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Removal and Recovery of Organic Pollutants from Aquatic Environment. V. Crosslinked Poly(hydroxystyrene) as a Polymeric Adsorbent for Removal and Recovery of ε-Caprolactam from Aqueous Solution

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Crosslinked poly(hydroxystyrene) (PHS resin) was found to be useful as a polymeric adsorbent for removal and recovery of ε-caprolactam from aqueous solution. The breakthrough capacity of PHS resins with $<$1-mg/l leakage in the effluent was 50—90 mg/dry g, which was scarcely affected by the presence of hydrochloric acid, sodium hydroxide, and inorganic salts such as sodium chloride, potassium chloride, calcium chloride, and magnesium chloride. Elution of the adsorbed ε-caprolactam from PHS resin was easily accomplished by a simple treatment with methanol, and PHS resin was efficiently regenerated. ε-Caprolactam was concentrated into 10—30 g/l solution.

In this series of investigations, attempts have been made to find new polymeric adsorbents which are useful for removal and recovery of organic pollutants from aquatic environment. This methodology is important not only in the protection of the environment from pollution, but also in the effective use of raw materials, because the organic pollutants can be recovered without chemical change. This paper deals with the removal and recovery of ε-caprolactam from aqueous solution by polymeric adsorbents.

ε-Caprolactam is the most important lactam in use by chemical industry. The wastewater from the manufacturing process contains some amount of the lactam, which is usually treated with activated sludge. However, the biological treatment needs a long time and a wide space. The adsorption process using a suitable polymeric adsorbent may be more convenient because the process saves time and space of the treatment, and makes it possible to reuse the recovered ε-caprolactam. We have tried to use various polymeric adsorbents for this purpose, and found that the crosslinked poly(hydroxystyrene) (PHS resin) was most useful.

Experimental

Materials. *p*-Acetoxystyrene provided by Maruzen Oil Co., Tokyo, was purified by distillation before use. Commercial products of divinylbenzene and toluene were purified by distillation before polymerization. Methanol, petroleum ether, ε-caprolactam, 2,2′-azobisisobutyronitrile, sodium hydroxide, hydrochloric acid, calcium hydride, and other chemicals were used without further purification.

Crosslinked Poly(hydroxystyrene) (PHS Resin). PHS resin was prepared by hydrolysis of the copolymer of *p*-acetoxystyrene with divinylbenzene according to the procedure of Packham[1] with minor modification. Dried copolymer of *p*-acetoxystyrene with divinylbenzene was ground using an ishiusu (a Japanese classical hand mill made of stone) and sifted out to 60—80 mesh. The sifted copolymer was hydrolyzed to give PHS resin. One sample of PHS resin (PHS-9) was prepared by a direct radical copolymerization of *p*-vinylphenol with divinylbenzene in benzene, which was ground and sifted out to 20—30 mesh. These PHS resins were rinsed with 10 Bed Volume (BV) of methanol by a batch method followed by washing with 30—40 BV of water by the continuous flow column method. Mole fraction of *p*-acetoxystyrene in the copolymer of *p*-acetoxystyrene with divinylbenzene before hydrolysis, and that of *p*-vinylphenol in PHS-9 were determined by elemental analysis. Content of water in the swollen state and the mean particle diameter of these PHS resins were determined, and results are given in Table 1.

Commercial Polymeric Adsorbents. For comparison with PHS resin, four commercial resins provided by Rohm and Haas Co., Philadelphia, Pa. were used. Amberlite IR-120B was used as a strong acid cation exchange resin which had a styrene–divinylbenzene matrix with sulfonate group. This

TABLE 1. CHARACTERISTICS OF CROSSLINKED POLY(HYDROXYSTYRENE) (PHS RESIN)

Crosslinked polyhydroxystrene	PHS-1	PHS-2	PHS-3	PHS-4	PHS-5	PHS-6	PHS-7	PHS-8	PHS-9[a]
Mole fraction of *p*-acetoxystyrene before hydrolysis	0.93	0.82	0.73	0.56	0.43	0.35	0.25	0.14	0.79[b]
Content of water in the swollen state (wt %)	44	32	25	33	41	29	47	52	62
Mean particle diameter in the dry state (mm)	0.28	0.30	0.23	0.33	0.25	0.30	0.33	0.30	0.65
Mean particle diameter in the wet state (mm)	0.38	0.40	0.33	0.40	0.38	0.38	0.35	0.38	1.03
Breakthrough capacity for sodium hydroxide adsorption (meq/dry g)	1.23	0.77	0.51	0.34	0.31	0.17	0.16	0.12	2.46
Total capacity for sodium hydroxide adsorption (meq/dry g)	1.45	0.87	0.70	0.49	0.38	0.31	0.25	0.16	2.60

a) Prepared by a direct copolymerization of *p*-vinylphenol with divinylbenzene. b) Mole fraction of *p*-vinylphenol.

