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ORIGINAL PAPER

Predominant hosting lead(II) in ternary mixtures of heavy metal ions by a novel of diethylaminomethyl-calix[4]resorcinarene

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Abstract Heavy metal ions from single and ternary systems of Pb(II), Cu(II), and Ni(II) adsorbed by calix[4]resorcinarenes in water–chloroform extraction were studied. Comparison was made of calix[4]resorcinarenes, 2,8,14,20-tetraundecyl calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol, and diethylaminomethyl-calix[4]resorcinarene, 5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20- tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol, for predominant extraction of their ions from the ternary mixture of aqueous solution at different pH in a water layer. The hosting of Pb(II) by the diethylaminomethyl-calix[4]resorcinarene occurred efficiently at pH 6–7. The hosting of Pb(II), Cu(II), and Ni(II) ions for the ternary aqueous mixture was applied to the Langmuir isotherm. Adsorption was studied using nuclear magnetic resonance spectroscopy in a water–deuterium chloroform extraction system. Results showed that as the heavy metal ions were included into the host cavity, the observation of shifted peaks of water molecules from downfield to higher field was visible in the nuclear magnetic resonance spectra, meaning that water molecules were included with heavy metal ion into the host cavity. The spectra also showed that the diethylamino group expressed formation of the coordination complex between the diethylaminomethyl-calix[4]resorcinarene and Pb(II) for the purpose of predominant hosting of Pb(II).

Keywords Calix[4]resorcinarenes · Langmuir isotherm · Nuclear magnetic resonance analysis · Wastewater treatment

Introduction

Recently, industrial wastewater effluents are often encountered in facilities conducting metal plating and electroplating, or producing fertilizers, batteries, dyes, chemical pharmaceuticals, and electronic devices, where considerable amounts of toxic and pollutant heavy metals are used. Such sites attract attention for development of effluent treatment in several fields. Heavy metals such as lead (Pb), copper (Cu), nickel (Ni), and others are well known to be associated with a tendency to accumulate in living organisms and are known to be highly toxic when absorbed into the human body (Friberg et al. 1979). Generally, the treatment of such industrial waste typically involves expensive techniques such as chemical precipitation, membrane adsorption, ion exchange, and adsorption on activated carbon (Rengaraj et al. 2001; Karthikeyan et al. 2005). Although adsorbents are obtainable at low cost, for example, natural adsorbents such as peanut pellets (Johnson et al. 2002), leaf powder (Ngah and Hanafiah 2008), and organosolv lignin (Acemioglu et al. 2003), active compounds in natural adsorbents are known to be insufficient for treating low levels of heavy metal ions in wastewater. Therefore, new processes including synthetic

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adsorbents must be developed to produce an alternative adsorbent. Especially, high activity of adsorbents is at meeting point of several areas in chemical sciences from the design of recognition and separation process. That is, a technique in the specificity for the recognition of specific analytes has attracted increasing interest in recent years.

Calix[4]resorcinarenes are known to be resorcinol-based macrocyclic or cyclic oligomers that possess a cone-shaped molecular cavity formed by four resorcinol units. These cyclic tetramers are prepared by acid-catalyzed condensation of resorcinol and aldehydes. Consequently, these interesting compounds are capable of forming host–guest complexes. In a pioneering work, Aoyama et al. (1989) demonstrated the potential of calix[4]resorcinarenes as a host–guest complex to interact with other molecules such as organic cations, anions, and molecules. Meanwhile, calix[4]arenes that were initially available for cation transport of Li(II), Na(II), and other cations from group I were investigated by Izatt et al. (1983, 1985). Furthermore, some reports have described the uses of calix[4]resorcinarene as a metal ion extraction agent as a single component of heavy metal ions. Such usefulness of the host, calix[4]resorcinarene, was used in many applications for liquid membranes (Minhas et al. 2010) and as an additive in chemical sensing for HPLC stationary phase and metal ion extraction agents (Jumina Sarjono et al. 2007). These works were focused in uses of only HPLC stationary phase for analytical field. Minhas and his co-workers (2010) studied the selectivity of Hg(II) as a carrier on the efficiency of transport process in extraction using a bulk liquid membrane containing calix[4]arene. However, the utilization of calix[4]resorcinarenes as an adsorbent in heavy metal ions remains limited. Little is known of details for separation mixtures of heavy metal. Therefore, challenges remain which hinder the study of separation behavior of such calix[4]resorcinarene by hosting the metal ions. In addition, these calix[4]resorcinarene hosts containing long-chain alkyl groups in the arene ring increase the solubility in organic solvents. Thus, they are having a potential as an application of additives, for example, used in coating with paint in order to appear heavy metal sorption. There would be possibility to such appearance of absorption specificity in several industrial products by paint and thin active layer formation on the bulk matrix for introducing heavy metal capture.

In the present study, two series of calix[4]resorcinarenes derivatives of 2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol (N-host) and 5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20-tetraundecyl calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol (DA-host) (Fig. 1) were synthesized and used as adsorbents for Pb(II), Cu(II), Ni(II) ions, and their mixtures for uptake in an aqueous medium at different pH. The intention was to investigate the competitive adsorption behavior of the series of the adsorbent in removal of ternary component of Pb(II), Cu(II), and Ni(II) from aqueous solution. The experimental factors such as pH variation and ion concentration in aqueous solution side for liquid–liquid extraction with chloroform which containing the hosts as adsorbent were reported in this paper. This research was completed during September 2011, at laboratory under Department of Materials Science and Technology of Nagaoka University of Technology, Japan.

