

Preparation of Mercaptoethylated Graft Fibers for Adsorption of Heavy Metal Ions

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Synopsis

Various kinds of mercaptoethylated graft fibers were prepared and the abilities to adsorb the heavy metal ions were studied. 2-Hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and vinyl acetate were graft-copolymerized by irradiation onto five kinds of synthetic fibers and two kinds of foam polymers. Preirradiation at low temperature was far more effective for grafting than simultaneous irradiation. The mercaptoethylation was carried out in the solution or in the vapor of ethylene sulfide onto the graft fibers treated with alkali. The mercaptoethylated graft fibers showed particular affinity for Hg and Ag ions. A few of the adsorption phenomena were pursued by flow experiment of the ionic solution through a column. The preliminary reduction of the mercaptoethylated graft fibers enhanced the capacity of adsorbing to three times that of the unreduced fibers. Effects of flow rate, pH, temperature, and concentration of Hg ion on the integrated adsorbed amount were also investigated.

INTRODUCTION

There are ever increasing occasions when large quantities of water must be purified within a reasonable time, though the extent of pollution may be light. To eliminate the dissolved pollutant rapidly from such water, stuffed fibrous materials made of functional polymer are considered to be fit especially for the purpose because the characteristics inherent in the fiber form are expected to favor rapid filtration with efficient adsorption and high reactivity.

We have endowed the capability to adsorb heavy metal ions selectively to ordinary synthetic fibers by introducing SH groups into the fibers. At first, monomers possessing hydroxyl group, such as 2-hydroxyethyl acrylate or methacrylate, were graft-copolymerized on several commercial synthetic fibers by radiation-chemical means. Besides, vinyl acetate was chosen as monomer because it was possible to convert the grafted polymer to poly(vinyl alcohol) branch by hydrolysis. Then the mercaptoethylation of hydroxyl group was performed by treating the grafted fibers with ethylene sulfide. The ability to adsorb the heavy metal ions by forming mercaptide or chelate was examined when the solution was supplied continuously through the column.

We also believe that syntheses of other functional fibers are possible without difficulty by applying a simple reaction on the synthetic fibers with the grafted polymers possessing hydroxyl group.

EXPERIMENTAL

Materials

The synthetic fibers employed in the experiment were Hizex (Mitsui Kagaku Co., 400 den. high-density) as polyethylene, nylon-6 (Toyo Rayon Co., 10 den.) as polyamide, Orlon (2.5 den., semidull) and Cashimilon (Asahi Kasei Co., 3 den.) as acrylic fibers, and Kanekalon (Kanekalon Co., 3.5 den., copolymer of acrylonitrile and vinyl chloride) as modacrylic fibers. They were washed in soap water and then subjected to Soxhlet extraction with ethanol for 8 hr, dried in air, and stored over silica gel.

A few of the open-cell synthetic foams, Moltopren SC ($d = 0.03$) and Color-Foam ECS ($d = 0.02$) (MTP Kasei Co., ester-type and ether-type, respectively) as polyurethane foams, and Eversoft AA ($d = 0.09$) (Bridgestone Co., made of natural rubber latex and SBR latex) were also adopted for the same purpose and treated as above.

2-Hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) were distilled under reduced pressure, and vinyl acetate (VAC) was distilled under ordinary pressure before use. Ethylene sulfide (bp 54–55°C) was synthesized by the reaction of ethylene carbonate with potassium thiocyanate.¹

Preparation of Graft Polymer

Several ways of radiation grafting were examined to obtain the most favorable result. The experimental procedure of grafting by the simultaneous irradiation technique using liquid-phase monomer and vapor-phase monomer was previously described in detail.^{2,3} The technique of low-temperature preirradiation grafting was also described in a previous report.³

After the reaction, the graft fibers and foams were subjected to Soxhlet extraction with ethanol or methanol, followed by drying under vacuum at room temperature. The extent of grafting was expressed as the weight increase ($P - P_0$) divided by the original weight P_0 of the backbone polymer.

The fibers on which VAC was graft copolymerized were hydrolyzed to produce hydroxyl groups on the grafted branch, by dipping them into 1.5% methanol solution of sodium hydroxide;⁴ after 2 or 3 min, the fibers were rinsed with methanol and dried *in vacuo*.

