Almost Complete Removal of Trace Amount of Halogenated Organic Compounds in Water: An Approach by Use of a Combination of Water-Soluble Thiacalixarene and Ion-Exchange Resins

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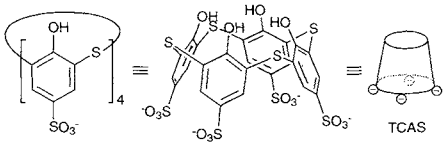
Two removal methods of small halogenated organic substances in water are proposed by formation of ternary complexes between the halides, thiacalix[4]arenetetrasulfonate (TCAS), and anion exchange resins, among which treatment of the polluted water with TCAS to form TCAS-guest complexes followed by trapping them onto the resin enables almost complete (more than 99.99%) removal of halogenated organic compounds such as CH_2Cl_2 and $CHCl_3$.

Removal of halogenated organic compounds in water is highly demanded in waste water and especially drinking water treatments. Most of the current techniques to remove these noxious substances rely on aeration and/or adsorption onto activated carbon.[1,2] These treatments, however, are far from satisfactory, because they can hardly accomplish sufficient removal of such substances. For example, it is obvious that aeration is not suitable for pollutants of low volatility such as $CHBr_3$. Adsorption of these organohalogen compounds to the adsorbent is rather weak so that they are readily expelled by other more strongly adhering materials. The short lifetime of the adsorbent is also another problem.

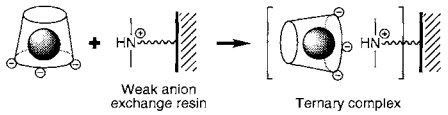
During the course of a project to develop novel functions of thiacalixarenes,[3] we recently synthesized a new water-soluble host molecule, thiacalix[4]arenetetrasulfonate (TCAS), and found that TCAS could bind small halogenated organic molecules such as CH_2Cl_2 and $CHCl_3$ in its hydrophobic cavity by 1:2 and 1:1 manner, respectively, in aq. soln. (eq. 1).[4]



(1)

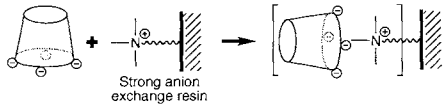
It has also been shown that addition of sodium chloride to the solution of the TCAS-halide complexes causes quantitative salting out of the sodium tetrasulfonate still including the halide.[4] From this observation, it occurred to the authors that removal systems of such halogenated compounds from water could be constructed only if the TCAS-halide complexes could be trapped onto a suitable solid support. Herein, we propose a supramolecular approach by forming a ternary complex consisting of an anion-exchange resin, negatively charged TCAS, and halogenated organic compounds, which is found to enable an unexpectedly high removing capability.

We tried two methods for the removal of the organic halides (hereinafter, denoted as guests or G) from water. In the first method (Method 1 illustrated in the graphical abstract), TCAS was first added to an aq. soln. of a guest, which was then allowed to stand for 1 h to form the host-guest inclusion complexes (eq. 1, $C_{initial}$ = 2.0 mM, $[TCAS]_{Total}$ = 5.0 mM). Then 25 cm^3 of the solution was passed through a column packed with 20 cm^3 of a weak anion-exchange resin having dimethylamino groups (Amberlite® IRA-93ZU) at 2 cm^3/min to trap the TCAS-guest complex as the ternary complex (eq. 2).



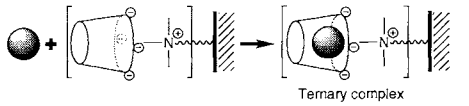
(2)

In the second method (Method 2), TCAS was initially immobilized onto an anion-exchange resin (eq. 3). It was found that a strongly basic resin having trimethylammonium function (Amberlite® IRA-900) bound with TCAS *ca.* 2 times faster than the weakly basic one (IRA-93ZU). Thus, TCAS (300 mg) was safely immobilized onto the strong anion-exchanger (8 cm^3) suspended in water (10 cm^3) by stirring for 5 h.



