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Reactive & Functional Polymers 36 (1998) 71–77

REACTIVE
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FUNCTIONAL
POLYMERS

Removal of nitrite ions from aqueous solutions by cross-linked polymer of ethylenediamine with epichlorohydrin

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Received 11 March 1997; accepted 19 July 1997

Abstract

We describe, for the first time, a polymeric sorbent which is specific for nitrite ions. We have demonstrated that an epoxy-amine resin obtained by suspension polycondensation of ethylenediamine with epichlorohydrin practically contains only secondary amino groups. The hydrochloride form of the resin is extremely efficient and highly selective in the removal of nitrite ions from aqueous solutions, even in very low concentrations. Nitrite binding occurs through formation of *N*-nitroso groups. The nitrite-loaded resin can essentially be regenerated by concentrated acid solutions, without losing its reactivity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Water purification; Nitrite ion; Epoxy-amine resin; Ethylenediamine

1. Introduction

Nitrite ion is one of the most hazardous chemicals which may be present in water. Its acid form nitrous acid is very reactive towards many organic compounds such as amines, phenols, alcohols, etc. Much of reactions involving nitrous acid proceed via radical mechanisms and these reactions are rapid. With nitrous acid, phenols give ortho- or para-hydroximino derivatives. Alcohols give nitrite esters. Primary amides readily decompose to give carboxylic acid and nitrogen. This approach have been demonstrated to be useful in controlling conversion of polyacrylamide into acrylic acid [1]. Aliphatic primary amines yield an unstable diazo compound which immediately decomposes into alcohol and nitrogen. This reaction is the basis of the Van-Slyke method which is used for the determination of amino acids [2].

Secondary amines or amides yield nitrosamines or nitrosamides respectively. Both products are well known carcinogens. Since the peptide linkages are secondary amides, nitrous acid is also a very harmful chemical for living organisms.

From an environmental point of view, pollution of water sources arising from nitrite ion is gaining increasing importance, due to extensive exploitation of nitrogen-containing fertilizers. Hence, nitrite-removal is a challenging issue that must be solved. To the best of our knowledge, there is no special sorbent for the removal of nitrite ions so far.

In the present study, we have targeted the removal of nitrite ions from aqueous solutions by using cross-linked polymers possess-

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PII S1381-5148(97)00122-3

ing secondary amines. For this purpose we have searched for a suitable polymer which would be regenerable. We have shown that an insoluble polymer obtained by reaction of ethylenediamine with epichlorohydrin practically does not contain primary amino groups and meets the above requirements.

In the study the use of the epoxy-amine polymer and its nitrite sorption kinetics have been investigated. Desorption of nitrite ions from the loaded polymer and regeneration conditions have been studied.

2. Experimental

All the chemicals were analytical grade chemical products: ethylenediamine (Merck), epichlorohydrin (Fluka), $NaNO_2$ (Merck), trisodium citrate (Merck), 2,7-dihydroxy napthalene (Merck) was crystallized from alcohol before use.

2.1. Preparation of the cross-linked polymer

50 ml of liquid paraffin was placed in a 250-ml volume two-necked flask equipped with a reflux condenser and a dropping funnel. The whole system was immersed in a ice bath. 10 ml (0.15 mol) ethylenediamine was added to the flask. While stirring with a magnetic stirring bar (350–400 rpm), 12.9 ml (0.165 mol) epichlorohydrin was added cautiously to the mixture through a dropping funnel. A white flocculant occurred after about 45 min stirring. Stirring was continued for another 18 h at room temperature. Then the mixture was heated to 70°C for 3 h. Solid particles precipitated were filtered and washed with 30 ml toluene. The product was dispersed in 30 ml toluene and refluxed for 30 min to remove paraffin residues and filtered, washed with ethanol and water. To obtain HCl-free resin the product was transferred into 50 ml of (5%) NaOH solution and stirred for 2 h. After filtration, white–yellow product was washed with excess of water and 20 ml of ethanol and dried at 50°C for 24 h under vacuum. Yield 15.7 g (86.0%).

2.2. Determination of accessible amine content

Accessible amine content was determined according to the procedure described elsewhere [3]. For this purpose, 0.1722 g of the resin sample was soaked in 25 ml of 1 M HCl solution and left in contact overnight, while stirring in a closed bottle. The excess of unreacted acid was titrated conductimetrically with 0.1 M NaOH solution. The accessible amine content was calculated as 11.9 mmol NH_2/g resin.

