

PREPARATION AND PROPERTIES OF MACRO-POROUS CHELATE RESINS OF CROSSLINKED POLYSTYRENE BEARING DITHIOCARBAMATE GROUPS

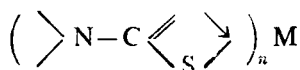
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ABSTRACT

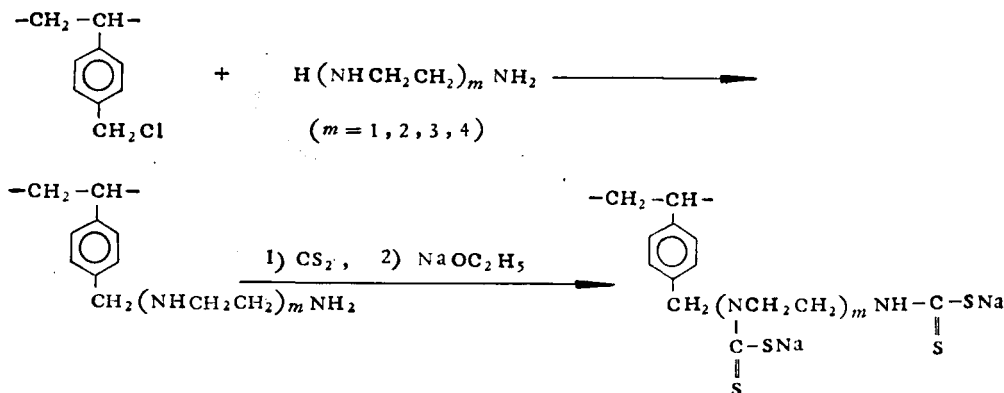
The title resins (DTC resins) with high adsorption capacity were prepared. The influences of various reaction conditions of amination and dithiocarboxylation were examined. The adsorption capacities of the produced DTC resin for Hg^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} are 4.40, 2.44, 1.77 and 1.36 mmol/g, respectively. It is highly effective in collecting traces of heavy metal ions in water over a wide pH range. The conversion of the functional groups were confirmed by the IR-spectra and elementary analysis.

Dithiocarbamates (DTC), a class of effective chelating agents, are characterized by their capability of forming very stable chelate compounds with a number of heavy metal ions except alkali and alkali-earth ions [1,2]:



Introducing the DTC group into a polymeric backbone not only maintains the good chelate property of the group but also gives the products the proper mechanical strength, which is of practical importance to water treatment, environment protection and chemical analysis, etc. This kind of chelate resins was being synthesized[3] and used in collecting heavy metal ions[4], chromatographic separation, etc.[5] with special advantages and produced on a commercial scale[6,7] in the last ten years.

DTC resins with polystyrene as backbone were reported in recent years [8-10]. By introducing amino groups into a gel type chloromethylated polystyrene beads (Gabriel method) we obtained DTC resin[11]. In the present work the DTC resin has been prepared by using good quality of macro-porous chloromethylated polystyrene beads and polyethylene polyamines according to the following processes:



The influence of the reaction conditions of amination and dithiocarboxylation on the properties of the product was investigated. The adsorption capacity and physical properties of the DTC resin which was prepared under the optimum reaction conditions were measured. The results of the adsorption capacity of the prepared resin for heavy metal ions are several times higher than that reported in the literature^[9].

EXPERIMENTAL

1. Amination

After swelling in the solvent the macro-porous chloromethylated polystyrene beads, the degree of crosslinking 6% (divinyl benzene), chlorine content 21.66%, were treated with amine in different mole ratio and under various temperatures and reaction time with stirring. The formed polystyrene beads bearing polyethylene polyamine (amine beads) were successively filtered by suction and rinsed with methanol and ether extensively, then dried at 50°C under vacuum.

2. Dithiocarboxylation (sodium alcoholate-ethanol method (1))

The beads with 23.20 millimole amino groups (calculated on the basis of elementary nitrogen analysis) were swollen in 20 ml of absolute ethanol. Various amounts (in mole ratio) of carbon disulfide were added and reacted at 20°C for a certain period of time. The mixture was heated to a fixed temperature after adding sodium ethanolate solution prepared with 0.75 g metallic sodium and 15 ml ethanol. The DTC resin thus formed was successively filtered by suction and rinsed with ethanol, toluene and ether extensively, then dried at 50°C under vacuum.