To investigate whether true grafting occurred or not, a selective elution method was adopted to separate the components of the graft fibers. The solvents used to extract the unreacted component of the fibers were boiling xylene for Hizex, formic acid for nylon, and dimethylformamide (DMF) for the other fibers.

Mercaptoethylation of Graft Fibers

The graft fibers possessing hydroxyl groups, 0.5 to 10 g, were soaked in 0.5% aqueous solution of sodium hydroxide or 5% methanol solution of sodium methylate for 30 min. Then, the fibers were pressed between filter paper to almost dryness and heated in boiling benzene containing 1% to 2% ethylene sulfide from 2 to 20 hr with bubbling of dry nitrogen. After the reaction, the mercaptoethylated graft fibers were washed with benzene and water.

The mercaptoethylation of graft fibers was also carried out with gaseous ethylene sulfide; the fibers treated with sodium methylate as above were exposed to the vapor of ethylene sulfide in sealed and degassed ampoules at 25°C for a given time, while the bottom of the ampoule containing the liquid ethylene sulfide was dipped in the thermoregulated water kept at 20°C. The extent of reaction with ethylene sulfide was checked by the weight increase of fibers after the reaction as well as by the sulfur analysis with a Yanagimoto microdetermining apparatus for halogens and sulfur Model MX-3. The mercaptoethylated graft fibers were examined by elution using the same solvents as were employed for the graft fibers.

Adsorption of Heavy Metal Ions

A part of the reactive SH groups in mercaptoethylated graft fibers thus prepared is suspected to be oxidized during the synthetic procedure.⁵ Therefore, the reducing reaction was applied to fibers before the adsorption experiment unless otherwise mentioned. The mercaptoethylated graft fibers were immersed in the mixture of zinc powder with glacial acetic acid and boiled for 1 hr. After that, the fibers were thoroughly rinsed with water and kept in it until used. When nylon was the backbone of the mercaptoethylated graft fibers, the glacial acetic acid was replaced by a mixture of acetic acid and water (1:4 by volume) to avoid the dissolution of nylon.

The adsorption of heavy metal ions was performed in two ways. In the batch experiment, 20 ml 0.005 mole/l. metallic salt solution containing 817mg/l. KH_2PO_4 and 94.7 mg/l. Na_2HPO_4 as buffer was added to 0.25 g of the mercaptoethylated graft fibers. Sometimes, a drop of dilute acid was required to bring the salt solution to the acidic region where no precipitation of hydroxide was observed. After 1 hr of stirring at room temperature, the fibers were removed from the solution, and the remaining ions were determined by the proper way referred to in Table VI.

Apart from the batch method described above, the change in the adsorbing capacity of the mercaptoethylated graft fibers was pursued when the HgCl_2 solution flowed through the column of the fibers. The fibers were loosely stuffed in a glass tube 0.8 cm in diameter equipped with an outer jacket for circulating thermoregulating water. One gram of the fibers extended to about 15 cm in the glass tube. The HgCl_2 solution, the pH of which was adjusted with 2% by volume of a 1/15 mole/l. phosphate buffer, was run down at a given rate and gathered in a fraction collector. The concentration of the remaining Hg^{2+} ion in each aliquot of 25 ml was measured by the spectrophotometric method with EDTA and KSCN.⁶

RESULTS AND DISCUSSION

Grafting by γ Ray Irradiation

In liquid-phase grafting by a simultaneous irradiation technique, the grafting onto fibers was nearly null, because the monomer was almost completely consumed by the formation of homopolymer. On the other hand, in vapor-phase grafting, as the homopolymerization could be suppressed or retarded by adding

TABLE I
Vapor-Phase Grafting of Monomers Onto
Various Fibers and Foams by Simultaneous Irradiation Technique^a

Fiber or foam	$100(P - P_0)/P_0$ for HEA	$100(P - P_0)/P_0$ for HEMA	$100(P - P_0)/P_0$ for VAC
Hizex (polyethylene) fibers	2.1	2.8	0.26
Nylon fibers	6.6	0.55	7.6
Orlon fibers	2.7	0.52	0.1
Cashimilon (acrylic) fibers	0.53	1.6	0.0
Kanekalon (modacrylic) fibers	0.24	0.1	0.0
Moltopren (ester-type polyurethane foam)	1.9	3.1 ^b	7.1
Eversoft (rubber foam)	4.3	0.0	0.24

^a Composition of liquid monomer phase for fibers: monomer, 5 ml; ethanol, 2 ml; DPPH, 5 mg; and water, 2 ml (for nylon and Orlon only); for foams: monomer, 5 ml; DPPH, 5 mg. Ethanol and water were used to swell the fibers. Irradiation, 24 hr at dose rate of 2×10^4 R/hr ⁶⁰Co γ rays at 25°C.