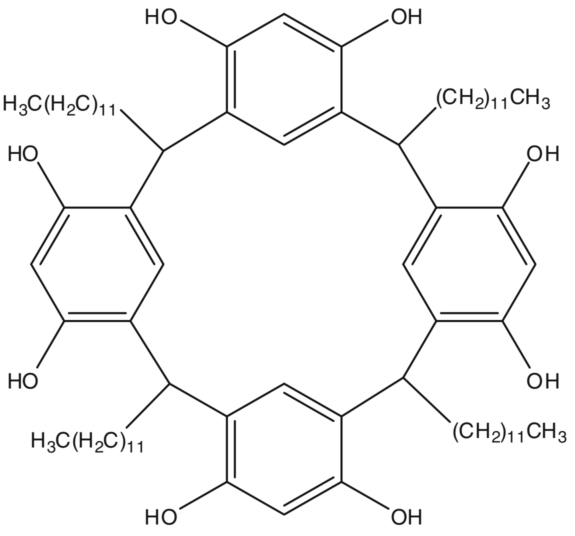
Materials and methods

Materials

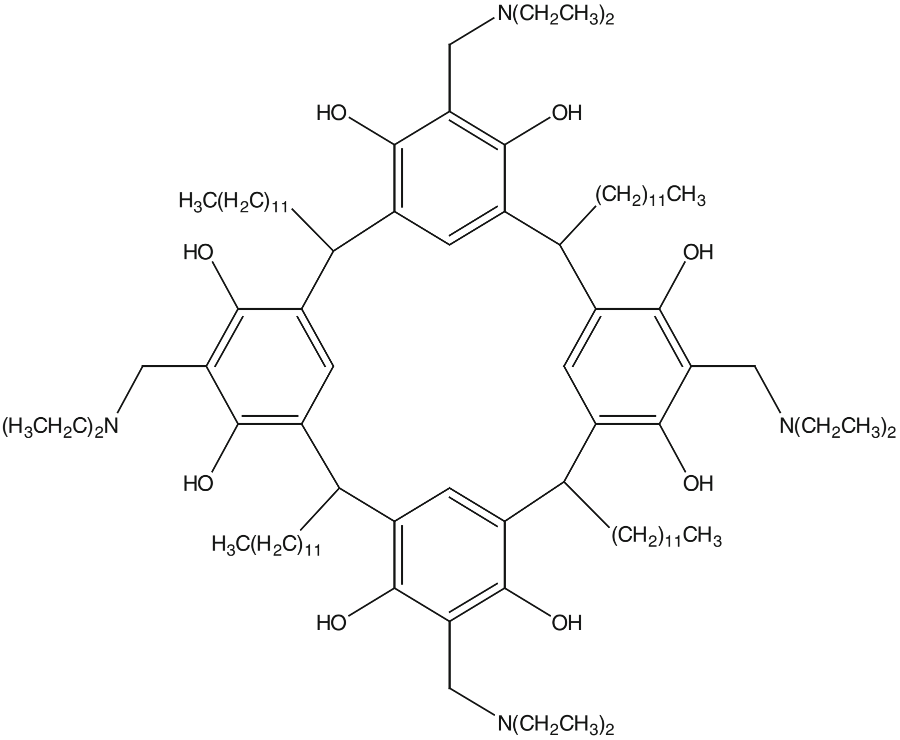
The materials used in this study consisted of resorcinol and dodecanal, which were purchased from Fluka Chemical Co. (Japan). Formaldehyde and diethylamine were purchased from Tokyo Chemical Industry Co. Ltd. (Japan). Benzene, ethanol, and 12 *N* hydrochloric acid (HCl) were obtained from Nacalai Tesque Inc. (Japan). All chemicals were used without further purification.

Preparation of 2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24–octol (N-host)

The N-host was synthesized by dissolving resorcinol (25.32 g, 0.23 mol) and dodecanal (42.39 g, 0.23 mol) in ethanol (300 mL). Then, 12 N HCl (50 mL) was added to the mixture of solution at 0 °C. The mixture was stirred and heated to 70 °C under nitrogen atmosphere for 10 h, after which the precipitates that had separated on cooling the mixture down to room temperature were recovered by filtration. Small amounts of additional precipitates were obtained by addition of water to the filtrate. The precipitates were combined, washed thoroughly with hot water (80 °C, 10 L), and then recrystallized twice from methanol and twice from hexane–acetone. Finally, the powders were dried at 0.2 mmHg for 24 h. This process gave the compound as a monohydrate as colorless needles (Faizal et al. 2009). The yield of the N-host was 50.2 %. Then, Fourier transform infrared spectroscopy (FT-IR) (IR Prestige-21 FTIR-8400s; Shimadzu Corp., Japan) and nuclear magnetic resonance spectroscopy (NMR) (JNM GX400; JEOL, Japan) were used to characterize the N-host. The FT-IR of the N-host in potassium bromide (KBr) method was



(a) 2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol



(b) 5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol

Fig. 1 Chemical structure of calix[4]resorcinarenes. **a** 2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol. **b** 5,11,17,23-tetra(diethylaminomethyl)-2,8,14,20-tetraundecylcalix[4]resorcinarene-4,6,10,12,16,18,22,24-octol

applied [cm^{-1}]: 3,469 (O–H), 2,900 (–C–H stretching), 1,616–1,496, and 837–719 (benzene ring of the N-host). ^{1}H-NMR of the N-host: in deuterium chloroform ($CDCl_3$) δ[ppm] = 9.68–9.32 (*m*, OH), 7.29–6.14 (*s*, H_1 and H_2), 4.60–4.33 (*s*, OH), 141–1.30 (*m*, 25H, CH_2), 0.93–0.90 (*m*, 4H, CH_3).