resin was used in the hydrogen ion form. Amberlite IRC-50 was used as a weak acid cation exchange resin which had a styrene–divinylbenzene matrix with carboxyl group. This resin was also used in the hydrogen ion form. Amberlite XAD-2 and XAD-4 were used as porous styrene–divinylbenzene resins with no ion exchange functional group. The surface area of XAD-2 and XAD-4 were claimed by the supplier to be 300 and 784 m^2/g, respectively.

Amberlite IR-120B was preconditioned and transferred to the hydrogen ion form as follows: (1) placing it in a column of 2.5-cm diameter with a fritted glass filter; (2) washing with 10 BV of methanol; (3) washing with 10 BV of deionized water; (4) slowly contacting with 10 BV of 2 mol/l hydrochloric acid; (5) washing with 10 BV of deionized water; (6) slowly contacting it with 10 BV of 2 mol/l sodium hydroxide; (7) washing with 10 BV of deionized water; (8) repeating steps 4 through 7 several times; (9) slowly contacting it with 20—30 BV of 2 mol/l hydrochloric acid; (10) extensive washing with deionized water until the effluent pH was close to the influent pH. The ion exchange capacity of the resin was 4.4 meq/dry g, which was determined by back titration with 0.1 mol/l hydrochloric acid using phenolphthalein as indicator in 1 mol/l sodium hydroxide after the addition of standard sodium hydroxide solution. Percentage moisture of the resin was determined after drying *in vacuo* to constant weight. Amberlite XAD-2 and XAD-4, and Amberilte IRC-50 in the hydrogen ion form were preconditioned by washing with 10 BV of methanol followed by washing with 30 BV of deionized water.

For comparison with the non-ionic XAD resins, we also used pulverized copolymer of styrene with divinylbenzene containing 57 mol% styrene, which was prepared as was described in a previous paper of this series.[2]

Adsorption Tests. Column studies were conducted using a 1.0-cm diameter glass column with a fritted glass filter connected with a 200-ml dropping funnel in a down-flow fashion at room temperature. The preconditioned polymeric adsorbent was placed in the column. The bed was carefully backwashed to eliminate entrained air and then tapped to ensure packing of the bed. The dropping funnel was used to contain influent solution. Samples were taken manually and were checked for the concentration of ε-caprolactam. The flow rate was 3 BV/h throughout this work. The influent concentration of ε-caprolactam was controlled to be about 2000 mg/l.

The capacity of polymeric adsorbents for the adsorption of ε-caprolactam was determined by continuous flow column method in two ways: (i) the breakthrough capacity, which was based upon the total amount of adsorbed ε-caprolactam before the effluent concentration reached 1 mg/l; (ii) the total capacity, which was determined based upon the total amount of adsorbed ε-caprolactam until the effluent concentration became close to the influent concentration.

The breakthrough capacity and the total capacity of the PHS resin for sodium hydroxide adsorption were determined using aqueous 0.02 mol/l sodium hydroxide solution by the continuous flow column method. Results are given in Table 1.

Equilibrium adsorption tests were conducted by placing weighed quantities of polymeric adsorbent and samples of aqueous solution of ε-caprolactam in a 300-ml Erlenmeyer flask sealed by rubber stopper in a water bath maintained at 30±1 °C with magnetic stirring. After the mixture reached equilibrium, the concentration of ε-caprolactam was determined.

Recovery of Adsorbed ε-Caprolactam from Polymeric Adsorbents. Polymeric adsorbents were saturated with ε-caprolactam by the continuous flow column method carried out until the effluent concentration became 1 mg/l using about 2000 mg/l of aqueous ε-caprolactam solution. Elution of the adsorbed ε-caprolactam from the polymeric adsorbents was conducted by the continuous flow column method using methanol as the eluant with flow rate of 3 BV/h in a down-flow fashion.