^b Irradiation, 2.5 hr without DPPH in liquid monomer phase.

TABLE II
Liquid-Phase Grafting of Monomers Onto
Various Fibers and Foams by Low-Temperature Preirradiation Technique^a

Fiber or foam	$100(P - P_0)/P_0$ for HEA ^b	$100(P - P_0)/P_0$ for HEMA ^c	$100(P - P_0)/P_0$ for VAC ^d
Hizex fibers	3.9	159	10.2
Nylon fibers	30.1	23.7 ^b	2.2
Orlon fibers	741	433	3.4
Cashimilon fibers	20.3	116 ^b	1.9
Kanekalon fibers	290	440	2.5
Color-Foam (ether-type polyurethane foam)	114	641	1.5
Eversoft	571	425	3.1

^a Preirradiation, 24 hr at a dose rate of 2×10^5 R/hr ⁶⁰Co γ rays at -78°C.

^b Grafting reaction, 4.0 hr at 40°C.

^c Grafting reaction, 48 hr at 40°C.

^d Grafting reaction, 3.0 hr at 45°C.

an inhibitor such as diphenylpicrylhydrazyl (DPPH) or benzoquinone to the liquid monomer, longer irradiation was possible compared with the liquid-phase grafting and better yield of grafting was obtained, as shown in Table I.

In the grafting by preirradiation technique, a very high extent of grafting was obtained without difficulty. Table II shows the results of grafting on fibers and foams preirradiated at -78°C. In these results, almost no homopolymer formation was observed, and it was apparent that more than 90% of the converted monomer was consumed by the grafting in the cases of HEA and HEMA. High efficiency of grafting when low-temperature preirradiation was applied was already mentioned in the previous paper.⁷ It may be inadequate to compare the ease with which the grafting proceeded on each kind of fibers, for the thicknesses of the original fibers differed widely from each other. The extent of grafting of VAC was rather low compared with that of other monomers.

TABLE III
Composition of Graft Fibers Prepared by Low-Temperature Preirradiation Technique

Graft fibers	Overall extent of grafting 100- (P - P ₀)/ P ₀	Solvent for Elution	Insoluble fraction, %	Un-reacted polymer fraction, %	Compo- sition of insoluble part (backbone polymer: branch polymer) ^a	Re- marks
Cashimilon-HEMA	66.0	DMF	41.2	58.8	1:35	c
Nylon-HEMA	23.7	formic acid	21.3	78.7	1:9	d
Kanekalon-HEA	95.1	DMF	44.6	55.4	— ^b	
Hizex-HEA	3.9	boiling xylene	6.3	93.7	1:1.5	

^a Calculated from overall extent of grafting and the amount of insoluble fraction.

^b Part of the grafted polymer seemed to be solubilized.

^c Insoluble fraction contained a minute amount of inorganic fillers.

^d Infrared absorption spectra of the unreacted polymer fraction showed the presence of very small amount of HEMA component.

Foam polymers lost their inherent flexibility by the grafting reaction and seemed to be inappropriate for the initial purpose as a selective adsorbent adaptable to any form and place.

Table III shows the result of the selective elution on several graft fibers. By treatment with the appropriate solvent, the unreacted polymer and the minute amount of inorganic filler, in some cases, were removed, whereas the remaining residue kept the form of fibers. The last column of Table III shows the composition of the remaining fibers, presumably the graft polymer. It is remarkable that the fiber-like residue consisted mainly of the grafted branch polymer.

As for the extraction of the occluded homopolymer, a sufficient result would be hardly obtainable in the case of HEA and HEMA grafting, because no solvent was reported on poly(HEA) and poly(HEMA)⁸ (some lower aliphatic alcohols were cited as solvents for poly(HEMA) in another paper⁹). By extended acetone and ethanol extraction of polyurethane foam with poly(VAC) grafted on, shown in Table I, about 2% of the attached polymer proved to be occluded. The amount of removed homopolymer was low in graft fibers prepared by low-temperature preirradiation technique.