Preparation of 5,11,17,23-tetra(diethylaminomethyl)–2,8,14,20-tetraundecyl calix[4]resorcinarene-4,6,10,12,16,18,22,24-octol (DA-host)

To a mixture of 10.0 g of the N-host (0.045 mol), 7.21 g of formaldehyde (0.12 mol) and 6.51 g of diethylamine (0.045 mol) were added to 1:1 % (v/v) benzene–ethanol solution for 100 mL. The mixture was kept under nitrogen atmosphere for 24 h at room temperature. Then, the mixture was heated for 120 min at 60 °C. The mixture of solution was cooled and then evaporated to obtain a viscous solution. The viscous solution was continued with recrystallization using a mixture of 1:1 % (v/v) benzene–ethanol solution until a white precipitate was obtained (Knyazeva et al. 2009). The DA-host was dried in vacuum (0.2 mmHg) to obtain a constant mass and was then characterized using (IR Prestige-21 FTIR-8400s; Shimadzu Corp., Japan) and NMR (JNM GX400; JEOL, Japan). The yield of the DA-host was 76.2 %. FT-IR of the DA-host using the KBr method was used [cm^{-1}]: 3,277 (O–H), 2,916–2,848 (–C–H stretching), 1,577–1,475 (benzene ring of the DA-host), 1,355–1,244, and 981–777 (–CH–N–($CH_2CH_3)_2$). ^{1}H-NMR of the DA-host: ($CDCl_3$) δ [ppm] = 3.87–3.72 (*m*, OH), 7.09 (*s*, H_3), 4.29–4.25 (*m*, CH_2), 2.18 (*s*, 3H, CH_2), 1.35–1.25 (*m*, 20H, CH_2), 1.06 (s, 6H, CH_3).

Adsorption experiments for single and ternary components of heavy metal ions in liquid–liquid extraction

The removal efficiency of single and ternary components of heavy metal ions was investigated. Standard solutions of Pb(II), Cu(II), and Ni(II) were prepared with appropriate concentrations using analytical reagent grades of each metal purchased from Nacalai Tesque Inc. (Japan). Experiments were performed with liquid–liquid extraction of the water–chloroform system by dissolving 0.2 g of the hosts to 5 mL chloroform. Then, 20 mL of each metal ion (10 mmol/L) was poured into a different centrifuge tube. The effects of Pb(II), Cu(II), and Ni(II) adsorption were studied at different pH. The mixture solution pH was adjusted to the necessary pH value by adding either 0.1 M sodium hydroxide (NaOH) or 1.0 M hydrochloric acid (HCl). The mixture was mixed well in centrifugation for 60 min with 600 rpm at different pH. The temperature was controlled to 20 °C. After 60 min, the aqueous solution was separated from the organic layer (chloroform phase). The concentrations of remaining heavy metal ions Pb(II), Cu(II), and Ni(II) in the aqueous solution were measured at a certain wavelength using an atomic adsorption spectrophotometer (AA-6300; Shimadzu Corp., Japan). Optimum conditions for adsorption equilibrium for the N-host and DA-host onto each metal were found to be 60 min at pH 6. Selectivity of the N-host and DA-host for the interfering metal ion was evaluated using the following equation (Castillo et al. 2005).

$$\text{Adsorption capacity}, q_e = \frac{(C_i - C_f)}{W} V \quad (1)$$

Therein, C_i signifies the initial concentration of metal ion (mmol/L) and C_f denotes the final concentration of metal ion (mmol/L) after equilibrium, V represents the volume of the metal ion solution (L), and W stands for the weight of the N-host or DA-host (g) used. The unit for the adsorption capacity q_e was mmol/g.

The adsorption experiment for the DA-host in ternary heavy metal ion solution was conducted in a similar manner to the N-host cases. For the ternary heavy metal ion solution, the concentration was fixed at 10 mmol/L of each Pb(II), Cu(II), and Ni(II) ion. The purpose was to study the comparison of adsorption capability of heavy metal ions by the N-host and DA-host in the ternary aqueous solution at different pH. Moreover, isotherm studies were conducted at a constant dosage weight (0.2 g) and by varying the concentration of heavy metal ions within the 10–50 mmol/L range. The amounts of heavy metal ion adsorption were calculated based on the difference of the heavy metal ions concentrations in aqueous solution before and after adsorption, the volume of the aqueous solution (20 mL) and the weight of the adsorbent (0.2 g) using adsorption capacity Eq. (1).

The interaction between the hosts and the heavy metal ions was investigated, and the binding properties were analyzed using NMR spectroscopy (AL-400; JEOL) in a water–$CDCl_3$ system for metal ions. The solid N-host or DA-host (0.08 g) was diluted in 2.0 mL $CDCl_3$ in a centrifuge tube (20 mL volume), and about 4.0 mL of heavy metal solution (100 ppm) was poured in the same centrifuge tube. They were mixed well in the centrifuge for 60 min at 600 rpm.

