Removal of Methyl Orange by Systems of Chloromethylated Polystyrene–Polyethylenepolyamines and –Polyethyleneimines

TATSUO TASHIRO, *Research Institute for Polymers and Textiles, 1-1-4, Higashi, Tsukuba, Ibaraki Pref., 305, Japan*

Synopsis

A study was made of the removal of methyl orange (MO) solutes in water by the reaction products of chloromethylated divinylbenzene crosslinked polystyrene (CMPS) with polyethylenepolyamines (PEPA), polyethyleneimines (PEI), and 2-methyl-2-oxazoline (MeOZO). This behavior of such polymers in regard to the Klotz equation and Freundlich adsorption formula was also examined and noted to conform better to the former than to the latter. The constants of the Klotz equation were calculated. The amounts of MO removed with unit masses of the polymers and the effects of salts on removal were studied. A possible mechanism for removal is discussed.

INTRODUCTION

It is difficult to remove nonionic, organic compounds dissolved in water, especially nonionic surfactants, dyestuffs, and phenol and its derivatives by ion exchange resins. For this purpose, adsorbents should be used, and a number of studies in this regard have been conducted.[1]

These studies include papers on interactions between natural macromolecules or synthetic polymers and methyl orange (MO), an acidic dyestuff. That is, they are papers on the binding of MO by bovin serum albumine,[2] polyethyleneimine,[3] polyvinylpyrrolidone and copolymers of vinylpyrrolidone with other monomers,[4] poly(crown ether),[5] polyvinylbenzoglyme,[6] polystyrene having a sugar group as a pendant,[7] the reaction products of poly(3-chloro-2-hydroxylpropylmethacrylate) with polyethylenepolyamines and those of chloromethylated polystyrene with triethylamine,[8] and powered nylon 66,[9] nylon 612,[10] and crosslinked poly(4-vinylpyridine).[11] The binding of other dyes by natural macromolecules and some of the above polymers has also been reported.[12]

However, all these are mainly studies on interactions between MO solutes and water-soluble macromolecules or polymers except nylon 66, 612, and crosslinked poly(4-vinylpyridine), and on the binding of MO solutes in water by insoluble polymers. Reference 8 alone deals with the study on the removal of MO by the insoluble complex formation of water-soluble polymers in aqueous solution.

Polyethyleneimine effectively binds solutes in water, and its binding affinity is large.[3] Polyethyleneimine immobilized on insoluble polystyrene should be capable of capturing MO solutes in water.

The present study was conducted to find means for removing MO solutes in industrial waste water from the standpoints of the reuse of waste water and preservation of the environment, using the reaction products of chloromethylated, divinylbenzene crosslinked polystyrene (CMPS) beads with polyethyleneimines (PEIs).

EXPERIMENTAL

Materials

CMPS was commercially obtained as beads (Polyscience Inc., 200–400 mesh), consisting of chloromethylstyrene 31.54 mol % (Cl content 2.63 meq/g, 9.32%), styrene 66.46 mol %, and divinylbenzene 2.00 mol %. The beads were used after being shaken in methyl alcohol for washing and to remove very fine powder beads by decantation. Tetraethylenepentamine (TEP) and pentaethylenehexamine (PEH) were commercially obtained (Woko Junyaku Co.). PEIs were supplied from Nippon Shokubai Kagaku Kogyo Co. These were used without further purification. Solvents such as dioxane and benzene were guaranteed reagents, and used after purification by drying and distillation.

Reactions of CMPS with PEI

Reactions were carried out as follows: CMPS beads 6.00 g (— CH_2Cl group 0.0158 mol) were placed in a three-necked flask followed by the addition of dimethylformamide 40 mL and PEI300 9.50 g. The mixture was stirred for 120 h at 100°C. When the reaction was complete, boiling water was added followed by stirring for about 10 min at 100°C. The reaction mixture was then filtered using a glass filter. The reaction product on the filter was washed with boiling water 200 mL, $1N$ HCl 20 mL, $1N$ NaOH 10 mL, and boiling water again until no alkali remained.

The product and water were placed in a flask and stirred for 24 h at 95–100°C and the former was collected by filtration. This procedure was repeated five times. The product was then washed for 96 h by a Soxhlet extractor: yield 8.38 g. The results of elemental analysis and molar number of PEI groups combined to the product [CMPS–PEI300 (4)] are shown at the 5th line in Table I.

