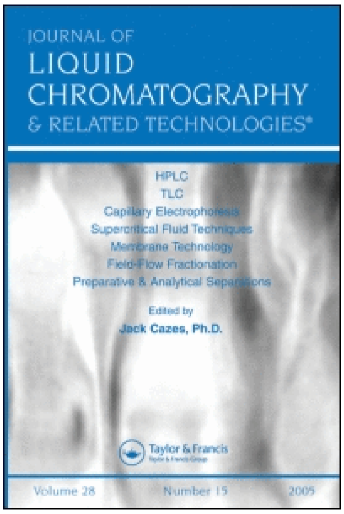

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REMOVAL OF ORGANIC COMPOUNDS FROM WATER VIA ADSORPTION ONTO POLYMETHYLHYDROSILOXANE PENTENYL-β-CYCLODEXTRIN

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ABSTRACT

A co-polymer of polymethylhydrosiloxane and pentenyl-β-cyclodextrin (PMSP-β-CD) is synthesized and used to extract various aromatic materials from water by adsorption onto the co-polymer matrix. The method of synthesis, separation scheme and parameters associated with adsorption are discussed. Salt and pH effects are also examined. The problems associated with other methods of removal are compared with those encountered by extraction using PMSP-β-CD. Most compounds studied can be quantitatively extracted from water if the extraction conditions are optimized. Removal is not greatly influenced by the addition of salt or change in pH. PMSP-β-CD is easily recycled at 80-100°C and both the organic analytes and PMSP-β-CD are recovered with a high efficiency. The results also indicate that extractions using PMSP-β–CD are not only possible but also advantageous in some cases.

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INTRODUCTION

Removal or preconcentration of organic compounds from water has been accomplished using various chemical techniques, such as polymeric membranes (1, 2), cloud point phenomena of surfactants (3, 4), cloud point phenomena of certain derivatized cyclodextrins (5) and, to a greater extent, liquid-liquid extractions (6, 7) and activated carbon (8, 9). Every method has certain strengths and limitations. A few of the more common problems associated with the aforementioned techniques include difficulties and expense in the regeneration of activated carbon, thermal degradation of analytes at the high temperatures required for surfactant cloud point extraction, as well as narrow surfactant concentration ranges in which separation by cloud point is feasible, small ranges of salt concentration or pH in which the extraction can be performed, cost of producing the temperatures needed for separation or regeneration and difficulties in monitoring various processes in the uv-vis spectral region.

Two of the more successful methods for the extraction of organic materials from water that have been used for many years are liquid-liquid extraction and adsorption onto activated carbon. The major disadvantage of liquid-liquid extraction is that large quantities of potentially hazardous organic solvents must be used to extract the required percentage of organic compounds from water. The purchasing, recycling and disposal of these solvents can also become expensive over time. Another widely successful extraction technique involves running wastewater containing organic compounds over a bed of activated carbon, where the compounds adsorb onto the surface of the carbon. The greatest drawback of this process is the limited capacity and the relatively high cost of producing temperatures required to reactivate the carbon after use. Producing these high temperatures usually represent up to 75% of the cost of the total recycling process (10). Consequently, any novel method that can perform nearly as well as activated carbon or liquid-liquid extraction, but does not require the use of large amounts of hazardous and expensive solvents and can circumvent the high cost of regeneration would be of general interest.

In this paper polymethylhydrosiloxane pentenyl-β-cyclodextrin (PMSP-β-CD) is synthesized and used to remove and recover aromatic organic compounds from water. The method of removal is adsorption onto the co-polymer and separation by sedimentation. Regeneration of PMSP-β-CD is accomplished by heating the polymer which has organic material adsorbed onto it, at 80-100° C in water. The solution is simply decanted or the the co-polymer is filtered while the solution is hot. The organics are released from the water insoluble PMSP-β-CD, forming a concentrated aqueous solution of organic compounds. This process operates with a high recovery of the organic materials in aqueous solution, as well as for the adsorbing media (PMSP-β-CD). This technique can be used for concentration of organic compounds as well. The results of this study indicate that removal of aromatic organic material from water using PMSP-β-CD is a viable alternative to other methods of extraction. This technique is particularly attractive because of the ease of recovery of organics, nonhazardous media, low temperatures required for regeneration of PMSP-β-CD, ease of recovery for PMSP-β-CD and the ability to successfully remove numerous compounds under a variety of conditions.

