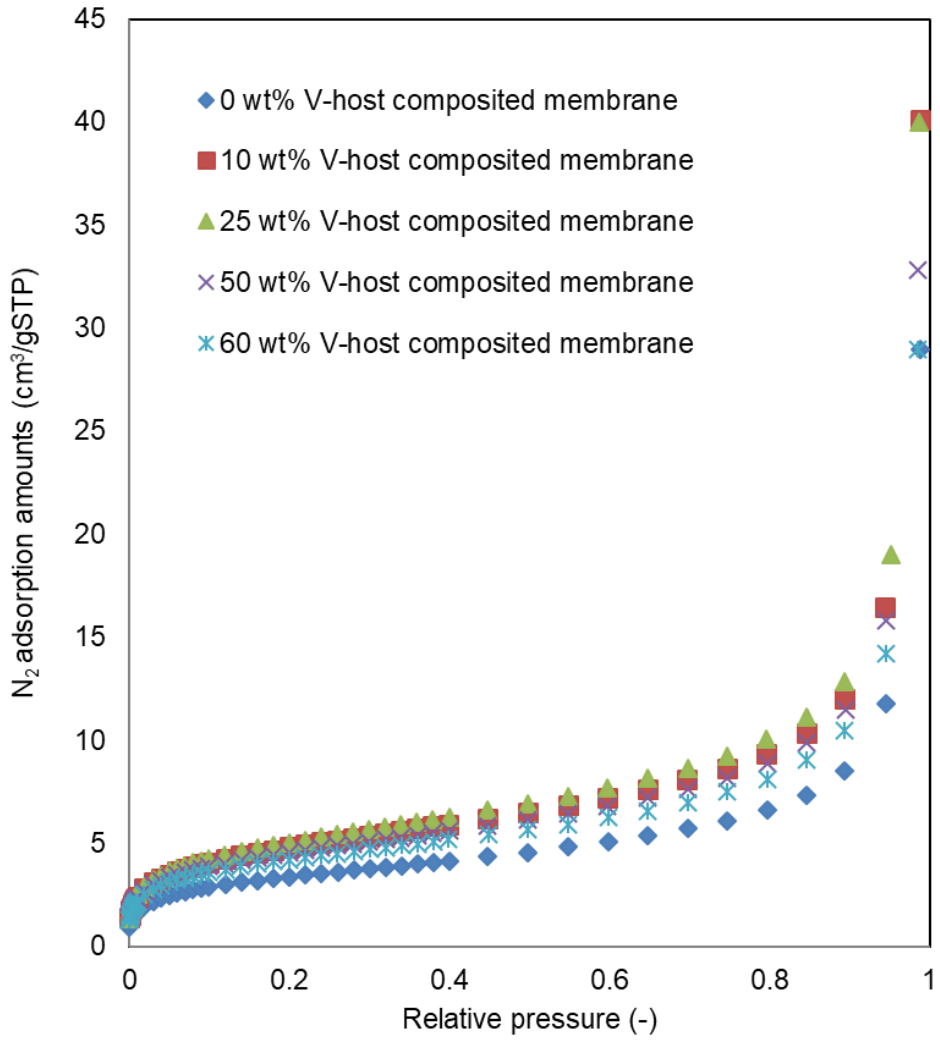


Figure 3.11 Nitrogen adsorption isotherm of PES membrane and the composited membranes having 10 wt%, 25 wt%, 50 wt% and 60 wt% loading of the V-host.

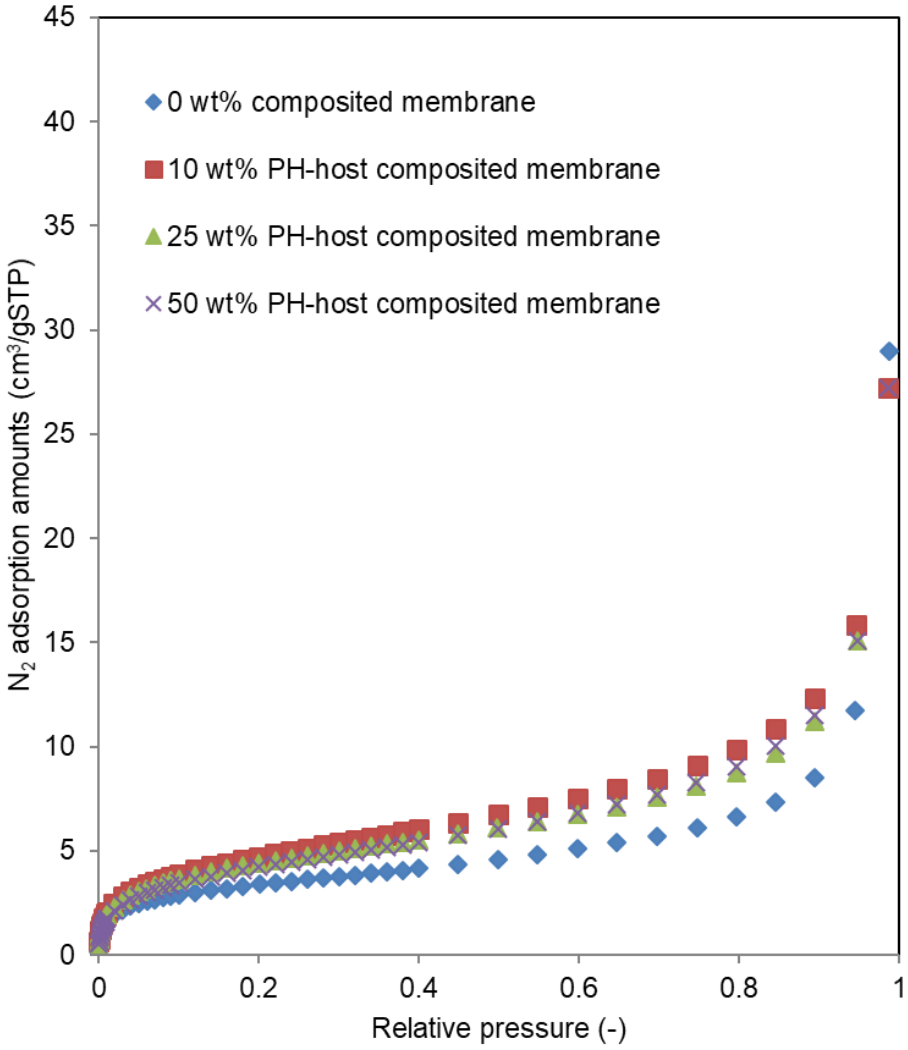


Figure 3.12 Nitrogen adsorption isotherm of PES membrane and the composited membranes having 10 wt%, 25 wt% and 50 wt% loading of the PH-host.

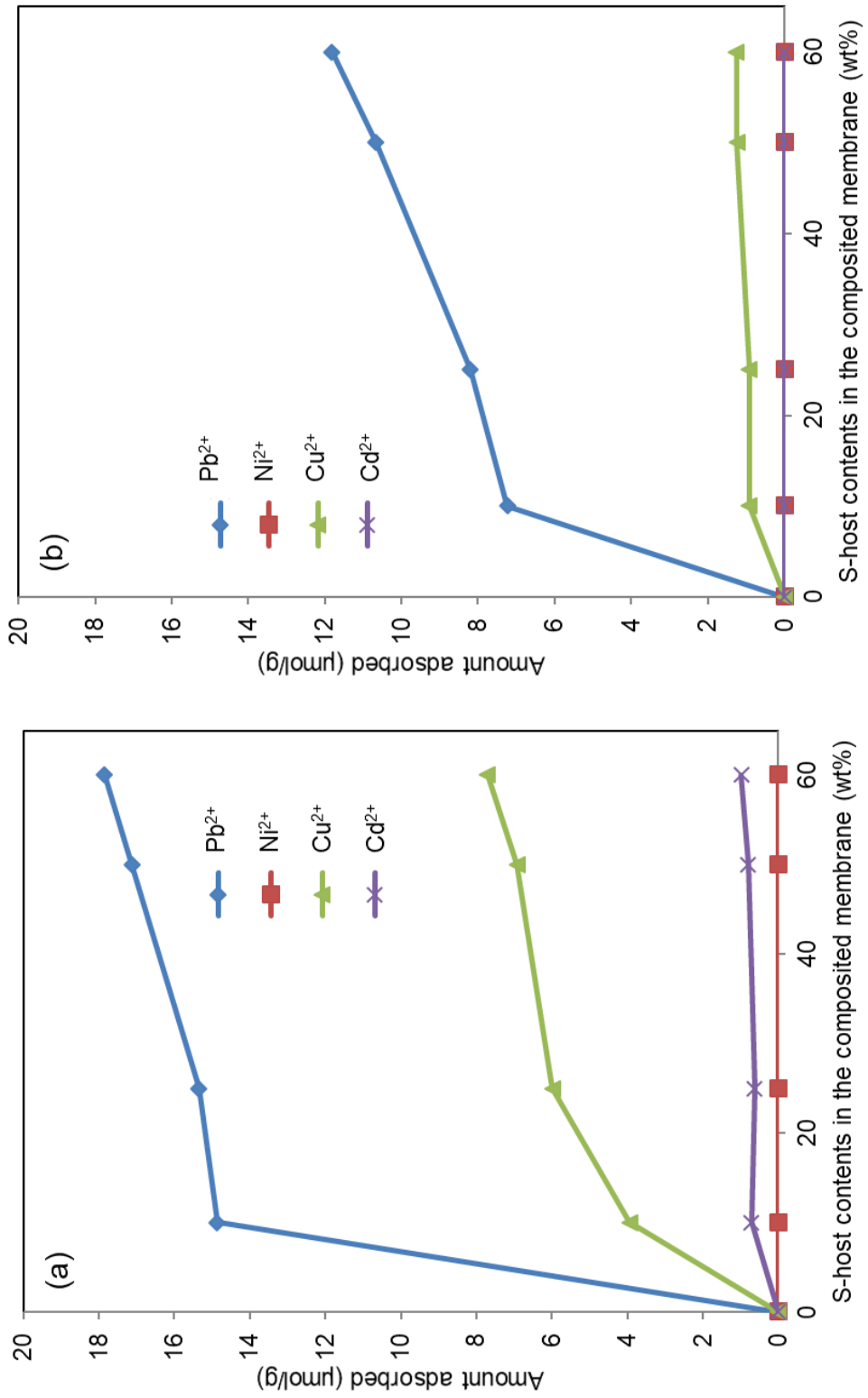
isotherms [27], which meant that the membranes consisted of macroporous structures. Compare the results of PES membrane with calix[4]resorcinarene composited membranes, the PES membrane had lower capacity of the N_2 adsorption amounts than each calix[4]resorcinarene composited membrane. It was also seen that, as the S-host, V-host and PH-host loading was increased in the membrane, the N_2 capacity amounts tend to be increased. However, when the S-host and V-host were added more than 50 wt%, the value of the N_2 capacity was decreased.

3.3.5 Binding experiments of the calix[4]resorcinarene composited membranes

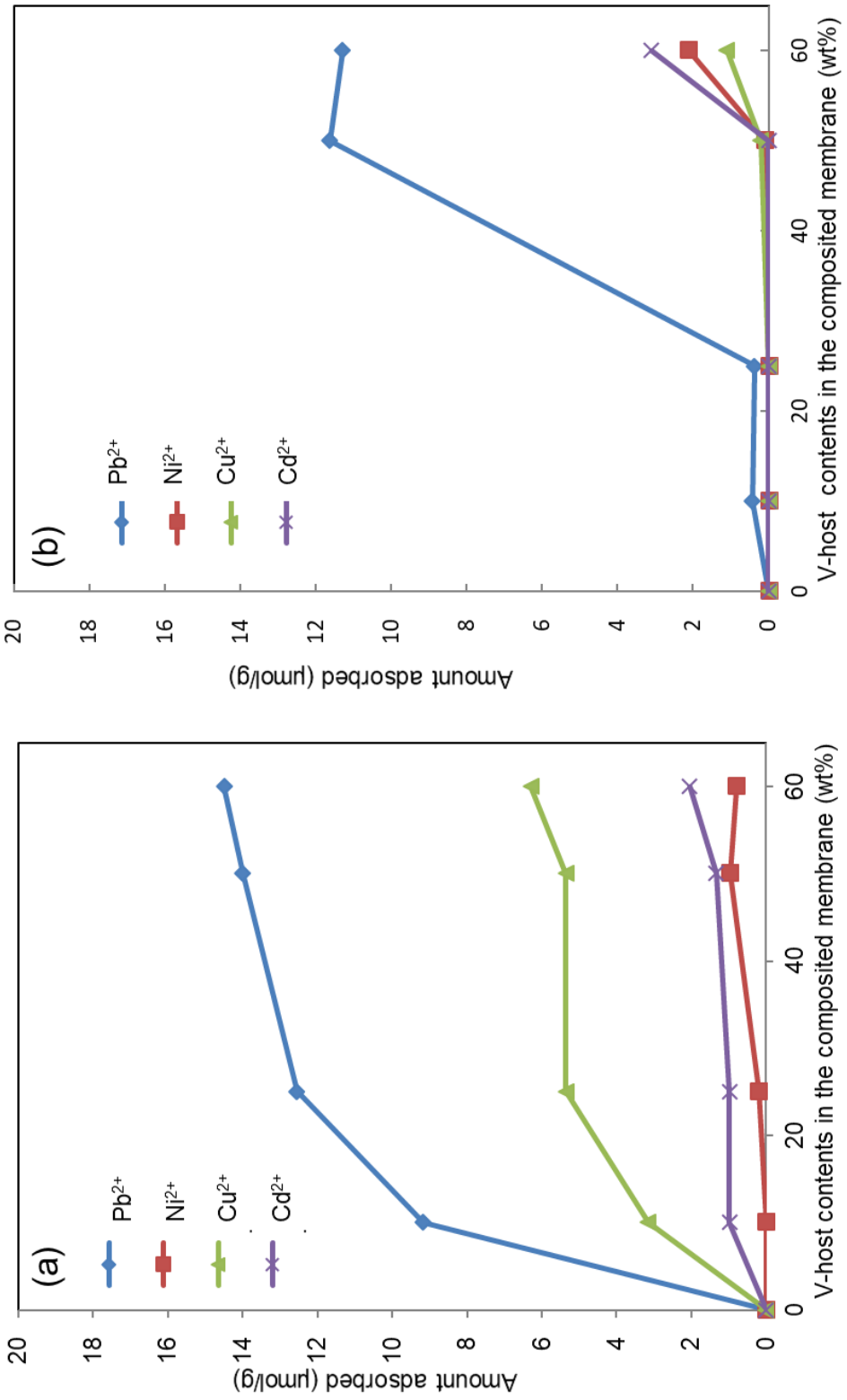
In the adsorption study of heavy metal ions, pH is one of the important parameters. As a result of adsorption experiment at different pH values (3, 5, 7 and 9) by using calix[4]resorcinarene powders, it was concluded that optimum condition was pH 5 in high adsorptivity. In acidic condition, the adsorption capacity of calix[4]resorcinarenes were relatively low. Increasing the pH enhanced the capacity until the pH 5 and the higher pH led to the decrease of adsorption capacity. These results might be explained by considering the electronic interaction between the adsorbent and the speciation of metal ions [28] at the different pH value. In terms of metal speciation, Pb^{2+}, Ni^{2+} and Cd^{2+} are mainly present under pH 6. By contrast, Cu^{2+} can be found under pH 2 and 4, respectively. Such calix[4]resorcinarenes, S-host, V-host and PH-host mostly contained OH groups as the binding site. Phenol is a weak acid (pKa is 9.95 in water) which will be mainly existed as its protonated form ($R\text{-}OH^{2+}$) at low pH. Increasing the pH may decrease the degree of protonation and led to the formation of free phenol (R-OH) [29]. The adsorbent and metal ions are present as positively charged species at low pH, so electrostatic repulsion occurs

and the adsorption capacity may decrease. In addition, protons may bind to the active site of the adsorbent in significant competition with metal ions. At higher pH values, adsorption capacity tended to increase due to the relatively large amount of free phenol that could coordinate with metal ions [29].

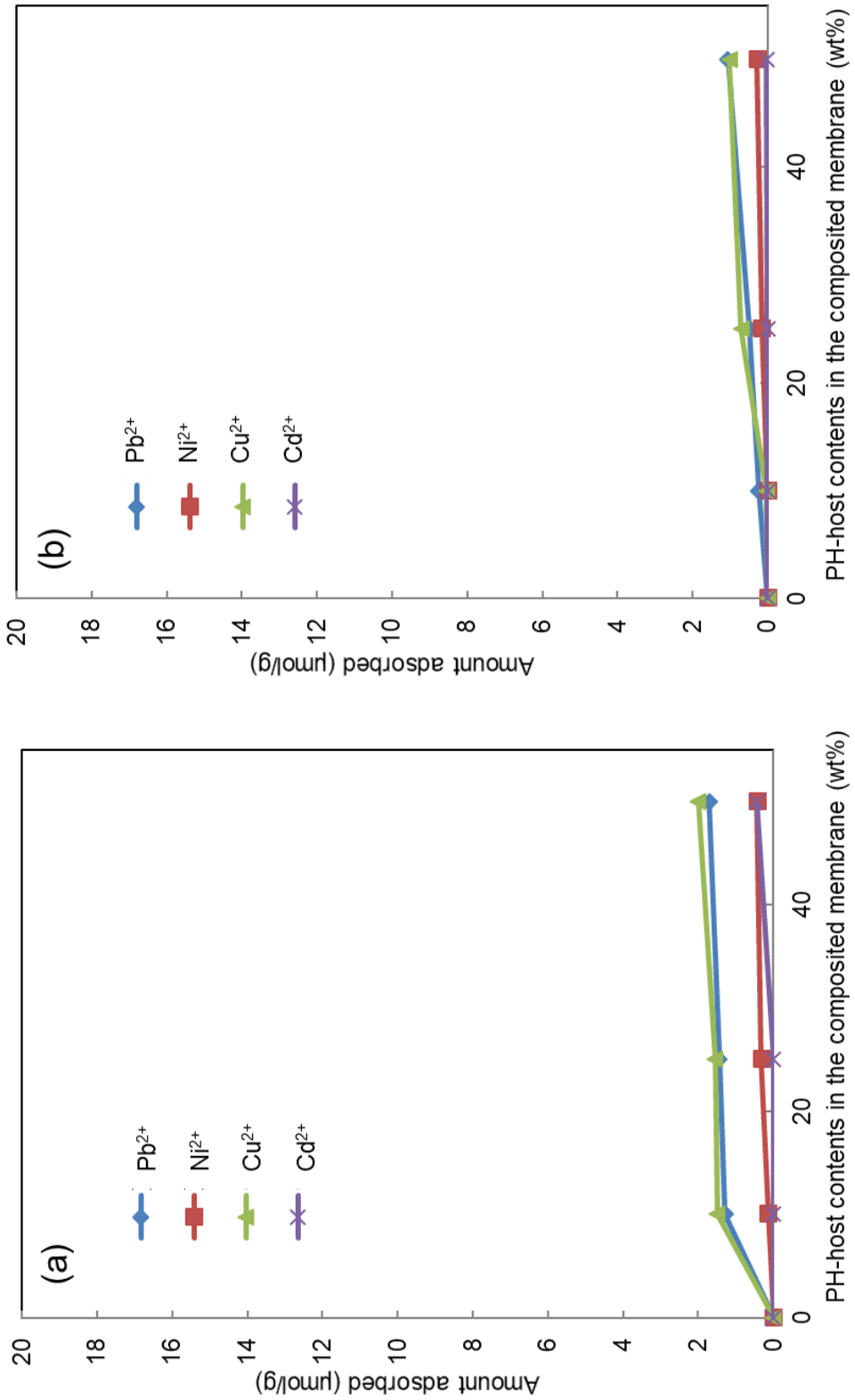
Similar batch binding experiment was performed to the calix[4]resorcinarene composited membranes. Figures 3.13(a), 3.14(a) and 3.15(a) show binding amounts of heavy metal ions on each adsorbent in single solution of Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} with 20 ppm concentration. The pH condition of their heavy metal ion solutions was controlled at pH5 by HCl and NaOH. Again, in the loading the membrane, apparently, the S-host composited membrane and V-host composited membrane showed higher adsorption of Pb^{2+}. With increasing the calix[4]resorcinarene loading in the membrane, the value of the adsorption amounts of Pb^{2+} was increased. For example, in non-loaded case, the PES membrane had no binding to the Pb^{2+} and other ions. However, ions of Ni^{2+}, Cu^{2+} and Cd^{2+} were less adsorbed. To confirm the effect of the heavy metal ions on the hosting properties, permeation experiments of each ion solute were carried out as shown in Figures 3.13(b), 3.14(b) and 3.15(b). The experiments were carried out at 20 ppm concentration in each heavy metal ion case. Here, the applied pressure of the permeation driving force was 4.0×10^4 Pa. It was noted that Pb^{2+} ion was highly taken by the S-host composited membrane and V-host composited membrane in the case of permeation experiment. When the calix[4]resorcinarene loading in the membrane was increased, there was a tendency to increase the binding of the Pb^{2+} ion to the membrane. It was apparent that the 60 wt% loading showed high rejection to the Pb^{2+} ion relative to other Ni^{2+} and Cu^{2+} ions. For the



Figures 3.13 Amounts adsorbed of heavy metal ions on each S-host composited membrane in single solution for (a) batch method and (b) permeation method.