Results and discussion

Selectivity and characterization of heavy metal ions

In the present work for the calix[4]resorcinarenes, both of the hosts consist the undecyl groups in the arene ring which could increase the solubility in organic solvents. The solubility of the obtained DA-host and N-host in number of organic solvents was evaluated. Both of the hosts were well soluble in tetrahydrofuran, toluene, dichloromethane, benzene, pyridine, *N*,*N*-dimethylformamide, and *N*-methyl-2-pyrrolidone; however, DA-host and N-host were insoluble in water, ethanol, hexane, and dimethyl sulfoxide. In addition, the present of DA-host consist four diethylamino groups in the ring, which is the weak base, and it would respond to the pH based on the equilibrium equation by diethylamino groups as follows:

$$-\mathrm{N(C_2H_5)_2} \overset{\mathrm{H^+}}{\rightleftharpoons} -\overset{+}{\mathrm{N}}\mathrm{(C_2H_5)_2H}$$

Generally, the pH of solution can affect the adsorption capacity of many adsorbents (Osu Charles and Odoemelam 2010). Therefore, the pH measurement was important in the present study to identify a suitable pH for the adsorption for each heavy metal ion because metal precipitation can occur at high pH to form insoluble hydroxide compounds, which would interfere with the adsorption experiments. Figure 2 shows the adsorption capacity of Pb(II), Cu(II), or Ni(II) on the DA-host and N-host. Here, the single component of aqueous heavy metal ion was present in the organic chloroform layer. In liquid–liquid extraction, free species of heavy metal ions were present in acidic solutions of pH 2–5. Relative to the low pH, the adsorptions at higher pH were found to be enhanced. At pH higher than 8.0, the precipitate occurred as a formation of a high concentration of hydroxide heavy metal ions leaching ion precipitation. Therefore, additional experiments were performed at pH 2–7 to confirm that the three metals were present in dissolved form. As Fig. 2b shows, the adsorption capacity of Pb(II) was higher than that of Cu(II) or Ni(II), especially for the DA-host in the higher pH region. The adsorption capacities of Pb(II) ion were 1.79 and 1.58 mmol/g for the DA-host and N-host, respectively.

The competitive extractions of Pb(II), Cu(II), and Ni(II) were further studied for a ternary mixture containing 10 mmol/L concentrations to investigate the separation of heavy metal ions. Thus, Fig. 3 presents the adsorption capacity of each component heavy metal ion at several levels of pH. The competitive adsorptions of the ternary component system are noteworthy. For pH 2–5, it was observed that the competitive adsorption behaviors of Cu(II) and Ni(II) ions showed their adsorption less than 0.15 mmol/g. At pH 5, the Pb(II) ion bound with 0.3–0.4 mmol/g for both hosts. At pH 6–7, the value of adsorption capacity was increased in both hosts. For example, the Pb(II) ion was adsorbed, respectively, with 1.06 and 0.89 mmol/g for the DA-host and N-host. However, comparison between single and ternary components indicated that the adsorption of Pb(II) was inhibited slightly by the presence of Cu(II) and Ni(II) ions, which indicates strongly that competitive adsorption occurred in the ternary component systems for both adsorbents.

