ELSEVIER

Journal of Hazardous Materials B80 (2000) 59–68

Journal of Hazardous Materials

www.elsevier.nl/locate/jhazmat

Removal of phenols from aqueous solution by XAD-4 resin

Young Ku*, Kuen-Chyr Lee

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

Received 21 March 2000; received in revised form 13 June 2000; accepted 13 June 2000

Abstract

The experiments on the adsorption of phenols from aqueous solution by Amberlite XAD-4, a polystyrene-divinylbenzene resin without functional group, were carried out under different conditions. The phenols studied in this research include 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 2,4-dinitrophenol, 2-methylphenol, and 2,4-dimethylphenol. The experimental observations indicate that adsorption behavior of various phenols by XAD-4 resin could be described by either Langmuir or Freundlich models. The removals of phenols by XAD-4 resin for solutions of different pH varied significantly and can be explained by the species distribution of phenols in aqueous solutions. Phenols were effectively removed by XAD-4 resin at acidic conditions where the presence of molecular phenol species dominates. The removal decreased sharply for alkaline solutions where the negatively-charged ionic species is the dominant phenol species. The proposed adsorption equilibrium model adequately describes the sorption behavior of phenols by XAD-4 resin. The presence of functional groups on the benzene ring of various phenols plays an important role on the extent of adsorption. The removals of phenols by adsorption were found to correlate with the octanol/water partition coefficients of various phenol compounds.

Keywords: Phenols; Adsorption; Resin

1. Introduction

Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. During the review of technologies for treatment of synthetic organic compounds, especially phenols, it was found that adsorption and oxidation processes were considered as possible treatment techniques. Even though activated carbon is the most frequently used adsorbent, some refractory organic compounds could also be

* Corresponding author. Tel.: +886-2-27333141; fax: +886-2-23785535.
E-mail address: ku@ch.ntust.edu.tw (Y. Ku).

0304-3894/00/$ – see front matter
PII: S0304-3894(00)00275-2

concentrated and removed from aqueous solution via adsorption by macroreticular resins without ion exchange functional groups. That is, the attachment of the nonionic portion of the organic solute to the surface of the resin by van der Waals interaction. Several previous researchers reported that the adsorption of phenols in aqueous solutions by various XAD resins was slightly exothermic with adsorption heat of 3–6 kcal/mole [4,9,14]. The adsorption behavior was reported to be highly dependent on the solution pH [2,6,7,11] because the species distribution of phenol compounds varies at different pH levels. The type and number of functional groups on benzene ring were also found important on the adsorption of phenol compounds [1,10]. This paper discussed the adsorption behavior of various phenols in aqueous solutions by XAD-4 resin. A conceptual model is established based on the elemental balances and equilibrium equations to describe the adsorption behavior and differentiate the extent of adsorption of various phenol species removed by XAD-4 resin under different experimental conditions.

2. Experimental

Amberlite XAD-4, a nonionic polymeric resin composed of polystyrene chains cross-linked with divinylbenzene, was used as the adsorbent for studying the adsorption behavior of various phenols in aqueous solution. The medium size of the resin is 35–40 mesh. Several surface characteristics of the resin were measured using a Micromeritics ASAP 2000 BET analyzer. The specific surface area, average pore volume, and average pore diameter were determined to be 820 m^3/g, 0.81 cm^2/g, and 23.8 Å, respectively. The phenols studied in this research including phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-tricholophenol, 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 2-methylphenol, and 2,4-dimethylphenol. Some characteristics of the phenols related to this research are summarized from various literatures [3,12,13,15–17] and listed in Table 1. All experimental solutions used in this research were prepared with certified reagent-grade chemicals (purity greater than 99%) and double-distilled water.