CMPS–PEI600(3) was prepared by a method similar to the above. Other CMPS–PEI and –PEPA (polyethylenepolyamine) used were the same as those prepared in the previous study.[13] Table I lists the reaction conditions, yields, and the elemental analysis results for the other products. CMPS–MeOZO(3)–Hy was derived from the alkaline hydrolysis of CMPS–MeOZO(3), the reaction product of CMPS with 2-methyl-2-oxazoline. This preparation is described in the previous paper.[13]

Removal of MO

One-tenth or one-twentieth gram of the polymer prepared was placed in a 30 mL flask, followed by the addition of 20 mL of 50–500 ppm solutions of MO dissolved in a pH 7 buffer solution containing $0.2M$ potassium dihydro-

TABLE I
Reaction Condition for the Preparation of CMPS–PEPA and –PEI,
and Their Elemental Analysis Results[a]

Polymers	CMPS (g)	PEPA PEI (g)	Solvent	(mL)	React. temp (°C)	React. time (h)	Yield (g)
CMPS–TEP(4)	3.00	4.47	Dioxane	20	100	51	4.15
–PEH(5)	2.00	3.66	Dioxane	20	50	240	2.54
–PEH(6)	2.00	3.66	Benzene	20	40	240	2.61
–PEI250(1)	3.00	3.94	Benzene	20	80	144	4.00
–PEI300(1)	3.00	4.74	Benzene	20	80	104	4.19
–PEI300(4)	6.00	9.50	DMF[b]	40	100	120	8.38
–PEI600(1)	3.00	9.46	Benzene	25	80	120	4.69
–PEI600(3)	6.00	9.46	D,B[c]	40	95	192	9.08
–PEI1800(1)	2.00	28.4	Benzene	20	80	192	2.50
–MeOZO(3)–Hy	2.00	20.0[d]			100	25	3.55

Reacted — CH_2Cl groups (mol %)	Combined PEI groups (mmol/g CMPS)	H (%) f	H (%) c	C (%) f	C (%) c	N (%) f	N (%) c	Cl (%) f[a]
17.0	1.42	8.87	8.62	78.89	81.46	8.26	8.32	+
16.0	1.33	9.07	9.00	79.21	80.55	8.96	9.08	–
17.4	1.45	9.32	8.78	78.77	80.07	9.57	9.65	–
24.6	2.05	9.07	8.99	75.96	77.12	8.50	8.69	–
14.5	1.21	8.94	8.83	79.90	79.57	9.91	9.92	–
13.0	1.08	8.35	8.29	74.36	78.37	8.99	8.94	4.24
10.3	0.859	9.02	9.12	76.35	76.89	11.93	12.05	–
12.0	1.00	8.87	9.28	74.29	75.75	12.97	13.29	0.00
3.3	0.275	9.37	9.06	77.20	77.03	11.35	11.33	–
		8.23		73.35		7.44		–

[a] + means that the Beilstein test showed the presence of chlorine, and "–" that the test did not.
[b] N, N'-dimethylformamide.
[c] Dioxane 20 mL + benzene 20 mL.
[d] MeOZO 20 mL.

gen phosphate (100 part)–0.2 N sodium hydroxide (59 part)–water (241 part, volume ratio). A blank specimen not containing MO was similarly prepared. The flasks were stoppered and the systems were allowed to stand in a thermostat bath at 25°C until the concentration of free MO scarcely decreased with the lapse of time.

The residual concentration of MO was determined as follows: A part of the supernatant liquid in the flask was withdrawn, and the residual concentration of MO was calculated from the difference between the absorbance of the MO solution and the blank specimen at 465 nm using a Hitachi double beam spectrophotometer 220 A. The amount of MO removed (mg/g polymer) was calculated from the difference between initial and residual concentrations. The measured supernatant liquid was returned to the flask.

RESULTS AND DISCUSSION

Reactions of CMPS with PEI

Table I lists the results of elemental analysis and calculated element contents of the polymers prepared. The method for calculating the reacted chloromethyl groups, combined PEPA or PEI groups, and element contents are described in detail in the previous paper.[13]

For the preparation of CMPS–PEI300(4), N, N'-dimethylformamide (DMF) was used as the solvent. The amounts of reacted $-CH_2Cl$ groups were smaller than those in reactions carried out in dioxane or benzene solvent. Although dioxane and benzene did not dissolve much PEI, the ability to cause the CMPS beads to swell appeared greater in dioxane and benzene than in DMF.

Removal of MO

The removal of MO by CMPS–PEPA or –PEI was slow. When 0.050 g of CMPS–PEI300(4) was put in 20 mL of 400 ppm of MO dissolved in the pH 7 buffer solution, more than 20 days were required for removal. When 0.100 g of this polymer was used, more than 8 days were necessary. CMPS–PEI300(4) of 0.100 g was placed in each of 20 mL of initial concentrations 80–500 ppm and allowed to stand at 25°C. After 10–31 days, the amounts removed and residual concentrations of MO were determined.

The values were examined for their conformation to the Freundlich adsorption formula [eq. (1)][14] and to Klotz equation [eq. (2)][15,3] (Fig. 1):

$$\log Q = \frac{1}{n'} \log C' + \log K \tag{1}$$

$$\frac{1}{r} = \frac{1}{nkC} + \frac{1}{n} \tag{2}$$

In eq. (1), Q is the adsorption amount (mg/g adsorbent) at the equilibrium state, C' the equilibrium concentration (ppm), n' a constant from 0.2 to 1, and K the adsorption amount at $C' = 1$. In eq. (2), r is the binding amount (mol/10^5 g polymer) at the equilibrium state, k the intrinsic binding constant of polymer, C the concentration (mol/L) of free solutes at the equilibrium state, n the number of binding sites per polymer 10^5g, and nk the first binding constant.

