

Removal of Nitrite Ions from Aqueous Solutions by Poly(*N,N*-Dimethylamino Ethylmethacrylate) Hydrogels

Z. Yılmaz, P. Kavakli Akkaş, M. Şen, O. Güven

Department of Chemistry, Hacettepe University, Beytepe, Ankara 06532, Turkey

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ABSTRACT: Removal of nitrite ions from aqueous solutions by protonated poly(*N,N*-dimethylamino ethylmethacrylate) hydrogels (P(DMAEMA)) was investigated. We have shown that polycationic and pendant secondary amine group containing P(DMAEMA) hydrogels is very efficient and highly selective for the removal of nitrite ions from aqueous solutions at even in very high concentrations. Adsorption studies have shown that pH of the nitrite solution has influence on the nitrite ion uptake capacity of P(DMAEMA) hydrogels.

The adsorption capacity of hydrogels had been increased up to 3100 mg NO₂⁻¹/g dry gel, by changing pH of the solution. The results of the adsorption studies showed that the interaction between nitrite ions and quaternized amine groups agree with the Langmuir-type isotherm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6023–6027, 2006

Key words: polyelectrolytes; adsorption; gels; hydrogels; radiation

INTRODUCTION

Nitrite ions constitute one of the most important wide-spread contaminants of aqueous environment and serve as significant indicators of natural water quality. The increasing level of nitrite in surface or ground waters results mainly from agricultural application of fertilizers as well as from many industrial processes.¹ Determination and speciation of nitrite and nitrate in waters and foodstuffs have received increasing attention in recent years because of their potential harmful impact on human health. NO₂⁻¹ is highly toxic to certain species of fish. NO₂⁻¹ enters the bloodstream through the gill by a mechanism that normally transports chloride.² After entering the bloodstream NO₂⁻¹ oxidizes iron in the hemoglobin molecule from ferrous state (Fe²⁺) to the ferric state (Fe³⁺). The resultant product, called methemoglobin, is incapable of reversibly binding with oxygen, so exposure to NO₂⁻¹ causes respiratory distress because of the loss in oxygen-carrying capacity of blood. It has been also reported that nitrite can react *in vivo* with secondary or tertiary amines to form *N*-nitroso compounds, some of which are known to be carcinogenic, teratogenic, and mutagenic.³ Kioussis et al. developed poly(allyl amine hydrochloride) polymer hydrogels that remove nitrate, nitrite, and orthophosphate nutrient anions from aquaculture wastewater.⁴ Bicak and Şenkal prepared epoxy-amine resins containing secondary amino

groups for removal of nitrite ions from aqueous solutions.⁵ They found that nitrite loading capacity of the resin was 11.7 mmol/g of HCl-free sample.

Polyelectrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole percentages to 100% of the repeating units. Polyelectrolytes may be anionic, cationic, or amphiphilic and may be synthetic or naturally occurring. The preparation of cationic poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) and its copolymers has gained noticeable interest and a series of articles were published by Siegel and Firestone in the late 1980s.^{6–8} They investigated the influence of comonomer *n*-alkyl methacrylate esters (*n*-AMA) and methyl methacrylate (MMA) on the pH-dependent swelling properties and swelling kinetics. It was found that the extent of the transition from the collapsed hydrophobic state to the hydrophilic state changed depending on the comonomer composition, and as the proportion of *n*-AMA to MMA is increased generally, the extent of the transition is reduced and shifted to lower pH. It was also observed that increasing the length of *n*-AMA side chain had also caused a reduction in the extent of the transition.