For the adsorption equilibrium experiments, predetermined amounts of XAD-4 resin were introduced into 100 ml reactors filled with aqueous solutions of known concentrations of phenol and the whole reaction setups were maintained at 25±1°C by containing in a shaker water bath. The solution pH was adjusted to desired level (between 3 and 11) by adding acidic or alkaline solutions to the reactor prior the addition of resin. The ionic strength of solution was kept constant with 0.5N $NaNO_3$. After 72 h of contact time for resin and phenol-containing solution, the solution pH was recorded and the resin was allowed to settle for about 5 min before the supernatant was withdrawn and filtered. The solution pH was recorded, and the concentrations of various phenols in the filtered samples were determined by measuring the absorption of specific wavelength with a Shimaszu model UV-160A UV/visible spectrophotometer.

3. Results and discussion

Several experiments were conducted to study the adsorption behavior under various solution pH conditions. Experimental results showed that most phenols studied in this

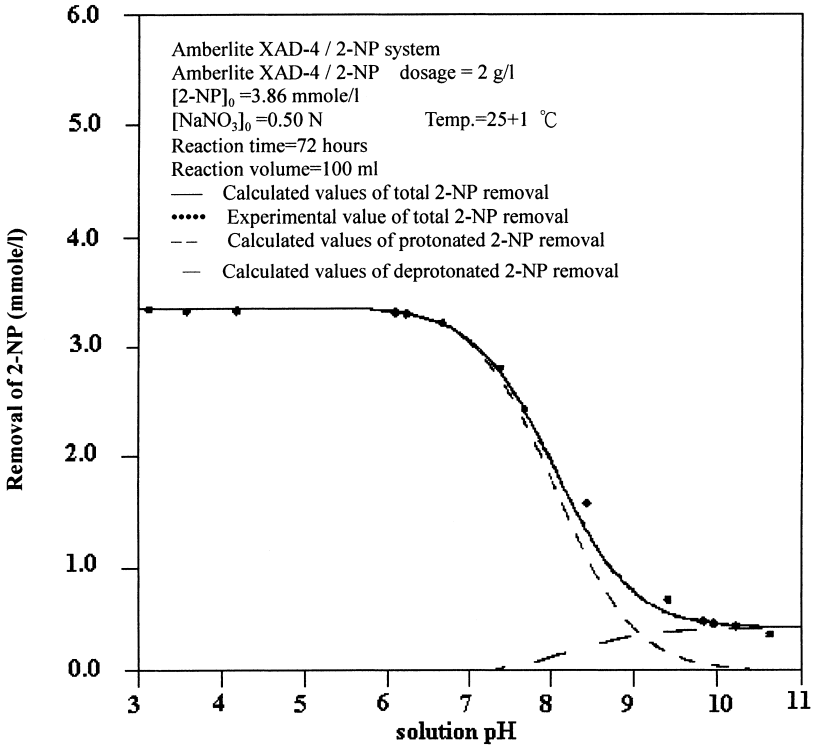

Fig. 1. Removal of 2-nitrophenol by XAD-4 resin at 25°C and different solution pH.

research were removed very effectively by XAD-4 resin for acidic solutions, the removals of phenols reduced sharply for alkaline solutions. For instance, the adsorption of 2-nitrophenol by XAD-4 at different solution pH is shown in Fig. 1, the removals were kept constantly high for solution pH below 8.5, and the removals reduced significantly for pH greater than 9.0. Almost no removal as found for solutions of pH 12.5 and higher. The experimental findings in this research are similar to the results reported by Kim et al. [11], much more 4-nitrophenol was adsorbed by XAD-7 resin for acidic conditions.

The effect of solution pH on the removal of various phenols from aqueous solutions by adsorption can be discussed by considering the theoretical distribution of various phenol species in aqueous solutions. Since most phenols (POHs) act like weak acids in aqueous solution, the dissociation of hydrogen ion from the phenol molecules strongly depends on the pH level of solution and can be expressed as

$$\mathrm{POH} \overset{K_a}{\rightleftharpoons} \mathrm{PO}^- + \mathrm{H}^+, \qquad K_a = \frac{[\mathrm{PO}^-][\mathrm{H}^+]}{[\mathrm{POH}]} \tag{1}$$

where [POH] and [PO] represents the concentrations of the molecular and dissociated ionic phenol species, respectively, and K_a is the dissociation constant of phenols shown in Table 1. Thus, the distribution of POH and PO species can be calculated as a function of solution