Figure 1 illustrates plots of $\log Q$ vs. $\log C'$ measured on the 10th–31st days after the start of the removal [–PEI300(4) 0.100 g, [MO]$_0$ (initial concentration of MO) = 80, 100, 140, 200, 300, 400, 500 ppm—20 mL]. Rough linear relations were obtained in certain narrow ranges of $\log C'$ [for example, $\log C' = -0.43$–0.30 (the 12th day), -0.50–0.65 (the 16th day), and -0.33–0.64 (the 31st day)]. Figure 2 shows the plots of $\log Q$ vs. $\log C'$ measured from the 10th to 37th days after the start of removal [–PEI600(3) 0.100 g, [MO]$_0$ = 160, 200, 250, 300, 350, 400, 500 ppm—20 mL]. Good linear relations were found in certain ranges of $\log C'$ [= -0.11–0.42 (the 10th day), -0.51–0.17 (the 37th day)].
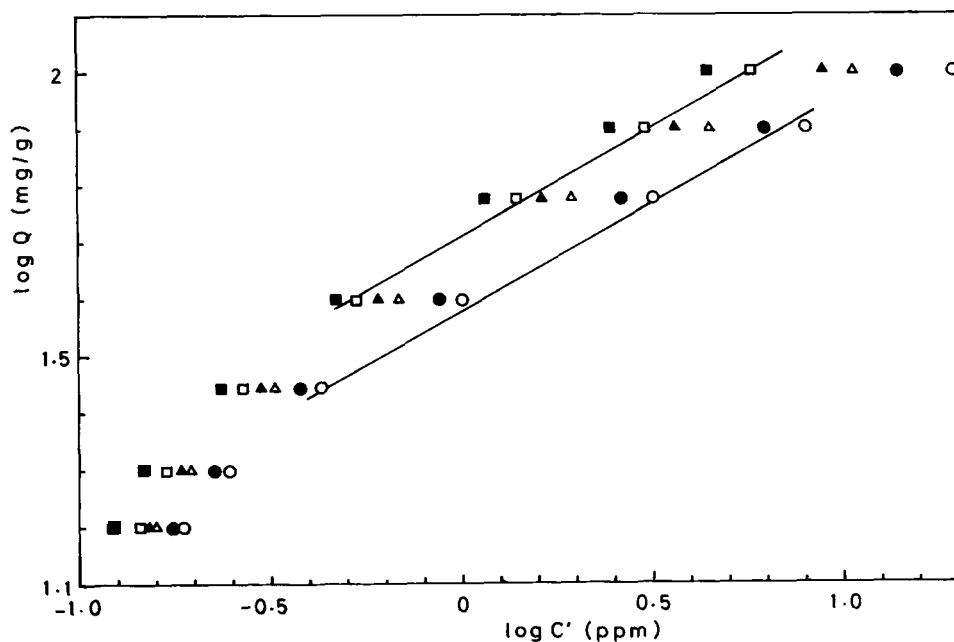
Fig. 1.   Plots of log Q vs. log C' in the removal of MO by CMPS–PEI300(4): CMPS–PEI300(4) = 0.100 g, $[MO]_0$ = 80, 100, 140, 200, 300, 400, 500 ppm, vol. = 20 mL. (○) 10th; (●) 12th; (△) 16th; (▲) 20th; (□) 24th; (■) 31st day after the start of the removal.
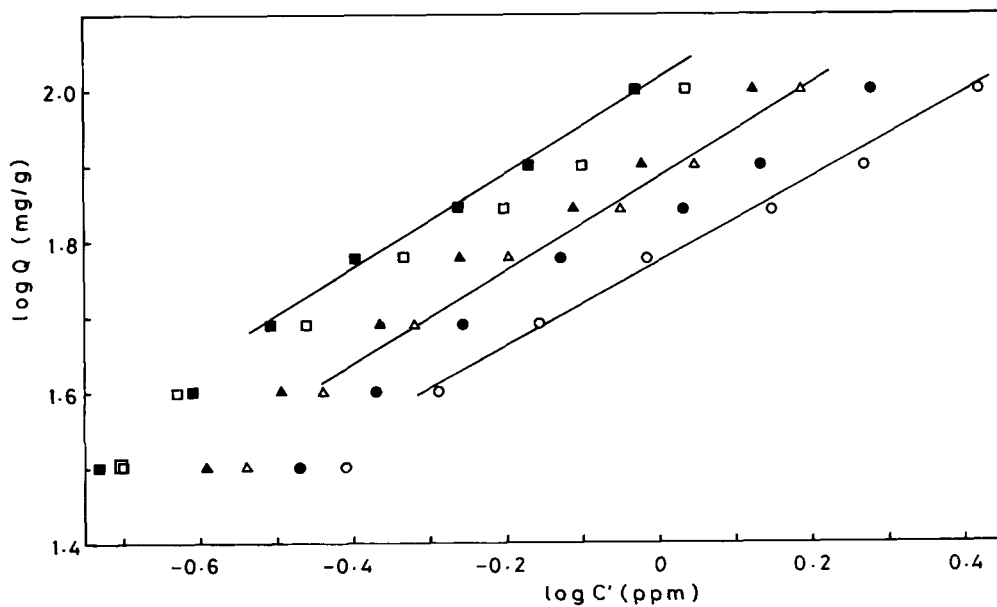