Analyses. Elemental analyses were performed at the Elementary Analyses Center of Kyoto University. Quantitative analysis of ε-caprolactam in aqueous and/or methanolic solution was performed with Shimadzu Model UV-200S spectrophotometer based upon the absorptivities at 203 nm. The pH value of solutions was determined with a Horiba Model F-7AD pH meter.

Results and Discussion

Adsorption of ε-Caprolactam on Various Polymeric Adsorbents Studied by the Continuous Flow Column Method. The breakthrough curves are illustrated in Fig. 1. PHS resin and XAD-4 showed the ability to adsorb ε-caprolactam in aqueous solution, but the cation exchange resins IR-120B and IRC-50 did not adsorb ε-caprolactam under our experimental conditions. We calculated the breakthrough capacity and the total capacity for the adsorption of ε-caprolactam. Results are summarized in Table 2. The adsorption capacity of the PHS resin was not very sensitive to the content of *p*-acetoxystyrene before hydrolysis, but showed a maximum at the content of about 40 mol%.

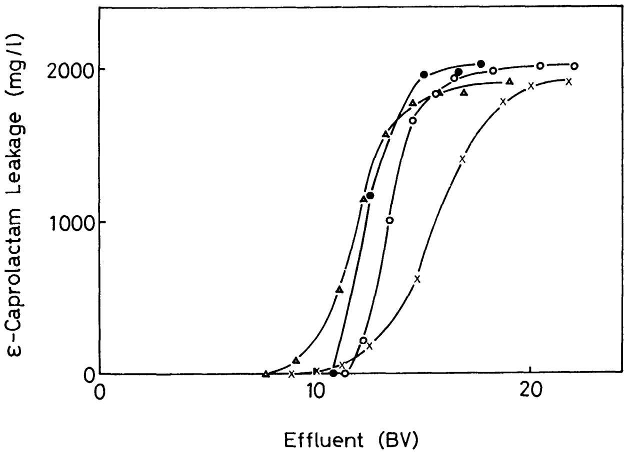


Fig. 1. Examples of the removal of ε-caprolactam from aqueous solution by polymeric adsorbents.
Conditions: influent concentration of ε-caprolactam, 2000 mg/*l*; flow rate, 3 BV/h; (▲) PHS-1; (○) PHS-4; (●) PHS-5; (×) XAD-4.

Among the styrene–divinylbenzene resins with no ion exchange functional group, XAD-4 (claimed by the supplier to have the surface area of 784 m^2/g) showed a breakthrough capacity of 55 mg/dry g, but XAD-2 (claimed by the supplier to have a surface area of 300 m^2/g) showed a much lower capacity to adsorb ε-caprolactam. This result indicates the importance of the surface area of the polymeric adsorbents. In this work, we used the PHS resins in the pulverized form, but they showed breakthrough capacities of 50—90 mg/dry g as can be seen in Table 2. If we supposed a

TABLE 2. CAPACITIES OF POLYMERIC ADSORBENTS FOR ε-CAPROLACTAM ADSORPTION[a]

Polymeric adsorbent	Breakthrough capacity (mg/dry g)	Total adsorption capacity (mg/dry g)
PHS-1	53	81
PHS-2	52	91
PHS-3	55	93
PHS-4	70	90
PHS-5	87	96
PHS-6	65	75
PHS-7	73	84
PHS-8	73	81
PHS-9	38	65
XAD-2[b]	12	—
XAD-4[c]	55	91

a) Determined by the continuous flow column method using about 2000 mg/l of aqueous ε-caprolactam solution. The flow rate was 3 BV/h. b) Claimed to have the surface area of 300 m^2/g. c) Claimed to have the surface area of 784 m^2/g.

TABLE 3. CAPACITIES OF POLYMERIC ADSORBENTS FOR ε-CAPROLACTAM ADSORPTION IN THE PRESENCE OF INORGANIC SALTS[a]

Polymeric adsorbent	Inorganic salt	Breakthrough capacity (mg/dry g)	Total adsorption capacity (mg/dry g)
PHS-5	none	87	96
PHS-5	NaCl	85	101
PHS-5	KCl	87	103
PHS-5	$MgCl_2$	89	103
PHS-5	$CaCl_2$	89	103
XAD-4	none	55	91
XAD-4	NaCl	57	96

a) Determined by the continuous flow column method using about 2000 mg/l of aqueous ε-caprolactam solution containing 0.1 mol/l of inorganic salts. The flow rate was 3 BV/h.

spherical form for PHS resins, the surface area of PHS-1—PHS-8 were assumed to be about 30 cm^2/g. Thus the actual surface area of the PHS resins would be less than 0.1 m^2/g. If porous PHS resins with large surface area were used, the adsorption capacity could be further improved. PHS-9 showed a lower capacity than the other PHS resins for the adsorption of ε-caprolactam. The result can be ascribable, at least partly, to the smaller surface area, because the particle size of PHS-9 was much larger than those of the other PHS resins as can be seen in Table 1.