Table 1
Some physical and chemical characteristics of various phenol

	Phenol	2-CP	2,4-CP	2,4,6-CP	2-NP	2,4-NP	2-Methyl phenol	2,4-Methyl phenol
Formula	C_6H_5OH	C_6H_4ClOH	$C_6H_3Cl_2OH$	$C_6H_2Cl_3OH$	$C_6H_4NO_2OH$	$C_6H_3(NO_2)_2OH$	$C_6H_4CH_3OH$	$C_6H_3(CH_3)OH$
Molecular weight	94.11	128.56	163.01	194.76	139.11	184.11	108.13	122.16
Melt point (°C)	41	43	45	68	45	113	31	26
Boil point (°C)	182	217	210	245	214	–	191	211.5
Vapor pressure (mm)	0.2[a]	0.10[a]	–	–	20[b]	–	0.24[c]	–
log(K_{ow})	1.46	2.17	3.23	3.72	1.79	1.53	1.98	2.50
pK	9.99	8.55	7.85	6.15	7.22	4.08	10.26	10.58
Specific graity	1.07	1.31	1.38	1.49	1.657	1.683	1.04	1.036
Bioeffect	0.53[d]	0.67[d]	0.58[d]	–	1000[e]	100[e]	60[e]	500[e]

[a] At 20°C.
[b] At 105°C.
[c] At 25°C.
[d] LD_{50} in g/kg.
[e] LD_0 in mg/l.

pH. The molecular species, POH, is the predominant in acidic solutions, whereas the ionic species, PO, predominates in alkaline solutions. The removal of phenols by XAD-4 resin may involve the adsorption of both molecular and ionic phenol species. The simplified overall scheme for the adsorption of phenols by XAD-4 resin can be expressed by following equations:

$$\mathrm{POH} + [\mathrm{R}]_{\mathrm{ad}} \overset{K_{\mathrm{ad1}}}{\rightleftharpoons} [\mathrm{RPOH}]_{\mathrm{ad}}$$

$$\mathrm{PO}^- + [\mathrm{R}]_{\mathrm{ad}} \rightleftharpoons [\mathrm{RPO}^-]_{\mathrm{ad}}$$

where R_{ad} is the adsorption sites on the XAD-4 resin, and $[RPOH]_{ad}$ and $[RPO]_{ad}$ are the molecular and ionic phenol species removed by XAD-4, respectively. In order to establish the site balance, the concentrations of the resin sites, either vacant or occupied by the various phenol species, R_{ad}, [RPOH], and [RPO], are defined as the ratio of the equivalent amount of sorption sites to the volume of reaction solution. The equilibrium adsorption constants for the molecular and ionic phenol species, K_{ad1} and K_{ad2}, are defined as followed:

$$K_{\mathrm{ad1}} = \frac{[\mathrm{RPOH}]_{\mathrm{ad}}}{([\mathrm{POH}] + [\mathrm{PO}^-])(1/(1 + (K_{\mathrm{a}}/[\mathrm{H}^+])))[\mathrm{R}]_{\mathrm{ad}}} \tag{2}$$

$$K_{\mathrm{ad2}} = \frac{[\mathrm{RPO}^-]_{\mathrm{ad}}}{([\mathrm{POH}] + [\mathrm{PO}^-])(1/(1 + ([\mathrm{H}^+]/K_{\mathrm{a}})))[\mathrm{R}]_{\mathrm{ad}}} \tag{3}$$

If the values of K_{ad1}, K_{ad2}, and K_a are known, the individual removals of molecular and ionic phenol species by XAD-4 adsorption, $[RPOH]_{ad}$ and $[RPO]_{ad}$ can be calculated simultaneously from the mass balance and equilibrium expressions shown in Eqs. (2) and (3), by using nonlinear Newton's method [8]. For highly acidic conditions (pH less than 4 in this research) where the presence of ionic phenol species is considered negligible, the phenol removed is assumed to be totally in the form of molecular phenol species, thus the values of K_{ad1} can be calculated. Similarly, K_{ad2} can be determined from the experimental results obtained for alkaline conditions (pH greater than 10 in this research) where the adsorption of molecular phenol species is considered negligible. With the determined adsorption equilibrium constants for various phenols summarized in Table 2, the established equilibrium