Fig. 2.   Plots of log Q vs. log C' in the removal of MO by CMPS–PEI600(3): CMPS–PEI600(3) = 0.100 g, $[MO]_0$ = 160, 200, 300, 400, 500 ppm, vol = 20 mL. (○) 10th; (●) 14th; (△) 18th; (▲) 22th; (□) 26th; (■) 37th day after the start of the removal.
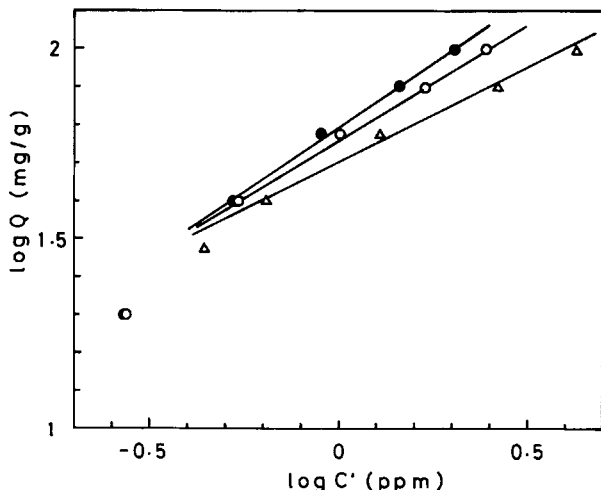
Fig. 3. Plots of $\log Q$ vs. $\log C'$ in the removal of MO solutes by CMPS–PEI600(1) and –PEI250(1) in water. CMPS–PEI600(1) = 0.100 g, $[MO]_0$ = 100, 200, 300, 400, 500 ppm, vol = 20 mL. (○) 8th; (●) 10th day after the beginning. CMPS–PEI250(1) = 0.100 g, $[MO]_0$ = 150, 200, 300, 400, 500 ppm, vol = 20 mL. (△) 8th day after the start.

In plots for CMPS–PEI600(1) (Fig. 3), a linear relation held approximately in the range of $\log C' = -0.26$—0.38, as measured on the 8th day after the start, and $\log C' = -0.28$–0.30, as measured on the 10th day [–PEI600(1) 0.100 g, $[MO]_0 = 100$, 200, 300, 400, 500 ppm—20 mL]. In plots for CMPS–PEI250(1) (Fig. 3), such a relation held in the range of $\log C' =$
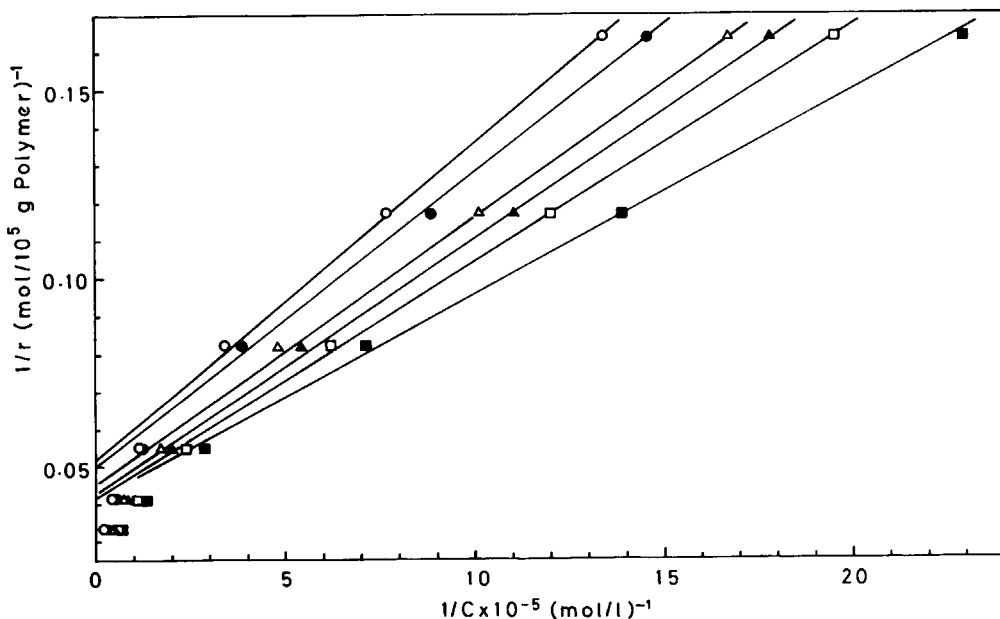