Figures 3.14 Amounts adsorbed of heavy metal ions on each V-host composited membrane in single solution for (a) batch method and (b) permeation method.



Figures 3.15 Amounts adsorbed of heavy metal ions on each PH-host composited membrane in single solution for (a) batch method and (b) permeation method.

mixture solution of each ion with 20 ppm concentration, all of the calix[4]resorcinarene composited membranes had no binding capacity to the Ni^{2+}, Cu^{2+} and Cd^{2+}, except for Pb^{2+} ion was rejected in the permeation for each calix[4]resorcinarene composited membrane (Table 3.5). Although the values of the adsorption amount for the Pb^{2+} were decreased one order to be 11 and 12 (μmol/g-membrane) for the 50 and 60 wt% of the S-host loading, respectively, the separation performance of Pb^{2+} binding was observed.

Consequently, these phenomena might be explained in terms of the different number of active sites of hydroxy group (-OH) and methoxy group ($-OCH_3$) on calix[4]resorcinarene more dispersed along the polymer chain. From the pH study, it was indicated that there was an adsorption competition between the proton (H^+) and metal ions Pb^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} that causes the metal ions adsorbed by the calix[4]resorcinarene. Especially, the adsorbent of the S-host and V-host contained additional methoxy groups, which might be responsible for the effectiveness of hosting sites of heavy metal ion compared with PH-host contained only hydroxyl groups for the capture of metal ions. Therefore, the adsorption amount of heavy metal ion on PH-host having no methoxy group was lower than that of them on S-host and V-host having four and eight methoxy groups.

The adsorption selectivity of calix[4]resorcinarene for heavy metal ions followed the order $Pb^{2+} > Cu^{2+} > Ni^{2+} \cong Cd^{2+}$. The order might be explained depending on ease of making complexes of heavy metals and OH groups. According to the HSAB theory [30] the phenol groups on the calix[4]resorcinarene was classified as a hard base. Pb^{2+}, Cu^{2+} and Ni^{2+} were moderate acid while Cd^{2+} was soft acid. Especially, compared to Cu^{2+} and Ni^{2+}, Pb^{2+} is more likely to form a complex with an OH group (Figure 3.16).

Figure 3.5 Binding amount of mixture of heavy metal ions to each calix[4]resorcinarene composited membrane by using batch method and perm-selective method.

Sample	Maximum binding amount of mixture of heavy metal ion(μmol/g)							
	Pb^{2+}		Ni^{2+}		Cu^{2+}		Cd^{2+}	
	Batch	Permeation	Batch	Permeation	Batch	Permeation	Batch	Permeation
10 wt% S-host composited membrane	**11**	**7.2**	0	0	**0.91**	**0.063**	0	0
25 wt% S-host composited membrane	**14**	**8.2**	0	0	**1.1**	**0.23**	0	0
50 wt% S-host composited membrane	**15**	**11**	0	0	**2.0**	**1.2**	**0.18**	0
60 wt% S-host composited membrane	**15**	**12**	0	0	**2.3**	**1.3**	**0.27**	0
10 wt% V-host composited membrane	0	0	0	0	0	0	0	0
25 wt% V-host composited membrane	0	0	0	0	0	0	0	0
50 wt% V-host composited membrane	**3.5**	**1.8**	0	0	**1.1**	0	0	0
60 wt% V-host composited membrane	**4.3**	**2.1**	0	0	**1.7**	0	0	0
10 wt% PH-host composited membrane	0	0	0	0	0	0	0	0
25 wt% PH-host composited membrane	0	0	0	0	0	0	0	0
50 wt% PH-host composited membrane	**1.7**	**1.4**	0	0	0	0	0	0

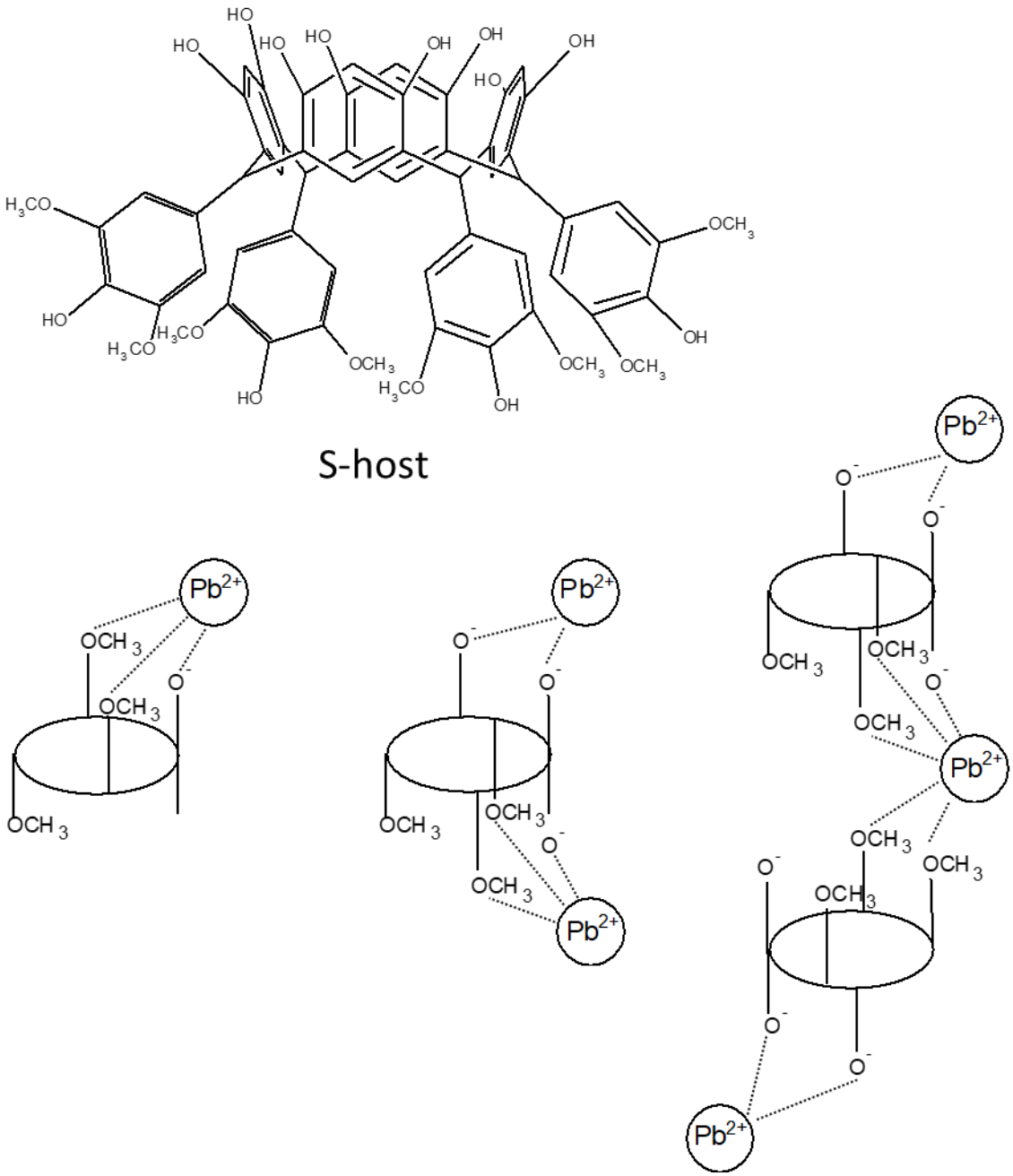


Figure 3.16 S-host-Pb^{2+} ion complex.

3.4 Conclusion

Novel calix[4]resorcinarene composited membranes were successfully prepared from PES and NMP by using the phase inversion process. As a result of adsorption experiments, it was concluded that the S-host composited membranes showed a high ability to reject Pb^{2+} ion. In particular, in quarterly mixture of aqueous heavy metal ions, the composited membrane having 50 and 60 wt% of S-host had host-guest properties and high retention of Pb^{2+} ion.

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Chapter 4

Application to alkali metal separation of organic hosting of calix[4]resorcinarene and their composited membranes

Abstract: This research discussed characterization and the evaluation of alkali metal adsorption properties of calix[4]resorcinarene hosts such as S-host, V-host and PH-host. Here, the adsorption behavior for their host of aqueous alkali metal ions, Na^+, K^+ and Cs^+, was examined in batch adsorption experiment. In single ion system for the adsorption process, the S-host showed that the highest adsorption capacity of Cs^+ ions was 22 μmol/g, while those for Na^+ and K^+ was 0.19 μmol/g and 2.1 μmol/g, respectively. In a ternary mixture of alkali metal ions, the S-host showed effective adsorption, even though other ion interfered the adsorptivity to Cs^+ ion. Therefore, herein, in addition to S-host composited membrane, S-host composited fiber were prepared by phase inversion process as shown in chapter 3. The composited membranes and fibers having different loading amounts of the S-host were prepared with 10, 25 and 50 wt% loading. The observation of N_2 adsorption isotherm indicated that the BET surface area of the composited fibers was significantly lower than that of the composited membranes. The adsorption behavior of aqueous alkali metal ions was examined for the composited membranes and fibers containing 10, 25 and 50 wt% of the S-host by using batch method and permeation method. Both composited membrane and fiber showed selectivity of Cs^+ ion in alkali metal ion mixture solution in batch methods, the adsorption capacity of Cs^+ of composited membrane and fiber were 9.8

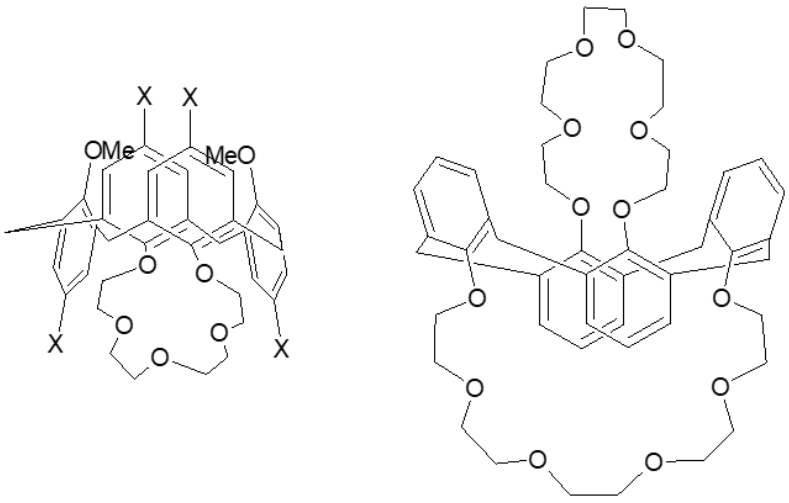
μmol/g and 0.72 μmol/g, respectively, even though they showed no adsorption capacity for Na^+ and K^+. When the composited membrane and composited fiber were compared for the alkali metal ion mix solution, Cs^+ could be effectively separated from the mixed solution in batch method. Especially, S-host composited membrane adsorbed effectively Cs^+, as the solution was permeated at 4.0×10^4 Pa applied pressure. The outstanding adsorption abilities of S-host composited membranes for Cs^+ ion have exhibited good prospects for disposal application of polluted water and environmental protection.

4.1 Introduction

Cesium (Cs) ion adsorbent has been attracting attention in the many fields, especially for the water environment after an accident at Daiichi Nuclear Power Plant hit by the Great East Japan Earthquake and tsunami in 2011. The plant meltdown and explosion brought about serious leakage of radioactive such as Cs and iodine (I), affecting pollution to a broad area in eastern Japan. Radioactive iodine has a short half-life of 8 days. But Cs^{134} has a half-life of about 2 years and Cs^{137} with a half-life of about 30 years [1] in long-term pollution. As the influences of radiation on the human body, there are fetal growth disorders, decreased hematopoietic function, infertility, burns and hair loss as acute disorders. Symptoms of cancer and leukemia are seen as late effects [2, 3]. Since radioactive Cs has been scattered in various places in the environment, the decontamination method differs depending on the target. For example, in the contaminated water containing radioactive Cs, water is carrier to extend the pollution. Therefore, Cs ion adsorbents were used for removal of the Cs. Nowadays, several clay minerals such as zeolite, bentonite

vermiculite, montmorillonite, geopolymer were utilized for the Cs removal from aqueous solution [4-8]. However, Na^+ and K^+ are competitive to Cs^+ adsorption in water and make such clay minerals as fewer effective adsorbents. In addition, Prussian blue (PB) particle (catena-[$MFe^{III}\{Fe^{II}(CN)_6\}$] (M = Li, Na, K, NH_4)) pigment is also known as having high Cs^+ adsorptivity [9-11].

As host-guest molecules for Cs^+ adsorption, macro porous silica based supra molecule [12], crown ether [13, 14] and calixarene [15, 16] were additionally known. Izatt et al. firstly used and developed *p*-tert-butylcalixarenes and *p*-tertpentylcalixarenes for the transport of alkali metal cations, especially for Cs^+, through bulk liquid membranes. As transport by the butyl (or pentyl) calixarenes is selective for Cs^+ over other alkali cations, the selectivity increases as the size of the calixarenes decreases: calix[8]arene < calix[6]arene < calix[4]arene [17, 18]. It was reported that calixarenes offer several advantages as carriers in low water solubility and forming neutral complexes with cations through loss of a proton. Also, the macrocyclic molecules have potentiality of coupling cation transport and reverse proton transport [18]. Moreover, many calix[4]arenes with crown ether moieties were produced and proved to be efficient for the complexation of alkali and alkaline earth cations due to the presence of the crown ether link [19]. Therefore, especially, some supramolecular recognition agents such as functionalized calix[4]arene with crown ether like dialkoxycalixarenes-crown-6 [20] and calix[4]arene-bis-crown-6 [21] showed much more efficient and selectivity for Cs^+ than crown ethers as shown in Figure 4.1.



[20] [21]

Figure 4.1 Functionalized calix[4]arene with crown ether, dialkoxycalixarenes-crown-6 [20] and calix[4]arene-bis-crown-6 [21].

However, the report to about Cs^+ adsorption based from calix[4]resorcinarene has not been found yet. In previous chapters 2 & 3, calix[4]resorcinarene such as S-host, V-host and PH-host were synthesized from plant-based chemicals and successfully prepared. Therefore, it is quite normal to test the S-host, V-host and PH-host for the Cs^+ adsorptivity. In this chapter, the hosts were used to test alkali ion adsorption for the selectivity of calix[4]resorcinarenes to Cs^+. Moreover, such calix[4]resorcinarene host composited with PES for membranes and fibers were described for Cs^+ adsorbents.

4.2 Experimental

4.2.1 Materials

The standard solution of NaCl, KCl and CsCl, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). KBr was produced from Tokyo

Chemical Industry Co., Ltd. (Tokyo, Japan). Poly(ethersulfone) (PES: MW = 50,000) was produced from BASF (Lud-wigshafen, Germany).

4.2.2 Alkali metal adsorption experiments of calix[4]resorcinarenes

In studying the binding ability of alkali metal ion for the calix[4]resorcinarenes such as S-host, V-host and PH-host, the batch binding experiment was carried out. Each metal ion solutions of Na^+, K^+ and Cs^+ were prepared as 20 ml at 20 ppm concentration in glass holder. In the single solution of each alkali metal ions, 0.05 g calix[4]resorcinarenes powder of S-host, V-host or PH-host was added. Then, the holder was shaken at 25 ℃ for 24 h by using TS-200 Shaking bath (Advantech, Taiwan). The concentrations of remaining alkali metal ions of Na^+, K^+ and Cs^+ in the aqueous solution were measured at a certain wavelength using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan). Optimum Selectivity of the calix[4]resorcinarene for the interfering metal ion was evaluated using the equation (2-1) as well as chapter 2. For calix[4]resorcinarenes, the single-point BET surface areas and particle size distribution were measured. In addition, the FT-IR spectra of calix[4]resorcinarene before and after alkali metal adsorption were measured.

4.2.3 Preparation of the calix[4]resorcinarene-composited membranes and fibers

PES-calix[4]resorcinarene composited membranes were prepared by phase inversion process as mentioned in chapter 3. PES-Calix [4] resorcinarene conjugate fiber was prepared by a modified phase inversion of PES - NMP solution in water to solid PES according to the previous procedure described. In the process of composited fibers, wet

spinning process explained in previous research [22] was used. Here, the fabrication process was followed. The PES was dissolved in NMP to prepare PES-NMP solution containing 20 wt% of PES concentration. Subsequently, a specific amount of S-host powder was added to the PES - NMP solution. Then, the calix[4]resorcinarene host was dispersed in the PES-NMP solution at concentrations of 10, 25 and 50 wt% and the mixed solution was stirred at 50 ℃ for 1 hour. After preparing the PES-calix[4]resorcinarene mixed solution, the mixture was extruded through a cylindrical needle with a needle hole diameter of 1.2 mm at an air pressure of 0.40 MPa. The extruded mixture was added dropwise to the water coagulation bath. The composite fiber was immersed in a water coagulation bath for 1 day and washed to remove residual NMP. Finally, the S-host bicomponent fiber was vacuum dried. Table 4.1 lists the composition of loaded calix[4]resorcinarene in PES and the content (%) of calix[4]resorcinarene powder in PES. The morphology of the composited fibers was observed by using a SEM after gold coating using a quick cool coater. Single-point BET surface areas of the fiber were measured. The fibers were cut to 5 cm for measurement of BET surface area.