(3)

Then the mixture was introduced into a column, at the bottom of which had previously been packed 2 cm^3 of the bare resin. Then, the water (25 cm^3) containing the guests (2.0 mM) was passed through the column at 2 cm^3/min to trap it as the ternary complex (eq. 4).



(4)

The ability of the two methods to remove the guests from water was assessed by removal ratio defined by eq. 5,

$$\text{removal ratio} \equiv 100\% - (C_{final} / C_{initial}) \times 100\% \quad (5)$$

where $C_{initial}$ and C_{final} are the concentrations of the guest in water before and after the treatment determined by GC-MS equipped with a head-space sampler (60 °C).

It had been shown that TCAS accommodates the guests listed in Table 1 to form the inclusion complexes having average number of the guest molecules $\bar{n} \approx 1$ (guests other than CH_2Cl_2) and $\bar{n} \approx 2$ (CH_2Cl_2).[5] Table 1 lists the results by Method 1, which contains $C_{initial}$ and C_{final} of the guest and the removal ratio. It can be seen that the concentrations of CH_2Cl_2 and $CHCl_3$ were reduced surprisingly from as high as several hundreds ppm to ppb level. This in turn means that the removal ratios were 99.99613 and 99.99485%, respectively, indicating that the removal was almost perfect. Even in the worst case, the removal ratio was 99.9094% for $CHBr_3$, confirming that the removal of the guests by Method 1 was satisfactory.

Table 1. Removal of halogenated organic compounds (Guests) from water by Method 1 (1 ppm = 1 μg/cm^3)

Guest	$C_{initial}$ / ppm	C_{final} / ppm	Removal Ratio
CH_2Cl_2	170	6.58×10^{-3}	99.99613%
$CHCl_3$	239	1.23×10^{-2}	99.99485%
$CHBrCl_2$	328	3.44×10^{-2}	99.9895%
$CHBr_2Cl$	417	2.33×10^{-1}	99.9441%
$CHBr_3$	508	4.60×10^{-1}	99.9094%
CH_2Cl-CH_2Cl	198	4.08×10^{-2}	99.9794%
CH_2Cl-$CHCl_2$	267	1.35×10^{-1}	99.9495%

On the other hand, Method 2 disclosed somewhat reduced removal ability ranging from 95.20% as the worst ($CHBr_3$) to 99.51% as the best ($CHCl_3$ and $CHBrCl_2$) (Figure 1). Even in the most favorable case, the final concentrations of CH_2Cl_2 and $CHCl_3$ were 2.68 and 1.17 ppm, respectively, which are higher by three order of ten than those attained by Method 1.

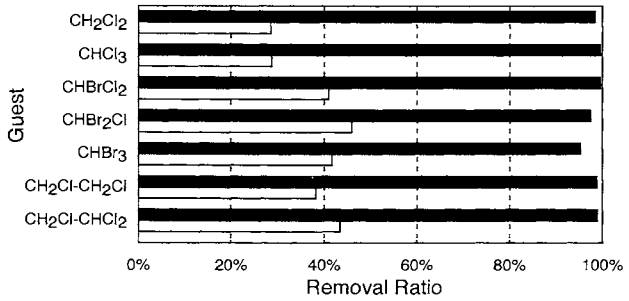


Figure 1. Removal of halogenated organic compounds from water by Method 2 with (■) and without (□) using TCAS on the resin.

Now, let us consider what makes the difference between the two methods in the removal performance. In Method 1, UV measurement did not indicate the presence of a detectable amount of TCAS in the effluent from the resin column. This strongly implies that the adsorption of the TCAS-guest complexes onto the ion exchanger (eq. 2) was sufficiently fast and almost quantitative and, once adsorbed, the TCAS-guest complexes did not leak out from the column (reverse process of eq. 2) at least during the treating period. No leakage of TCAS from the TCAS-bound column in Method 2 was also confirmed by UV. On the basis of these considerations, the amount of the guests remaining in the treated water should be controlled by the complexation steps (eqs. 1 and 4). Contrary to the fast and quantitative complexation of TCAS with the guests in a homogeneous phase (eq. 1) as studied previously,[4] complexation of the resin-bound TCAS with the guests involves solid-liquid two phases process which must be subjected to many factors. For instance, hence G cannot penetrate into the cavity of TCAS through the lower rim (cyclic array of OH groups), the TCAS fixed on the resin must change its conformation, or the host must once be desorbed from the resin into the bulk liquid phase to accommodate the guest. These events should be highly inhibited by the coulombic interaction between the sulfonate groups of the TCAS and ammonium groups of the resin, letting some part of the guests go through the column without retention.