Fig. 4. Plots of $1/r$ vs. $1/C$ in the removal of MO by CMPS–PEI300(4): CMPS–PEI300(4) = 0.100 g, $[MO]_0$ = 80, 100, 140, 200, 300, 400, 500 ppm, vol = 20 mL. The symbol marks are identical to those described in Figure 1.
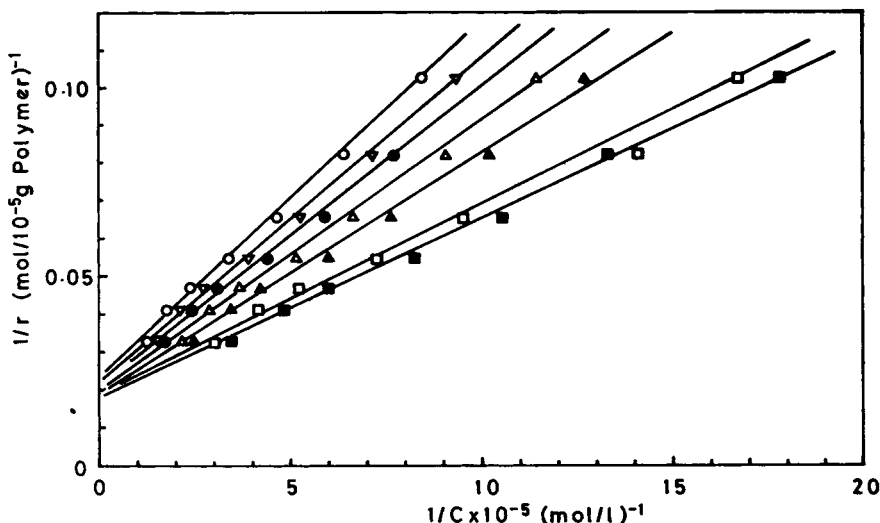
Fig. 5. Plots of $1/r$ vs. $1/C$ in the removal of MO by CMPS–PEI600(3): CMPS–PEI600(3) = 0.100 g, $[MO]_0$ = 160, 200, 300, 400, 500 ppm, vol = 20 mL. The symbol marks are identical to those described in Figure 2.

−0.19–0.62, as measured on the 8th day [−PEI250(1) 0.100 g, $[MO]_0$ = 150, 200, 300, 400, 500 ppm—20 mL].

In plots of $1/r$ vs. $1/C$ for CMPS–PEI300(4) (Fig. 4), linear relations were observed in the range from $1/C \times 10^{-5}$ = 3.4–13.3 (the 8th day), 2.9–23 (the 31st day) [removal by CMPS–PEI300(4) 0.100 g in 20 mL of the initial concentration of MO from 100 to 300 ppm, the 24th day], and in plots of $1/r$ vs. $1/C$ for CMPS–PEI600(3) (Fig. 5), linear relations were found in the range of $1/C \times 10^{-5}$ = 1.8–8.3 (the 10th day) and 3.5–17.5 (the 37th day). For CMPS–PEI600(1) and −PEI250(1) (Fig. 6), plots of $1/r$ vs. $1/C$ also showed linear relations. In plots for CMPS–PEI300(4) (Fig. 4), deviations from the lines were observed in the region below $1/C \times 10^{-5}$ = 3.5 and also in plots for removal by CMPS–1800(1) and −PEI300(1) (Fig. 6). (The causes for this are discussed later).

From Figures 1–6, it can be concluded that removal of MO solutes by CMPS–PEPA and −PEI conforms better to the Klotz equation than the Freundlich adsorption formula, especially in the region over $1/C \times 10^{-5}$ = 1.

In the removal of MO solutes in water by CMPS–PEI, no residual concentration attained a constant even after 37 days from the start of removal. However, in the present experiments, values measured on the 8th to the 10th day showed linear relations between $1/r$ and $1/C$. Therefore, constants of the Klotz equation were calculated by the least square method from $1/C$ and $1/r$ obtained after 10 to 31 or 37 days. $1/nk$ and $1/n$ for CMPS–PEI300(4) are as follows:

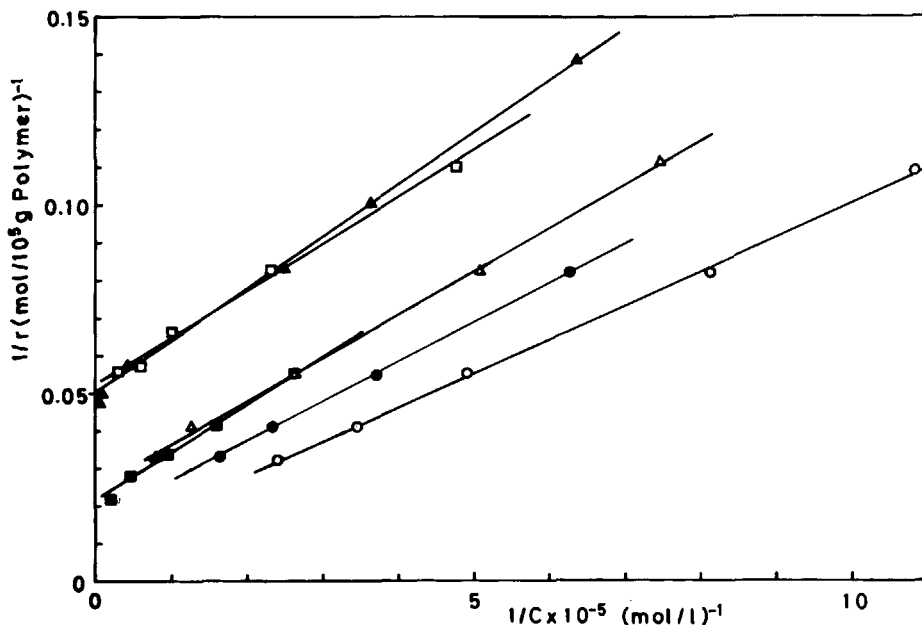| ith day	10	12	16	20	24	31
$1/nk \times 10^5$	0.00855	0.00767	0.00715	0.00682	0.00630	0.00538
$1/n$	0.051	0.050	0.045	0.043	0.041	0.042

