

Pre-concentration of Anions on Poly(N-acetyl-D-glucosamine) Derivative - Modified Carbon Paste Electrode

Clovis A. Rodrigues, Valfredo T. de Fávère, Eduardo Stadler* and
Mauro C.M. Laranjeira

*Departamento de Química, Universidade Federal de Santa Catarina, CP 476,
88.040-900 Florianópolis, SC, Brasil*

Received: april 27, 1992; january 10, 1993.

Neste trabalho foi estudada a capacidade do biopolímero quitina e seus derivados (quitosana, quitosana enxertada com acrilonitrila e quitosana acetilada) em acumular ânions (nitrito, permanganato, iodeto e ferricianeto). Esta capacidade foi estudada através da técnica de voltametria de redissolução, utilizando os polímeros como componente dos eletrodos modificados de pasta de carbono (EMPC). A varredura de potencial foi precedida de uma etapa de pré-concentração, por um determinado tempo e potencial adequado, dependente do tipo de ânion. A quitosana enxertada com poli(acrilonitrila) é muito eficiente na acumulação de todos os ânions estudados. A quitosana acumula os íons nitrito, iodeto e ferricianeto. A quitina acumula todos os ânions, mas com menor eficiência. A quitosana acetilada acumula íons permanganato.

In this work the capacity of the biopolymer chitin and its derivatives (chitosan, polyacrylonitrile-grafted chitosan and acetylated chitosan) to accumulate the anions nitrite, permanganate, iodide and ferricyanide was studied. This capacity was monitored by stripping voltammetry, using the polymers as modified carbon paste electrodes (MCPE). The measurement, by cyclic voltammetry, of the static capacities of the polymers was preceded by a pre-concentration step during a specific period of time at an appropriate potential. The MCPE-polyacrylonitrile-grafted chitosan and MCPE-chitosan were very efficient in accumulation of nitrite, ferricyanide, permanganate and iodide ions. Chitin, has a capacity to accumulate anions, but its efficiency is lower than that of modified chitin.

Key words: *stripping voltammetry; carbon paste electrode; chitin derivatives; pre-concentration.*

Introduction

Industrial and analytical utilization of the biopolymer chitin [poly (N-acetyl-D-glucosamine)] and its derivatives has recently gained growing importance in pre-concentration and separation of ions¹⁻⁵. They provide efficiency in the removal of ions and are promising as adsorbent resins.

In the recent report, Bai *et alii*⁶ used chitin in the pre-concentration and characterization of nitrite, permanganate, chromate, vanadate and ferricyanide anions by stripping voltammetry with a modified carbon paste electrode (MCPE).

In the present work we report the comparative pre-concentration capacity of chitin derivatives (chitosan, polyacrylonitrile-grafted chitosan and acetylated chitosan) for nitrite, ferricyanide, permanganate and iodide ions.

Experimental

The commercial potassium salts (reagent grade), nitrite, permanganate, iodate and ferricyanide (Merck) were used in standard aqueous (Milli-Q water) solution.

Chitin (85% N-acetylated) was obtained according to the literature method from shrimp shells⁷⁻⁹. Chitosan (20% N-acetylated) was prepared by basic hydrolysis of chitin following the methods described in previous reports⁷⁻⁹.

The N-acetylated chitosan with a degree of N-acetylation of 100% was synthesized by the reaction between chitosan and acetic anhydride¹⁰ and polyacrylonitrile-grafted chitosan using ceric ammonium nitrate (CAM) as the redox initiator⁹.

The cyclic voltammograms were obtained using a CV-27 Cyclic Voltammeter (Bioanalytical System Inc.), with an

associated X-Y plotter (Omnigraphic 100, of Houston Instruments). A system of three electrodes was used: a carbon paste as working electrode, a reference electrode (Ag/AgCl-KCl) and a platinum wire as auxiliary electrode. The carbon paste electrode was prepared using a mixture of 0.4 g of electrolytic carbon powder (Rekipro) in 0.2 g mineral oil (Nujol) and 0.06 g of the polymer. The standard electrode carbon paste (ECP) was prepared using a 2:1 mixture of electrolytic carbon powder with mineral oil.