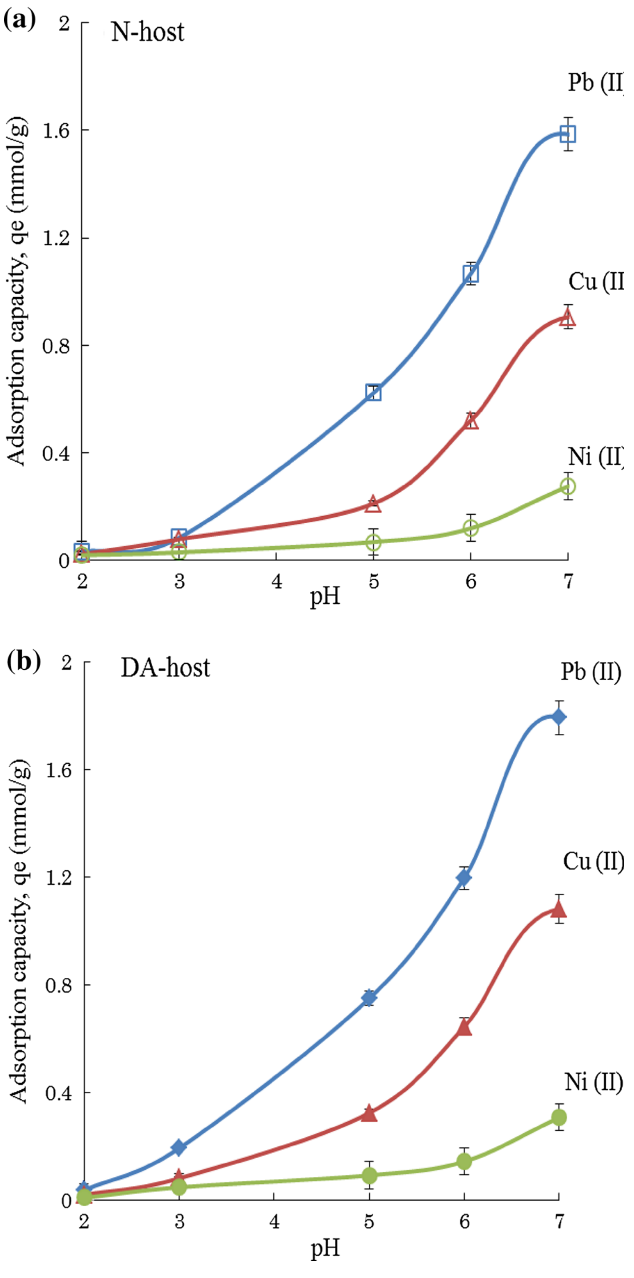


Fig. 2 Effect of pH on the adsorption capacity of single-component heavy metal ions onto **a** N-host and **b** DA-host [Initial concentration of each heavy metal = 10 mmol/L; Volume = 20 mL; Dosage of the hosts = 0.2 g; Agitation period = 60 min]

Slight differences were apparent in the adsorption behaviors of the N-host and DA-host. Data of the ternary component confirmed that the adsorption capacity of the DA-host became higher than that of the N-host. The diethylamino groups were present on the DA-host, showing a positively changed group at lower pH. Therefore, these phenomena agreed well with the fact that the host expressed electrostatic repulsion against the metal ions. However, the DA-host showed good potential for heavy metal adsorption at pH 6–7. At pH 7, the adsorption capacities were 1.06 and 0.89 mmol/g, respectively, for the DA-host and N-host, indicating that the calix[4]resorcinarene frame can fit with