Fig. 6.   Plots of $1/r$ vs. $1/C$ in the removal of MO by CMPS–PEI: (○) –MeOZO(3)–Hy; (●) –PEI600(1); (■) –PEI300(1); (△) –PEI250(1), (□) –TEP(4); (▲) –PEI1800(1). For measurement day and the amounts of the polymers, see Table II.

The values for CMPS–PEI600(3) are as follows:

ith day	10	12	14	18	22	28	37
$1/nk \times 10^5$	0.00928	0.00852	0.00778	0.00722	0.00652	0.00496	0.00480
$1/n$	0.023	0.022	0.022	0.019	0.017	0.019	0.017

Since the residual concentrations of MO decreased gradually even after 31 or 37 days from the start of the removal at 25°C, $1/nk$ and $1/n$ could not actually be determined. However, $1/nk$ on the 10th day were less than twice those on the 31st or 37th day. That is, the differences were not significant. $1/n$ on the 10th day was essentially the same as on the 31st or 37th day. From the residual concentration measured on about the 10th day at 25°C, when $1/r$ was plotted against $1/C$, linear relations were found. Thus, $1/nk$ and $1/n$ calculated from those on about the 10th day were comparable to each other.

Thus, $1/r$ and $1/C$ for removal by other polymers were calculated from the residual concentration of MO measured on about the 10th day. Linear relations were observed for all CMPS–PEPA and –PEI in the region over $1/C \times 10^{-5} = 1$. Table II lists nk and n calculated from $1/r$ and $1/C$. The nk and n of these polymers exceeded those of powered nylon 66 ($nk = 0.585 \times 10^5$, $n = 1$ at 25°C),[9] 612 ($nk = 2.74 \times 10^5$, $n = 2.86$ at 25°C),[10] and crosslinked poly(4-vinylpyridine) ($nk = 12.4$–34.7×10^5, $n = 3.33$ at 30°C),[11] and were less than that of the reaction product of chloromethylated polystyrene with triethylamine (PS–TEA) ($nk = 165 \times 10^5$, $n = 250$ at 30°C and 193×10^5, $n = 333$ at 20°C).[8]

TABLE II
Constants of Klotz Equation[a]

	$nk \times 10^{-5}$	n	$[MO]_0$ (ppm)	ith day[b]
CMPS–TEP(4)	81.0	18.4	100–400	10
–PEH(5)	69.0	14.8	100–300	10
–PEH(6)	64.9	26.3	160–400	10
–PEI250(1)	89.3	38.9	100–250	8
–PEI300(1)	84.0	44.8	100–500	10
–PEI300(4)	117	19.6	30–300	10
–PEI600(1)	96.2	64.9	100–500	10
–PEI600(3)	108	43.5	160–500	10
–PEI1800(1)[c]	64.	21.8	60–250	16
–MeOZO(3)–Hy	110	100.7	150–500	9

[a]The removal was carried out under the condition of the amount of polymer = 0.100 g except CMPS-PEI1800(1), MO solution = 20 mL, and at 25°C.
[b]The day which $1/r$ and $1/C'$ were determined after the start of the removal.
[c]0.050 g.

Although powered nylon 66 and 612 appeared to have far larger surface areas per unit mass due to fine particles, their nk and n were smaller than those of CMPS–PEIs. These and the greater nk for binding by PS–TEA are discussed later.

That nk is large (that is, slope of line is small) means small change in the amount removed with change in concentration. Large n means that the amount removed is large. These are desirable factors for removal. A large removal rate is also an important factor. Thus, CMPS–MeOZO(3)–Hy, –PEI600(1), and –PEI600(3) should be good removal agents in the polymers studied here.