In recent years much more attention has been directed to P(DMAEMA) hydrogels that undergo controllable volume changes in response to small variation of pH and temperature changes in solution condition for use in a variety of novel applications, including controlled drug delivery^{9–10} and gene transfer agent.^{11–13}

In our previous study, we proposed that small amount of ethylene glycol dimethacrylate (EGDMA) can facilitate the crosslinking of DMAEMA effectively, during low dose rate γ -irradiation and improve the

Correspondence to: M. Şen (msen@hacettepe.edu.tr).

crosslink efficiency to ~8-fold, when used only 0.05% concentration in the initial monomer mixtures.¹⁴

In this study, protonated P(DMAEMA) hydrogels were used to remove nitrite ions from aqueous systems. Sorption kinetics and effects of initial NO_2^- concentration and pH have been investigated.

EXPERIMENTAL

Chemicals

The monomer used in the preparation of hydrogels, namely *N,N*-dimethylaminoethyl methacrylate (DMAEMA), was obtained from Aldrich (USA). Ethylene glycol dimethacrylate (EGDMA), used as crosslinking agent, was obtained from BDH (UK).

Preparation of hydrogels

Ternary mixtures of DMAEMA, EGDMA, and water were used in the preparation of P(DMAEMA), hydrogels. Aqueous solutions of DMAEMA containing 35% water were prepared and 0.1% volume of EGDMA were added into these solutions. Aqueous monomer solutions thus prepared were placed in polyvinyl chloride (PVC) straws of 3-mm diameter and irradiated with γ -rays up to 8.0 kGy in air at ambient temperature in a Gammacell-220 type γ -irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogels obtained in long cylindrical shapes were cut into pieces of 2–3 mm and stored for later evaluations.

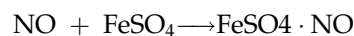
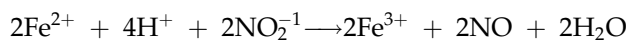
Monomer-gel conversion

Pieces of hydrogels were dried in a vacuum oven at 40°C to constant weight and subjected to Soxhlet extraction with water as solvent. Uncrosslinked polymer and/or residual monomer were removed with the extract of the gel structure. Extracted gels were dried again in vacuum oven at 40°C to constant weight. Percentage gelation i.e., percentage conversion of monomer and crosslinking agent into insoluble networks, was determined as the ratio of total weight of monomer and crosslinking agent in the initial mixture to the dried weight of hydrogel. The amount of uncrosslinked DMAEMA in monomer, polymer, and/or copolymer form was determined by titration of extract against 0.02M HCl to phenolphthalein end point. The experimental details related to gel preparation and characterization of hydrogel have already been given elsewhere.^{14,15}

Determination of the nitrite ion concentration

For the determination of nitrite ion concentration ferrous sulfate method was used. In an acidic medium ferrous sulfate reduces nitrogen in nitrite (NO_2^-) to

form nitrous oxide (NO). Excess ferrous ions combine with the nitrous oxide to form a brown-colored complex ion, the color intensity of which is in direct proportion to the nitrite present in the water sample.



Concentration of brown-colored complex ion was determined at 333 nm by using Philips 8710 UV-vis spectrophotometer.

Determination of the nitrite adsorption capacity

To determine the maximum nitrite loading capacity of P(DMAEMA) hydrogel, ~ 0.05 g of dry hydrogel was placed into 50 mL of 1M HCL solution for over night. The swollen protonated hydrogel was removed, washed with distilled water, and transferred into 100 mL of NaNO_2 solutions with various initial concentrations ranging from 0 to 2000 ppm and stirred for 24 h at room temperature. The pH of the NO_2^- solution in 0–2000 ppm concentration range is 5.5–5.7. The nitrite ion remaining in the solution was determined by using before mentioned ferrous sulfate method.

Nitrite adsorption kinetics

The adsorption kinetics of nitrite ion from 500 ppm NO_2^- solution was followed by a simple batch experiment. The amount of nitrite ion adsorbed was checked at certain time intervals. Aliquots of 100 μL taken at predetermined time interval from the solution were used for the determination of concentration of remaining NO_2^- ions at certain time intervals. The adsorbed amount was calculated, as the difference between the nitrite contents of the initial and final solutions.