2.3. Swelling of the resin sample

Upon standing we observed that small polymer particles dissipate in water. To avoid any probable error, disc-shaped sample with a diameter of 1 cm and 3.3 mm thickness was prepared from 0.25 g dry polymer, by IR pellet sampler under 10 tons/cm^2 of pressure. The disc was placed in a 100-ml volume sintered glass funnel, which was kept in a closed bottle containing 150 ml 1 M HCl solution. The level of solution was adjusted so that the upper level was 5 cm higher than that of the sample. The bottle was sealed to prevent any CO_2 uptake which might cause shifts in pH.

The sample was allowed to stand in contact with acid solution for 6 weeks at room temperature. From time to time the glass funnel was taken out, filtered by suction and weight. The swelling ratio (w/w_0) was found to be 14.3.

2.4. Determination of the nitrite ion concentrations

Nitrite ion concentrations were determined by a colorimetric method which is described elsewhere [4]. This method is based on absorption measurements at 440 nm, which is characteristic for the nitroso derivative of 2,7-napthalenediol in acid solutions.

2.5. Determination of the nitrite loading capacity

In order to estimate maximum nitrite-loading capacity of the resin, 0.5 g resin sample was placed in contact with 30 ml of 15% HCl solution and left overnight. The swollen polymer was decanted and washed many times with distilled water. Then it was transferred into 50 ml of 0.6 M $NaNO_2$ solution, in which total amounts of nitrite is about 10% excess of the theoretical amine content. The mixture was stirred for 24 h at room temperature. The concentration of the nitrite ion remaining unreacted in the solution was determined colorimetrically. Sorbed nitrite content was calculated as the difference between the nitrite contents of the starting and final solutions. Nitrite-loading capacity of the resin was found to be 11.7 mmol/g dry resin.

2.6. *Kinetics of the nitrite ion sorption*

Kinetics of nitrite sorption was investigated by simple batch experiment as follows: 0.5 g sample of the polyamine resin was soaked in 50 ml of 0.2 M $NaNO_2$ solution. While stirring gently at room temperature, at appropriate times aliquots were transferred into volumetric flasks by filtering. The sample solutions were diluted properly and their nitrite concentrations were assayed colorimetrically. The sorbed amount was calculated as the difference between the nitrite contents of the initial and final solutions.

2.7. *Efficiency for trace amounts*

0.5 g of the resin sample was acidified as described above and interacted with 50 ml of 32.5 ppm NO_2 solution. 2 ml aliquots were taken out at appropriate time intervals and their nitrite contents were assayed similarly. Variation of the nitrite concentration of the solution was plotted as a function of time (Fig. 1).

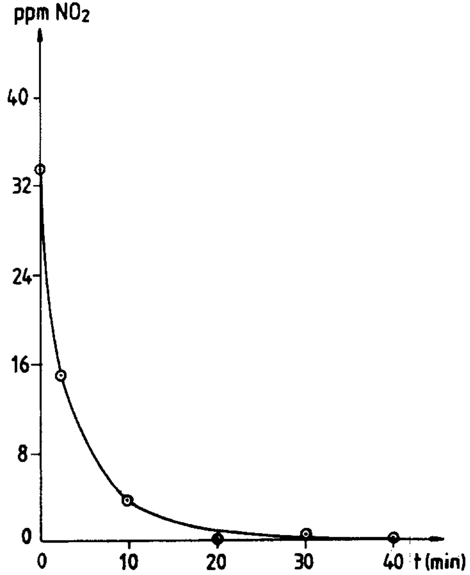


Fig. 1. Kinetics of nitrite sorption.