Effect of Some Inorganic Salts in Aqueous Solution on the Breakthrough Capacity of Polymeric Adsorbents for ε-Caprolactam Adsorption. In the practical use of polymeric adsorbents for removal and recovery of ε-caprolactam from wastewater, it is difficult to avoid the presence of some inorganic salts. Inorganic cations in wastewater might reduce the capacity of PHS resin for the adsorption of ε-caprolactam if it adsorbed through an ion exchange mechanism. In order to obtain some information on this subject, we have investigated the effect of the presence of some inorganic salts in aqueous solution on the breakthrough capacity of PHS resin for ε-caprolactam adsorption.

Since major inorganic cations commonly appearing in natural water are sodium, potassium, calcium, and magnesium cations, we first determined the breakthrough capacities of PHS resins, and XAD-4 for comparison, for the adsorption of ε-caprolactam in the presence of sodium chloride, potassium chloride, calcium chloride, and magnesium chloride. Results are given in Table 3. The capacity did not decrease in the presence of these inorganic salts.

Effect of Acid and Alkaline Materials in Aqueous Solution on the Breakthrough Capacity of Polymeric Adsorbents for the Adsorption of ε-Caprolactam. In the practical use of polymeric adsorbents for wastewater treatment, it is also difficult to avoid the presence of acid and alkaline materials. In order to obtain some information on this subject, we have investigated the effect of hydrochloric acid and sodium hydroxide in aqueous solution on the capacity of PHS resin, and XAD-4 for comparison, for the adsorption of ε-caprolactam. Results are summarized in Table 4. The breakthrough capacity was scarcely affected by the presence of these acid and alkaline materials.

TABLE 4. EFFECT OF ACID AND ALKALINE METERIALS IN AQUEOUS ε-CAPROLACTAM SOLUTION ON THE CAPACITY OF POLYMERIC ADSORBENTS FOR ε-CAPROLACTAM ADSORPTION[a]

Polymeric adsorbent	HCl (mmol/l)	NaOH (mmol/l)	pH of the solution		Breakthrough capacity (mg/dry g)	Total adsorption capacity (mg/dry g)
			influent	effluent[b]		
PHS-5	20.1		2.77	2.78	82	103
PHS-5	1.58		4.05	4.05	91	101
PHS-5			5.48	5.69—5.87	87	96
PHS-5		0.009	6.40	5.79—6.29	89	102
PHS-5		0.18	10.40	6.84—6.87	81	99
XAD-4	15.3		3.00	2.78—2.89	42	96
XAD-4	0.57		4.22	5.74—5.78	40	94
XAD-4			5.62	5.50—5.62	55	91
XAD-4		0.07	7.43	6.00—6.03	32	93
XAD-4		1.07	10.77	10.08—10.35	41	94

a) Determined by the continuous flow column method using about 2000 mg/l of ε-caprolactam solution containing acid or alkaline materials. The flow rate was 3 BV/h. b) Before the breakthrough point.

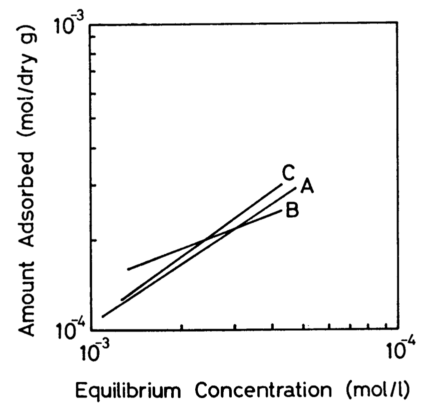


Fig. 2. ε-Caprolactam adsorption isotherms on polymeric adsorbents at 30±1°C.
(A) PHS-4; (B) PHS-5; (C) XAD-4.

Adsorption Equilibrium for ε-Caprolactam and Polymeric Adsorbents. The experimental isotherms of ε-caprolactam adsorption on PHS resin are shown in Fig. 2. Similar results were obtained with PHS resins and XAD-4.