Mercaptoethylation

The results of mercaptoethylation with ethylene sulfide are shown in Table IV on several kinds of graft fibers. Among the few reports concerning mercaptoethylation with this compound, Chaudhuri and Hermans⁵ reported the preparation of mercapto cellulose derivatives by the reaction of dry cellulose and ethylene sulfide in a stream of dry nitrogen. But, in our experiment, no reaction of ethylene sulfide whatsoever occurred on graft fibers or even on cotton under their condition, as is seen in the first row of Table IV, unless the hydroxyl group was activated by alkali.¹⁰ The reaction of pretreated graft fibers, inclusive of those on which the hydrolyzed poly(VAC) was grafted, proceeded easily with dissolved ethylene sulfide as well as with the gaseous one. The extent of reaction

TABLE IV
Mercaptoethylation of Graft Fibers with Ethylene Sulfide (ES)

Graft fibers	Overall extent of grafting $100(P - P_0)/P_0$	Pretreatment	Concn. of ES in benzene, %	Reaction time, ^a hr	Wt. increase by mercaptoethylation $100(P' - P)/P$	S content of ethylated graft fibers, ^b %	Grafted monomer: reacted ES ^c
Cashimilon-HEMA	66.0	—	2.0	20	0.0	0.00 (0.00)	—
Cashimilon-HEMA	66.0	NaOCH ₃	1.0	20	15.9	5.35 (7.31)	1:0.87
Nylon-HEMA	23.7	NaOCH ₃	1.0	20	23.9	7.84 (10.29)	1:2.7
Kanekalon-HEMA	21.8	NaOH	1.0	4.0	11.0	— ^d (5.29)	1:1.3
Kanekalon-HEA	95.1	NaOCH ₃	vapor (25°C)	4.0	15.7	— ^d (7.24)	1:0.62
Hizex-VAC (hydrolyzed)	10.2	NaOCH ₃	2.0	20	4.4	0.82 (2.39)	1:0.68

^a Reaction temperature, 75° to 80°C.

^b Values in parentheses are %S calculated from the weight increase by mercaptoethylation.

^c Calculated as the ratio of numbers of monomeric units from the weight increase.

^d S content cannot be determined separately by the adopted analytical method when S and Cl coexist in the sample.

TABLE V
Elution of Mercaptoethylated Graft Fibers

Mercaptoethylated graft fibers	Overall extent of grafting $100(P - P_0)/P_0$	Wt. increase by mercapto-ethylation $100(P' - P)/P$	Solvent for elution	Insoluble fraction, %	S content of insoluble fraction, %	S content of soluble fraction, %	Remarks
Cashimilon-HEMA-ES	66.0	15.9	DMF	29.5	6.46	0.67	a
Nylon-HEMA-ES	23.7	23.9	formic acid	17.7	25.4	0.56	b
Kanekalon-HEA-ES	95.1	15.7	DMF	57.7	— ^c	— ^c	b
Hizex-VAC-ES	10.2	4.4	Boiling xylene	7.3	1.24	0.77	b

^a Insoluble fraction contained a minute amount of inorganic fillers.

^b Soluble fractions showed the same infrared absorption spectra with those of the original fibers.

^c S content cannot be determined separately by the adopted analytical method when S and Cl coexist in the sample.

TABLE VI
Adsorption of Heavy Metal Ions by Mercaptoethylated Graft Fibers^a

Metal ion(salt)	pH	Exchange capacity, mg ion/g fiber	Method of determination
Hg ²⁺ (HgCl ₂)	5.6	37.5	spectrophotometry ⁶
Ag ⁺ (AgNO ₃)	3.7	29.8	titration with KSCN
Cu ²⁺ (CuSO ₄)	4.3	1.48	titration with Na ₂ S ₂ O ₃
Zn ²⁺ (ZnCl ₂)	4.1	1.02	titration with EDTA
Cd ²⁺ (CdCl ₂)	4.8	0	titration with EDTA
Cr ³⁺ (CrCl ₃)	5.8	0	titration with MnSO ₄ and EDTA

^a Mercaptoethylated graft Cashimilon: 100($P - P_0$)/ P_0 of HEMA, 66.0; and 100($P - P$)/ P of ES, 15.9; ca. 200 mg fibers stirred in 20 ml 0.005 mole/l. solution. Reaction time, 1.0 hr at 20°C.

of ethylene sulfide was apt to be less than the equivalent of the grafted monomeric unit in many cases, although it increased with increasing reaction time. However, as the reaction product looked inhomogeneous and the agreement between observed and calculated contents of sulfur was poor, all the hydroxyl groups could not necessarily react with ethylene sulfide, or else a considerable portion of the reacted ethylene sulfide was supposed to form homopolymer.