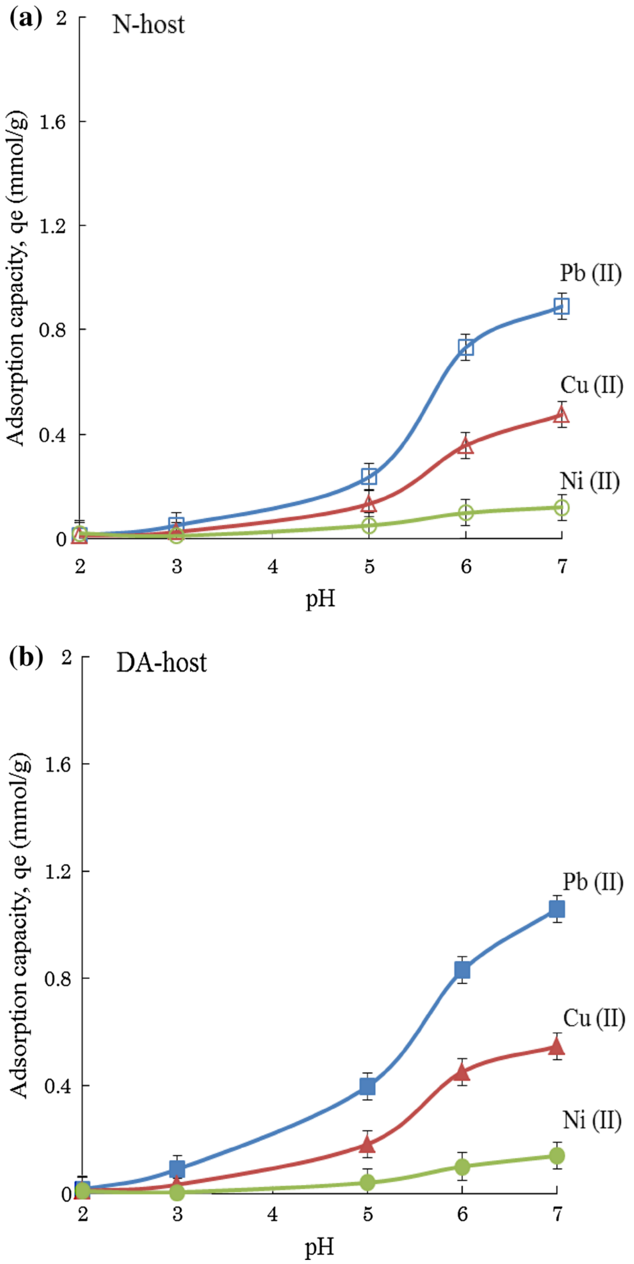


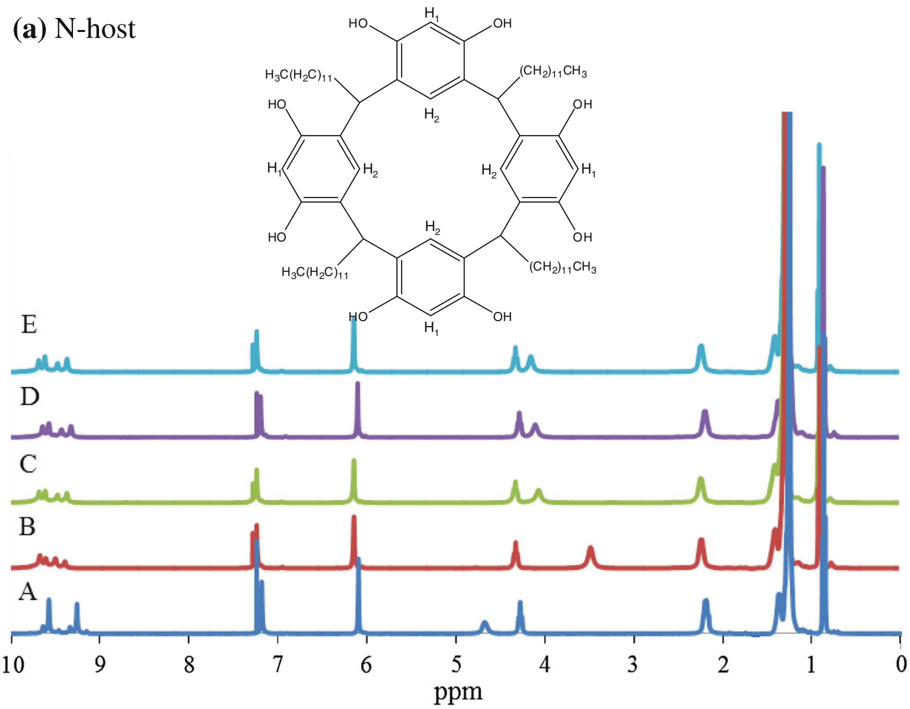
Fig. 3 Effect of pH on the adsorption capacity of each ion in ternary component heavy metal ions onto **a** N-host and **b** DA-host [Initial concentration of each heavy metal = 10 mmol/L; Volume = 20 mL; Dosage of the hosts = 0.2 g; Agitation period = 60 min]

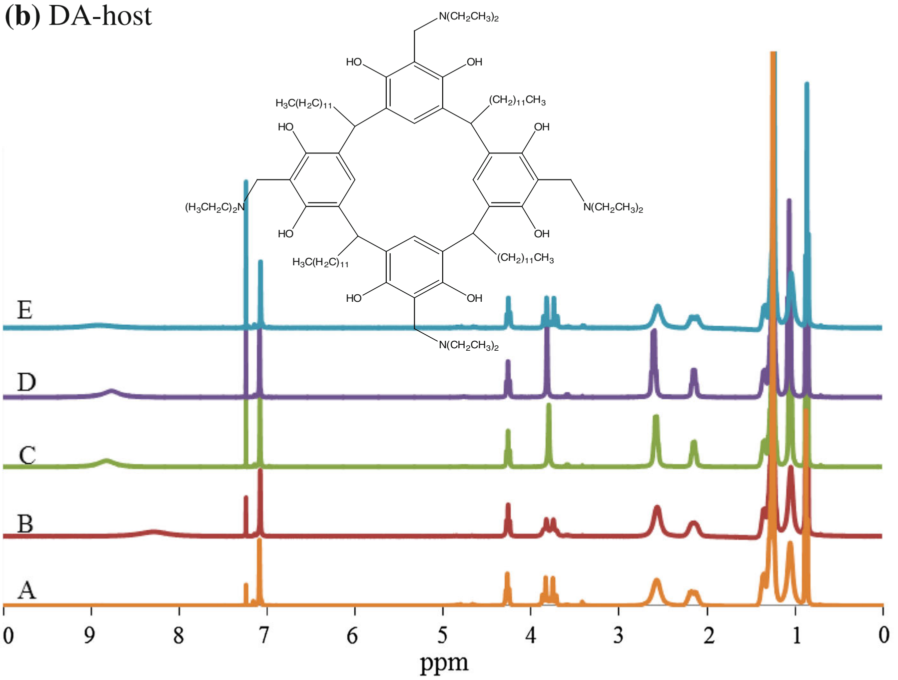
such a Pb(II) ion because less electrostatic repulsion was present at this pH for the DA-host. In addition, the higher capability of the DA-host was presumed to be attributable to the presence of coordination of diethylamino groups to the ions. Consequently, the adsorption capacity of Pb(II) in ternary components of heavy metal ions was found in both hosts to be a tendency for high adsorption capacity to others.

The adsorption behavior of the heavy metal ions on the DA-host and N-hosts was analyzed by using NMR spectroscopy in water–$CDCl_3$ containing 10 mmol/L concentrations of respective heavy metals. Figure 4a and b present a comparison of the ^{1}H-NMR spectra of the N-host and DA-host as measured at room temperature in $CDCl_3$ for each extraction experiment. Figure 4a shows that the signals at 7.21 and 6.10 ppm were indicated, respectively, in outer and inner aromatic protons in the host ring for H_1 and H_2. In spectrum A for the N-host, the singlet peak intensity of the H_2 protons was weakened and the outer proton peak at 6.10 ppm was enhanced in Pb(II) extraction. The OH proton appeared as multiplet peaks of equal intensities centered at 9.58 and 9.26 ppm. However, the N-host expressed a lower magnetic shift, meaning that the leaving metal inclusion unshielded with the inner ring current effect of the calix[4]resorcinarene. It is noteworthy that the peak of water, which was present in the N-host, appeared at 4.68 ppm and showed a higher chemical shift at 4.07 ppm for Pb(II) systems. Results show that water coordinated to the OH group of the N-host when the Pb(II) ion was included. The signals at 1.41 and 0.90 ppm corresponded to the alkyl hydrophobic region for the resorcinol units. In panel (a), spectrum A shows one molecule of water, suggesting that this was assigned at 4.68 ppm for the crystalline N-host (Ma et al. 2001). For spectrum B, the water molecule peak appeared in a higher field at 3.49 ppm when the N-host in $CDCl_3$ was washed with water. This shift indicates that water was included in the inner arene cone. However, when Pb(II) ion was present in the water layer, the water peak shifted forward to the lower field at 4.07 ppm, which strongly suggests that the water molecule supported the Pb(II) ion hosting to the inner N-host.