3. Determination of the adsorption capacity of DTC resin

Table 1 Determination of the adsorption capacity of DTC resin*

Items	Ion solution to be determined				DTC amount (mg)	Shaking period (h)	Analytical method for determination of residual ion
	Ion to be determined	Conc. (mole / l)	Volume (ml)	pH			
The effect of pH on the adsorption capacity	Cu ²⁺ , Cd ²⁺ , Zn ²⁺ mix.	0.025 resp.	20	1.0—8.5	100 ± 0.5	24	Atomic absorption spectrometry
	Hg ²⁺	0.025	20	1.0—5.5	100 ± 0.5	24	EDTA titration
Rate of adsorption	Cu ²⁺	0.025	20	5.5	100 ± 0.5	1—72	Iodometry
Adsorption capacity	Hg ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺	0.025	20	5.5	100 ± 0.5	72	Hg ²⁺ , Zn ²⁺ , Cd ²⁺ EDTA titration; Cu ²⁺ Iodometry

* The adsorption capacity of the resin for Cu²⁺ was determined after shaking 24 h to evaluate the reaction conditions.

RESULTS AND DISCUSSION

1. Factors which affect the amination and the quality of beads

The amination of chloromethylated polystyrene has been reported^[12-14]. We chose diethylene triamine with medial amino group numbers from four different amines for amination and investigated the influence of reaction conditions such as reaction temperature, time, solvents, amine/chlorine mole ratio, and amine concentration on the nitrogen content and residual chlorine content of amine beads. The results are listed in Table 2.

Table 2 The effect of reaction conditions of amination on the quality of amine beads

No.	Reaction temp. (°C) / Reaction time (h)	Solvent	Amine/ Chlorine (mole ratio)	Conc. of amine (wt. %)	Elementary anal. of amine beads	
					N (%)	Cl (%)
A2	20 / 24 then 70 / 3	Toluene	4	10	11.43	0.94
A3	100 / 3	Toluene	4	20	11.85	0.41
A4	20 / 24	Toluene	4	20	12.05	0.80
A5	20 / 24 then 70 / 3	Toluene	4	20	12.47	0.75
A6	Same	Dioxane	6	Volume of solvent same as A7	12.62	0.81
A7	Same	Toluene	6	30	12.79	0.63
A8	Same	Benzene	6	Volume of solvent same as A7	12.42	0.78
A9	Same	Toluene	2.5	30	12.18	0.77
A11	Same	Toluene	4	30	12.81	0.54

In Table 2, the amination reaction is indicated to be influenced by the effect of reaction temperature and time in A3, A4, A5, by the effect of solvents in A6, A7, A8, by the effect of amine/chlorine mole ratio in A7, A9, A11, by the effect of amine concentration in A2, A5, A11, respectively.

From the results of elementary analysis of formed amine beads, it is clear that A11 (toluene as solvent, amine/chlorine mole ratio=4, amine concentration 30% (wt.), reaction at 20°C for 24 h and then at 70°C for another 3 h) produces the amine beads with the highest nitrogen content and lower residual chlorine content.

If each chlorine atom is replaced by one diethylene triamine molecule, the theoretical nitrogen content of the amine beads will be 18.24%. The fact that the nitrogen contents of all prepared amine beads in Table 2 are much lower than this value and the residual chlorine contents are very small indicates that more than one amino group per amine molecule may take part in the reaction to replace chlorine atom resulting in additional crosslinking.

Table 3 shows the results of amination with four different amines under the A11 reaction conditions. The nitrogen content of formed amine beads increases with the number of amino group in the amine molecule but the percentage of conversion of functional group decreases contrarily because of the increase of additional crosslinking.

Table 3 Different amines effect on the amination reaction

No.	Amine	Amino grs./ Amine molecule	Elementary analysis		% Conversion of functional group* (mole %)	Additional crosslinking** (%)
			N (%)	Cl (%)		
A10	Ethylene diamine	2	11.25	0.53	69.7	30.3
A11	Diethylene triamine	3	12.81	0.54	58.9	41.1
A12	Triethylene tetramine	4	13.34	0.71	49.1	50.9
A13	Tetraethylene pentamine	5	13.94	1.39	45.5	54.5

* Conversion from Cl group into $-(\text{NHCH}_2\text{CH}_2)_m\text{NH}_2$, $m = 1, 2, 3, 4$.