Recovery of ε-Caprolactam from Polymeric Adsorbents. In addition to the removal of ε-caprolactam from aqueous solution, the major objective of this work is to recover as much ε-caprolactam as possible from the polymeric adsorbents. This is necessary not only in the effective regeneration of the polymeric adsorbents, but also in the reuse of the recovered ε-caprolactam. We examined the elution of ε-caprolactam from PHS resin and XAD-4 by the continuous flow column method using methanol as the eluant. Results are shown in Fig. 3. The adsorbed ε-caprolactam was quantitatively recovered using 2—3 BV of methanol as the eluant, and PHS resin and XAD-4 were efficiently regenerated. ε-Caprolactam was concentrated into 10—30 g/l solution.

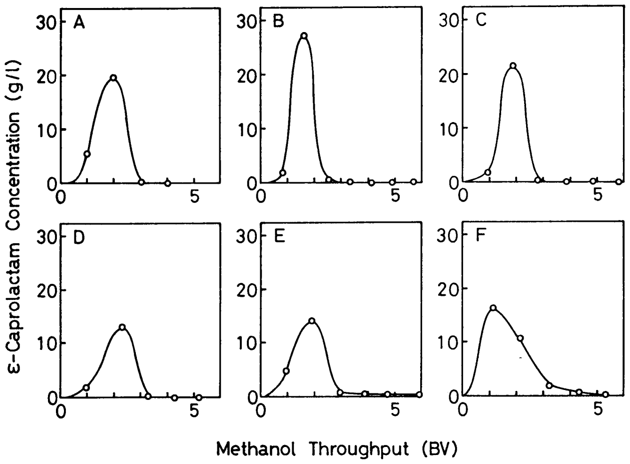
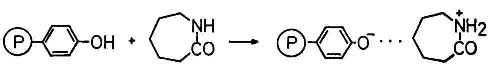


Fig. 3. Elution of adsorbed ε-caprolactam from polymeric adsorbents using methanol as the eluant by the continuous flow column method.
Flow rate was 3 BV/h; (A) PHS-5; (B) PHS-6; (C) PHS-7; (D) PHS-8; (E) PHS-9; (F) XAD-4.

Mechanism of the Adsorption of ε-Caprolactam on PHS Resin. Although mechanism of the adsorption of ε-caprolactam on PHS resin has not been elucidated as yet, experimental results gave some suggestions on this problem. It is reasonable to speculate that the adsorption of ε-caprolactam by PHS resin was derived from an intermolecular interaction between ε-caprolactam and phenolic hydroxyl group of PHS resin, because PHS resin showed a comparable or a rather higher capacity than the porous styrene–divinylbenzene resin with no ion exchange functional group, in spite of the fact that we used PHS resin in a pulverized form.

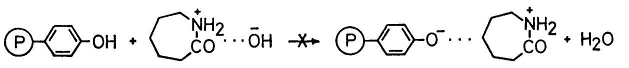
Although we used PHS resin in a pulverized form, it showed a high hydrophilicity and considerably swelled in water as can be seen in Table 1. Thus the effective surface area in water might be unexpectedly large. However, this high hydrophilicity would not wholly explain the adsorption capacity of PHS resin for ε-caprolactam, because a vinylpyridine–divinylbenzene copolymer in a pulverized form[2) did not adsorb ε-caprolactam under similar conditions, in spite of the fact that the copolymer also showed a high hydrophilicity. Therefore, the high hydrophilicity of PHS resin can not wholly explain its capacity for ε-caprolactam adsorption. The intermolecular interaction between ε-caprolactam and phenolic hydroxyl group of PHS resin appears to be an important factor for the adsorption.

Since phenol is a weak acid, and ε-caprolactam is a very weak base, the following interaction was hypothesized between PHS resin and ε-caprolactam:



Here, ε-caprolactam uptakes a proton from phenolic hydroxyl group of PHS resin and forms a complex with phenoxide anion as the associated counterion.

On the other hand, since weak acid and strong acid cation exchange resins did not adsorb ε-caprolactam under our experimental conditions, the following ion exchange mechanism would not be suitable for the adsorption of ε-caprolactam by PHS resin.



Further research is required to determine the mechanism of the interaction between ε-caprolactam and PHS resin.

References

1) D. I. Packham, *J. Chem. Soc.*, **1964**, 2617.

2) N. Kawabata and K. Ohira, *Environ. Sci. Technol.*, **13**, 1396 (1979).