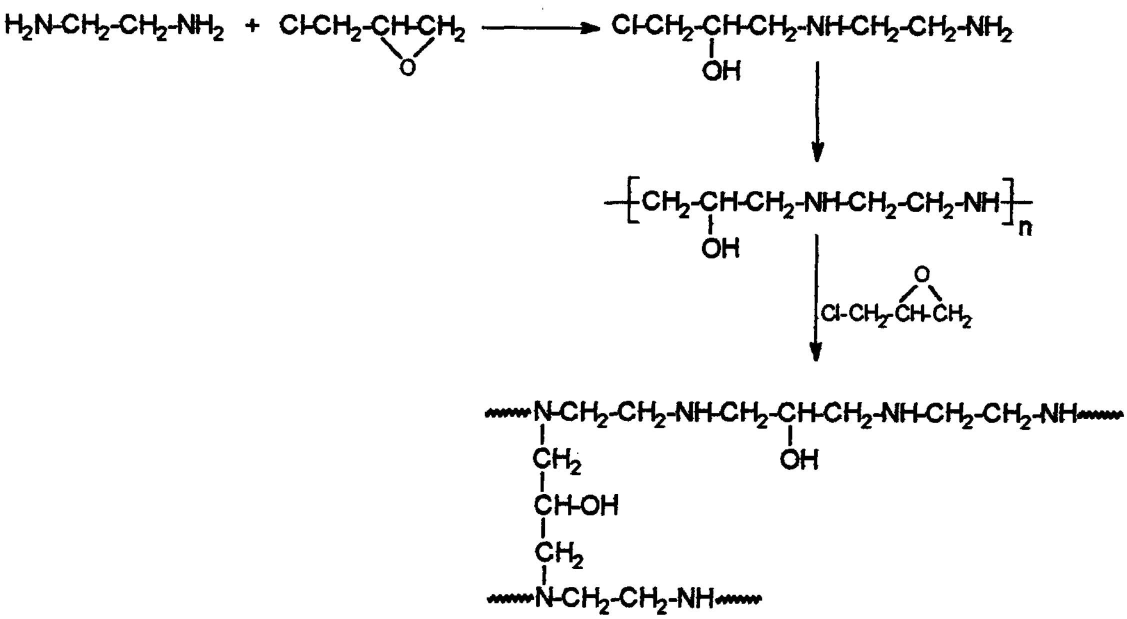
2.8. *Desorption of the nitrite ions*

In concentrated acid solutions *N*-nitroso groups decompose to give nitrous acid. However, in acid solutions nitrous acid tends to escape as nitrogen oxides. To prevent nitrous acid escaping, a modified version of Libermann's qualitative method was used for quantitative determination of nitrous acid. For this purpose the desorption process was performed in acidified solution of 2,7-napthalenediol, which serves also as trapping agent, in that the nitrous acid is fixed as soon as it is liberated from the polymer. In the procedure, 0.5 g of the loaded polymer was added to a 50-ml volume of 3 M HCl solution containing 1.2 mmol 2,7-napthalenediol in a closed bottle. The mixture became red within a few minutes due to the formation of 1-nitroso 2,7-napthalenediol. The mixture was stirred for 24 h at room temperature. 2 ml aliquots were used for direct determination of the nitrous acid content.

This inspection reveals that nitrite ion content of the desorbing solution was 76% of the expected value. We have observed that heating at 40–50°C for 3 h in 15% HCl solution is enough for a complete decomposition of *N*-nitroso groups. After that the polymer becomes regenerated and is free of nitroso groups.

3. Results and discussion

Synthesis of the epoxy-amine resin from ethylenediamine and epichlorohydrin has been described in the patent literature [5,6]. The re-



Scheme 1.

action of epichlorohydrin with ethylenediamine is exothermic and severe explosions occur even when a few millilitres of the reagents are mixed. The reaction can be achieved safely by suspension polycondensation using liquid paraffin as continuous phase, at 0°C. Thermal curing of the precipitated polymer at 80°C for 6 h gives rise to an insoluble resin. The reaction is believed to occur in two steps, (i) ring opening of the epoxy group, (ii) condensation through chloromethyl group. Excess of epichlorohydrin causes cross-linking (Scheme 1).

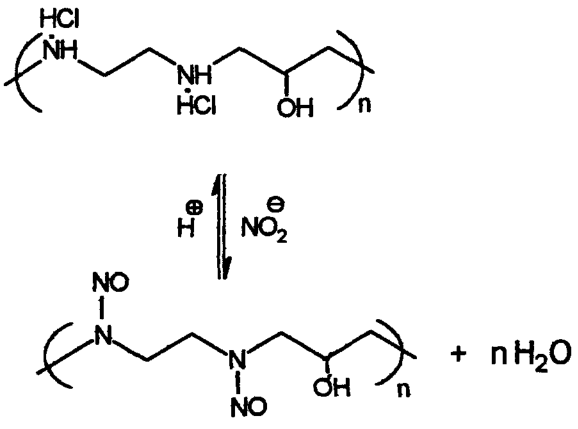
Nitrous acid test indicates that the product practically does not contain primary amino groups. This result seems to be surprising. However, in a recent study it has been demonstrated that reactivity of primary amines toward epoxides is higher than that of the secondary amines [7]. Hence, the product practically consists of secondary and tertiary amino groups. Swelling ratio of the resin in 1 M HCl solution is about 14.3 (w/w_0).

3.1. Nitrite ion sorption

Acidified resin reacts with nitrite ions in aqueous solutions to form *N*-nitroso compounds (see Scheme 2).