** 100%—% Conversion of functional group.

In Table 4 we list the analytical data of the DTC resins produced by dithiocarboxylation with five different amine beads including the macro-porous primary amine beads which were prepared according to the previous report^[11]. The amino group content of formed amine beads increases with the number of amino group in the amine molecule. On the other hand, the additional crosslinking enhances the stereo hindrance for the reaction and a great quantity of tertiary amine is produced which is useless for the dithiocarboxylation. As a result the percentage of mole conversion of amino to DTC group decreases progressively. These effects lead to the change of the sulfur content of product from going up slowly to coming down. The actual adsorption capacity of the products for Cu^{2+} decreases progressively except the DTC resin corresponding to the primary amine beads because the stronger additional crosslinking effect not only limits the orientation of the ligands but also hinders the transference of the metal ions, making them difficult to place in suitable stereo position for chelation.

Table 4 The results of dithiocarboxylation* with different amine beads

No.	Amine	N (%) of amine beads	S (%) of DTC resin	% Conversion of functional gr.** (mole %)	Adsorption capacity of DTC resin (mmol Cu ²⁺ /g)
D1	Ammonia	7.51	19.59	81.4	2.10
D2	Ethylene diamine	11.25	21.19	60.9	2.14
D3	Diethylene triamine	12.81	21.67	55.3	1.91
D4	Triethylene tetramine	13.34	22.27	55.3	1.37
D5	Tetraethylene pentamine	13.94	19.83	44.6	1.07

* Alcoholate-ethanol method (1)

CS₂/Amino group 2.5 (in mole) reaction at 20°C for 24 h and then at 60°C for 12 h after adding alcoholate solution.** Conversion from amino group into >NCSSNa and —NHCSSNa .

Thus it is concluded that ethylene diamine is the most suitable amination agent for the preparation of the DTC resin with high adsorption capacity.

2. Factors in dithiocarboxylation affecting the quality of DTC resin

Dithiocarbamate is usually prepared by reaction of an amine with carbon disulfide under alkaline condition using alcohol or water as reaction medium^[1]. The amine beads made from ethylene diamine were dithiocarboxylated under the conditions based on the previous report^[11] and other reference works^[8,9,15]. A comparison was made for five combinations of different alkali and medium in dithiocarboxylation. Table 5 shows the sulfur content of the produced DTC resins and the adsorption capacities for Cu²⁺. The products prepared

Table 5 Comparison of the properties of DTC resins prepared by different dithiocarboxylation methods

No.	Method	Reaction condition	Ref.	DTC resin anal.	
				S(%)	Adsorption cap. (mmol Cu ²⁺ /g)
D6	Sodium alkoxide-ethanol (1)	Amino gr. : CS ₂ : C ₂ H ₅ ONa = 1:3:1.4 (mole ratio), resin swelling with ethanol, 20°C/24 h after CS ₂ added, and then 60°C/12 h after EtONa-EtOH added		23.22	2.18
D10	Sodium alkoxide-ethanol (2)	Amino gr. : CS ₂ : C ₂ H ₅ ONa = 1:2.5:0.9 (mole ratio), resin swelling with ethanol, 60°C/12 h after CS ₂ added, and then 20°C/24 h after EtONa-EtOH added	[9]	14.35	1.02
D7	Sodium hydroxide-water	Amino gr. : CS ₂ : NaOH = 1:3:3, resin soak in aq. NaOH solution, 50°C/36 h after CS ₂ added	[8]	23.10	2.13
D8	Without base-ethanol	Amino gr. : CS ₂ = 1:3 (mole ratio), resin swelling with ethanol, 20°C/36 h after CS ₂ added	[15]	11.71	1.47
D9	Pyridine-isopropanol	Amino gr. : CS ₂ : pyridine = 1:4.8:2.6, resin react with the mix. of CS ₂ , pyridine, and isopropanol at room temp. for 3 weeks	[11]	11.85	0.96

from alcoholate-ethanol method (1) and sodium hydroxide-water method give the highest sulfur content and the higher adsorption capacity. Alcoholate-ethanol method (2) is similar to that of Saegusa, et al.^[9] Alcoholate-ethanol method (1), our improved method, differs from other methods in the heating procedure after adding alcoholate solution. When amine beads react with carbon disulfide some amino groups will form inner salts with dithiocarbamic acid presented^[15]. These amino groups can be converted to dithiocarboxyl groups by addition of alcoholate solution and the higher temperature in proposed alcoholate-ethanol method (1) promotes such conversion resulting in a great increase in sulfur content and adsorption capacity of the products.

Furthermore, the effects of the reaction parameters on the dithiocarboxylation of ethylene diamine beads by alcoholate-ethanol method (1) such as mole ratio of reagent, temperature and time on the sulfur content and adsorption capacity of the products were investigated. The results are shown in Figs. 1, 2 and listed in Table 6.