Table 4.1 Components of the calix[4]resorcinarene composited fibers

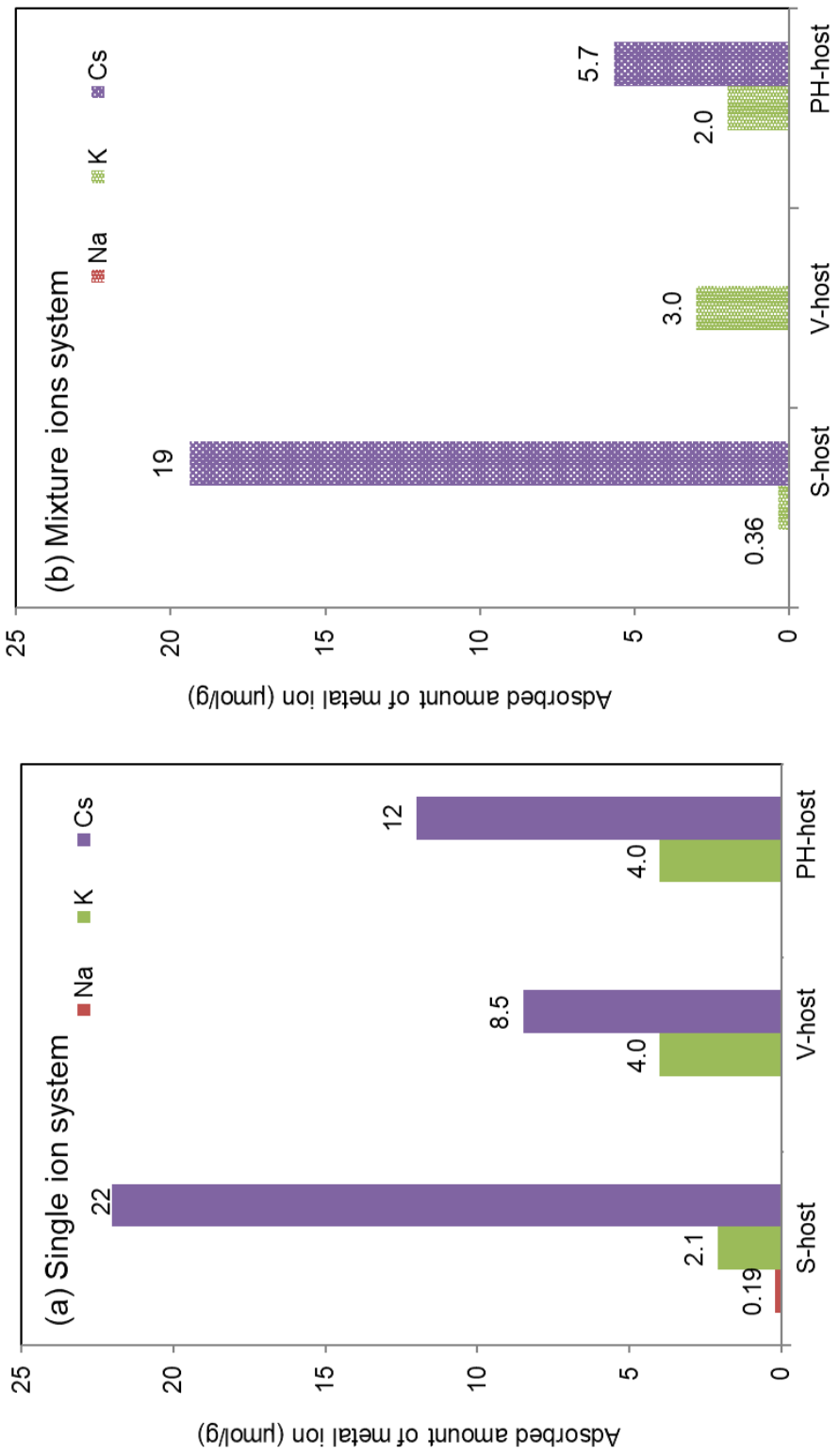
20 wt% PES-NMP solution (g)	Calix[4]resorcinarene (g)	Calix[4]resorcinarene composited fiber (wt%)
20	0	0
	0.4	10
	1.0	25
	2.0	50

The prepared calix[4]resorcinarene composited membranes and fibers were used for alkali metal batch binding experiment. In the adsorption experiment of calix[4]resorcinarene composited membranes (diameter 45 mm, thickness 70−90 μm), batch binding method and permeation methods were carried out. In the case of batch binding experiment, 0.05 g of calix[4]resorcinarene composited membrane was put in 20 ml of metal ion solutions of Na^+, K^+ and Cs^+ at 20 ppm concentration in glass holder. Then, the holder was shaken at 25 ℃ for 24 h for saturation binding. On the other hands, single or quarterly mixture of aqueous alkali metal ions was permeated through the composited membrane by using same Amicon cell folder previously mentioned in chapter 3 under 4.0×10^4 Pa applied pressure. The batch adsorption experiments for alkali metal ions were conducted when 0.10 g of calix[4]resorcinarene composited fibers were used.

4.3 Results and discussion

4.3.1 Cs^+ ion separation from alkali metal ion mixture by calix[4]resorcinarene

Figure 4.2(a) shows binding amounts of metal ions on each calix[4]resorcinarene in a single solution of Na^+, K^+ and Cs^+. As seen, it was noted that the S-host, V-host and PH-host adsorbed Cs^+ with adsorption amounts of 22, 8.5 and 12 (μmol/g), respectively, in Cs^+ single solution. Moreover, all hosts exhibited K^+ adsorptivity, whereas Na^+ was only adsorbed by the S-host. As seen, the Cs^+ selectivity is an important factor because the several co-existing metal ions such as Na^+ and K^+ influences the adsorptivity. Then, to confirm the selectivity of the alkali metal ions on the hosting properties, the mixtures of each 20 ppm of Na^+, K^+ and Cs^+ were also applied to test the similarity in batch adsorption



Figures 4.2 Amounts adsorbed of alkali metal ions on each calix[4]resorcinarenes in (a) single solution and (b) mixture solution.

experiment. The results are shown in Figure 4.2(b). The adverse effect brought by coexisting Na^+ and K^+ could be produced in two ways of competitive adsorption or acting as counter ions during adsorption. The Cs^+ adsorption efficiency was decreased as the Na^+ or K^+ existed, as presented in Figure 4.2(b). However, the S-host kept the high adsorptivity to Cs^+, whereas V-host and PH-host decreased their Cs^+ adsorption amount. From these results, it was observed that the mixed Na^+ and K^+ interfere Cs^+ adsorption. However, the S-host still effectively adsorbed the Cs^+ even in the mixture solution, suggesting high Cs^+ selectivity.

To investigate properties of calix[4]resorcinarenes for the Cs^+ adsorber, BET surface area of calix[4]resorcinarene was measured as seen in Figure 4.3. The resultant of BET surface areas of each calix[4]resorcinarene was 5.8, 7.5, and 12.0 m^2/g, for S-host, V-host and PH-host, respectively. In general, if the physical adsorption occurs on the surface of the host molecules, when BET surface area of host molecules was increased, the value of the adsorption amounts of guest molecules was also increased. Even though the S-host had a lowest BET surface area, the results showed the highest ability of Cs^+ adsorption. Furthermore, particle size distribution of the calix[4]resorcinarenes in water was measured. As shown in Figures 4.4, it was observed that the average values of particle size of the powders of S-host, V-host and PH-host were about 21 μm, 20 μm, and 3 μm, respectively. In the case of the adsorption experiment for each aqueous host solution, the hydrophilic host is advantageous to approaching guest molecule. As seen, the chemical structure of the S-host has eight methoxy groups, V-host has four methoxy groups and PH-host has no methoxy group. Therefore, the methoxy groups seem to make the calix[4]resorcinarene

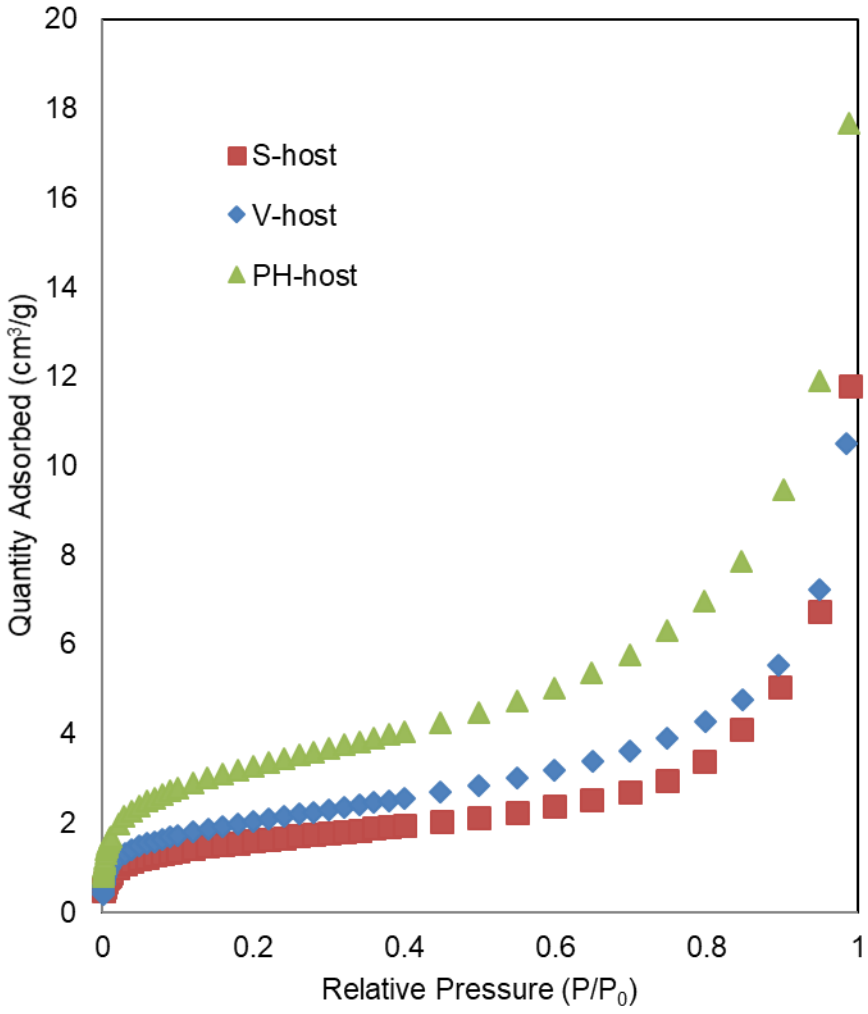
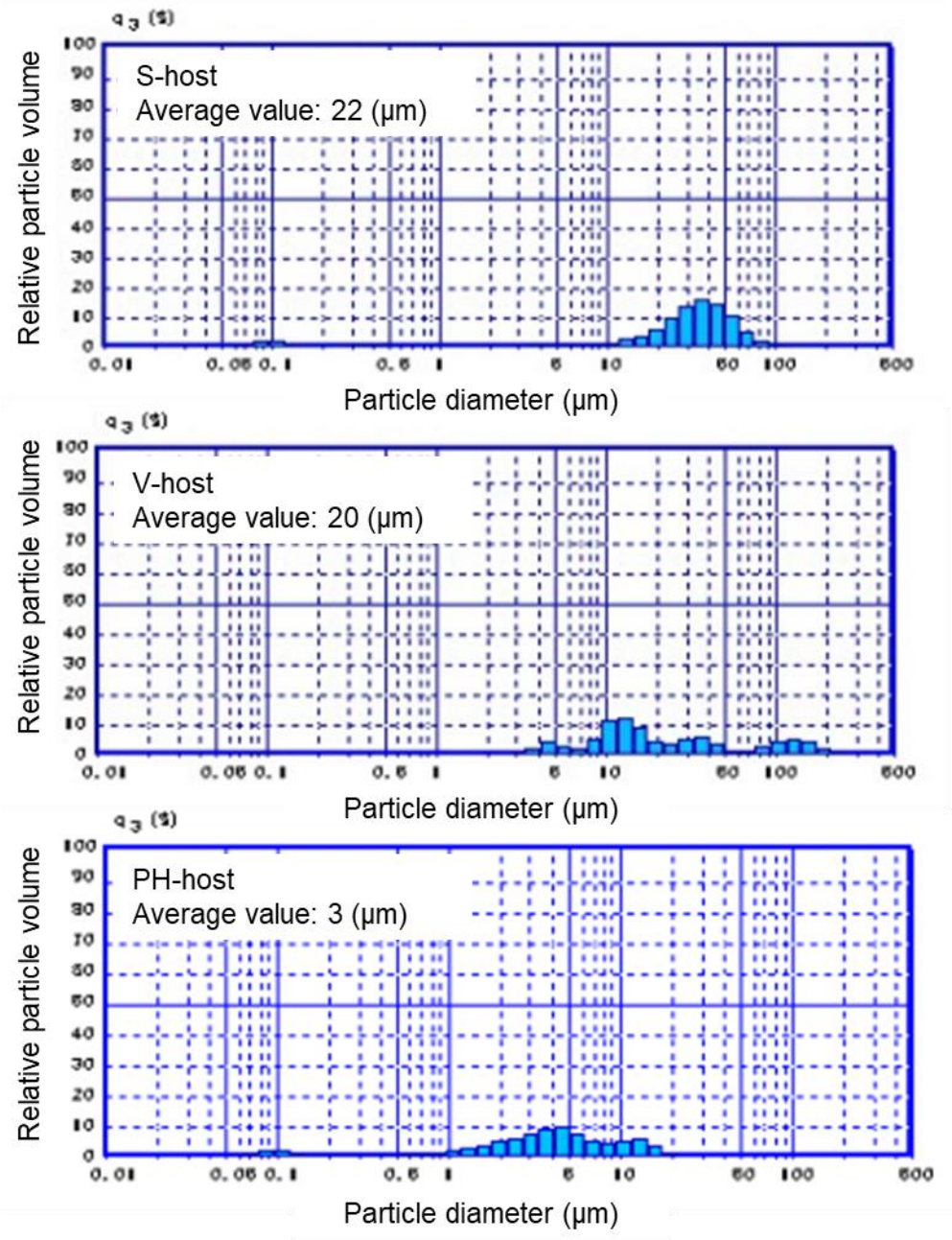


Figure 4.3 Nitrogen adsorption isotherm of S-host, V-host and PH-host.

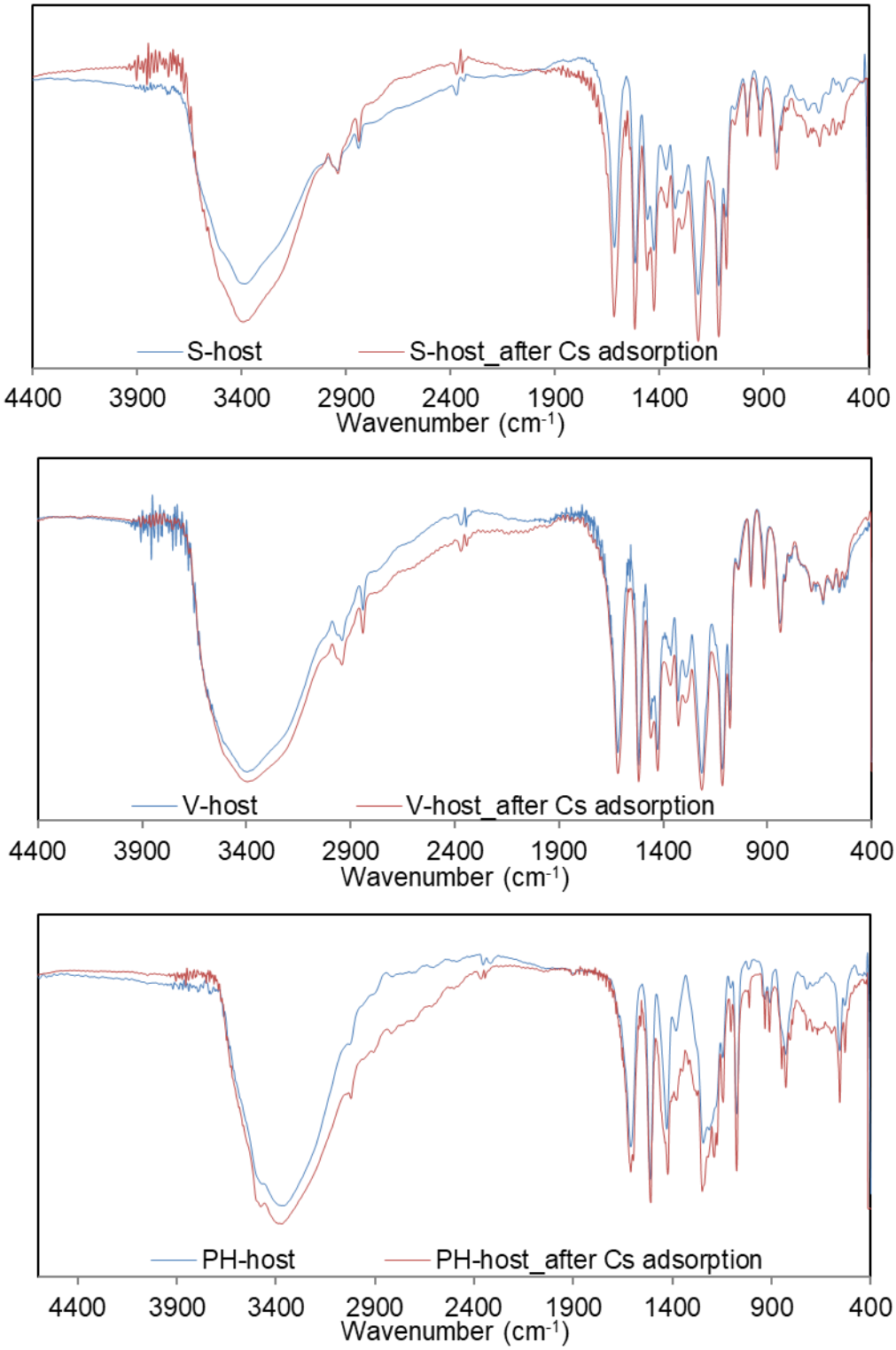


Figures 4.4 Particle size distribution of S-host, V-host and PH-host in water.

hydrophobic, so probably the S-host had lowest hydrophilicity in these calix[4]resorcinarenes. These results were due to one of reason for that the calix[4]resorcinarene adsorbed highly Cs^+ ion.

4.3.2 FT-IR analysis for the host-guest interaction

Fourier transform infrared (FT-IR) spectroscopy is known as a powerful tool to examine the chemical bonds in molecules by producing infrared absorption. Figures 4.5 show FT-IR spectra obtained for the before and after Cs^+ adsorption of S-host, V-host and PH-host, respectively. For the S-host, V-host and PH-host, there was O-H stretching vibration band around 3400 cm^{-1}. This band was one of the main chemical bonds in calix[4]resorcinarenes for the interaction to various metal ions. In addition, S-host and V-host having methoxy group therefore, showed C-O-C ring breathing vibration at 1254 cm^{-1} and 1046 cm^{-1}. So, it was expected that the Cs^+ chemisorption at the O atoms located caused the significant shift of the O-H or C-O-C stretching vibration band. The O-H stretching vibration band for the Cs-adsorbed calix[4]resorcinarene was not shifted, but because somewhat larger area peak in the presence of Cs^+ was seen, when the spectra were compared for that of Cs^+ un-adsorbed host in S-host. However, the V-host and PH-host showed less change. Moreover, the C-O-C stretching vibration band at 1254 cm^{-1} and 1046 cm^{-1} for Cs-adsorbed case appeared larger peak than that for Cs^+ un-adsorbed, for the S-host. From these results, it was suggested that Cs^+ was might be included by calix[4]resorcinarene through oxygen of phenol and $-OCH_3$ group.



Figures 4.5 FT-IR spectra of obtained for the Cs un-adsorbed and adsorbed each calix[4]resorcinarene, S-host, V-host and PH-host.