However, in Fig. 4b for the DA-host with diethylamino groups, protons from CH_2 and CH_3 were observed, respectively, at 3.72–3.78 ppm and 1.06 ppm. The water was present, showing its signal at 2.57 ppm. The broad OH signal was shown in the lower field at 8.25 ppm for the spectrum B when the water layer contained Pb(II) ion with 10 ppm concentration. In addition, the OH signal was shifted to about 8.80 ppm. The downfield shift indicated that the OH groups positioned on the aryl ring were directed outward when the metal ion was included. Additionally, it was noted that the signal splitting of the multiplet for the CH_2 group of diethylamino group on the DA-host was changed to a singlet peak when the metal ion for Pb(II) and Cu(II) was included in the cone. The significance meant that such metal ion coordinated with the nitrogen atom of the diethylamino group. Consequently, the neighboring CH_2 group of the nitrogen atom, which was coordinated, was influenced strongly by the effect of the heavy metal ion. Results of NMR analysis revealed that the heavy metal ion was included in the host cavity through the aid of water molecules in the N-host and also through interaction with the OH group of the DA-host.

Fig. 4 Comparison of ^{1}H-NMR spectra of **a** N-host and **b** DA-host for water-$CDCl_3$ extraction. Here, $CDCl_3$ was used as organic solvent and water layer contained 10 ppm metal ions. Spectra *A*, *B*, *C*, *D,* and *E* were for crystalline samples, washing the hosts in $CDCl_3$ by water, Pb(II), Cu(II), and Ni(II) aqueous solution with the 10 ppm concentration


(a) N-host


(b) DA-host

Adsorption isotherms

Adsorption isotherms are known to be fundamental in describing the adsorption behavior of adsorbate ions. Therefore, analyses of Pb(II), Cu (II), and Ni(II) with the N-host and DA-host were conducted for two phases applied in Langmuir equilibrium isotherms (Panida and Pisit 2010). To inform the adsorption isotherms of the calix[4]resorcinarene host and the ion guest, the relation between the concentration of the ion adsorbate in the aqueous solution and the amount of ion adsorbed onto the adsorbent was examined using the Langmuir equation.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (2)$$

In that equation, Q_m signifies the maximum amount of hosting capacity of heavy metal ions adsorbed for a complete monolayer (mmol/g), C_e represents the equilibrium concentration of heavy metal ions (mmol/L), Q_e denotes the amount of heavy metal ions adsorbed at the equilibrium concentration (mmol/g), and b stands for the Langmuir constant related to the affinity of the binding sites (L/mmol). Figure 5 shows the equilibrium adsorption isotherms of Pb(II), Cu(II), and Ni(II) onto the N-host and DA-host as a function of the initial concentration among heavy metals. The calculated results of Langmuir isotherm constants are presented in Table 1. The experimental data show that the maximum adsorption capacity for hosting each heavy metal was obtained. The data revealed that the adsorption capacity of heavy metal ions onto DA-host was higher than the adsorption capacity of heavy metal ions onto the N-host. These assignments might be explained by the differences of their chemical structures of the N-host and DA-host. The adsorbent of the DA-host contained additional diethylamino groups, which might be responsible for the effectiveness of hosting sites of heavy metal ions through coordination interaction with nitrogen atom and metal ions. However, the N-host contained only hydroxyl groups for the capture of metal ions. Therefore, the analytical results showed that the DA-host expressed a great amount of hosting capacity Q_m and equilibrium constant b for Pb(II) adsorption.

Langmuir isotherms showed that the adsorption capacity of Pb(II) was higher than those of Cu(II) and Ni(II) for both adsorbents. The respective values of adsorption capacity of Pb(II), Cu(II), and Ni(II) with the concentration 10 ppm were 5.75, 3.79, and 1.15 mmol/g for the N-host, although those for the DA-host were 6.10, 3.63, and 4.48 mmol/g. Results show that Pb(II) adsorption by the N-host and DA-host became higher values than those of other metals. Furthermore, the adsorption of Pb(II) by the DA-host showed higher adsorption than that of the N-host. Here, NMR data suggest that both hosts were cone configurations of calix[4]resorcinarenes (Gutsche 1989). Consequently, these phenomena might be explained in terms of the size of the studied heavy metal ions. For heavy metal ions in this study, the size order is shown below.

$$\mathrm{Pb}^{2+}(1.19\text{Å}) > \mathrm{Cu}^{2+}(0.73\text{Å}) > \mathrm{Ni}^{2+}(0.69\text{Å})$$

Regarding comparison of the ion diameter and host cavity size, Pb(II) had ion diameter of 1.19 Å. The cavity size of calix[4]resorcinarene was 2.59 Å (Gutsche 1989), although the respective ion diameters of Cu(II) and Ni(II) were 0.73 and 0.69 Å. Therefore, Pb(II) was the right choice to fix into the cone shape of the N-host and DA-host, in contrast to Cu(II) and Ni(II) (Jain and Kanaiya 2011; Turshatov et al. 2004).