In Fig. 1 the sulfur content and adsorption capacity does not increase anymore when the CS_2 /amino mole ratio goes up to 3, which is considered as the optimum value.

The temperature in Fig. 2 refers to the highest temperature after alcoholate solution is added. The curves show the maximum at 65°C . Table 6 indicates that the best total reaction period is 18 h.

Several reaction conditions such as over high temperature and prolonged reaction time

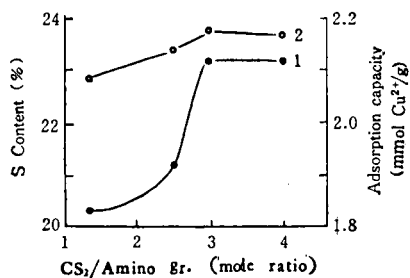


Fig. 1 Influence of CS_2 quantity on the dithiocarboxylation reaction
1—S content, 2—adsorption capacity, other reaction condition same as Table 4.

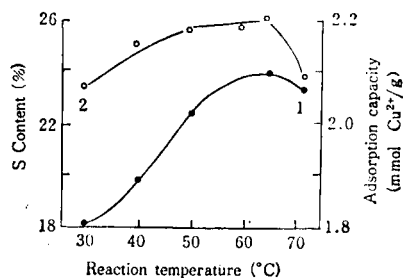


Fig. 2 Influence of temperature on the dithiocarboxylation
1—S content, 2—adsorption capacity, CS_2 /amino gr. mole ratio = 3, other reaction condition same as Table 4.

Table 6 Effect of reaction time on dithiocarboxylation*

No.	Reaction time (h)			Analysis of DTC resin	
	Before EtONa added	After EtONa added	Total time	S (%)	Adsorption cap. (mmol Cu^{2+} / g)
D17	3	3	6	23.59	2.24
D19	9	9	18	24.15	2.33
D20	12	12	24	24.08	2.20
D13	24	12	36	24.08	2.20

* CS_2 /Amino gr. (mole ratio) = 3, 65°C after EtONa-EtOH added.

will cause a little reduction in sulfur content and adsorption capacity of the DTC resin (see Fig. 2 and Table 6). It may be attributable to the escaping tendency of carbon disulfide at elevated temperature resulting in a reduction in actual mole ratio of the reagents, or the decomposition of the resin during prolonged reaction time.

3. The properties of DTC resin

The percentage of synthetic conversion and general properties of DTC resin prepared by amination with ethylene diamine and dithiocarboxylation under the optimum conditions mentioned above are listed in Table 7.

Table 7 Percentage of conversion, general properties, and appearance of DTC resin

N (%) amine beads	(% of conversion of amination*	S(%) DTC resin	(% of conversion of dithiocarboxy- lation**	General properties and appearance of DTC resin			
				Appear- ance	Grain (mesh)	Wet apparent density (g / ml)	Wet true density (g / ml)
11.25	69.7	24.15	74.4	Yellow beads	30—60	0.40	1.47

* Conversion from Cl group into $\text{—NHCH}_2\text{CH}_2\text{NH}_2$.

** Conversion from amino gr. into >NCSSNa and —NHCSSNa .

The chelating properties of the resin was determined. Figs. 3 and 4 show the effect of pH on the adsorption capacity of the resin. Under the experiment conditions, the adsorption percentage of the resin for Cu^{2+} , Cd^{2+} , Zn^{2+} is as high as 98—100% over a wide pH range (2—7.5) as shown in Fig. 3. The adsorption capacity of the resin of Hg^{2+} is over 4 mmol/g at pH 4—5.5; but decreases rapidly below pH 4 (see Fig. 4).

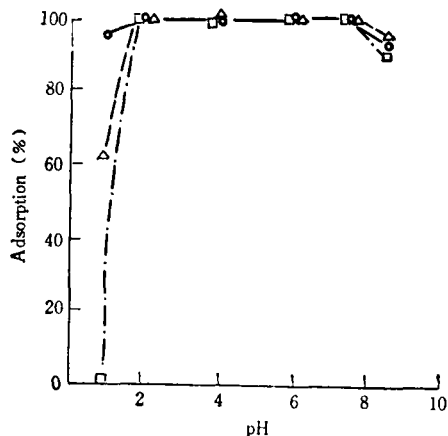


Fig. 3 The effect of pH on the adsorption percentage for Cu^{2+} , Cd^{2+} , Zn^{2+}
—○— Cu^{2+} ; —△— Cd^{2+} ; —□— Zn^{2+} .