Amounts Removed by the Polymers

One-twentieth gram of each polymer was placed in 20 mL of 500 ppm of MO dissolved in the pH 7 buffer solution, followed by standing at 25°C. The amounts removed (mg/g) were determined on the 14th day after the start. The amounts removed (mmol) per mmol of PEPA or PEI group were calculated as follows: Amounts removed (mmol/g polymer) were divided by the molar numbers of combined PEPA or PEI groups in 1 g of each polymer. These quotients corresponded to the molar number of MO removed by 1 mmol of PEPA or PEI group (Table III). Plots of the amount of MO removed (mmol/mmol PEPA or PEI group) vs. that of the PEPA or PEI group (mmol/g polymer) (Fig. 7) failed to show a correlation, as was also noted in the plots for the removal of polyethylene glycol mono-p-nonyl-phenyl ether (NP) using the same polymers.[13]

Generally, however, the amount removed (mmol/mmol group) increased with decrease in the molar number of the combined group. This was also observed in the removal of NP by CMPS–PEG [poly(ethylene glycol)][16] and the polymers[13] used here, and thus the amount of MO solutes removed by a polymer is generally larger when the polymer has a PEI group with relatively larger molecular weight.

TABLE III
The Amounts of MO Removed from the Solutions of Initial Concentration
of 500 ppm[a]

Polymer[b]	N content (%)	Combined groups (mmol/g polymer)	Removed amount	
			(mg/g polymer)	(mmol/mmol group)
CMPS–TEP(1)	9.99	1.45	196	0.413
–TEP(4)	8.26	1.19	66	0.169
–PEH(2)	10.16	1.20	199	0.507
–PEH(5)	8.96	1.09	99	0.277
–PEH(7)	10.05	1.18	95	0.246
–PEH(8)	10.37	1.25	193	0.472
–PEI250(1)	8.50	1.39	187	0.411
–PEI250(2)	6.73	1.11	34	0.093
–PEI300(1)	9.91	0.936	179	0.584
–PEI300(2)	9.16	0.882	172	0.596
–PEI300(3)	11.29	1.07	101	0.288
–PEI300(4)	8.99	0.843	132	0.478
–PEI600(1)	11.93	0.592	197	1.02
–PEI600(3)	12.97	0.640	189	0.902
–PEI1000(1)	9.12	0.298	88	0.902
–PEI1200(1)	9.22	0.248	57	0.702
–PEI1200(2)	10.24	0.261	79	0.925
–PEI1800(1)	11.35	0.191	64	1.02

[a] The amounts were determined on 14th day after the start of the removal at 25°C. Polymer = 0.050 g, MO solution 20 mL.

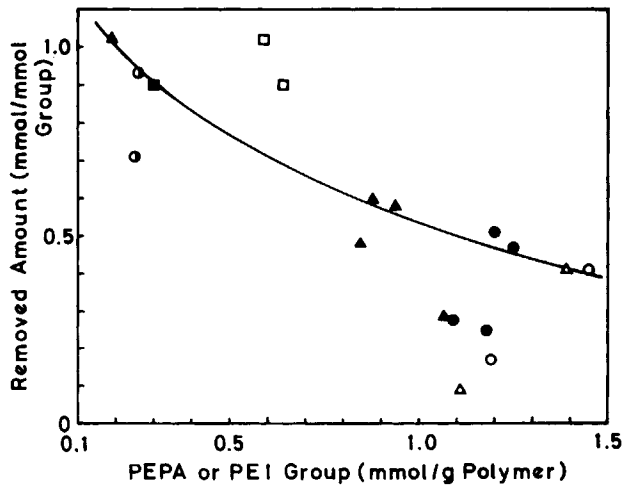[b] The preparation conditions of polymers except for those in Table I have been described in Ref. 13.

Fig. 7. Plots of the amounts of MO removed vs. molar numbers of combined PEPA or PEI groups in 1 g of the polymers: (O) CMPS–TEP: (●) –PEH; (△) –PEI250; (▲) –PEI300; (□) –PEI600; (■) –PEI1000; (◐) –PEI1200; (▲) –PEI1800.

Removal of MO by the Polymers

Generally, some polymers comprised of hydrophobic and hydrophilic parts can bind some organic compounds consisting of hydrophobic and hydrophilic parts. This is due to interactions between the hydrophobic parts of the polymers and those of the organic compounds.[7,17,18]

The polymers used here captured NP, a nonionic surfactant, by hydrophobic interaction.[13] PEI binds MO by hydrophobic interaction.[3] Since PEI molecules are protonated to a considerable degree in an aqueous solution of pH 7, the protonated parts of PEI bind MO solutes having negative charges.[19] That is, PEI binds by both hydrophobic and electrostatic interactions. Although the present polymers are insoluble in water, the PEPA or PEI groups in these polymers may possibly be protonated in water of pH 7. Thus, they may be able to bind MO anions in water by electrostatic interaction and remove MO solutes in water by both types of interactions.

As described before, nk and n of powered nylon 66, 612, and crosslinked poly(4-vinylpyridine) were less than those of CMPS–PEI. This may be attributable to the fact that the hydrophobicity of the PS part of CMPS–PEI is greater than that of methylene chain parts of nylon and vinylpyridine part of poly(4-vinylpyridine). Also, the basicity of amino groups of PEI is greater than that of acid amide groups of nylon. Although the basicity of the pyridine part of poly(4-vinylpyridine) is greater than that of PEI, the hydrophobicity of this polymer is much less than that of PS part of CMPS–PEI, and thus nk and n appear smaller than those of CMPS–PEI. The larger nk and n of PS–TEA is ascribable to the following: Since this polymer is water-soluble, binding occurs between the molecules of the polymer and MO in the solution.