Table 2
The calculated equilibrium constants for various phenols

	K_p	K_{ad1} (l/mmole)	K_{ad2} (l/mmole)
Phenol	0.50	0.0930	0.0030
2-Chlorophenol	1.34	0.37	0.018
2,4-Dichlorophenol	3.38	0.93	0.029
2,4,6-Trichlorophenol	7.36	2.32	0.12
2-Nitrophenol	6.22	1.90	0.018
2,4-Dinitrophenol	0.96	0.20	0.007
2-Methylphenol	1.11	0.24	0.022
2,4-Dimethylphenol	1.33	0.30	0.029

Table 3
The correlated parameter of Freudlich and Langmuir isotherms for the adsorption of 2-nitrophenol by XAD-4 resin

	Freundlich				Langmuir			
pH	Fitted equation	r^2	K	n	Fitted equation	r^2	X_m	b
pH=3.0	$\log(X)=0.42\log(Ce)+0.93$	0.95	13.51	2.01	$(1/X)=0.0376\,(1/Ce)-0.0746$	0.98	6.70	2.38
pH=11.3	$\log(X)=1.26\log(Ce)-0.67$	0.97	0.21	0.79	$(1/X)=4.082\,(1/Ce)-0.15$	0.97	–	–

equations expressed below can adequately describe the adsorption behavior of phenols by XAD-4 resin.

$$K_{ad1} = \frac{[RPOH]_{ad}}{([P]_0 - ([RPOH]_{ad} + [RPO^-]_{ad}))(1/(1 + K_a/[H^+]))\,([R]_{0,ad} - ([RPOH]_{ad} + [RPO^-]_{ad}))} \quad (4)$$

$$K_{ad2} = \frac{[RPO^-]}{([P]_0 - ([RPOH]_{ad} + [RPO^-]_{ad}))(1/(1 + ([H^+]/K_a)))\,([R]_{0,ad} - ([RPOH]_{ad} + [RPO^-]_{ad}))} \quad (5)$$

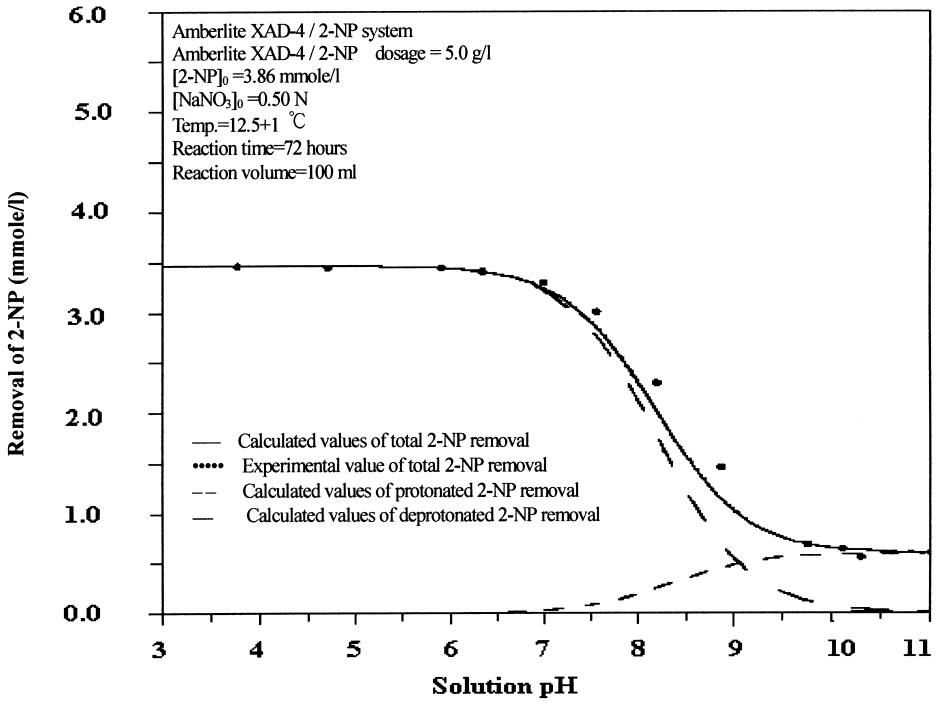

Fig. 2. Removal of 2-nitrophenol by XAD-4 resin at 12.5°C and different solution pH.