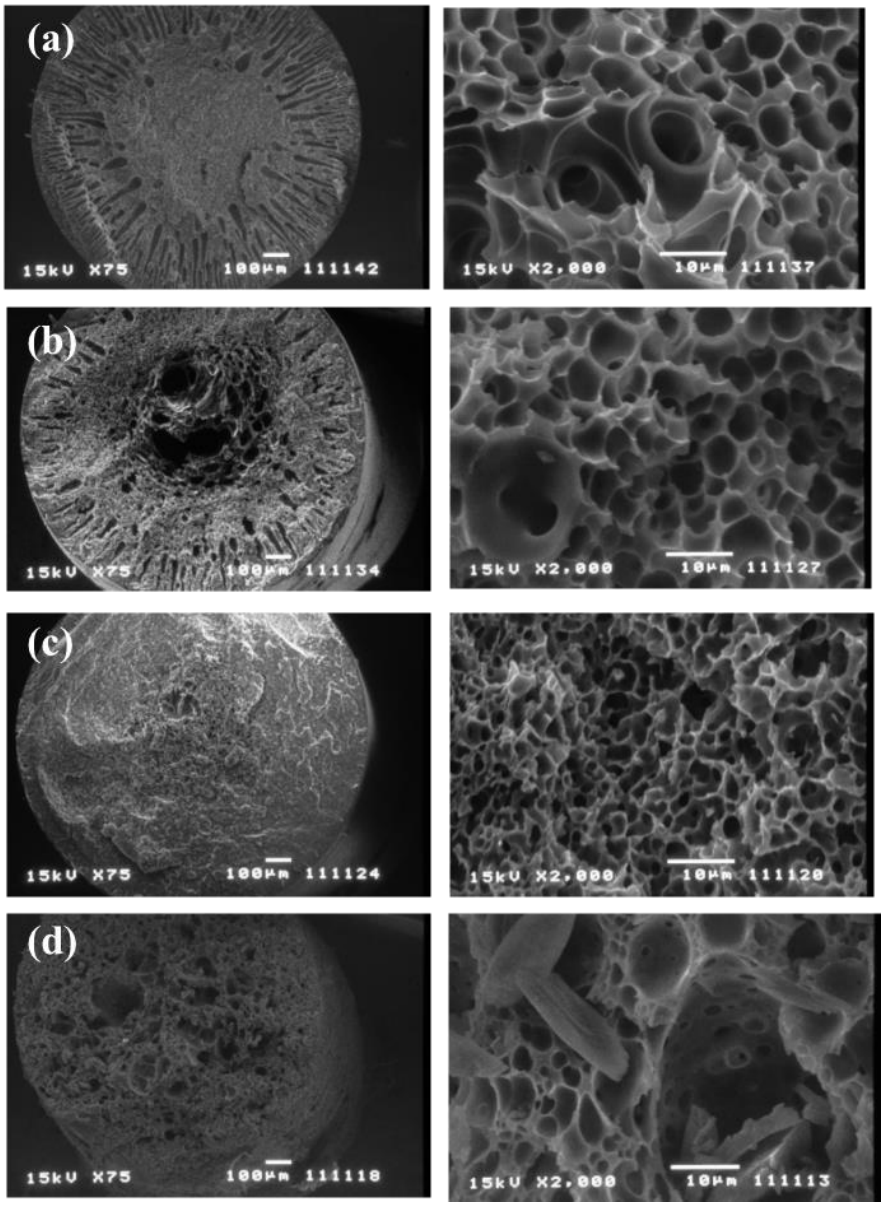
Table 4.2 Attribution list of FT-IR spectra of before and after Cs^+ adsorption of S-host, V-host and PH-host.

	O-H (cm^{-1})	C-O-C (cm^{-1})
S-host	3398	1220
S-host-Cs	3387	1213
V-host	3399	1215
V-host-Cs	3409	1213
PH-host	3390	-
PH-host-Cs	3359	-

4.3.3 Characterization of calix[4]resorcinarene composited fibers

As a result of 4.3.1, it was appeared that S-host showed the highest Cs^+ adsorptivity and selectivity in three kinds of calix[4]resorcinarenes. Therefore, to investigate the application of calix[4]resorcinarene composited membrane and fiber for alkali metal adsorbent, S-host composited membranes and fibers were prepared and used for adsorption experiments.

Figures 4.6 show the morphology images of PES fiber and the obtained 10, 25 and 50 wt% S-host composited fibers. From he appearance of the S-host composited fibers, it was indicated that the phase inversion of the wet spinning produced fibrous composites satisfactorily. In SEM date as seen in chapter 3, Figures 3.4 were pictures of the cross section (left sides) and focused one's (right sides). Also, in their SEM pictures, the cross-sectional views showed that the fiber had a diameter of about 1.2 mm and that it had a porous structure in the composited fiber. It was shown that the fiber morphology of PES without the S-host was porous and had a finger-like structure. As the carrying amount of S



Figures 4.6 SEM images of (a) PES fiber and S-host composited fibers with (b) 10 wt%, (c) 25 wt% and (d) 50 wt% loading.

host increased, the finger structure of the section disappeared. In SEM images with the magnification ×2000, when the S-host was loaded 50 wt% in PES fiber, the S-host well distributed in the PES network, showing a sponge structure. Therefore, SEM images showed that the micropore structure of the composite fibers decreased with increasing loading of S-host. To confirm the interaction of S-host in the PES fiber, FT-IR spectra of the composited fibers were measured. As shown in Figure 4.7, in the case of S-host, for the 1650-1700cm^{-1} region, the peak of A of PES (b) with composited fiber shifted toward shorter wavenumber side for B at 1664 cm^{-1} and C at 1656 cm^{-1} in 10 and 50 wt% loading of the S-host, respectively. From 1100 to 1238 cm^{-1} bands was attributed to >S(=O)$_2$ stretching vibration. It was revealed that the S=O groups of the PES were interacted with the S-host in the composited fiber as same as in the case of producing the composited membrane in chapter 3. In addition, the appearance of 1510 cm^{-1} and 1600 cm^{-1} band of C=C stretching vibration in the phenyl rings in all S-host composited fiber represented the presence of the S-host in the fiber. The peak shift of the stretching band was surely seen in the composite fibers, meaning the formation of interaction between PES and S-host as well as the composited membranes in chapter 3. These indicated that the S-host was properly composited in PES fiber. Table 4.3 includes the data of tensile strength, water content and BET surface area of each S-host composited fibers. The tensile strength of the composited fiber decreased, when the loading of the S-host was increased. It was noted that the value of water content became high as the S-host was loaded in the fibers. In the similarity of the case of producing the calix[4]resorcinarene composited membranes, the values were higher than that of 100 % for the loading fibers. This meant that the porous volume in their fibers

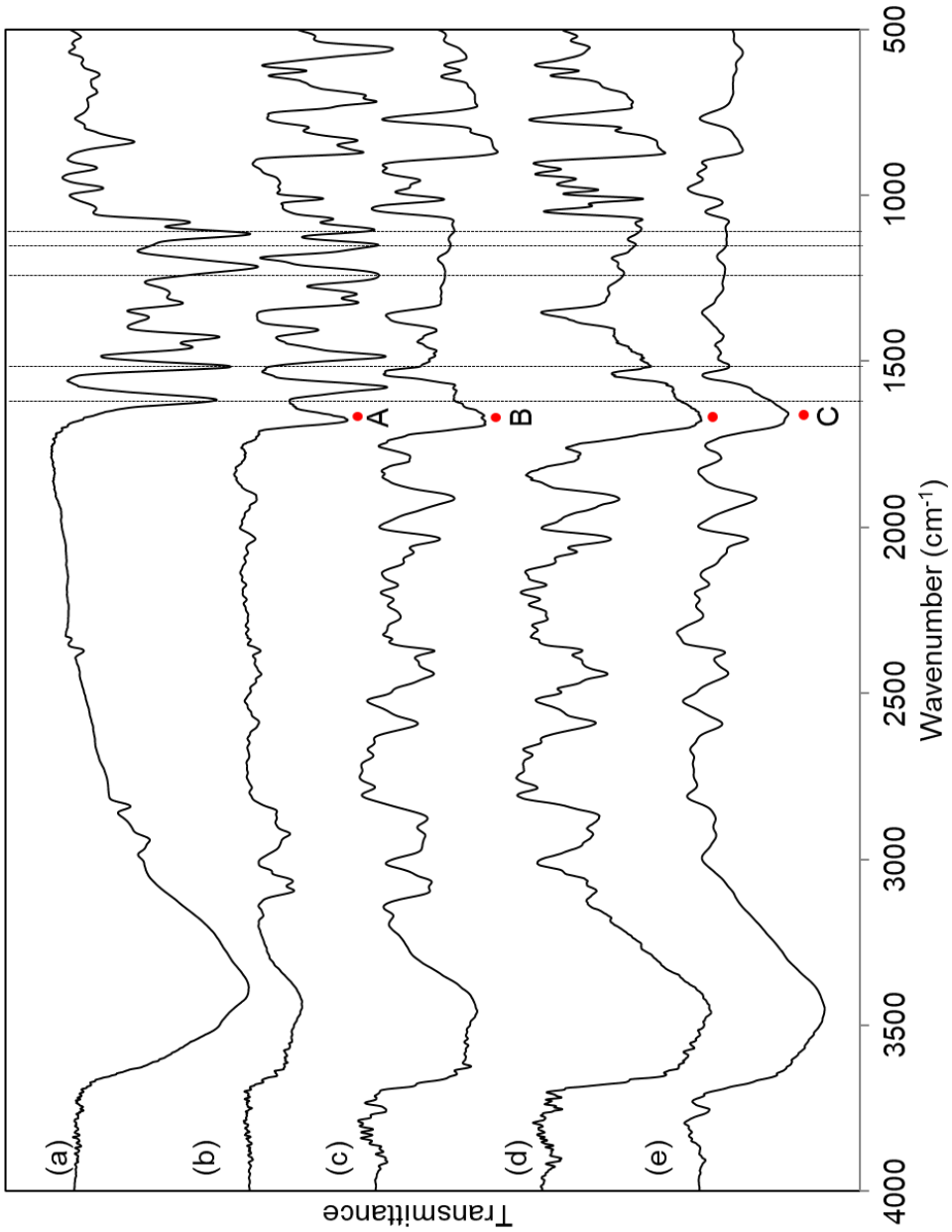


Figure 4.7 FT-IR spectra of (a) S-host, (b) PES and S-host composited fibers with (c) 10 wt%, (d) 25 wt% and (e) 50 wt% loading.

Table 4.3 Properties of PES fiber and S-host composited fibers.

Host	Loading (wt%)	0	10	25	50
S-host	Tensile strength (MPa)	21±0.11	7.56±0.22	5.32±0.05	2.29±0.13
	Water content (%)	40	201	185	312
	BET surface area (m^2/g)	2.81	2.91	2.12	3.35

easily took water. This also suggested that the introduction of the S-host consisting of OH groups led to the improvement in water access. Thus, the S-host loading in the fiber changed the hydrophilic city of the composited fiber, even though the scaffold PES had hydrophobic nature. In order to analyze porous properties of the S-host composited fibers, the BET surface area was evaluated by nitrogen adsorption to the dried fibers. When the S-host loading was changed from 10 to 25 wt%, the values of BET surface area were decreased. Then, as the S-host loading was increased 50 wt% in the fiber, the surface area was a little bit increased to 3.35 m^2/g of BET surface area. The values of BET surface area of the composited fibers became low relative to those of the composited membranes (Figure 3.10). Figure 4.8 shows nitrogen adsorption isotherm of the PES fiber and each S-host composited fiber. According to their adsorption behavior, the PES fiber and S-host composited fibers belonged to type II isotherms [23], showing the similarity of the composited membranes meant that the fibers consisted of macroporous structures. As compared with the results of PES fiber having S-host in the composited fibers, there is not so much difference of the N_2 adsorption amounts, depending on the S-host presence.

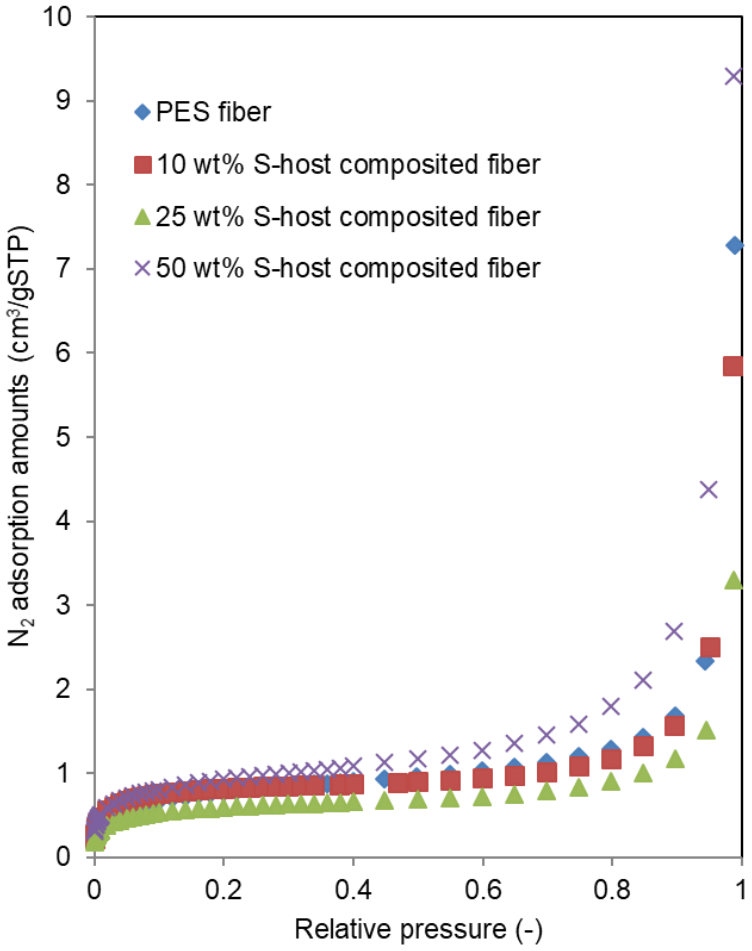
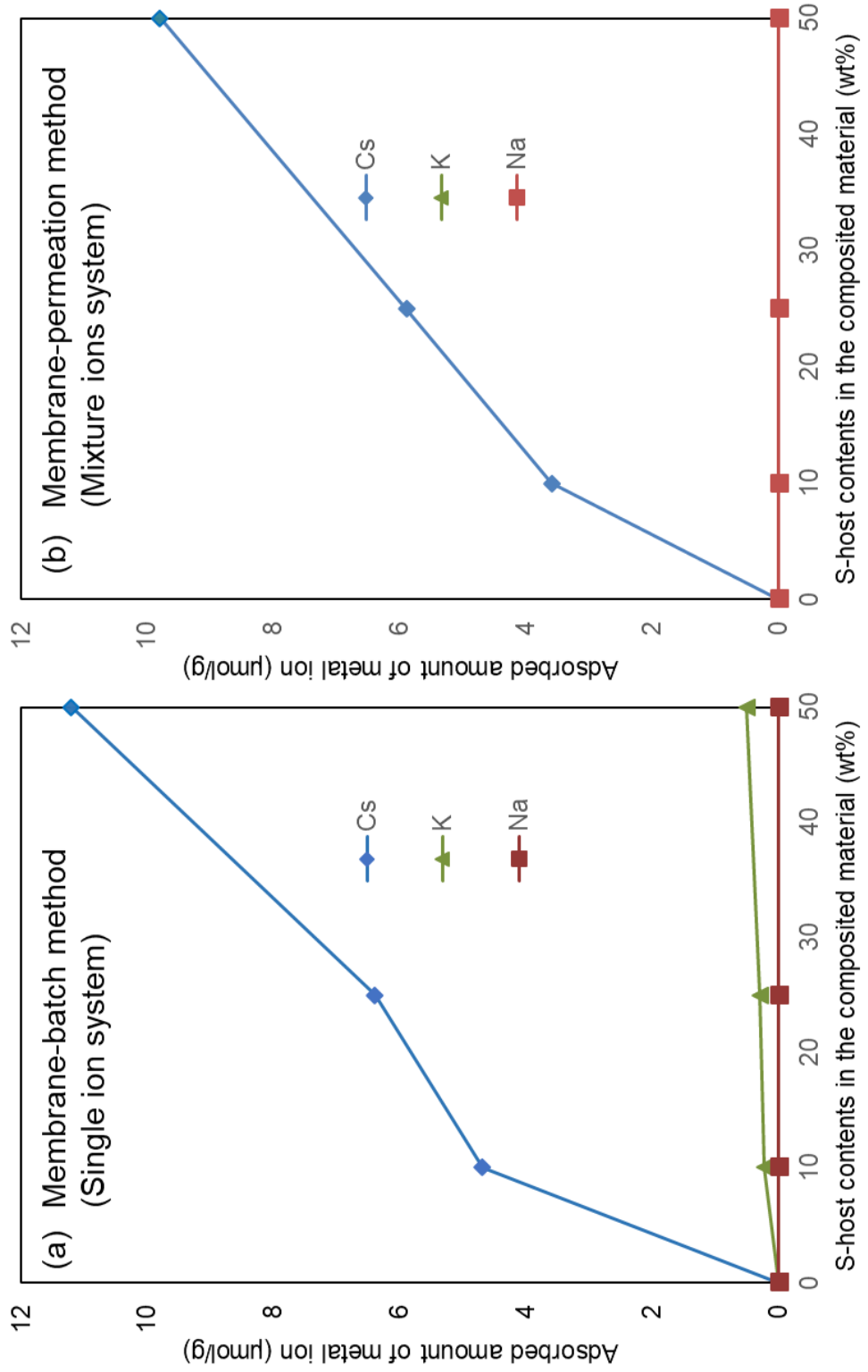


Figure 4.8 Nitrogen adsorption isotherm of PES fiber and the S-host composited fibers having 10 wt%, 25 wt% and 50 wt% loading of the S-host.