EXPERIMENTAL

Materials

Chemicals were obtained from various companies as follows: Aldrich Chemical Company: acetanilide, aniline, o,p-chloroaniline, dimethyl sulfoxide - 99% anhydrous, o-nitroacetanilide, o,m,p-nitroaniline, nitrobenzene, o,m,p-nitrophenol, p-nitrotoluene, 4-phenylazophenol, 2-phenylbenzimidazole, 3-phenylphenol and phosphorous pentoxide; Fisher Chemical Company: bromopentene, sodium hydride, sodium propionate, chlorisplatinic acid, tetrahydrofuran, methanol, polymethylhydrosiloxane (PS 122), glacial acetic acid and anhydrous sodium sulfate; Sigma Chemical Company: 2,2' dihydroxybiphenyl, sodium chloride and 2-naphthol; Matheson, Coleman and Bell: 1-naphthol ; Mallinkrodt Chemical Company: benzoic acid; ASTEC: β-cyclodextrin.

Synthesis of Cross Linked Polymethylhydrosiloxane Pentenyl-β-Cyclodextrin

In a nitrogen atmosphere, 6.79 g of β-cyclodextrin which had been previously dried in a heated vacuum drying chamber overnight with phosphorous pentoxide as the drying agent, was added to 150 ml of dimethyl sulfoxide in a three neck round bottom flask. With continuous stirring, 0.72 g of sodium hydride was added and allowed to react for 90 minutes at 50° C. Bromopentene (3.55 ml) was added to 25 ml DMSO. The solution was dropped into the flask over a one hour period and stirred for 25 hours at 50° C. The flask was then removed from the nitrogen atmosphere, the DMSO layer removed by vacuum distillation at 60° C and 100 ml of methanol was added. The methanol was removed by rotorevaporation until only 5 ml remained. This product (pentenyl-β-CD in methanol) was added to 100 ml of ice water, filtered and rinsed with 3 x 50 ml of ice water. The pentenyl-β-CD was dried overnight in a drying chamber. In a nitrogen atmosphere, 5.0 g of previously prepared pentenyl-β-CD was dissolved in 100 ml tetrahydrofuran at 53° C. To this, 3.5 g of polymethylhydrosiloxane (PS 122) and 10 mg of sodium propionate were added with stirring. Chlorocisplatinic acid (8.8 mg) was dissolved in 1 ml THF and added to the system. The solution was stirred for 4 hours at 53° C and then removed from the nitrogen atmosphere. The product, PMSP-β-CD, was filtered and dried overnight in a drying chamber.

Apparatus and Procedure

A Shimadzu LC-6A liquid chromatographic system with a SPD-2AM variable wavelength spectrophotometric detector and Linear 1200 strip chart recorder was used to quantitate each sample. The detector was operated at a different wavelength for each compound analyzed. The flow rate and sample loop were 1.0 ml/min and 20 µm respectively. A C_8 or C_{18} column (5µm x 25cm) from Advanced Separation Technologies Incorporated was used to separate each compound.

All samples were prepared using the following method. Distilled water was added to each compound to make the desired concentration. Two ml of the aqueous solution, to which the specified amount of cross linked PMSP-β-CD had been added, was mechanically shaken for twenty hours. The cyclodextrin was allowed to settle to the bottom and the sample was decanted. This sample was then injected into the HPLC system without further preparation. The pure compound was also analyzed to obtain percent removal data. Sodium hydroxide and acetic acid were used for pH adjustment in the pH study. Sodium chloride was used in varying concentrations for the ionic strength study. The mobile phases were mixtures of methanol and water which were filtered through a membrane filter of 0.45 µm pore size and degassed by vacuum-ultrasonication method prior to use. Peak areas of both the sample containing the PMSP-β-CD and the pure compound were calculated by triangulation and used to determine percent of compound removed.