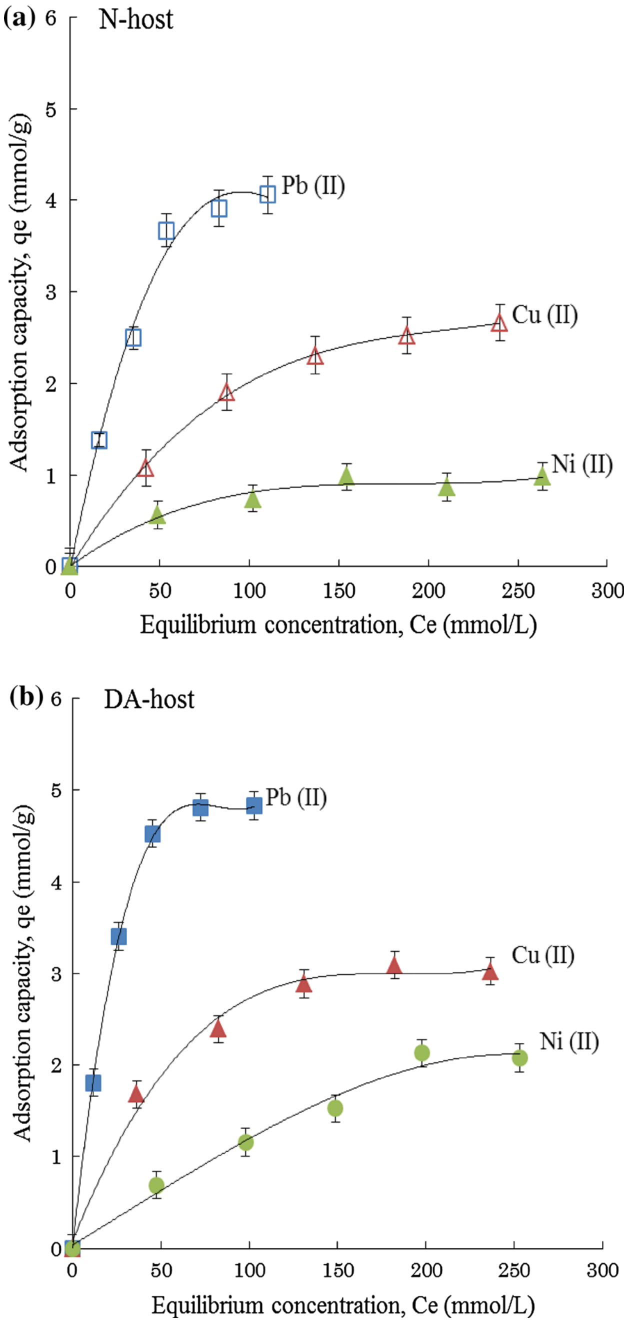


Fig. 5 Comparison of equilibrium adsorption of heavy metal ions from aqueous solution using **a** N-host and **b** DA-host [Initial Pb(II), Cu(II), and Ni(II) concentration = 10–50 mmol/L; Volume = 20 mL; Dosage of N-host and DA-host = 0.2 g; pH = 6; Agitation = 600 rpm]

Among the three metal ions, the adsorbents of the N-host and DA-host exhibited the lowest adsorption efficiency for Ni(II). Results of the Langmuir isotherm underscored that both hosts showed a low adsorption capacity for Ni(II) adsorbent, perhaps because Ni(II) is somewhat smaller than the host cone.

Table 1 Langmuir isotherms with constant and correlation coefficient for the adsorption of Pb(II), Cu(II), and Ni(II) onto the hosts

Adsorbent	Heavy metal	Langmuir		
		Q_m (mmol/g)	b (L/mmol)	R^2
N-host	Pb(II)	5.75	0.02	0.96
	Cu(II)	3.79	0.01	0.99
	Ni(II)	1.15	0	0.97
DA-host	Pb(II)	6.1	0.04	0.98
	Cu(II)	3.63	0.03	0.99
	Ni(II)	4.48	0.02	0.88

Langmuir isotherm constant are presented in Table 1 and shows the maximum adsorption capacity, Q_m for hosting each heavy metal

Q_m maximum amount of adsorption, b Langmuir constant, R^2 correlation coefficient

Conclusion

In the present study, the capacities of the N-host and DA-host to adsorb Pb(II), Cu(II), and Ni(II) ions from aqueous solutions were examined by separation experiment of Pb(II), Cu(II), and Ni(II) at different pH. Predominant hosting of Pb(II) was observed on the DA-host at the neutral pH region in the separation process. The evidence showed a first report on separation of heavy metal mixture by calix[4]resorcinarene. The equilibrium isotherms revealed that the adsorption of Pb(II), Cu(II), and Ni(II) onto N-host and DA-host adsorbents mainly fitted the Langmuir model. In addition, the adsorption of the metal ions on the calix[4]resorcinarene hosts was studied using ^{1}H-NMR analysis. The obtained findings supported that the DA-host showed potential for use as an adsorbent for heavy metal Pb(II) because the diethylamino groups can coordinate with the heavy metal ions. This point might be important for further development of a new adsorption system for use with actual wastewater containing a mixture of heavy metals. There are also possibilities to apply the DA-host and N-host in specificity of heavy metal ion on bulk materials by some chemical treatments. Therefore, the progresses in these hosts are focused on several industrial applications in the field of wastewater treatment for elimination of such toxic ion from the wastes. The present results provide useful and variable information for further investigation of wastewater treatments.

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