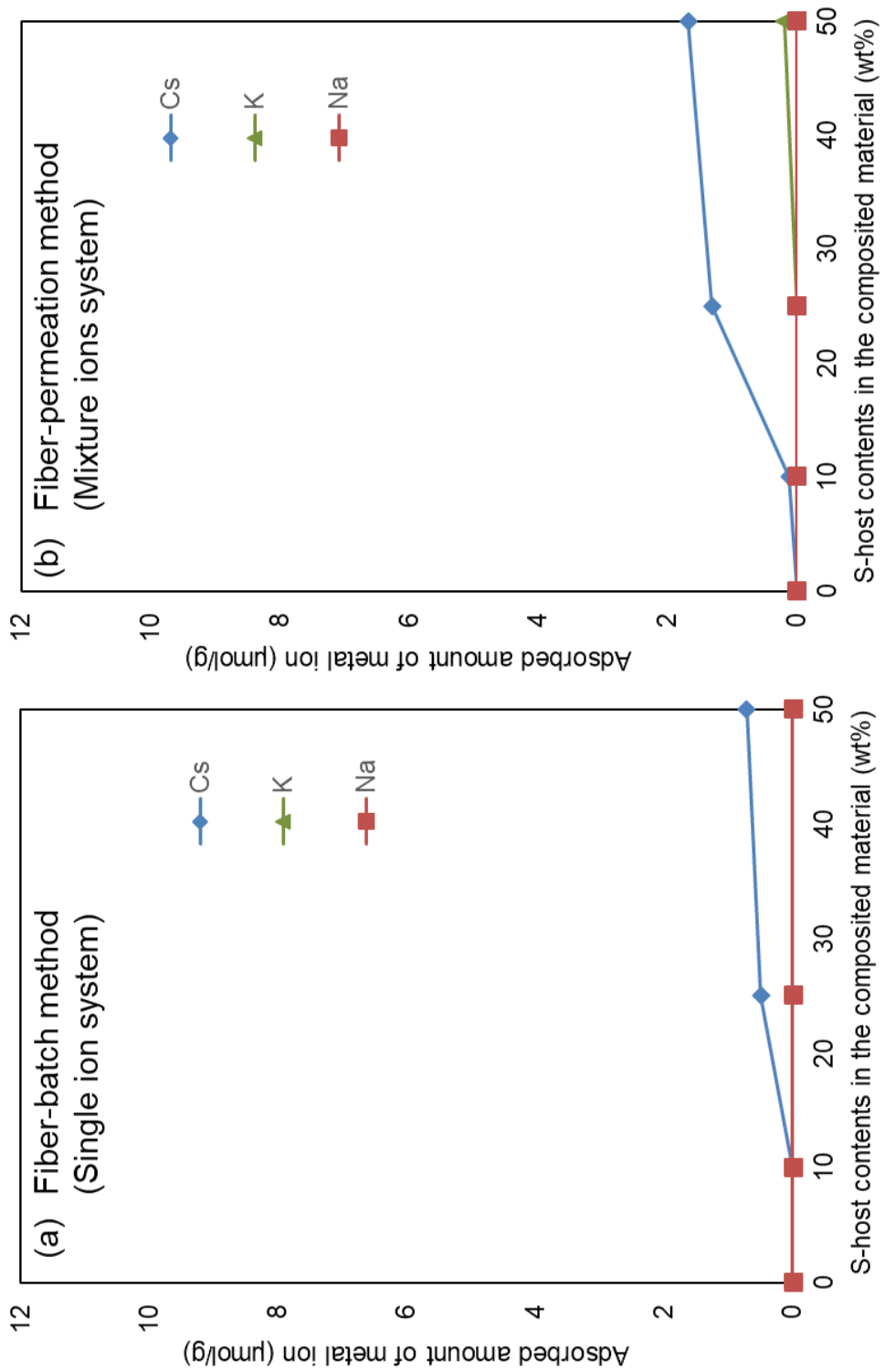
4.3.4 Cs^+ ion separation from alkali metal ion mixture by calix[4]resorcinarene composited membranes and fibers

Figures 4.9 and 4.10 show the results of alkali metal ions adsorption experiment for batch method on each adsorbent of the S-host composited membranes and fibers in single and mixture solution of Na^+, K^+ and Cs^+ with 20 ppm concentration. In non-loaded case of S-host, the PES membrane had no binding to the Cs^+ and other ions. With increasing the S-host loading in the membrane and fiber, the value of the adsorption amounts of Cs^+ was increased. Comparing composited membrane and composited fiber, it was noted that the membranes showed higher adsorption amount for Cs^+ relative to the composited fibers. At 50 wt% loading, the Cs^+ adsorption amount in single solution system was 11.2 and 1.68 μmol/g for the composited membrane and fiber, respectively. As a result of BET surface area, it was appeared that the surface area of composited fibers was quietly lower than composited membrane. Since S-host was completely distributed in PES layer, it was considered that the imbedded S-host was difficult to contact with Cs^+ in batch experiment.

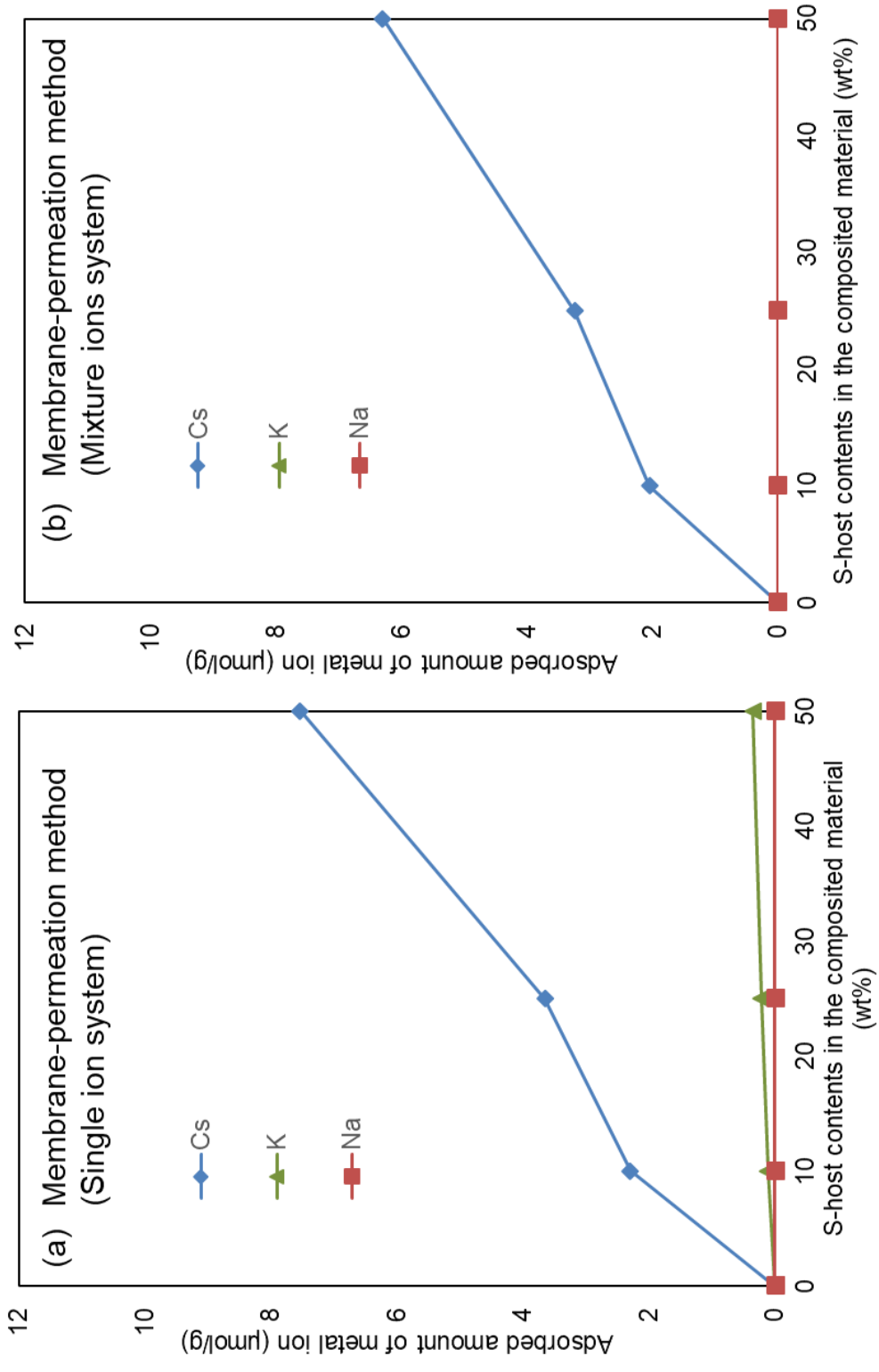
To confirm the effect of the alkali metal ions on the hosting properties, permeation experiments of each ion solution were carried out for S-host composited membranes as shown in Figures 4.11. The experiments were conducted at 20 ppm concentration in each metal ion or mixture. Here, the applied pressure of the permeation driving force was fixed at 4.0×10^4 Pa. When the S-host loading in the membrane was increased, there was a tendency to increase the binding of the Cs^+ ion to the membrane. It was apparent that the 50 wt% loading showed high rejection to the Cs^{2+} ion relative to other Na^+ and K^+ ions, meaning that the effect was due to the S-host loading in the membrane. For the mixture



Figures 4.9 Amounts adsorbed of alkali metal ions on each S-host composited membrane for batch method in (a)single solution and (b) mixture solution.



Figures 4.10 Amounts adsorbed of alkali metal ions on each S-host composited fiber for batch method in (a)single solution and (b) mixture solution.



Figures 4.11 Amounts adsorbed of alkali metal ions on each S-host composited membrane for permeation method in (a)single solution and (b) mixture solution.

solution of each ion with 20 ppm concentration with Na^+, K^+ and Cs^+, the S-host composited membranes had no binding capacity to the Na^+ and K^+. However, Cs^+ ion was quietly and highly rejected in the permeation process for the S-host composited membranes containing 50 wt% of the S-host. Although the values of the desorption amount for the Cs^+ were decreased to be 6.3 μmol/g-membrane for the 50 wt% loading membrane, the separation performance of Cs^+ binding was observed in the presence of the other ions of Na^+ and K^+.

To evaluate the S-host composited membrane in permeation process, volume flux of each permeation solution, water, Cs^+ single solution with a concentration of 20 ppm, and alkali metal ion (Na^+, K^+ and Cs^+) mixed solutions each ion contained at 20 ppm were passed through the membrane at 4.0×10^4 Pa. For both the PES membrane and the S-host composited membranes, the void space rate (%) was calculated as shown with water content and BET surface area in Table 4.4. When water was permeated through the membrane, the PES membrane showed the lowest value of the volume flux with 6.9×10^{-3} m^3/m^2min. The values of the volume flux for 10, 25 and 50 wt% loading of the S-host in the composited membranes were 1.4×10^{-2}, 1.8×10^{-2} and 2.8×10^{-2} m^3/m^2min, respectively. So, it was cleared that the S-host loading in the PES membrane made that the water permeability was increased. When Cs^+ single or Na^+, K^+ and Cs^+ alkali metal mixture in the aqueous solution was permeated through the membrane, it was observed that the volume flux decreased for all membranes relative to the water. Particularly, as permeating through the mixed ion solution, the volume flux was the lower than those of water and the single ion solution. As a result of SEM images of the S-host composited membranes

Table 4.4 Water contents, BET surface area, void space rate of PES and S-host composited membranes and volume flux of the permeation solutions when water, Cs^+ solution and alkali metal ion mixture were permeated through membrane at 4.0×10^4 Pa.

Sample	Water contents (%)	BET surface area (m^2/g)	Void space rate (%)	Volume flux (m^3/m^2min)		
				Water	Cs^+ single solution	Na^+, K^+ and Cs^+ mixture
PES membrane	42	12.3	9.4	6.9×10^{-3}	2.6×10^{-3}	2.1×10^{-3}
10 wt% S-host composited membrane	214	16.3	47	1.4×10^{-2}	3.9×10^{-3}	2.8×10^{-3}
25 wt% S-host composited membrane	301	17.6	55	1.8×10^{-2}	7.1×10^{-3}	5.4×10^{-3}
50 wt% S-host composited membrane	358	13.9	63	2.8×10^{-2}	1.3×10^{-2}	1.1×10^{-2}

(Figure 3.4), the S-host influenced to the membrane morphology. This meant that the solvent exchange became slow and a sponge-like membrane in the phase inversion process as formed the membrane by coagulation in water medium. In general, finger like structure provides higher volume flux than sponge like structure. However, in the case of the S-host composited membrane, the volume flux increased as the S-host content in the membrane increased, even though the high S-host loading provided sponge like morphology of the composited membrane. This might be explained from the result of the values of the void space rate of the composited membrane containing different loading S-host. Here, the value of the void space rate was evaluated by the following equation (4-1).

$$void\ space\ rate\ (\%) = \frac{W_{before} - W_{after}}{V} \times 100$$

where W_{before} and W_{after} represents the volume of water remaining before and after immersion of S-host composited membrane and V is the volume of S-host composited membrane. As the loading amount of S-host in the composited membranes was increased, the void space rate also increased. So, it was easily considered that the higher void space in the spongy membrane increased the permeability of water medium through the membrane. Consequently, it was confirmed that S-host composited membrane showed higher Cs^+ adsorptivity than composited fiber in bath binding method. In addition, considering the adsorption process, it was found that thin membrane process was selectable for the permeation to separate alkali metal ion mixture for the perm-selection of Cs.

4.4 Conclusion

This study investigated to develop the calix[4]resorcinarene from natural chemicals such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde for Cs^+ adsorption for the applicability of the efficient Cs^+ decontamination. The resulting data clarified that the Cs^+ adsorption efficiency of S-host was high rather than V-host and PH-host. In addition, at the presence of competing ions of Na^+ and K^+ was slightly affected for Cs^+ adsorption by S-host. These results indicated that the S-host could be used as an effective adsorbent for the selective removal of Cs^+ with high adsorption capacity.

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Chapter 5

Application of vegetable plants and calix[4]resorcinarene for novel adsorbents for ethylene gas

Abstract: This chapter described the behavior of ethylene gas (C_2H_4) adsorption of the calix[4]resorcinarene and vegetable wastes occurred annually at the end of production like tomato stem, squash stem, cucumber stem, red perilla stem and bract of corn as a application. The derived vegetable plants were washed with distilled water and then dried more than 5 days at room temperature and used to C_2H_4 adsorption. The C_2H_4 and nitrogen adsorption was examined in vegetable plants, which were dried, and the gases adsorption performance was compared with those of zeolite, activated carbon and synthesized calix[4]resorcinarenes from syringaldehyde, vanillin and *p*-hydroxybenzaldehyde, which are having plant components. The results showed that the tomato stem having fine cell walls composed of cellulose fibers had the highest C_2H_4 adsorption quantity in tested vegetable plants samples. The C_2H_4 adsorption volume per unit area of the tomato stem was 0.35 cm^3/m^2 and was 2.5 times higher than that of zeolite and the adsorption was obeyed Freundlich model. On the other hand, much higher C_2H_4 adsorption was firstly found in the calix[4]resorcinarenes condensed with resorcinol and syringaldehyde and vanillin, S-host, and V-host. The adsorption quantities of C_2H_4 of the S-host and V-host were 3.9 and 2.2 cm^3/m^2, respectively. Evidence was presented that the methoxy groups in their hosts was important in the C_2H_4 adsorption in the calix[4]resorcinarenes to adsorb the C_2H_4 gas.

5.1 Introduction

Ethylene (C_2H_4) gas is known as growth hormone in plants, some fruit and vegetable produce C_2H_4 as ripening begins [1]. For these cases, C_2H_4 promotes the aging and maturing fruit [2]. However, C_2H_4 can also cause plants to the excessive aging. So, to keep the freshness of fruit and vegetable in the food industry, the controlling of C_2H_4 amount is important by adsorbents for the practical uses. Therefore, the material capturing C_2H_4 is increasingly alternative in the industrial field, because of importance in keeping the freshness of perishable food during the its transportation with extremely huge amounts. At present, the most widely used technology for capturing C_2H_4 for perishable food is physisorption on porous materials such as activated carbon [3, 4] and zeolite [5, 6]. Therefore, the effective way for capturing C_2H_4 for perishable food is physisorption on porous materials. It is known that perishable vegetables and fruits are grown by adsorbing such growth hormone of C_2H_4 [7]. This is because that the phytohormone C_2H_4 inhibits cell expansion in plants, when the gas is present in cellulose microfibers. So, cellulose microfiber in plants seems to include C_2H_4 adsorption sites. However, very limited research was reported [8, 9]. Among them, Walten et al. reported growth cotton in effect on C_2H_4 [8]. David et al. also reported that tomato showed insensitivity to their growth [9]. This strongly suggests that such plant has C_2H_4 insensitive sites inside plat. Thus, it is interesting to apply such vegetable plant to C_2H_4 adsorber, especially in their inedible parts such as leaves and stems as a recycle green product.

On the other hand, calix[4]resorcinarene has attracted attention for two decades because of macrocycle based on a hydroxyl alkylation product of phenols and aldehydes

and on a hydrophobic cavity that can hold smaller molecule or ion [10]. Until now, little is known in organic molecules few reports on its chemisorb for C_2H_4 adsorption [11, 12]. Especially for these hosts, which were synthesized from plant chemical components. So, calix[4]resorcinarene has been used as interesting materials in their adsorption properties for several processes [13, 14]. The molecular recognition behavior to gas adsorption is one of great interest by hosting for calixarenes, if the cyclic organic molecule effectively includes gas, especially in C_2H_4. According to the prior studies of such supramolecular action of calixarene, hosting action supported by a Lewis acid-base [15] and van der Waals forces [16] was reported by constructive inclusion found with the calixarene cavity [17] in gas separation [18] and gas sensor [19] for CO_2, NO_2, CH_4, CO, toluene vapor, natural gas. However, such gaseous molecular recognition is still at an early stage and the application of calix[4]resorcinarene for C_2H_4 adsorbent has never been reported.

In this background, the present work described C_2H_4 adsorber in calix[4]resorcinarenes as challenging to the topic and the adsorption behavior was compared with vegetable samples. This is because that such natural chemical involves plant cell having lignin components, and chemical components of syringaldehyde and vanillin. Therefore, such phytochemical approach including natural chemical component in plant source seems to be possible to fabricate calix[4]resorcinarene host. In the previous chapter, calix[4]resorcinarenes introduced with syringaldehyde, vanillin and *p*-hydroxybenzaldehyde were mentioned to metal ion adsorbers. The raw chemicals of syringaldehyde, vanillin and *p*-hydroxybenzaldehyde having aldehyde group, are found in plant cell from the maple tree, vanilla bean and gastrodia elata as natural chemicals and

these contain different numbers of the methoxy group within the chemical structure in their plant cells. Therefore, this chapter described the C_2H_4 adsorption behavior of the calix[4]resorcinarenes and comparison of the adsorptivity with plant vegetable samples.

5.2 Experimental

5.2.1 Materials

Ethanol was purchased from Nacalai Tesque Inc (Tokyo, Japan). Zeolite originally comes from Iizaka Mine was supplied from Nitto Funka Trading Co., Ltd. (Tokyo, Japan). Activated carbon (FP-3) was obtained from JEChem (Osaka, Japan). Tomato stem, squash stem, and bract of corn were made from Fukushima (Japan), cucumber stem was obtained from Aomori (Japan) and the red perilla stem was supplied from Niigata (Japan).

5.2.2 Preparation and characterization of vegetable plant samples

All vegetable plants were washed with distilled water and dried more than 5 days at room temperature. The morphology of the vegetable plant was observed by using a scanning electron microscope (SEM, JSM-5300 LV; JEOL, Japan) after gold coating using a quick cool coaster (Sanyu Denshi K.K, Japan). Functional group analysis of the treated vegetable plant was carried out using Fourier transform infrared (FT-IR) spectroscopy (FT-IR 4100 series, Jasco Corp. Japan) over a frequency range 500-4000 cm^{-1}. Pellets were made from samples with KBr. Moreover, each vegetable plant was cut 5 mm×5 mm for BET surface area measurement and C_2H_4 adsorption experiment.

5.2.3 Gas adsorption experiments for the vegetable plants and calix[4]resorcinarene

For the prepared samples of vegetable plants of tomato stem, squash stem, cucumber stem, red perilla stem and bract of corn, BET surface area of these samples was measured using a Micromeritics Automatic Surface Area and porosimetry Analyzer Tristar II (Shimadzu, Japan). The calix[4]resorcinarenes were also used for the similar procedure. The vegetable samples (5 mm × 5 mm) were put in the sample tube and dried by using the micromeritics VacPrep061 (Shimadzu, Japan) at 25 ℃ for 24 h. Then, the sample tube was launched in the analyzer in the relative pressure range of 1.0×10^{-4} to 9.9×10^{-1} at 77.3 K. Similar experiments for the N_2 adsorption of the vegetable plants, C_2H_4 adsorption was also measured in the range of 1.0-100k Pa at 273.15 K. These gas adsorption results were compared with those of zeolite and activated carbon. In their experimental results, to compare each value in unit area, the quantity adsorbed of C_2H_4 per unit (Q) was derived from the maximum quantity adsorbed of C_2H_4 (Q_m) and the BET surface area (V) according to following equation (5-1).

$$Q = Q_m / V \quad (5\text{-}1)$$

5.2.4 Analyze for C_2H_4 adsorption in the vegetable plants and calix[4]resorcinarene

Langmuir and Freundlich analyze were followed by standard methods for analyzing the equilibrium binding parameters for the homogeneous and heterogeneous surface, respectively [20]. In order to investigate the adsorption ability for C_2H_4 in the resultant vegetable plants, Langmuir (Eq.5-2) and Freundlich (Eq.5-3) analyze was taken as follows

equations from the result of their C_2H_4 adsorption experiments.

$$p/n^a = \frac{1}{n_m^a} + \left(\frac{1}{n_m^a}\right)p \qquad (5\text{-}2)$$

$$\ln n^a = ln\ a + \left(\frac{1}{u}\right) lnP \qquad (5\text{-}3)$$

where a is constant, u is adsorption intensity, p is the adsorbate's partial pressure, and n_a represent the binding capacity of the substrate to vegetable plants.