Regeneration of Polymethylhydrosiloxane Pentenyl-β-Cyclodextrin

PMSP-β-CD that had been used to remove organic material from water was added to 500 ml of water. After one hour of heating above 80° C, the mixture was vacuum filtered using Whatman filter paper. The polymer was allowed to air dry for one day. The extracting power of this recycled polymer was measured using a test compound and compared with that of freshly synthesized PMSP-β-CD.

RESULTS AND DISCUSSION

PMSP-β-CD appears to be a hard, brittle solid with negligible solubility in most solvents, including methanol, acetonitrile, ether, water, methylene chloride, hexane, isopropanol, chloroform, DMSO and DMF. Since this material has both a siloxane and cyclodextrin portion, it may be possible to have both nonspecific, hydrophobic adsorption as well as complexation into the cyclodextrin cavity as means for removing organic compounds from water. Using an optical microscope with 22x and 57x magnification, a photograph of PMSP-β-CD was taken (Figure 1). This image suggests that PMSP-β-CD has a nonporous, glass-like structure. The average partial size was 0.9 mm and the range was from about 0.5 - 1.6 mm.

In the course of studying data from different removal trials, it became obvious that the time allowed for adsorption was important. Consequently, a time study was performed. This data for the unstirred, "stagnant" system is shown in Table I. Three compounds were studied at two different PMSP-β-CD concentrations. After 48 hours, equilibrium is reached in all cases. In a stationary system, the dissolved components must diffuse through the solution until an available adsorption site is found. Shaking or stirring produces rapid mixing, which brings analytes into contact with the surface more efficiently. As expected, equilibrium times were greatly reduced. Consequently all further experiments were done with mechanically shaken mixtures. Table II is a typical comparison of equilibration times in mixed versus unmixed extractions. The time in which maximum removal is achieved is reduced to three hours with mechanical shaking.

Table III shows the relative removal of various aromatic compounds from water using PMSP-β-CD. At the high PMSP-β-CD concentration of 500 g/mmol, all but three compounds were removed at levels greater than 90%. The three that are removed at less than 90% are acetanilide, o-nitroacetanilide and p-nitroacetanilide. This suggests that acetanilide and substituted acetanilides are more poorly adsorbed onto PMSP-β-CD than other compounds. The addition of slightly more PMSP-β-CD will raise removal of the acetanilides to nearly 100%. Clearly the capacity of the PMSP-β-CD in its present state (*i.e.*, relatively large average particle size) is not high. Further grinding of the adsorbent to increase

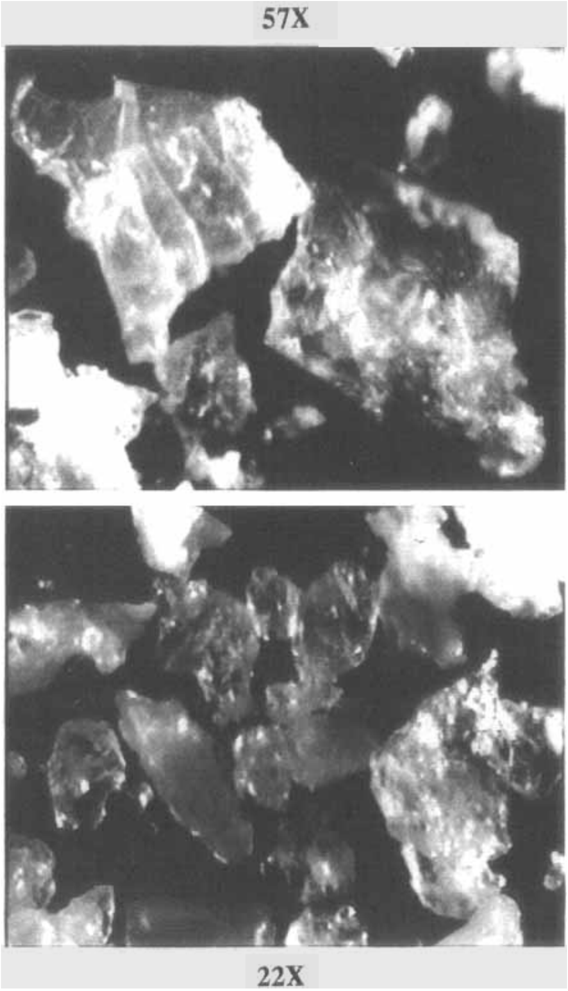

Figure 1: Optical Microscope Photograph of PMSP-β-CD at 22X and 57X magnification.