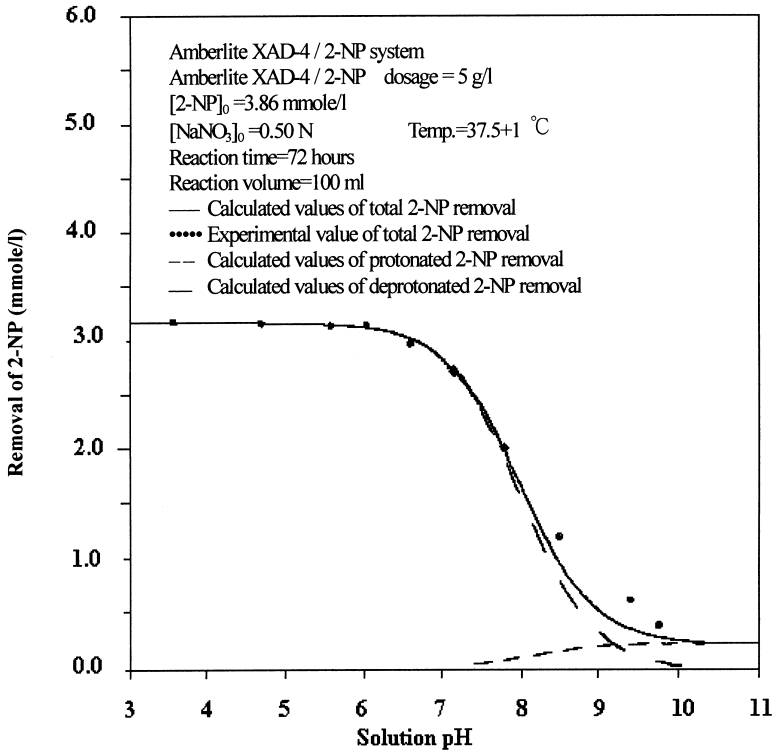

Fig. 3. Removal of 2-nitrophenol by XAD-4 resin at 37.5°C and different solution pH.

The effect of initial concentration on the adsorption of 2-nitrophenol by XAD-4 resin was studied at 25°C in order to establish the adsorption isotherm. The Langmuir and Freundlich models were used to correlate the experimental equilibrium data. The values of Langmuir and Freundlich parameters are summarized in Table 3 with relatively good applicability. The fitted results also indicate that adsorption of 2-nitrophenol in aqueous solutions was considered to be unfavorable for alkaline conditions.

For experiments conducted at same solution pH, the removal of 2-nitrophenol by XAD-4 resin slightly decreased with increasing temperature, as shown in Figs. 2 and 3, indicating the adsorption is endothermic. The equilibrium adsorption constants at different temperatures are summarized in Table 4. The adsorption heat for the adsorption of 2-nitrophenol by

Table 4
The calculated adsorption equilibrium constants at different solution temperature for the adsorption of 2-nitrophenol by XAD-4 resin

Temperature (°C)	K_{ad1}	K_{ad2}
12.5	2.73	0.03
25.0	1.90	0.018
37.5	1.32	0.01

XAD-4 at various solution pH was calculated by correlating the equilibrium constants with solution temperature via van't Hoff equation, and determined to be about −5 kcal/mole at pH 3 and −7.5 kcal/mole at pH 11.