For isotherm data, Scatchard analysis, which was used as modified Langmuir plot, was the standard method for analyzing the equilibrium binding parameters of acceptor with a receptor. For C_2H_4 adsorption in the resultant S-host, V-host, PH-host, zeolite and activated carbon, the Scatchard equation (5-4) [21] was applied.

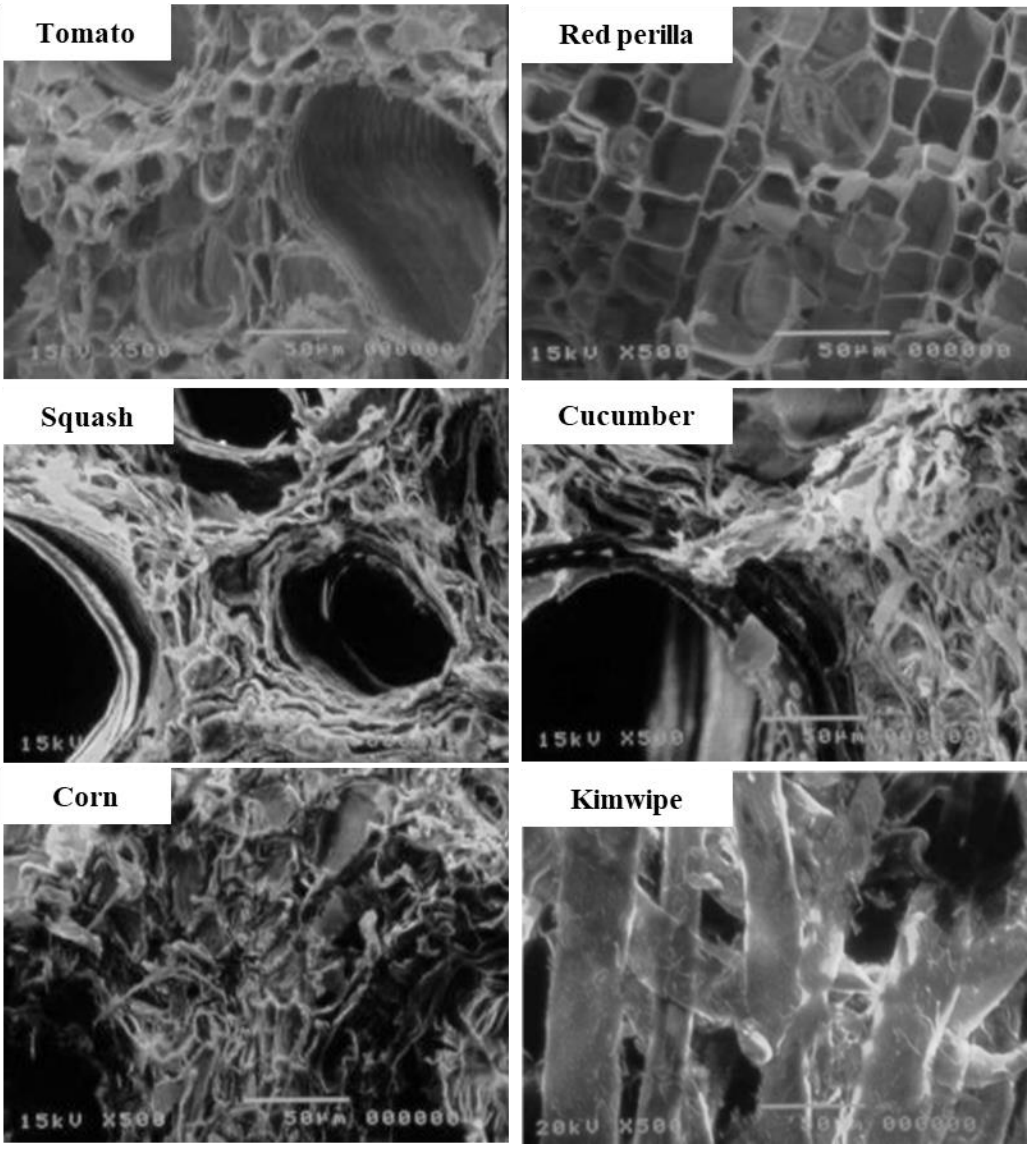
$$[S]/C_e = -[S]K_a + nK_a \qquad (5\text{-}4)$$

Here, K_a is the intrinsic equilibrium association constant, C_e and n represent the free concentration of substrate in equilibrium condition and binding capacity of substrate to S-host, V-host, PH-host, zeolite and activated carbon, respectively.

5.3 Results and discussion

5.3.1 Characterization of vegetable plants

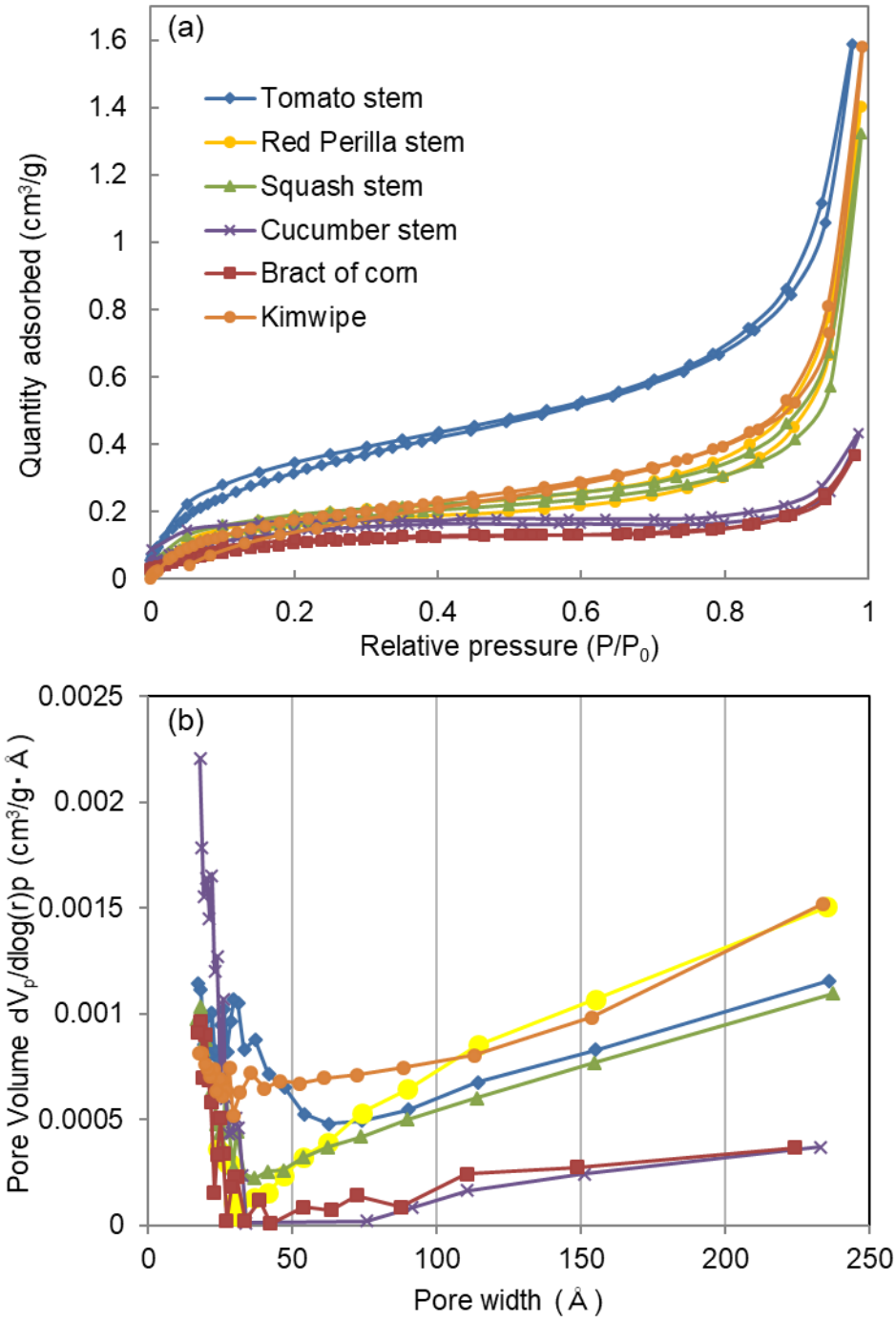
Figure 5.1 shows the SEM micrographs of the tensile fractured surface of tomato stem, squash stem, cucumber stem, red perilla stem, bract of corn and kimwipe at a magnification of 500×. As seen, the tomato stem, squash stem, cucumber stem and red perilla stem exhibited a fractured surface with many cell walls. Especially tomato stem and



Figures 5.1 SEM image of vegetable plants after washing with distilled water and dried for 5 days at room temperature and kimwipe.

red perilla stem had many fine cell walls. However, in the cases of squash stem, cucumber stem and bract of corn, the SEM micrographs exhibited no fine cell walls on the fracture surfaces. The pictures of the squash stem and cucumber stem suggested that fibrous cellulose had strongly aggregated each other. For the comparison, cellulose fiber, kimwipe, was used as a reference sample (Figures 5.1, bottom right). In order to examine their porous properties for gas adsorptivity, N_2 adsorption experiment was carried out. Figure 5.2(a) shows N_2 adsorption isotherms for their samples. The tomato stem showed the highest BET surface area in vegetable plants and BET surface area of tomato stem, red perilla stem, squash stem, cucumber stem and bract of corn were 0.76, 0.68, 0.66, 0.54 and 0.43 m^2/g, respectively. As seen in the isotherm of the tomato stem, the type was followed in type II for macro porous structure [22]. In Figure 5.2(b), meso pore distribution was calculated by Barrett-Joyner-Halenda method (BJH methods) [23]. The kimwipe, tomato stem and red perilla stem had pore distribution in the range of 150-200 Å. Also the tomato stem and red perilla stem had fine pores in the less than 40 Å regions. This well corresponded to the presence of the many fine cell walls on fractured surface. This also meant that these cells provided a wide surface area. In contrast, the bract of corn and the cucumber stem exhibited the lowest BET surface area in vegetable plants. The BJH pore distribution also suggested less pore volume distribution. The comparison of the BJH results suggested that red perilla stem having fine cell walls had very less pores in less than 50 Å regions, although the stem contacted larger pores having 150-200 Å size.

As seen in Figure 5.3, C_2H_4 adsorption experiment was carried out for the vegetable plants. The C_2H_4 isotherm of the tomato stem had higher adsorption to C_2H_4. The



Figures 5.2 N_2 isotherm (a) and BJH pore distribution (b) of vegetable plants and kimwipe.

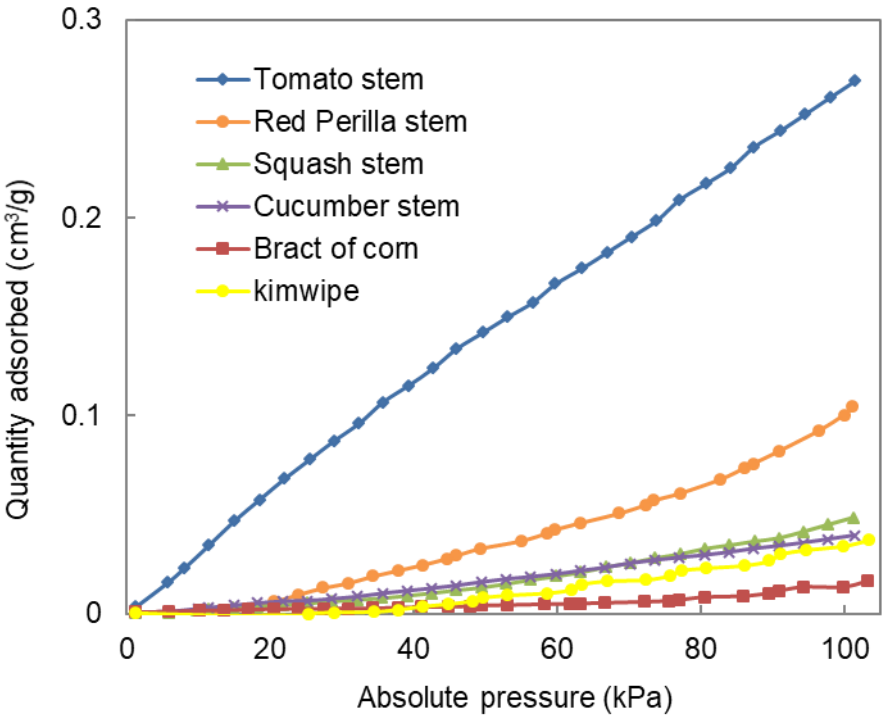


Figure 5.3 C_2H_4 isotherm of vegetable plants and kimwipe

adsorption quantities of tomato stem, red perilla stem, squash stem, bract of corn, cucumber stem and kimwipe were 0.27, 0.10, 0.05, 0.02, 0.04 and 0.04 cm^3/g, respectively, at 100k Pa. It was clear that the tomato stem showed the highest C_2H_4 adsorption capacity in the vegetable plans, meaning the presence of many fine cell walls on fractured surface. However, the red perilla and kimwipe having a similar BET surface area with tomato stem showed one-third and one-seventh lower than C_2H_4 adsorption quantity of the tomato stem, respectively. Therefore, it was indicated that not only physisorption of C_2H_4 occurred on vegetable plant, but also chemisorption occurred especially in tomato stem. The FT-IR spectra of vegetable plants and lignin (Figure 5.4) are comparable with vegetable plants, as shown in all vegetables. These vegetable plants spectra revealed a broad and intense peak at

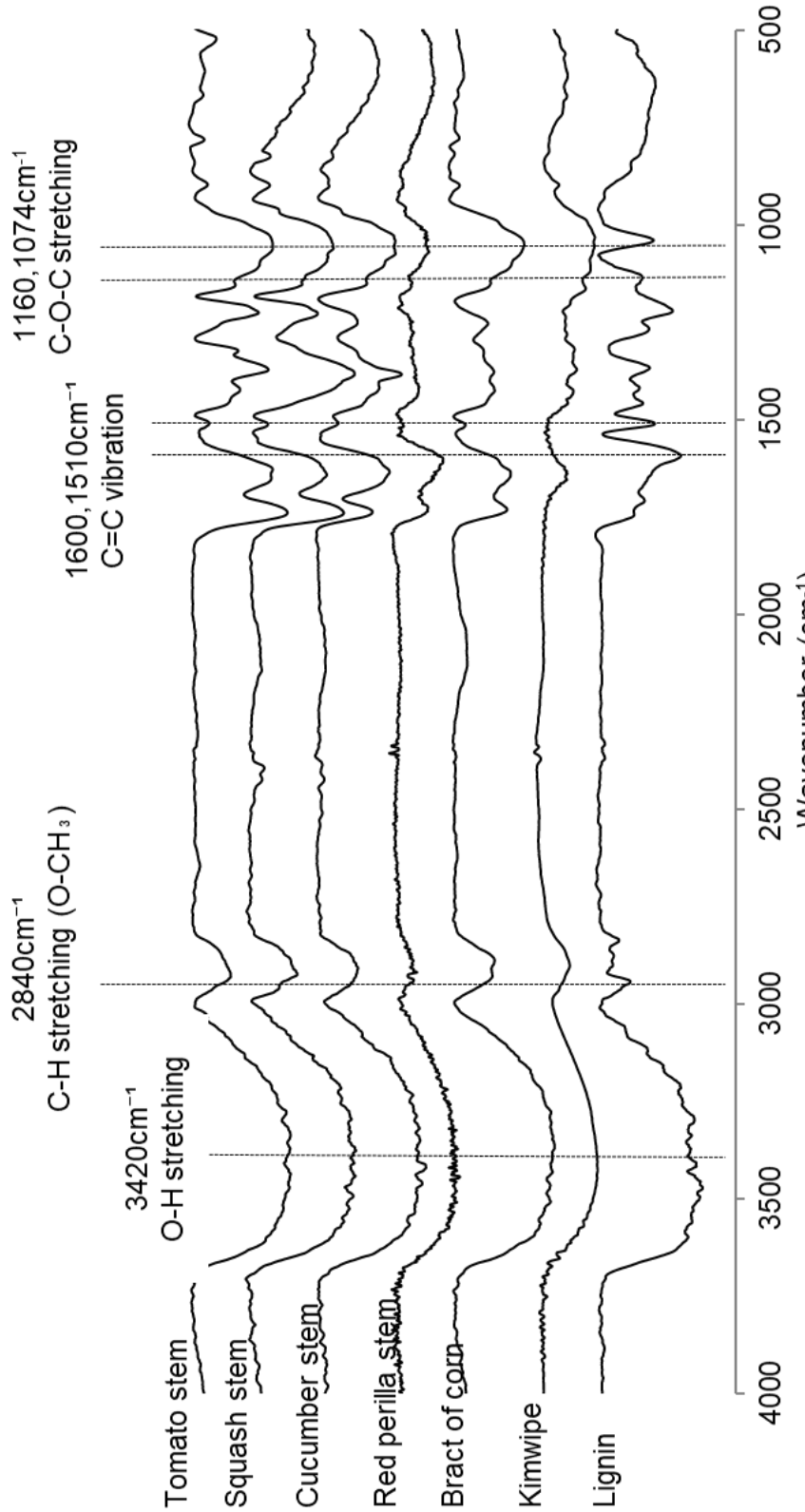
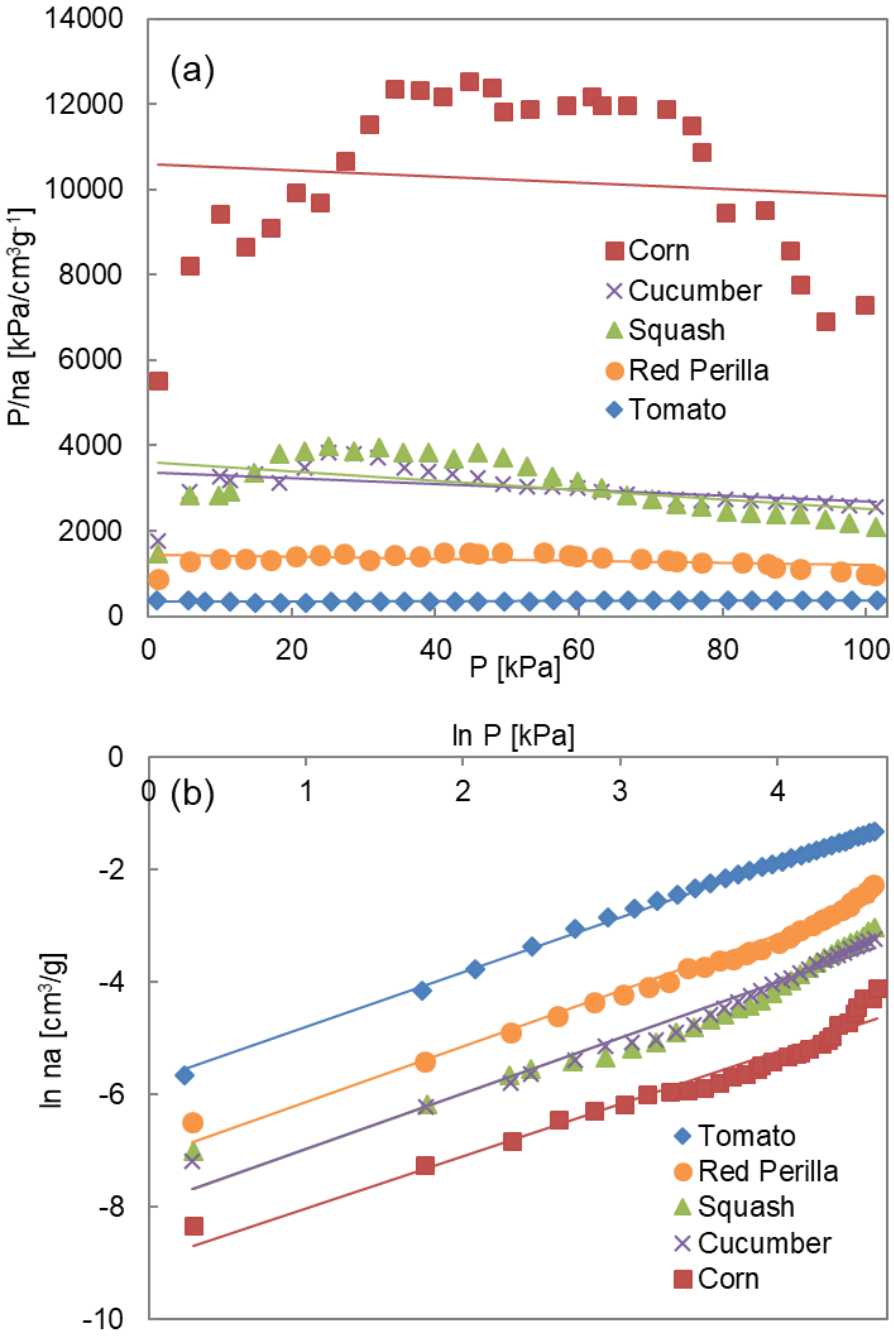


Figure 5.4 FT-IR spectra of vegetable plants, kimwipe and lignin.