TABLE I. EFFECT OF TIME ON PERCENT REMOVAL[a]

COMPOUND	TIME (hours)	% REMOVED (0.100 mmol/g)[b]	% REMOVED (0.025 mmol/g)[b]
m-nitrophenol	1	2	13
	6	8	30
	23	27	47
	48	24	62
	68	20	63
	140	27	62
o-nitroaniline	1	8	23
	6	19	37
	23	18	56
	48	32	62
	68	34	68
	140	31	69
p-nitrophenol	1	5	17
	6	12	28
	23	20	44
	48	22	53
	68	24	50
	140	28	58

[a] Two ml of aqueous sample is used. All compound concentrations are 1×10^{-3} M.

[b] mmol/g refers to mmol of analyte per gram of PMSP-β-CD.

TABLE II. PERCENT REMOVAL OF M-NITROPHENOL: TIME SHAKEN VERSUS TIME STATIONARY[a]

TIME (hours)	STATIONARY % REMOVED	SHAKEN % REMOVED
0.5	--	40
1.0	13	--
1.5	--	60
2.0	--	78
3.0	--	77
4.0	--	80
6.0	30	--
23.0	47	--
48.0	62	--
68.0	63	--

[a] Two ml of aqueous sample is used. Concentration of m-nitrophenol is 1×10^{-3} M. Analyte per PMSP-β-CD concentration is 0.025 mmol/g for stationary sample and 0.020 mmol/g for shaken sample.

TABLE III. PERCENTAGE OF AROMATIC MATERIAL REMOVED FROM WATER USING PMS PENTENE-β-CYCLODEXTRIN[a]

ANALYTE	% REMOVED (0.002 mmol/g)[g]	% REMOVED (0.025 mmol/g)[g]	ANALYTE CONC (M x 10^{-5})
acetanilide	81	34	1.0
aniline	98[b]	--	2.5
benzoic acid	90[c]	--	5.0
2,2' dihydroxybiphenyl	93	--	1.0
o-chloroaniline	99[d]	--	1.5
p-chloroaniline	99	--	1.0
N-methylaniline	99[e]	--	1.9
1-naphthol	99	--	1.0
2-naphthol	98	57[f]	1.0
o-nitroacetanilide	70	20	1.0
p-nitroacetanilide	89	--	1.0
o-nitroaniline	95	59	1.0
m-nitroaniline	90	--	1.0
p-nitroaniline	96	--	1.0
nitrobenzene	99	91[f]	1.0
o-nitrophenol	99	--	1.0
m-nitrophenol	96	63	1.0
p-nitrophenol	91	58	1.0
p-nitrotoluene	97	--	1.0
4-phenazophenol	99	--	1.0
3-phenylphenol	90	--	1.0
2-phenylbenzimidazole	98	--	1.0

[a] A two ml aqueous sample is used in all cases. *All samples were shaken mechanically for 20 hours.*

[b] PMSP-β-CD concentration is 0.005 mmol/g.

[c] PMSP-β-CD concentration is 0.01 mmol/g.

[d] PMSP-β-CD concentration is 0.003 mmol/g.

[e] PMSP-β-CD concentration is 0.004 mmol/g.

[f] PMSP-β-CD concentration is 0.025 mmol/g.

[g] mmol/g refers to mmol of analyte per gram of PMSP-β-CD.

the surface to volume ratio can increase the capacity by nearly two orders of magnitude. However, in this initial study the coarse material was preferred due to the ease of isolation via decantation or fast filtering. Also shown in Table III, PMSP-β-CD is able to extract a significant portion of extremely dilute organic compounds (1 x 10^{-5} M). With EPA guidelines on allowable organic levels in wastewater becoming more stringent, novel techniques may be needed to remove such trace organics from water. Also, it should be noted that o-chloroaniline and p-chloroaniline are effectively removed with PMSP-β-CD. This is significant because many halogenated organics cannot be removed by derivatized cyclodextrins in cloud point extractions (5). This is because these particular compounds interfere with the phase separation process.