During this process the swelled resin sample shrinks and becomes light yellow in colour. Nitrite loading capacity of the resin was found to be 11.7 mmol per g of HCl-free sample. This amount is 85.0% of the theoretical secondary amine content.

The nitrosoation proceeds via nitrous acid and the free amine. To form nitrous acid from nitrite ion, secondary amino groups in the polymer were transformed to ammonium chloride by treating with 15% HCl solution. Being weak acid the



Scheme 2.

ammonium cation forms nitrous acid upon interacting with nitrite ion. Then *N*-nitroso groups form and the polymer becomes light yellow in colour. So here, the nitrite sorption is not an ion-exchange process and does not depend on the anion of ammonium cation associated.

In order to see any difference in the nitrite sorption, the loading experiment was repeated with the polymer treated with acetic acid instead of HCl solution. The nitrite sorptions of the polymers with acetate and chloride anions were almost equal, as it is expected.

In the FT-IR spectra of the nitrosoated polymer, characteristic N–O stretching vibration was exhibited at 1490 cm^{-1} (Fig. 2).

Kinetic experiments indicate that, in about 20 min, 90% of the nitrite content of the solution is consumed (Fig. 3). This amount is almost equal to the maximum sorption-capacity of the polymer. Also, the polymer is quite sensitive to trace quantities. Fig. 1 shows that upon interacting 0.5 g of the acidified the polymer sample with 50 ml of nitrite solution, 32.5 ppm concentration closes to zero in about 20 min. Hence, nitrite binding of the polymer is reasonably fast and the equilibrium establishes within 20 min.

The nitrite-loaded polymer decomposes in acid solutions to give nitrous acid, and HCl salts of the secondary amine groups remain on the polymer. This process is the basis of the regeneration procedure. However, even in concentrated acid solutions (3 M) desorption of the nitrite ions from the polymer does not complete at room temperature for 24 h. In fact, the regeneration with acid is also followed visually by the disappearance of the yellowish colour of the loaded sam-

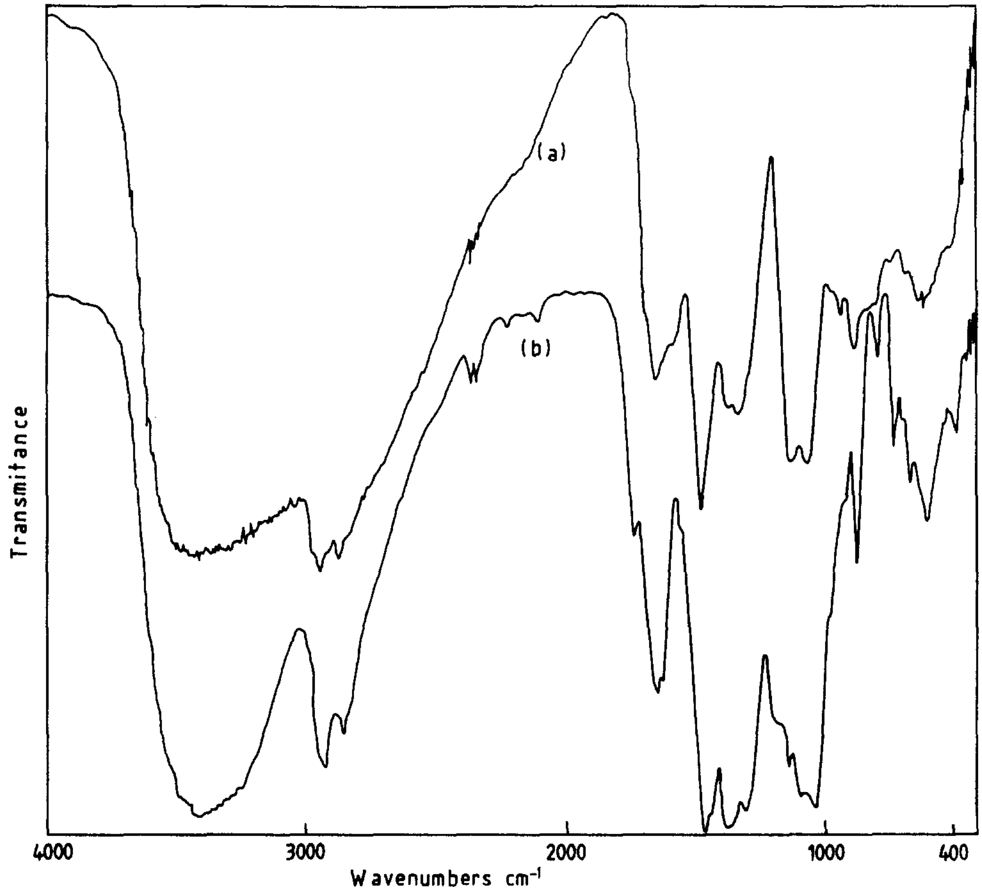


Fig. 2. FT-IR spectra of (a) original polymer, (b) nitrite-loaded polymer.