3400 cm^{-1} attributed to hydrogen bonded (O-H bond) stretching vibration from the cellulose, whereas a weak absorption peak in the range of 1160-1050 cm^{-1}. These were assigned to C-O-C, C-OH and C-C bonded stretching vibration from the β-(1 → 4')-glycosidic bond. Moreover, they also had a weak absorption peak at 2840 cm^{-1} and 1600-1510 cm^{-1} assigned to C-H bonded stretching from the methoxy group and C=C bonded stretching vibration from the aromatic rings of the lignin, suggesting to their presence in vegetable plants. With these results, it was confirmed that tomato stem, squash stem, cucumber stem, red perilla stem, bract of corn showed the presence of IR peaks of lignin and cellulose. However, kimwipe composing the fibrous structure also exhibited strong O-H bond peak and C-O-C, C-OH and C-C bond at 3400, 1160-1050 cm^{-1}, respectively. These peaks were characterized from cellulose, but there were no peaks at 2840, 1600 and 1510 cm^{-1} for lignin.

5.3.2 Analyses of C_2H_4 adsorption to vegetable plants

To know the adsorption behavior of vegetable plants, the results of the C_2H_4 adsorption were applied for Langmuir and Freundlich analyzes. The Langmuir plots were obtained by C_2H_4 adsorption experiment for each vegetable plant in Figure 5.5(a). From the obtained date, the correlation coefficient (R_2) was calculated of tomato stem, red perilla stem, squash stem, cucumber stalk and bract of corn for -7.52, 0.49, -2.23, -10.92, -6.52 and -7.52, respectively. This was indicated that these C_2H_4 adsorption isotherm were not related to unimolecular adsorption on the surface. Figure 5.5(b) is Freundlich plots of the C_2H_4 adsorption. In the case of Freundlich plots, the values of R_2 of tomato stem, red perilla stem,



Figures 5.5 Langmuir plots (a) and Freundlich plots (b) for C_2H_4 in vegetable plants.

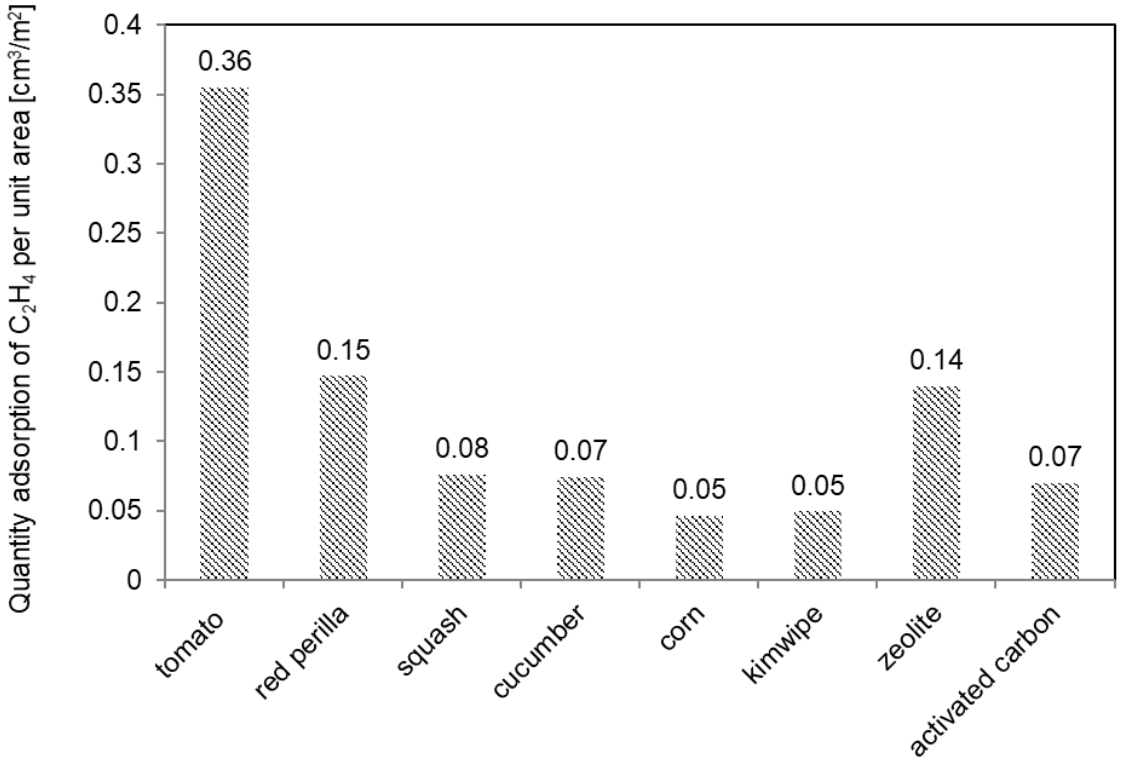


Figure 5.6 Quantity adsorption of C_2H_4 gas per unit area of each host.

squash stem, cucumber stem and bract of corn were 0.97, 0.99, 0.99, 0.98 and 0.93, respectively. This strongly indicated that the C_2H_4 adsorption isotherm of the vegetable plant obeyed with Freundlich relation, meaning that multi-layer adsorption of C_2H_4 was occurred on vegetable plants. The constant *a* is an approximate indicator of adsorption capacity, while 1/*u* is a function of the strength of adsorption in the adsorption process [24]. The values of the constant *a* were 0.0031, 0.0008, 0.0003, 0.0003 and 0.0001 for tomato stem, red perilla stem, squash stem, cucumber stem and bract of corn, respectively. The adsorptivity of C_2H_4 for the tomato stem was compared with those of zeolite and activated carbon. So, the volume of the C_2H_4 adsorption quantity (Q_a) and BET surface area was converted to the adsorptivity per unit area in the vegetable plants, zeolite and activated

carbon. Figure 5.6 shows the quantity of adsorption of C_2H_4 per unit area cm^3/m^2 for each sample. The zeolite and activated carbon had 0.14 and 0.07 cm^3/m^2 in the unit area adsorption to C_2H_4. In contrast, for the case of tomato stem, high adsorption to C_2H_4 occurred with 0.35 cm^3/m^2. This result meant that the tomato stem contained efficient adsorption sites to C_2H_4 in the microfibrous cellulose.

5.3.3 C_2H_4 adsorption experiment of calix[4]resorcinarenes

In order to compare C_2H_4 adsorptivity to calix[4]resorcinarenes with vegetable plants, the gas adsorption was measured. Figure 5.7 shows N_2 quantities adsorpted to

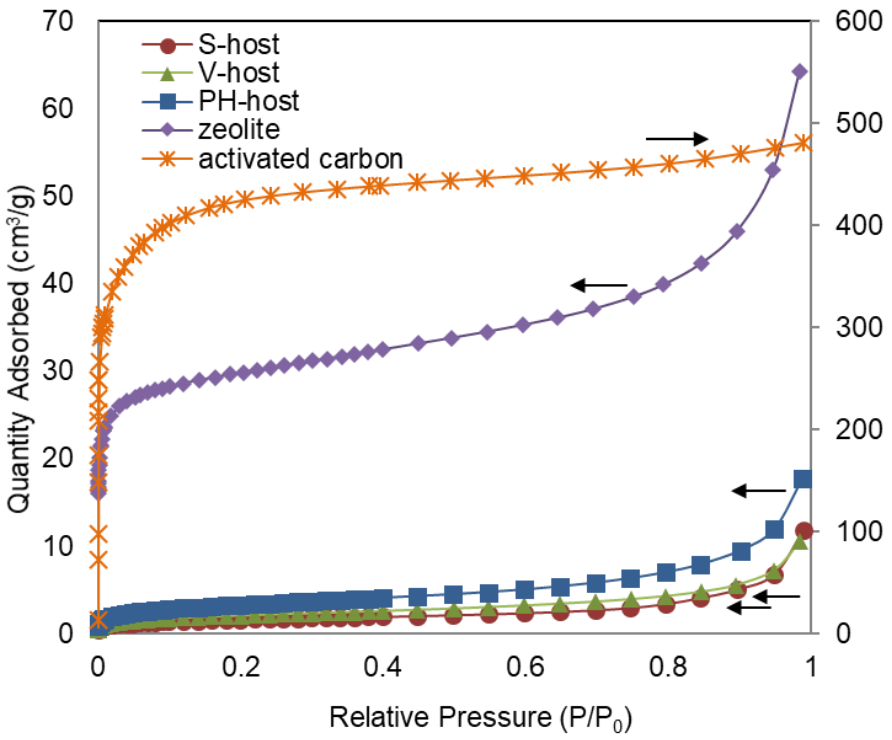


Figure 5.7 N_2 adsorption isotherms of S-host, V-host, PH-host, zeolite and activated carbon.

calix[4]resorcinarenes, zeolite and activated carbon. As seen, activated carbon and zeolite were much superior to N_2 adsorption than calix[4]resorcinarenes. This meant that their surface areas of activated carbon and zeolite were much larger than those of calix[4]resorcinarenes powder. The BET surface area was evaluated as 1431 and 102 m^2/g for the activated carbon and zeolite, and the values were 12.0, 7.5 and 5.8 m^2/g for PH-host, V-host and S-host, respectively, in their powers. In these cases of the N_2 adsorption isotherm for activated carbon, the curve was resembled in type I adsorption isotherms [22], meaning that those typically were microporous materials. On the other hands, all calix[4]resorcinarenes showed type II adsorption isotherms, which meant that the powders consisted of macroporous structures for the N_2 adsorption. These results suggested that the calix[4]resorcinarenes had less ability of physical adsorption of N_2 molecule whereas activated carbon and zeolite showed highly physical adsorption.

For testing C_2H_4 adsorptivity, the C_2H_4 adsorption isotherms were measured in the calix[4]resorcinarenes having different numbers of methoxy groups. Figure 5.8 shows C_2H_4 isotherms for the calix[4]resorcinarenes, zeolite and activated carbon. Here, the quantity of C_2H_4 was expressed in a unit surface area of the plots of the adsorbed volume (cm^3). From the result of the adsorption experiments of C_2H_4, it was noted that the S-host and V-host showed high C_2H_4 adsorptivity. The values of C_2H_4 adsorption amounts for S-host, V-host, PH-host, zeolite and activated carbon were obtained for 3.9, 2.2, 0.49, 0.14 and 0.064 cm^3/m^2, respectively, at 100 kPa of C_2H_4 pressure. So, the calix[4]resorcinarenes showed a higher C_2H_4 capacity than zeolite and activated carbon, when the value was converted to the C_2H_4 capacity of per unit area. It is known that the kinetic diameter of the C_2H_4 is 3.90

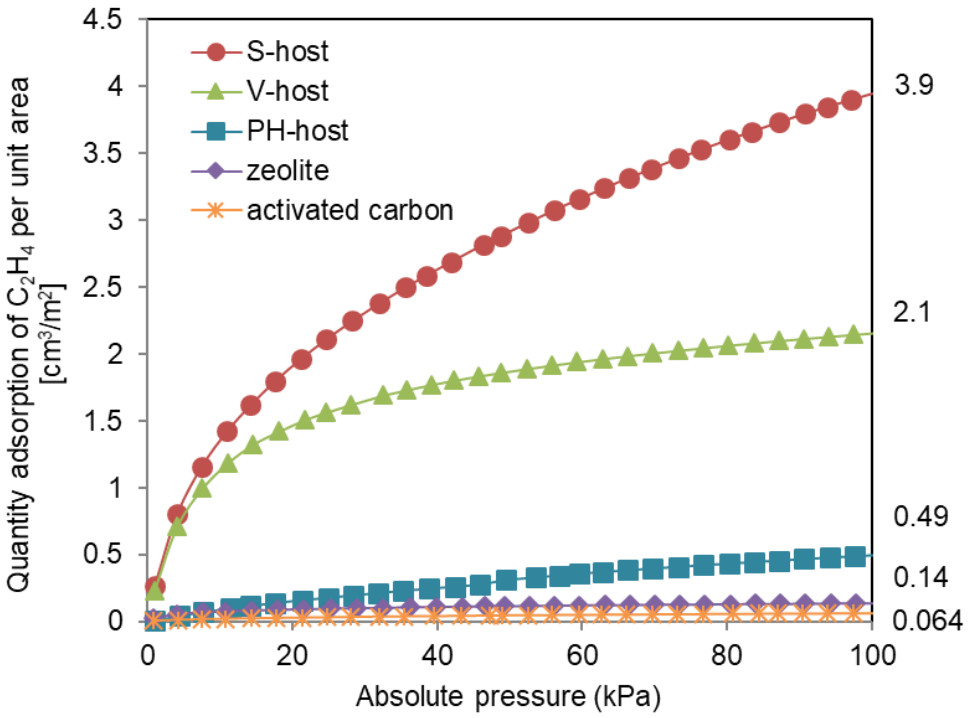
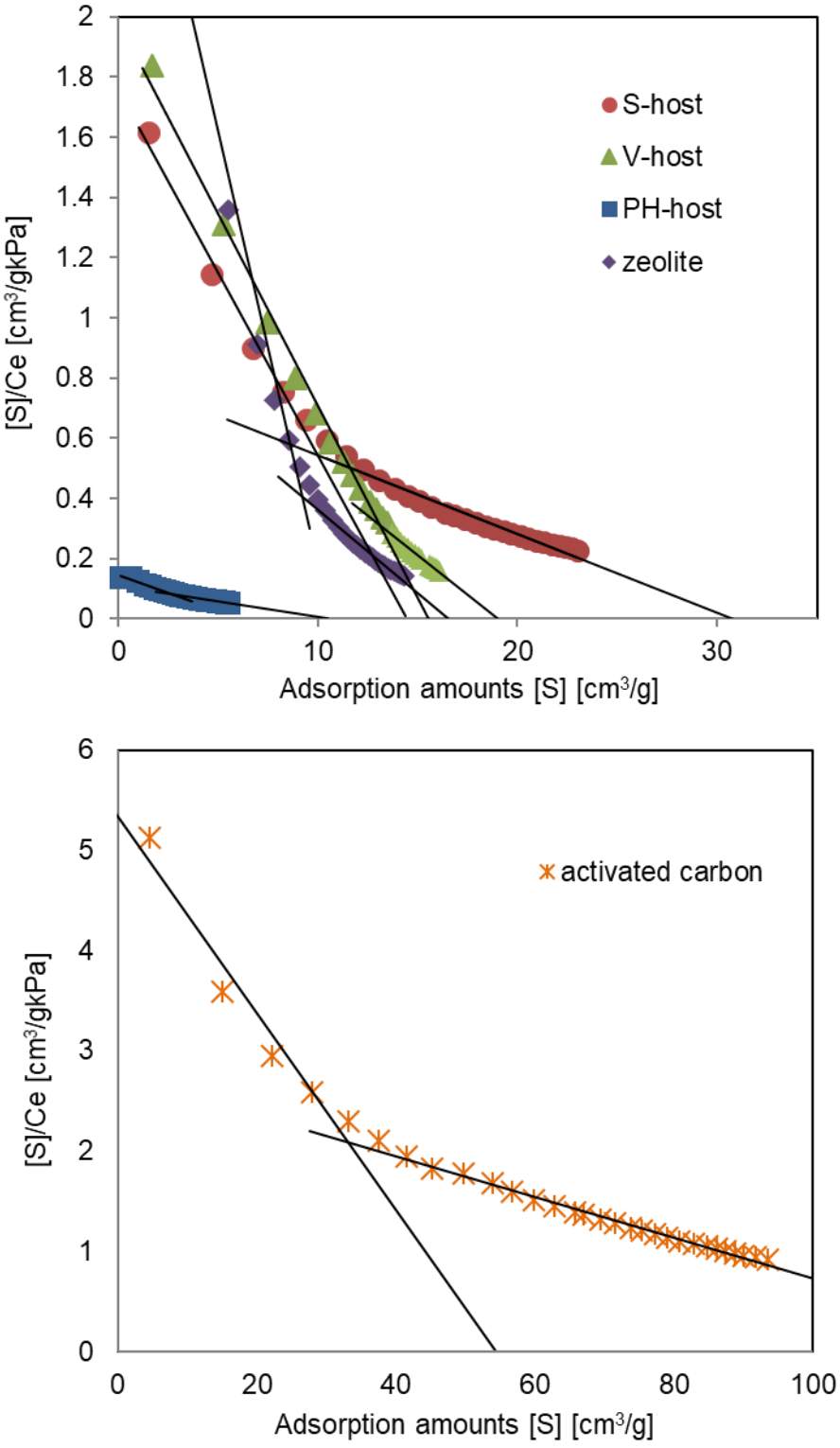


Figure 5.8 C_2H_4 adsorption isotherms of S-host, V-host, PH-host, zeolite and activated carbon.

Å and the inner cavity of zeolite and activated carbon are 2 Å-10 Å and 10 Å-200 Å, respectively [25, 26]. From these comparisons, it could easily understand that such C_2H_4 was well adsorbed on activated carbon with 93.5 cm^3/g adsorption amounts. On the other hand, the cavity size of calix[4]resorcinarene was estimated 2.59 Å [10]. This seems to be difficult to exclude the C_2H_4 molecular in the calix[4]ewsorcinarene cavity, although S-host and V-host behaved higher C_2H_4 adsorbers.

To know adsorption parameters and adsorption site for C_2H_4, the isotherm plots were represented in the modified Langmuir model, Scatchard analysis [27]. Figure 5.9 presents Scatchard plots obtained by C_2H_4 adsorption experiments for each calix[4]resorcinarene,



Figures 5.9 Scatchard plots for C_2H_4 in S-, V-, PH-hosts, zeolite and activated carbon.