Effect of pH on the nitrite adsorption

For the investigation of the effect of pH on the NO_2^- adsorption, solutions were prepared in pH ranging from 2 to 7 by using HCl. The 500 ppm NO_2^- solution was used in these experiments.

RESULTS AND DISCUSSION

Preparation of hydrogels

When pure DMAEMA monomer was irradiated with γ -rays, both polymerization and crosslinked reactions took place simultaneously. The total dose required for the onset of gelation was determined to be 40 kGy for this system. The hydrogels prepared above gelation dose showed low mechanical stability and ruptured upon swelling. This is most probably

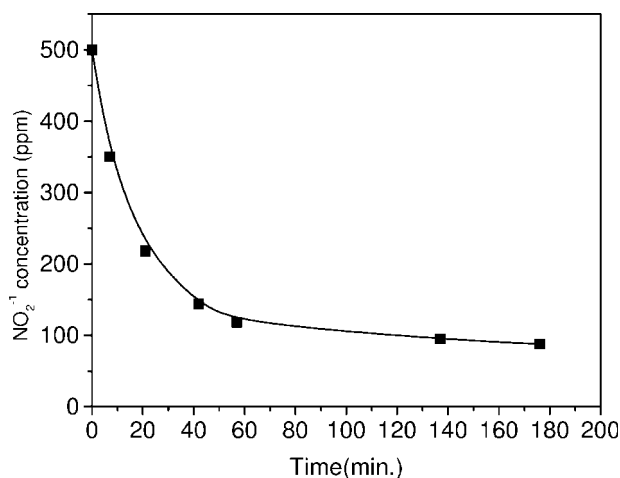


Figure 1 Adsorption kinetic of nitrite ion from 500 ppm solution.

because of the presence of polymerized, but not crosslinked, DMAEMA chains entrapped in the gel structure. Their loss as sol fraction upon contact with water will naturally weaken the mechanical stability of gel. When DMAEMA irradiated at high doses i.e., 70 kGy, only 10% conversion from monomer to gel structure was observed.

To decrease the gelation dose and increase the crosslink density at the same time, a difunctional crosslink agent, EGDMA was added to monomer. The hydrogels obtained in the presence of 0.1% EGDMA behaved similarly to pure PDMAEMA gels that is upon swelling the geometric shape of the gel was destroyed. This is probably because of the insufficient formation of crosslinks. The sensitizing effect of water for the gelation of *N*-vinyl 2-pyrrolidone (VP), acrylamide (AAm) and copolymers of AAm and VP were very well demonstrated in our previous studies.^{16–19}

To make mechanically stable hydrogels, water is added to DMAEMA/EGDMA system. The percentage gelation from monomer to insoluble network increases with increasing irradiation dose until 4.0 kGy. After that, gelation remains almost constant. When DMAEMA/EGDMA/water mixture irradiated at 8.0 kGy, 95% conversion from monomer to gel structure was observed. Characterization of network structure of this hydrogel system and determination of crosslink density and polymer-solvent interaction parameter were in detail in our previous study.¹⁵

NO₂⁻¹ ion adsorption

To investigate the adsorption kinetics of nitrite ion onto P(DMAEMA) hydrogels, ~ 0.05 g of gel was treated with 500 ppm nitrite ion solutions at room temperature. Figure 1 shows the adsorption curve of nitrite ion onto P(DMAEMA) hydrogels. The adsorption values are given as adsorbed nitrite, mg/g dry gel. High

adsorption rates are observed within 20 min for nitrite ions and after 1 h the plateau value was reached. Approximately 82.5% removal of nitrite ions was achieved within 1 h from 500 ppm nitrite solution.

The effect of the initial concentration of nitrite ions on the adsorption behavior of protonated P(DMAEMA) hydrogel (0.05 g) was determined in 24 h contact times for NO₂⁻¹ ion and for 11 different NO₂⁻¹ ion concentrations (75, 150, 200, 250, 500, 1000, 1500, 2000, 2500, 3000, and 3500 ppm) are given in Figure 2. Figure 2 shows that adsorption of nitrite ions increased continuously with increasing initial NO₂⁻¹ concentration. NO₂⁻¹ ion adsorption reached equilibrium after 3000 ppm initial concentration.