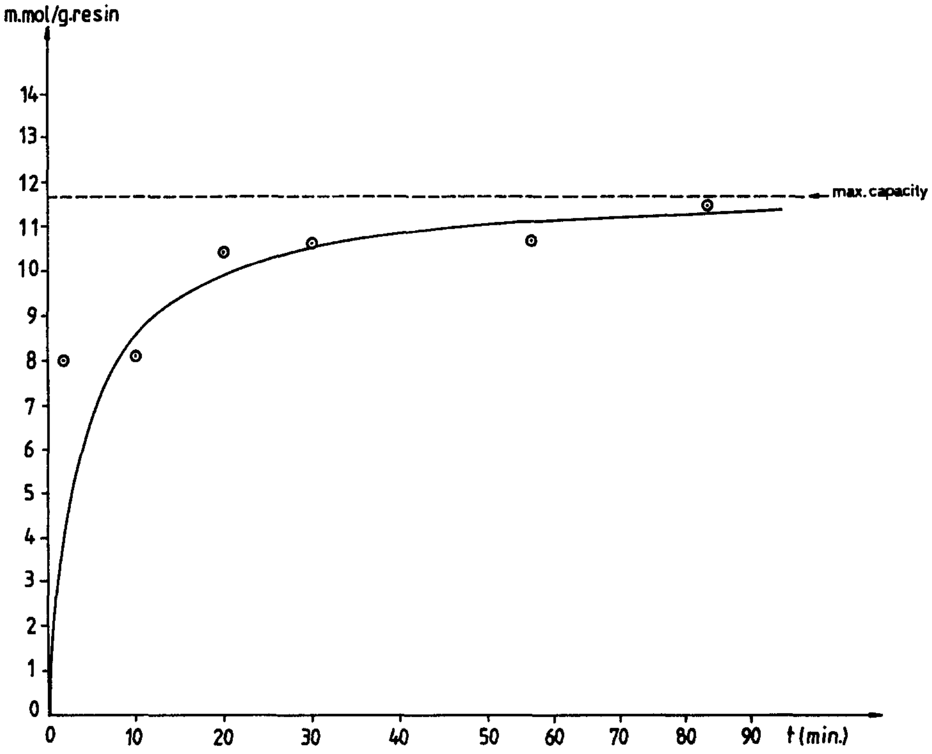


Fig. 3. Concentration–time plot of the dilute nitrite solution in contact with 0.5 g polymer sample.

ples. For a quantitative desorption, heating at 40–50°C (in an efficient fume cupboard) for 3 h with 15% HCl solution is satisfactory. By this way the used polymer becomes regenerated. Indeed, the polymer sample regenerated by this way does not give colour when treated with 2,7-dihydroxy napthalene solution.

FT-IR spectra of the regenerated sample show almost the same pattern with those of the original sample. In the study we have not used the regenerated samples more than once. But a simple test on the regenerated polymer shows that its nitrite-sorption capacity is very close to those of the original polymer sample. This is not surprising, because its structure does not contain hydrolysable linkages in the main chain. We did not examine the effects of interfering entities on the nitrite sorption process. However, according to the studies relating with metal uptakes, some metal ions capable of anionic complexes, especially in higher oxidation states such as Fe(III) or Cr(III), can be sorbed as complex salts through ammonium cations in concentrated acid solutions. But in previous reports it has been claimed that this type of complexation is favoured in high acid concentrations [8]. Whereas, in our case, only the HCl form of the polymer is used and pH of the solution during the nitrite sorption is between 3.2–6.4, which is not suitable for sorption of those kind of metal ions. The polymer itself in free amine form is an excellent chelating agent for transition metal ions. The chelation is followed visually by coloration of the polymer particles. But in the acid form the amino groups of the polymer lose their electron donating character and do not coordinate with transition metal ions. This has been studied and reported by us in another paper [9]. As a consequence, the polymeric sorbent presented seems to be highly selective for nitrite ions in the conditions studied. Its efficiency for trace quantities and regenerability makes it a promising material for water purification. Its use in packed columns may also be of interest, provided that its high swelling can be controlled. The chemistry of the process implies that this approach can be extended to the other polymeric materials possessing secondary amine functions. Further studies on the subject are in progress.

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