In Table V, which shows the results of elution and the sulfur content of the fraction, it is seen that fractionation in regard to the poly(ethylene sulfide) or grafted poly(ethylene sulfide) was possible in every instance. But owing to the lack of a good solvent for poly(ethylene sulfide), which does not dissolve in any solvent except sulfuric acid,¹¹ the amount of homopolymeric poly(ethylene sulfide) occluded into the mercaptoethylated graft fibers could not be ascertained. When the mercaptoethylated graft fibers were soaked in the solvents, most of the insoluble fraction kept the form of fibers, and the powder-like residue

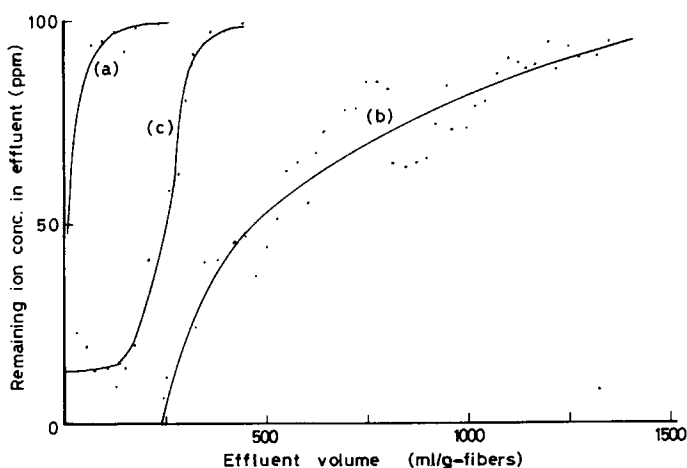


Fig. 1. Changes of ion concentrations in effluents as function of flowed volume of solutions: mercaptoethylated graft Cashimilon, same as used in Table VI, 1 g; (a) reduced fibers for 100 ppm Cd²⁺ solution; (b) reduced fibers for 100 ppm Hg²⁺ solution; (c) unreduced fibers for 100 ppm Hg²⁺ solution. pH of solution, 5.5; flow rate, 3 ml/min.

was very small. Therefore, it is concluded that ethylene sulfide reacted fairly effectively with the hydroxyl group of the grafted branch. We cannot give an appropriate interpretation at present of the fact that the amount of insoluble fraction was smaller than expected in many cases. Perhaps, a part of the graft polymer was decomposed or solubilized to some extent during the reaction.

Adsorption of Heavy Metal Ions by Mercaptoethylated Graft Fibers

It was shown that the mercaptoethylated graft fibers adsorbed particular heavy metal ions, presumably forming a mercaptide or chelate with them. The behavior was revealed to be very selective; the fibers strongly adsorbed Hg^{2+} and Ag^+ , but affinities of the fibers to other ions were poor. Table VI shows the results of the batch experiment, where a bundle of mercaptoethylated graft fibers was reduced by zinc in glacial acetic acid before the adsorption experiment. As is seen in Figure 1, the reduction procedure enhanced the capacity of the fibers to adsorb the Hg^{2+} ion. Oxidation of the SH group to disulfide linkage seems to be more or less unavoidable during the mercaptoethylation. It would be worthwhile mentioning that no adsorption whatsoever was observed when the original or the graft Cashimilon was used without mercaptoethylation.

Because of the loose stuffing of fine fibers, the rapid elimination of the heavy metal ions from the solution was expected when the solution was forced to flow through the column. Figure 1 shows the result of the continuous flowing experiment of Hg^{2+} and Cd^{2+} ion solutions. While Cd^{2+} was hardly removed, Hg^{2+} was completely eliminated from solution up to 250 ml/g, and then the fibers showed incomplete elimination of the ion in a long range of flowing period. Such a phenomenon, being affected by the rate of flow, was more or less generally observed throughout the continuous flow experiments through the column. This may be so because some of the reaction sites existed in such inner parts of the fibers which take a long time for ions to reach.