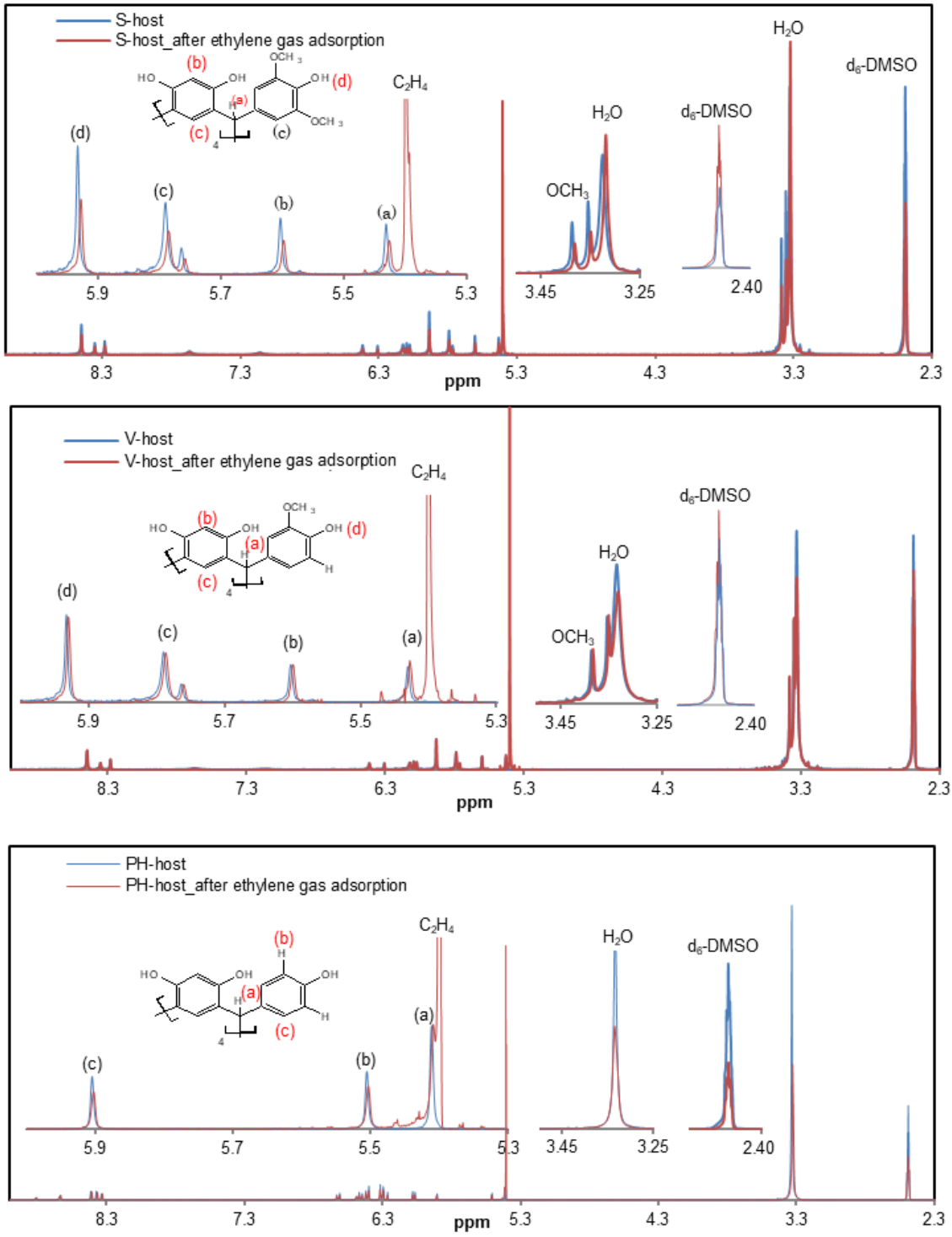
zeolite and activated carbon. In the resulting data, two straight line regions were obtained, meaning that these had different binding abilities for the C_2H_4 adsorption to non-specific and specific bindings [27]. From the straight areas, values of binding equilibrium constants (K_a and K_{ah}) were estimated as shown in Table 5.1. At low adsorption amount region, the obtained values of K_a for the S-host and V-host were higher than that of the activated carbon. But zeolite had higher value for the K_a, although zeolite had the lower binding capacity of 10.6 cm^3/g in comparison with those of the S-host and V-host of 14.5 and 15.5 cm^3/g. In the region of the adsorption at larger than 10 cm^2/g of [*S*], the S-host, V-host and zeolite showed K_{ah}=0.026, 0.053, and 0.055 K/Pa, respectively, for physical of C_2H_4 adsorption. It was cleared that the S-host and V-host exhibited higher C_2H_4 adsorption sites relative to that of PH-host having no methoxy group in the calix[4]resorcinarene structure. In addition, both former calix[4]resorcinarenes had higher adsorptivity than zeolite and activated carbon in unit area base.

Table 5.1 C_2H_4 binding abilities in S-, V-, PH-hosts, zeolite and activated carbon.

	BET surface area	K_a	Binding capacity (n)	K_{ah}
	[m^2/g]	[kPa^{-1}]	[cm^3/g]	[kPa^{-1}]
S-host	5.8	0.12	14.5	0.026
V-host	7.5	0.13	15.5	0.053
PH-host	12	0.024	6.2	0.010
Zeolite	102	0.29	10.6	0.055
Activated carbon	1431	0.098	53.4	0.020

5.3.4 ^{1}H-NMR analysis for estimation of the host-C_2H_4 interaction

To investigate the chemical interaction of the calix[4]resorcinarene with C_2H_4, NMR analysis was carried out when C_2H_4 was saturated by C_2H_4 babbling purge in the d_6-DMSO solution. Figure 5.10 shows ^{1}H-NMR spectra of calix[4]resorcinarene solution at room temperature before and after C_2H_4 purged in the solution. Each NMR spectrum had a strong peak at 5.4 ppm for C_2H_4 in addition to the peak at 5.41 to 5.44 ppm originating from the ring current effect of the formation of the calix[4]resorcinarene ring. The OH proton from resorcinol of S-host and V-host appeared at 8.34 ppm. In the case of the PH-host, the OH proton peaks for the resorcinol and *p*-hydroxybenzaldehyde were appeared as the multiple peak at 8.37 and 8.60 ppm, respectively. The chemical shift was observed in the absence and presence of C_2H_4 adsorption in slight shift toward higher magnetic field at the 5.4-6.4 ppm for the C-H bond. This was attributed to outer and inner aromatic protons in the host ring and methoxy group, and O-H group. However, the PH-host had no tendency on the peak shift even though C_2H_4 was present. Additionally, the S-host and V-host spectra revealed a multiple peak at 3.38-3.35 ppm attributed to C-H bonded from the methoxy group and expressed chemical shift at 3.38-3.35 ppm due to the presence of methoxy group in their structure. This indicated that the introduction of C_2H_4 made electron density of the whole calix[4]resorcinarene increase. Because of the interaction between calix[4]resorcinarene and C_2H_4, especially, the S-host had the highest shift in the range of 5.4-6.4 ppm in the calix[4]resorcinarene. As mentioned before, the diameter of the C_2H_4 is 4.163 Å, whereas calix[4]resorcinarene has 2.59 Å cavity. So, it might be thought that S-host, V-host and PH-host had difficulty for the gas molecule inclusion. But the NMR



Figures 5.10 ^{1}H-NMR spectra of calix[4]resorcinarene solution before and after C_2H_4 purged in the solution.

results suggested that by using their -OCH_3 group. Therefore, it was might be expected interactions of C_2H_4 adsorption which was well occurred in the S-host having -OCH_3 group. However, as considered about the result of C_2H_4 adsorption in PH-host having same number of OH groups without -OCH_3 group, the no chemical shift meant quietly lower interaction. When the -OCH_3 group was bonded to an aromatic ring, the electron donating property acted as donating electrons to the guest molecule. Therefore, the host-guest interaction for electron deficient C_2H_4 occurred with -OCH_3 groups for chemisorption and efficiently performed by the S-host calix[4]resorcinarene.

5.4 Conclusion

In this chapter, high C_2H_4 adsorption was found in tomato stem because the stem morphology developed fine cell walls, showing to isotherm obeyed by Freundlich plots. Moreover, the C_2H_4 adsorption on calix[4]resorcinarenes synthesized from syringaldehyde and vanillin by condensation with resorcinol were much higher than the tomato stem sample. In the analyzed Scatchard plots, the calix[4]resorcinarenes having hydrogen and -OCH_3 group had high ability of C_2H_4 adsorption, especially in depending on the number of the -OCH_3 groups in the host. The ^{1}H-NMR analysis revealed that a -OCH_3 group effectively help to adsorb the C_2H_4 in calix[4]resorcinarene, suggesting that chemisorption site includes in the green aldehydes.

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Chapter 6

Summary

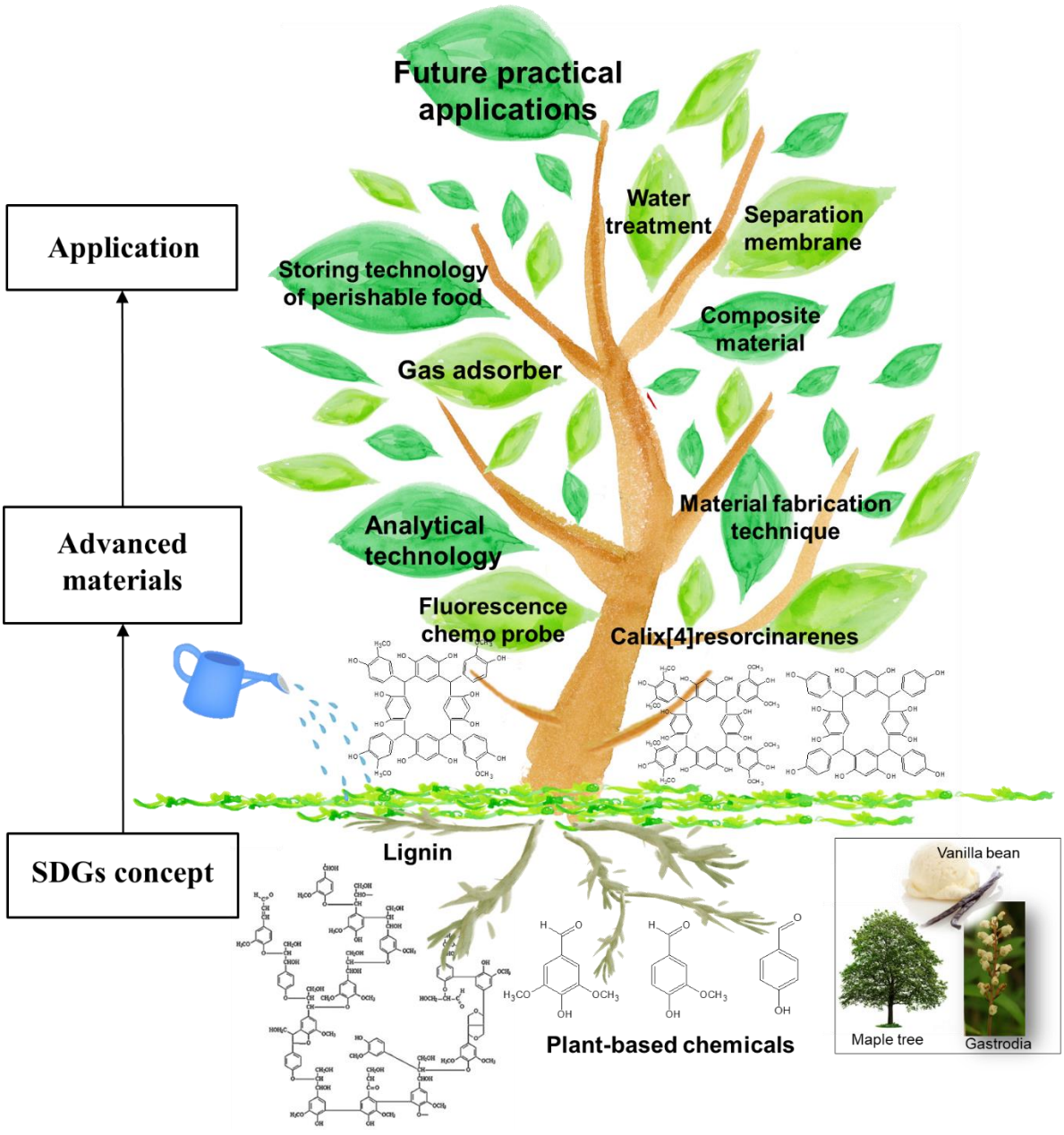
The present thesis has focused on synthesis of novel calix[4]resorcinarenes and their applications used as adsorbents for mainly heavy metal ion and Cs^+. Here, because of importance of SDGs, using plant-based aldehyde is adopted for water decontaminant adsorbers, the calix[4]resorcinarenes, were synthesized for purpose of hosting molecules to the targeted metal ions and ethylene in their separator uses. Especially, this demonstrated versatile technologies in analytical chemo diagnosis and composite membranes as first report in these fields. This thesis discussed and expected the contribution to understanding of these calix[4]resorcinarene prepared from such lignin-derived aromatic aldehydes in points of view of green chemistry. Chapter 1 summarized a brief introduction of the related topics to the water environment pollution. Also, in a sustainable issue, the importance of plant derived materials was mentioned in the point of view of host-guest materials. Among them, especially, the synthetic approach of calix[4]resorcinarene derivatives and basic properties and applications were described in this chapter. Chapter 2 revealed that the facile synthesis of calix[4]resorcinarene by condensation of resorcinol and plant derived aromatic aldehyde such as syringaldehyde, vanillin and *p*-hydroxybenzaldehyde. In this chapter, the comparative investigations of adsorption behaviors of several heavy metal ions for the obtained calix[4]resorcinarenes were conducted as fluorescence analysis of the calix[4]resorcinarenes. The quenching process of the fluorescence of the

calix[4]resorcinarene was applicable for sensitive selectivity toward Pb^{2+} ion. In combination with UV spectroscopic analytical data, the potential ability was introduced to sensitive fluorometric detection of the Pb^{2+} ion. Chapter 3 focused on the fabrication of composite membrane consisting of poly(ethersulfone) and calix[4]resorcinarene. With increasing the amount of calix[4]resorcinarene in composited membranes, these were porous structure with higher surface area and improve their heavy metal adsorptivity due to the introduction of calix[4]resorcinarene having selective hosting. It was evidenced that PES-calix[4]resorcinarene composited membrane showed innovative nature in separator to Pb^{2+} through the membrane filtration process. It was firstly reported that calix[4]resorcinarene hosting composition in porous PES membranes was efficient for the effect permeably and selective separation. Chapter 4 described investigation of Cs^{+} ion separation from alkali metal ion mixture in the presence of such Na^{+} ion and K^{+} ion for using the calix[4]resorcinarenes. The adsorbent performance was worked well even in the co-presence of Na^{+} and K^{+} ions for Cs^{+} ion, showing highly separated selectivity to the ion. The investigation of Cs^{+} adsorptivity and selectivity of calix[4]resorcinarene composited membrane and fiber reveled that the filtration process of composited membrane was efficient for Cs^{+} separation from alkali metal ion mixture. Chapter 5 revealed ethylene gas adsoptivity of calix[4]resorcinarene. Comparative investigations revealed that the calix[4]resorcinarene having methoxy group showed a higher adsorption capacity towards C_2H_4 gas. The evidence of the synthesized calix[4]resorcinarenes maintained chemical interaction with electron deficient C_2H_4 occurred with methoxy groups, leading chemisorbed binding with calix[4]resorcinarene. The C_2H_4 adsorptivity was also compared

plant material such as vegetable plants like tomato stem, squash stem, cucumber stem, bract of corn and red perilla stem. The comparison was indicated that the present calix[4]resorcinarenes were highly adsorbed in C_2H_4.

As a conclusion of this thesis, the resultant concerned with synthesis and fabrication of advanced materials which sourced from green chemicals and then functional adsorbents contain innovative applications for future practical uses. These concepts are illustrated as last figure for growing tree scheme according to concept of SDGs. As possible future applications, because there is no such ethylene gas adsorbent by organic material, it would be expected that the calix[4]resorcinarene can composite with inorganic plastic material to develop a novel wrapping bag for food industry area, since the composites can effectively adsorb ethylene gas to keep vegetable fresh.

In addition, the contents of such calix[4]resorcinarenes and their functional materials for significant selectivity to ion and molecule are quite meaningful for future development to separation and decontamination fields as new technologies. I hope that this study can contribute to extend to be attractive for their future applications in global industry.


Future practical applications
Application
Advanced materials
SDGs concept
Water treatment
Separation membrane
Storing technology of perishable food
Composite material
Gas adsorber
Material fabrication technique
Analytical technology
Fluorescence chemo probe
Calix[4]resorcinarenes
Lignin
Plant-based chemicals
Vanilla bean
Maple tree
Gastrodia

List of Publications

1. Lisa Nakajima, Nor Nadiah Mohamad Yusof and Takaomi Kobayashi, "Calixarene-Composited Host–Guest Membranes Applied for Heavy Metal Ion Adsorbents", Arabian Journal for Science and Engineering, Vol. 40, 2015, p. 2881–2888.

2. Lisa Nakajima and Takaomi Kobayashi, "Calixarene Hosts Synthesized from Green Chemicals of Vanillin and Syringaldehyde: Fluorescence Probes for Pb^{2+}", Journal of Chemical Engineering of Japan, Vol. 49, Issue 9, 2016, p. 878–883.

3. Lisa Nakajima, Mako Nishiduka, Shuji Uchida and Takaomi Kobayashi, "Vegetable waste adsorbers for ethylene gas", International Journal of Engineering and Technical Research, Vol. 7, Issue 10, 2017, p. 10-13.

Other related papers

1. Anyaporn Boonmahitthisud, Lisa Nakajima, Khoa Dang Nguyen and Takaomi Kobayashi, "Composite effect of silica nanoparticle on the mechanical properties of cellulose-based hydrogels derived from cottonseed hulls", Journal of Applied Polymer Science, Vol. 134, Issue 10, 2016, p. 44557(1-12).

2. Nuttida Srirachya, Kanoktip Boonkerd, Lisa Nakajima and Takaomi Kobayashi, "Bio-composite hydrogels of cellulose and vulcanized natural rubber with nano interconnected layers for reinforced water-retaining materials", Polymer Bulletin, Vol. 75, Issue 12, 2018, p. 5493–5512.

Presentations in International Conferences and Symposiums

1. **5th International Conference for Young Chemists (ICYC 2015)**, Penang, Malaysia, "Natural Chemicals Calixarene Hosts Synthesized for Fluorescence Chemo-Probes to Heavy Metal Ions", Lisa Nakajima, Nor Nadia Mohamad Yusof and Takaomi Kobayashi, August 5-7, 2015.

2. **The 4th Joint Symposium CU-NUT**, Bangkok, Thailand, "Green Chemicals Calixarene Hosts Synthesized for Highly Selective Fluorescence Chemo Sensor for Pb^{2+}", Lisa Nakajima and Takaomi Kobayashi, October 21-22, 2015

3. **The 5th international GIGAKU Conference in Nagaoka (IGCN2016)**, Nagaoka. Niigata, Japan, "Synthesis and Use of Green-Chemical Calix[4]resorcinarenes Applied for Ethylene Gas Adsorbent", Lisa Nakajima and Takaomi Kobayashi, October 6-7, 2016.

4. **International Symposium on Local Innovative Activation by Food and Energy (2nd ISLife2017 Summer),** Nagashima, Kagoshima, Japan, "An efficient approach toward C_2H_4 adsorbent by calixarenes synthesized with plant aldehydes having different number of methoxy groups", Lisa Nakajima and Takaomi Kobayashi, August 9-10, 2017

5. **2nd International Conference on Materials Engineering and Functional Materials (ICMFM2018)**, Da Nang, Vietnam, "Calixarenes Prepared from Plant Aldehydes Having Methoxy Groups and Their Cecium(I) Adsorbers", Lisa Nakajima and Takaomi Kobayashi, May 5-7, 2018.