It can be seen from Figure 8 that the amounts removed do not always depend on the nitrogen content of the polymers. This apparently indicates that MO solutes are captured not only by electrostatic, but by hydrophobic interactions as well. The amount removed also appears to be influenced by the preparation conditions, but this has yet to be confirmed.
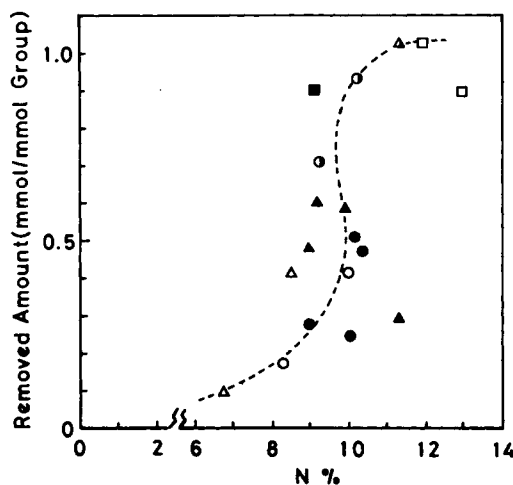
Fig. 8. Plots of the amounts of MO removed vs. nitrogen content: The symbol marks are identical to those described in Figure 7.
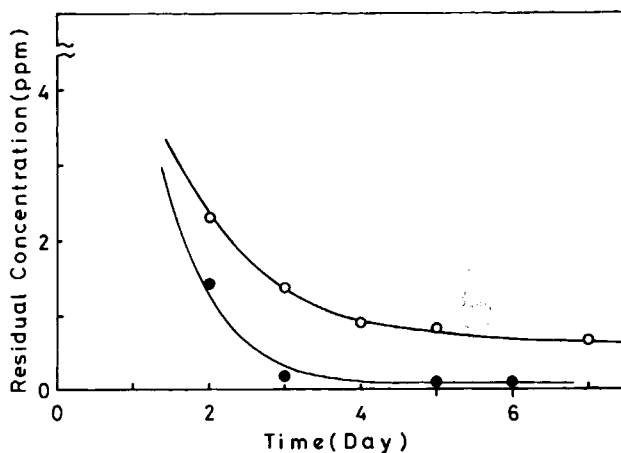
Fig. 9. The decrease in the concentration by the removal of MO with CMPS–PEI600 in the presence and absence of salts with lapse of time. CMPS–PEI600 = 0.100 g, $[MO]_0$ = 200 ppm, vol = 20 mL. (○) Removal in distilled water; (●) removal in pH 7 buffer solution (0.2M KH_2PO_4 100 parts + 0.2N NaOH 59 parts + H_2O 241 parts, volume ratio).

In Figures 4 [CMPS–PEI300(4)] and 6 [CMPS-PEI300(1), –PEI1800], the plots of $1/r$ vs. $1/C$ deviate from the lines in the region below $1/C = 1$. (In Fig. 5, the plots of $1/r$ vs. $1/C$ are presumed to deviate from the line in the region over $[MO]_0 = 600$ ppm, i.e., $1/C < 1$–4.) This has been also observed in the binding of butyl and propyl orange by powered nylon 66.[9] A possible explanation has been proposed by Lim et al.[9] as follows: Binding increases sharply with concentration of the free dye. This clearly indicates that hydrophobic and electrostatic interactions work together in this binding, reflecting the stacking of dye molecules bound to the polymer.

The effect of salt on removal was examined by placing CMPS–PEI600(1) 0.100 g in 20 mL of 200 ppm concentration of MO dissolved in the pH 7 buffer solution and in distilled water without the salt (Fig. 9). In the former, more than 5 days were required to attain an equilibrium state, while only 3–4 days in the latter case. The residual concentrations were about 0.65 ppm (the amount removed = 39.97 mg/g) and about 0.15 ppm (the amount removed = 39.87 mg/g), respectively. The differences in these values may be considered small, judging from the initial concentration. The effect of the salt present in MO solution on removal is small.

SUMMARY

The removal of MO dissolved in pH 7 buffer solution (K_2HPO_4–NaOH) by CMPS–PEPA and PEI was studied and found to conform to the Klotz equation, whose constants were determined. The first binding constant (nk) and n for MeOZO(3)–Hy, the maximum for the polymers studied here, were smaller than those of water-soluble polystyrene–triethylamine. The binding affinity of PEPA or PEI per mmol group was greater in the group with a larger molecular weight. Removal occurs by hydrophobic interactions between hydrophobic groups of MO and the polymers and electrostatic interactions between the anion groups of MO and amino or imino nitrogens of the

polymers. CMPS–PEI600 and –MeOZO–Hy removed MO solutes in water more efficiently than crosslinked poly(4-vinylpyridine), nylon 66, or 612.

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