Figure 2 illustrates the effect of PMSP-β-CD concentration on percent removal of m-nitrophenol and 2-naphthol. As expected, until maximum removal is reached, a higher percentage of both compounds is removed as more PMSP-β-CD is introduced into the system. For m-nitrophenol, the maximum point of removal occurs after the addition of 0.005 mmol/g. For 2-naphthol, maximum removal occurs after only 0.016 mmol/g. This suggests that each compound has a different adsorption affinity for PMSP-β-CD. Any given compound's affinity for PMSP-β-CD is probably dependent on many properties such as size of the molecule and functional groups present in the compound. Adsorption isotherms are easily measured for most compounds. Figure 3 shows the isotherm for m-nitrophenol. Adsorption on PMSP-β-CD seems to be a classic Langmurian process. It seems that there are primary adsorption sites but little, if any, secondary adsorption under the conditions of this experiment. Hence, characterization of this adsorbent may be more straight forward than would be indicated from its relatively complex chemical make-up.

Table IV compares extraction values of four compounds at three pHs. 2-Naphthol and m-nitrophenol are weak acids which become ionized under basic conditions. o-Nitroaniline is a weak base which is ionized in acidic solutions. Nitrobenzene does not ionize to an appreciable extent under basic or acidic

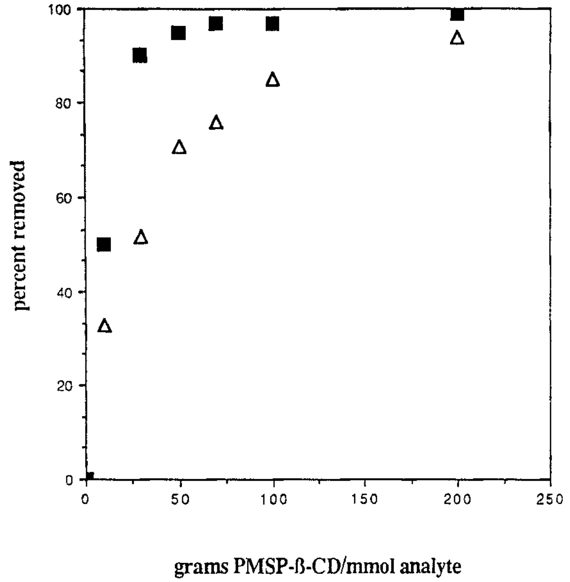

Figure 2: Effect of PMSP-β-CD concentration on percent removal of 2-naphthol (■) and m-nitrophenol (▲). Two ml aqueous samples of varying concentrations were analyzed in all cases. All samples were mechanically shaken for 20 hours.

conditions. While removal is constant for 2-naphthol and nitrobenzene, a slight change is recorded for o-nitroaniline and m-nitrophenol. The small difference in removal for o-nitroaniline and m-nitrophenol is likely due to the ionized species (pH 10.0 for m-nitrophenol and pH 1.5 for o-nitroaniline) having a different affinity of the adsorbent than the corresponding neutral species. Apparently 2-naphthol is sufficiently hydrophobic that it is strongly absorbed whether or not it is ionized. As expected, the percent removal remains constant for nitrobenzene, which was chosen as the reference compound since it should not ionize within the pH range studied. It should be noted that the pH dependence is only a factor when small amounts of PMSP-β-CD are used. If large amounts of PMSP-β-CD are added to the aqueous system, the more weakly absorbing species still can be quantitatively removed.