The total amount of the adsorbed Hg^{2+} calculated by the integration was 60.7

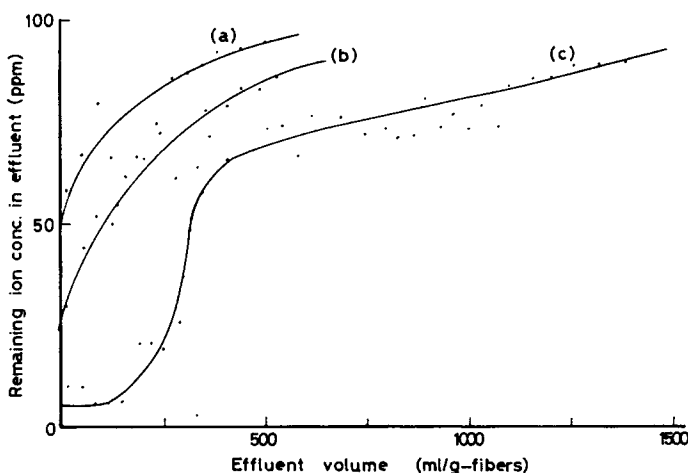


Fig. 2. Effect of flow rate on Hg^{2+} concentration in the effluent: mercaptoethylated graft nylon, 0.65 g; $100(P - P_0)/P_0$ of HEMA, 23.7, and $100(P' - P)/P$ of ES, 23.9; pH of solution, 7.0; flow rate, (a) 30 ml/min, (b) 15 ml/min, (c) 5 ml/min; concentration of Hg^{2+} , 100 ppm.

TABLE VII
Effect of Various Reaction Conditions on Integrated Adsorbed Amount of Hg^{2+} ^a

Mercaptoethylated graft fibers	pH	Temperature, °C	Concentration of Hg^{2+} , ppm	Integrated adsorbed amount of Hg^{2+} , mg/g
Cashimilon-HEMA-ES ^b	5.7	18	100	56.1
	6.6	18	100	51.6
	7.5	18	100	22.1
	8.0	18	100	12.1
Nylon-HEMA-ES ^c	7.0	18	100	24.9
	7.0	45	100	22.2
	7.0	18	37	9.5
	7.0	18	100	24.9
	7.0	18	150	43.2

^a Rate of flow, 2 to 3 ml/min.

^b Mercaptoethylated graft Cashimilon: $100(P - P_0)/P_0$ of HEMA, 115.8; and $100(P - P)/P$ of ES, 10.9.

^c Same fibers as used in Fig. 2.

mg/g fiber in the case (b) in Figure 1. If all the grafted ethylene sulfide was active for Hg^{2+} , the largest possible amount adsorbed should be 228 mg/g of this fiber; that is, only one fourth was effective for Hg^{2+} . It seems that a considerable amount of ethylene sulfide was consumed to form a polymeric chain without producing SH groups at the end. Iodometry¹² revealed that about one-fifth of the reacted ethylene sulfide unit seemed to be active as SH group, although the strong adsorption of iodine on the fibers made the results obscure in many cases. Comparing (b) with (c) in Figure 1, it is seen that the reducing procedure made the total adsorption three times larger than ever.

Adsorbed Hg^{2+} ion was shown to be easily recovered by soaking the fibers in acidic aqueous solution. When the fibers which had adsorbed Hg^{2+} ion by run (b) were dipped in 100 ml aqueous solution containing 1% hydrochloric acid for 1 hr, 16 mg at the first time and 4.7 mg at the second time of Hg^{2+} were desorbed.

Figure 2 shows the effect of flow rate of Hg^{2+} solution on the elimination of Hg^{2+} with mercaptoethylated graft nylon. With increasing rate of flow, the escaping ions increased and a range of complete elimination was not observed.

Table VII shows the effect of several factors, such as pH of the solution, adsorption temperature, and concentration of Hg^{2+} ion. The adsorption was more effective at lower pH in the range from 5 to 8. Temperature of operation did not seem to have a serious effect on adsorption. It was rather an unexpected fact that the concentration of Hg^{2+} affected the integrated adsorbed amount, perhaps because an equilibrated state was not attained in the adsorption of Hg^{2+} ion.

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