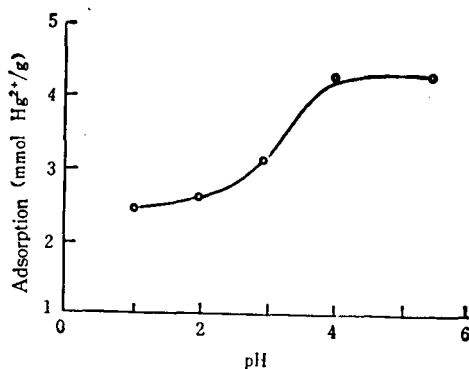


Fig. 4 The effect of pH on the adsorption for Hg^{2+}

The adsorption rate of DTC resin for Cu^{2+} is shown in Fig. 5. The adsorption of the resin for Cu^{2+} in 2 h is greater than 50% of the adsorption capacity and in 24 h is 95.5%.

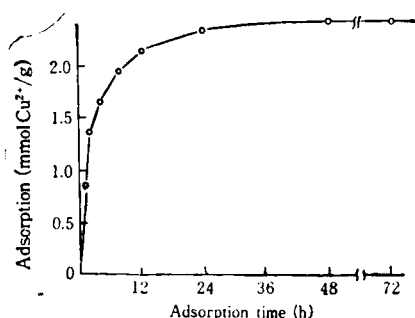


Fig. 5 The relation between the adsorption of Cu^{2+} with DTC resin and adsorption time

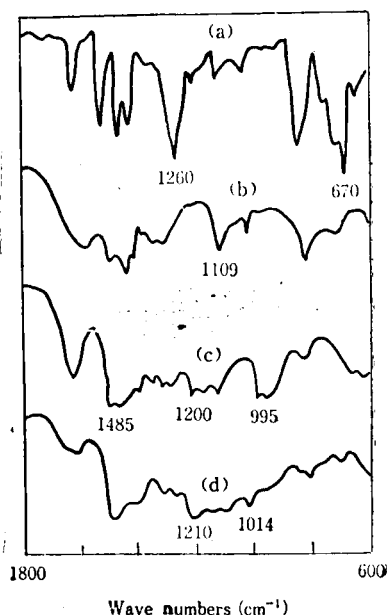


Fig. 6 IR spectra of various resins (a) chloromethylated polystyrene, (b) amine beads, (c) DTC resin, (d) DTC resin chelated with Cu^{2+} .

Table 8 shows the adsorption capacities of DTC resin for Hg^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} . The results indicate that as far as the adsorption capacity is concerned the DTC resin made from ethylene diamine is better than those from long chain polyethylene polyamines. Whereas Saegusa et al. prepared the DTC resin with the long chain polyethylene polyamine in which some amino groups were still acetylated resulting from incomplete hydrolysis of the product, which was prepared from chloromethylated polystyrene and 2-methyl-2-oxazoline and probably did not carry out the dithiocarboxylation reaction under optimum conditions, the authors synthesized the DTC resin under optimum condition, using a macro-porous chloromethylated polystyrene bead as the raw material. Consequently the adsorption capacities of the DTC resin made in the present work for Hg^{2+} , Cu^{2+} , Cd^{2+} are greater than that made by Saegusa et al. by a factor of 1.6 to 3.8 respectively.

Table 8 Adsorption capacity of DTC resin for some heavy metal ions

Heavy metal ions		Hg^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
Adsorption capacity (mmol ion / g)	This paper	4.40	2.44	1.77	1.36
	Saegusa et al.	1.44	0.91	—	0.28

4. IR spectrometrical analysis

Fig. 6 shows the IR spectrograms of chloromethylated polystyrene beads, the corresponding amine beads, DTC resin, and Cu^{2+} chelated DTC resin. The conversion of the functional

groups in the synthesis and chelation processes was confirmed qualitatively.

C—Cl bond strong absorption band at 670 cm^{-1} and CH_2 nonplanar wagging vibration absorption band enhanced by neighbouring Cl at 1260 cm^{-1} (a) are weakened considerably or almost disappear in (b) indicating the absence of chlorine linked with benzyl group. The C—N stretching vibration band at 1109 cm^{-1} (b) indicates the introduction of amine.

The characteristic new bands at 1200 cm^{-1} (C=S bond) and at 1485 cm^{-1} , 995 cm^{-1} (N—C=S bond) in (c) indicate the formation of dithiocarboxyl group. On account of chelation these new bands show hypsochromic shift of more than ten wave number except that at 1485 cm^{-1} which does not shift apparently.

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