In order to further identify the effect of solution condition on the removal of various phenols, a partition constant, K_p, defined as the ratio of the amount of a specific phenol species adsorbed by XAD-4 resin to the total amount of phenol in aqueous solution, is introduced. For instance, K_p for the removal of molecular phenol species by adsorption can be expressed as

$$K_p = \frac{[\text{RPOH}]_{ad}}{[\text{POH}]} \tag{6}$$

Several previous researches reported that the adsorption behavior of phenol compounds by natural adsorbents is highly influenced by hydrophobic interaction. In most cases, the affinity between an adsorbent and a hydrophobic solute can be linearly corrected with the organic carbon content of the adsorbent [5,15] as shown by the following equations:

$$K_p = (\text{foc})(b)(K_{ow})^a \tag{7}$$

where foc is adsorbent as carbon, a and b are constants.

As shown in Fig. 4, the experimental results in this research indicate that the partition constant (K_p) could be empirically correlated with the octanol/water partition coefficient

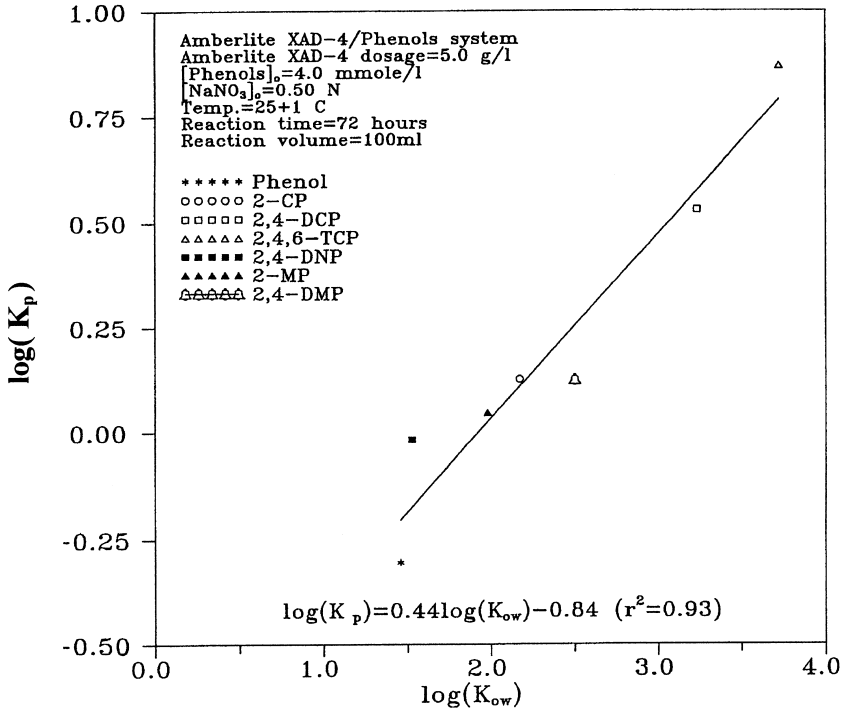

Fig. 4. Correlated results of K_p and K_{ow} for various phenols.

(K_{ow}) for various phenols adsorbed by XAD-4 resin. Thus, the adsorption equilibrium and partition constants of phenols adsorbed by XAD-4 resin can be roughly estimated from the octanol/water partition coefficient of the phenol compounds by using Eq. (7). Also, because the K_{ow} value of different phenols usually varied with the type and number of functional groups on the benzene ring as listed in Table 1. For chlorophenols, the K_{ow} increases with the number of chlorine on the benzene ring and is consistent with the trend of adsorption and partition constants. Similar results can be elucidated for various nitrophenols and methylphenols.

4. Conclusion

The removal of phenols by XAD-4 resin was found to be feasible for acidic conditions, but decreased significantly with increasing solution pH level. Experimental results indicated that adsorption equilibrium behavior of various phenols by XAD-4 resin can be described by either Langmuir or Freundlich models. The effect of solution pH on the removal of phenols can be discussed by considering the predominant phenol species present in the solution. The extent of phenol removal by XAD-4 adsorption was found decreased with increasing solution temperature. The equilibrium model based on species distribution and mass balance considerations is capable of describing the adsorption behavior at different solution pH conditions and calculating the individual removals of various phenol species presented in the investigated systems. Despite the different type and number of functional groups on the benzene ring, the adsorption equilibrium constants of various molecular phenol species by XAD-4 resin were found to correlate well with the octanol/water partition coefficients of the phenols.