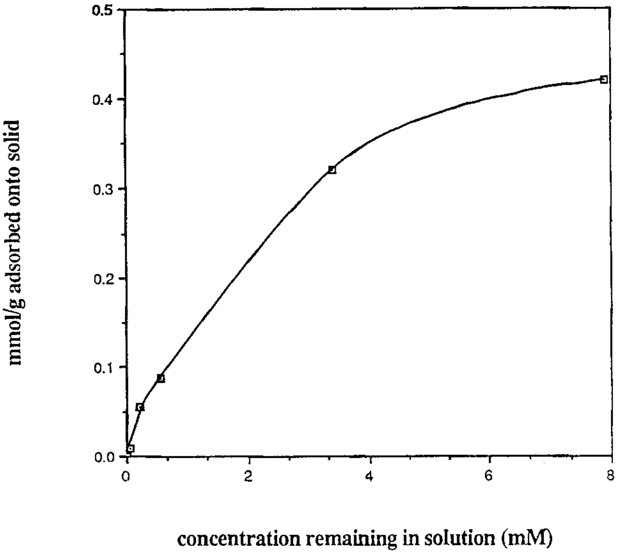

Figure 3: Adsorption isotherm of m-nitrophenol on PMSP-β-CD. Two ml aqueous samples of varying concentrations were analyzed in all cases. All samples were mechanically shaken for 20 hours. All analyzes were performed at room temperature (see Experimental). PMSP-β-CD concentration was 50 mg/ml for each sample.

The effect of salt on percent removal is presented in Table V. Surprisingly extraction of many organic compounds from aqueous solution are not effected by a salt concentrations as high as 0.5 M NaCl. There seems to be no evidence for the 'salting out' effect of organic compounds that is seen in many other circumstances. Another important aspect of removal in salt water is that the separation mechanism (sedimentation) is not effected by the addition of salt. Most cloud point extractions are influenced by even a small salt concentrations (3). This could be an important consideration in applications that require a constant separation mechanism in conditions of varying ionic strength.

Perhaps the most interesting aspect of this method for the separation and removal of organic compounds from water is that it is possible to easily recover both the PMSP-β-CD and organic compounds at high efficiencies. To recycle the

TABLE IV. pH EFFECT ON PERCENT REMOVAL[a]

COMPOUND	pH	%REMOVED (0.017 mmol/g)[b]	% REMOVED (0.002 mmol/g)[b]
o-nitroaniline	1.5	45	99
	7.0	59	99
	10.0	55	99
2-naphthol	3.0	58	92
	7.0	-	98
	10.0	56	94
nitrobenzene	3.0	91	99
	7.0	91	99
	10.0	89	99
m-nitrophenol	3.0	63	92
	7.0	58	90
	10.0	48	95

[a] Two ml of 5 x 10^{-5} M aqueous sample is analyzed in all cases. All samples are mechanically shaken for 20 hours.

[b] mmol/g refers to mmol of analyte per gram of PMSP-β-CD.

PMSP-β-CD, all that is needed is a small amount of water and a source of energy sufficient to heat the water to between 60 and 80° C. Different compounds are released from the adsorbent at different temperatures. However all compounds investigated were completely removed at temperatures between 80-100° C. The PMSP-β-CD is simply added to the water and heated at 80-100° C for a few minutes or until all adsorbed organic material is released. The PMSP-β-CD used in this study was recycled approximately thirty times over a six month period. There was no significant difference found between new and recycled adsorbent. The fact it is relatively easy to induce the release of organic compounds by PMSP-β-CD means that this method can be used in analytical procedures as a preconcentration technique. The low temperature recycling combined with the hardiness of this material makes PMSP-β-CD an interesting alternative for either the concentration or removal of organic materials from water.

TABLE V. SALT EFFECT ON PERCENT REMOVAL[a]

COMPOUND	SALT CONC (M)	% REMOVED (0.017 mmol/g)[b]	% REMOVED (0.002 mmol/g)[b]
o-nitroaniline	0.00	59	98
	0.01	69	98
	0.05	59	98
	0.10	62	96
	0.50	60	99
2-naphthol	0.00	57	99
	0.01	52	97
	0.05	68	98
	0.10	64	97
	0.50	57	97
nitrobenzene	0.00	91	99
	0.01	94	99
	0.05	96	99
	0.10	95	99
	0.50	97	99

[a] Two ml of 5 x 10^{-5} M aqueous sample is analyzed in all cases. All samples are mechanically shaken for 20 hours.

[b] mmol/g refers to mmol of analyte per gram of PMSP-β-CD.

CONCLUSIONS

PMSP-β-CD is a very hardy material that can be used to remove a variety of organic compounds from water. The cost of recycling or reusing this material is inexpensive because low temperatures are used (<100°C). Recovery of PMSP-β-CD is accomplished with simple decantation or filtration. The organic compound that is removed from water, also can be concentrated and quantitatively recovered making it a potentially useful analytical methodology. Both recovery of the PMSP-β-CD and the organic material are quantitatively performed.

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