Adsorption isotherm of P(DMAEMA) was analyzed according to the linear form of the Langmuir isotherms for NO₂⁻¹ ion by using the following expression,

$$\frac{C_e}{q_e} = (1/K_L q_{\text{mon}}) + (1/q_{\text{mon}})C_e$$

where C_e is the equilibrium concentration of NO₂⁻¹ ion in solution, q_e represents the adsorbed nitrite ion per unit mass of adsorbent at equilibrium, q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage, K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon} .²⁰

The plot of isotherm shown in Figure 3 seems to be linear over the high concentration range (\gg 500 ppm) studied. K_L and q_{mon} values calculated from Langmuir equation are 2.86×10^{-3} and 3333, respectively. The constant, K_L , contains enthalpic interaction the binding of metal ions with polymer, and can be found from the intercept of the lines given in Figure 3. q_{mon} is a quantity representing adsorption capacity, also known as monolayer coverage of the surface. q_{mon} value of P(DMAEMA) for ion was found to be 3333 mg/g. This is very good in accordance with the result previously seen in Figure 2.

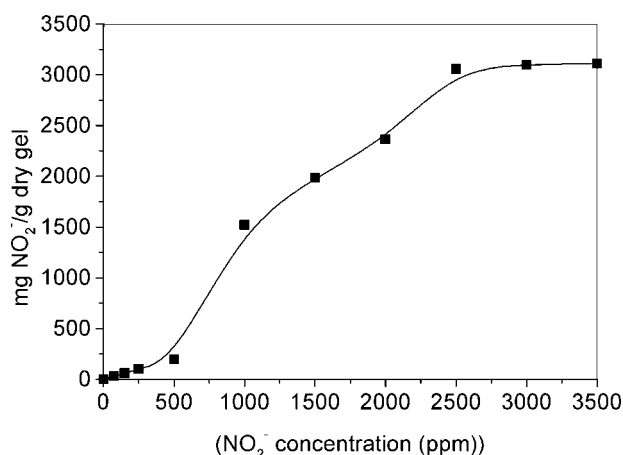


Figure 2 Dependence of nitrite ion uptake on the initial concentration of nitrite ions.

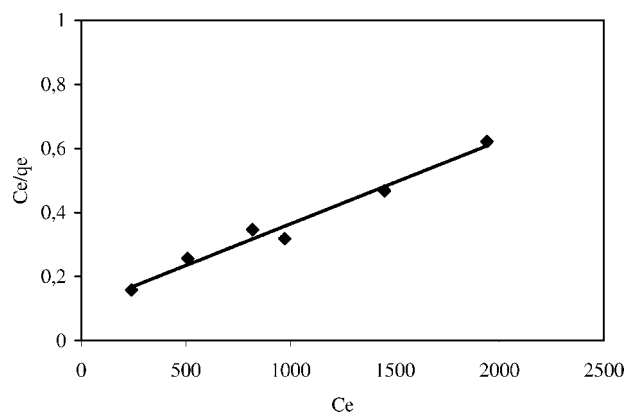


Figure 3 Langmuir isotherm for nitrite ion adsorption on P(DMAEMA).