List of symbols

$[POH]$	concentration of phenol in molecule species (mM)
$[PO^-]$	concentration of phenol in ionic species (mM)
$[H^+]$	concentration of hydrogen ion (mM)
$[RPOH]_{ad}$	concentration of adsorption of phenols by XAD-4 resin in molecule species (mM)
$[RPO^-]_{ad}$	concentration of adsorption of phenols by XAD-4 resin in ionic species (mM)
$[R]_{ad}$	concentration of adsorption site on XAD-4 resin (mM)
K_{ad1}	equilibrium adsorption constants for the molecular phenol species, (l/mmole)
K_{ad2}	equilibrium adsorption constants for the ionic phenol species, (l/mmole)
K_p	partition constant
foc	adsorbent as carbon
a,b	constants

References

[1] A.K. Burnham, G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec, R. Willis, Identification and estimation of nature organic contaminants in portable water, Anal. Chem. 44 (1972) 139.

[2] R.M. Carlyle, Use of synthetic adsorbents in chemical processes, Effl. Water Treat. 2 (2) (1982) 55.
[3] J.A. Dean, Lang's Handbook of Chemistry, 13th Edition, McGraw-Hill, New York, NY, USA, 1981.
[4] D.S. Farrier, A.L. Hines, S.W. Wang, Adsorption of phenol and benzoic acid from dilute aqueous solution onto a macroreticular resin, J. Colloid Interface Sci. 69 (1979) 233.
[5] C.T. Jafvert, J.C. Westall, E. Grieder, R.P. Schwarzenbach, Distribution of hydrophobic organic compounds between octanol and water: organic acids, Environ. Sci. Technol. 24 (1990) 1795.
[6] R.L. Jolley, Concentrating organics in water ffor biological testing, Environ. Sci. Technol. 15 (1981) 984.
[7] G.A. Junk, J.J. Richard, M.D. Grieser, D. Witiak, J.L. Witiak, M.D. Arquello, R. Vick, H.J. Svec, J.S. Fritz, G.V. Calder, Use of macroreticular resins in the analysis of water for trace organic contaminants, J. Chromatogr. 99 (1974) 745.
[8] D. Kahaner, C. Moler, S. Nash, Numerical Methods and Software, Prentice-Hall, Englewood, NJ, USA, 1989.
[9] N. Kawabata, I. Higuchi, J.I. Yoshida, Removal and recovery of organic pollutants from the aquatic environment. VII. Adsorption of phenol and carboxylic acids on crosslinked poly(4-vinylpyridine), Bull. Chem. Soc. Jpn. 54 (1981) 3253.
[10] D.C. Kennedy, Macroreticular polymeric adsorbent, Ind. Eng. Chem. Prod. Res. Dev. 12 (1973) 56.
[11] B.R. Kim, V.L. Snoeyink, F.M. Saunders, Adsorption of organic compounds by synthetic resins, J. Water Pollut. Control Fed. 48 (1976) 120.
[12] A. Leo, C. Hansch, D. Elkins, Partition coefficients and their uses, Chem. Rev. 71 (1971) 525.
[13] D.R. Lide, CRC Handbook of Chemitry and Physics, CRC Press, Ann Arbor, MI, USA, 1992.
[14] J. Paleos, Adsorption from aqueous and nonaqueous solutions on hydrophobic and hydrophilic high surface area copolymers, J. Colliod Interface Sci. 31 (1969) 7.
[15] K. Schellenberg, C. Leuenberger, R.P. Schwarzenbach, Sorption of chlorinated phenols by natural sediments and aquifer, Environ. Sci. Technol. 18 (1984) 652.
[16] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, 3rd edn., 1997.
[17] J.C. Westall, C. Leuenberger, R.P. Schwarenbach, Influence of pH and ionic strength on the aqueous–nonaqueous distribution of chlorinated phenols, Environ. Sci. Technol. 19 (1985) 193.