As can be seen from Figure 1, the anion-exchange resin *per se* possessed considerable capability to hold the halogenated guests, probably due to hydrophobic interactions. Therefore, there remains some ambiguity as to the intrinsic ability of the resin-bound TCAS to remove the guest by inclusion depicted in eq. 4.[6] It should, however, be noted that substantial part of the removal of the guests should still be ascribed to the TCAS introduced onto the resin.

Although many operation variables need to be clarified before the proposed methods could be applicable to a practical use, it is highly desirable that the trapped pollutants can readily be recovered and TCAS and the resin regenerated. In this regard, the choice of ion-exchange resin is an important factor: Preliminary experiments indicated that the recovery of TCAS from a weak anion exchange column was quite promising, as the positive charge of the ion-exchange group could easily be neutralized by use of a strong base.[7] On the other hand, strong anion-exchanger may be more advantageous from the viewpoint of the capacity and speed of the water treatment.

In conclusion at this point, Method 1 is more promising as judged from the capability of removal of the pollutant and recycling of the materials. The high removal performance was attributed to the fast kinetics of the inclusion step (eq. 1), which should greatly rely on the sulfo group to allow TCAS to be highly soluble in water.[8] Since Methods 1 and 2 proposed here are of potential importance as practical removal methods of halogenated organic substances in water, we are now optimizing such variables as the kind of ion-exchange material, immobilizing conditions of TCAS, the concentration of TCAS on the column, flow rate, and so on.

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References and Notes

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2 "Suido to Trihalomethane (Drinking Water and Trihalomethanes)," ed by N. Tanbo, Gihodo, Tokyo (1983).
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4 N. Iki, T. Fujimoto, and S. Miyano, *Chem. Lett.*, **1998**, 625.
5 The average number of binding, $\bar{n}$, was evaluated by $\bar{n} \equiv ([G]_{total} - [G]_{free})/[TCAS]_{total}$.[4] The $\bar{n}$ values for guest molecules containing bromine were determined in this study; CH_2BrCl: 1.16, 0.98; CH_2Br_2: 1.19, 1.04; $CHBrCl_2$: 1.11, 0.84; $CHBr_2Cl$: 1.11, 0.88; and $CHBr_3$: 1.06, 0.88 by precipitation and NMR methods, respectively.
6 The outer surface of TCAS bound to the resin may also provide hydrophobic environment to trap the guests.
7 For instance 82.3% of TCAS could be recovered by flushing the column with 250 cm^3 of 1 M NaOH at 5 cm^3/min. In this respect, the strong anion exchange group in Method 2 is not suitable because TCAS was strongly retained regardless of pH. In fact, only 19.1% of TCAS could be recovered by flushing the resin with 300 cm^3 of 5 M HCl at 5 cm^3/min.
8 The necessity of the sulfo group is obvious by the fact that the suspended powder of *p-tert*-butylthiacalix[4]arene (TCA) could not remove these guests in water,[9] although it could include small solvent molecules by recrystallization from CH_2Cl_2, $CHCl_3$, 1,2-dichloroethane, and so on.[10]
9 Solutions of D_2O (1 cm^3), which had previously been saturated by CH_2Cl_2 (47.5 mM) or $CHCl_3$ (18.6 mM), were stirred with the solid powder of TCA (72.1 mg, 0.1 mmol) for 24 h. The remaining concentrations were 37.6 and 14.0 mM, respectively, meaning that only 9.9 and 4.5% of guests in water were removed by solid TCA.
10 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, and S. Miyano, *Tetrahedron Lett.*, **38**, 3971 (1997); T. Sone, Y. Ohba, K. Moriya, H. Kumada, and K. Ito, *Tetrahedron*, **53**, 10689 (1997).