The binding of nitrite ion onto P(DMAEMA) hydrogels was confirmed by FTIR analyses. The FTIR spectra of P(DMAEMA), unprotonated P(DMAEMA), protonated P(DMAEMA), and nitrite ion adsorbed forms are given in Figure 4. Difference spectra obtained by subtraction of protonated P(DMAEMA) FT-IR spectrum from unprotonated P(DMAEMA) FT-IR spectrum, and nitrite ion adsorbed P(DMAEMA) FT-IR spectrum from protonated P(DMAEMA) FT-IR spectrum are also given in Figure 4. After protonation of P(DMAEMA), a broad stretching band was observed between 2700 and 2300 cm^{-1} region which was characteristic for NR_3H^+ . For the spectrum of nitrite ion adsorbed form, nitrite displayed $\text{N}=\text{O}$ stretching band at 1385 cm^{-1} and the $\text{N}-\text{O}$ stretching bands at 825 cm^{-1} as given in literature.²¹

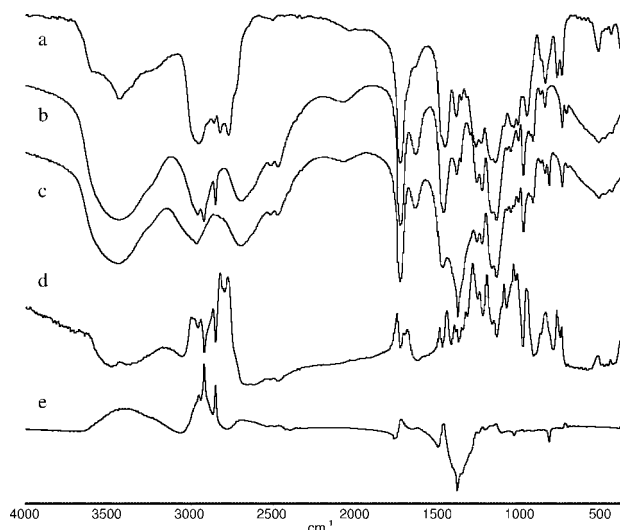


Figure 4 FTIR spectra of P(DMAEMA) (a) unprotonated, (b) protonated, (c) nitrite ion adsorbed, (d) spectrum difference between (b) and (a), and (e) spectrum difference between (c) and (b).

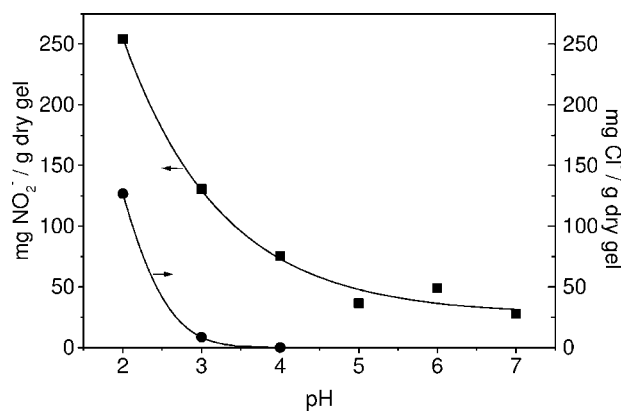


Figure 5 Effect of pH on NO_2^- and Cl^- ions adsorptions.

Effect of pH on the nitrite adsorption

To determine the effect of pH on the adsorption characteristic of hydrogels, adsorption studies were conducted in solutions with different pH's, pH 2–7. As can be seen from Figure 5, NO_2^- ion adsorption capacity strongly depends on the pH of the medium. Because of the deprotonization of tertiary amine groups, adsorption rapidly decreased and the specific interactions between quaternized amine groups and nitrite ions also decreased.

For the adjustment of the pH, HCl was added in the solution so NO_2^- adsorption was achieved in the presence of Cl^- ions. For the investigation of selectivity of hydrogels to Cl^- ions the amount of adsorbed Cl^- ions in the presence of NO_2^- ions was determined between pH 2 and 4. The amounts of adsorbed Cl^- ions per gram dry gel are given in Figure 5. Maximum Cl^- ion adsorption was observed at pH 2 because of the complete protonization of hydrogel. This value decreased to 0.35 mg Cl^- /g dry gel at pH 4.

As a conclusion, these results show that P(DMAEMA) hydrogels may be considered as a potential adsorbent for the selective removal of nitrite ions from wastewaters.

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