Results and Discussion

The electrochemical behavior of nitrite, ferricyanide, permanganate and iodide ions was observed in the different modified carbon paste electrodes (MCPE) used. Measurement by cyclic voltammetry of the static capacities of the polymers was preceded by a pre-concentration step during a specific period of time at an appropriate potential. The ex-

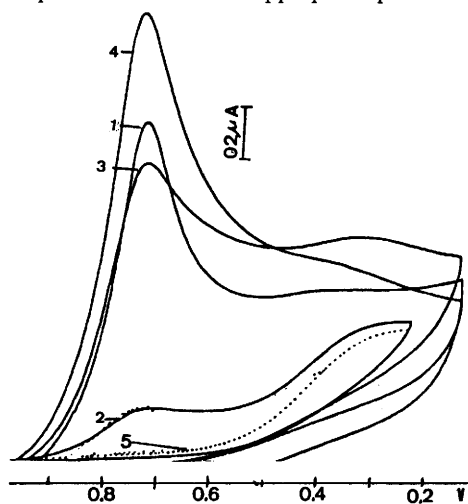


Figure 1. Cyclic Voltammograms for $2.5 \times 10^{-6} M MnO_4^-$ ion, in HCl (pH 3.1) at electrodes polarized at +1.3V for 10 min, scan rate 10 mV/s. MCPE with : 1-polyacrylonitrile-grafted chitosan, 2- Chitosan , 3- Chitin, 4- Acetylated chitosan 5- Standard electrode carbon paste (ECP).

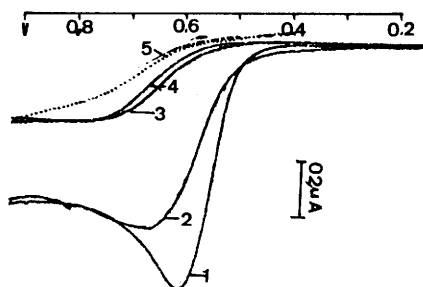


Figure 2. Cyclic Voltammograms for $1.8 \times 10^{-5} M NO_2^-$, in HCl (pH 3.1) at electrodes polarized at 0.0V for 10 min, scan rate 10 mV/s. MCPE with : 1- polyacrylonitrile-grafted chitosan, 2- Chitosan , 3- Chitin, 4- Acetylated chitosan.

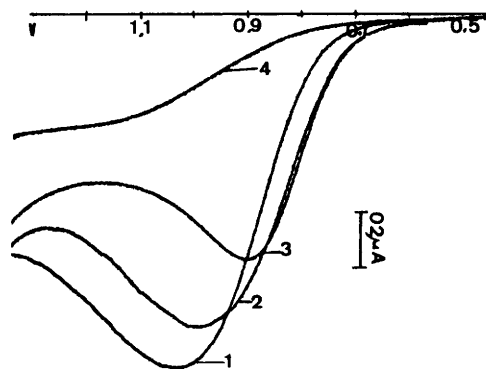


Figure 3. Cyclic Voltammograms for $1.5 \times 10^{-5} M I^-$, in HCl (pH 3.07), at electrodes polarized at 0.0V for 10 min, scan rate 10 mV/s. MCPE with : 1- polyacrylonitrile-grafted Chitosan, 2- Chitosan , 3- Chitin, 4- Acetylated chitosan 5- Standard electrode carbon paste (ECP).

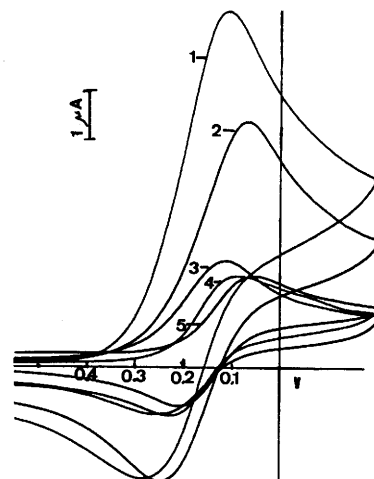


Figure 4. Cyclic Voltammograms for $4.0 \times 10^{-5} M [Fe(CN)_6]^{3-}$ in 0.01 M KCl+HCl (pH 3.0), at electrodes polarized at 0.8V for 15 min, scan rate 100 mV/s. MCPE with : 1- polyacrylonitrile-grafted chitosan, 2- Chitosan , 3- Chitin, 4- Acetylated chitosan 5- Standard electrode carbon paste (ECP).

perimental conditions (deposition time and concentration of sample, polymer:graphite ratio in the MCPE) and the voltammetric parameters (scan rate and sensibility) were maintained constant for each species and MCPE. Thus, the absorption capacity of different polymers corresponds to a difference in the intensity of the cathodic or anodic peak current.

Figure 1 shows the cyclic voltammograms for $2.5 \times 10^{-6} M MnO_4^-$ in HCl, pH 3.1. Under this condition, the MCPE-acetylated chitosan is the most effective in anion accumulation. However, a less effective anion accumulation was verified for a second potential scan. It was observed that for standard electrode carbon paste (ECP) and MCPE-chitosan accumulation is ineffective for permanganate ion.

Figure 2 shows the cyclic voltammograms for $1.8 \times 10^{-5} M NO_2^-$ in HCl, pH 3.1. Under this condition, MCPE-polyacry-

lonitrile-grafted chitosan is effective for nitrite ion. However, the anion accumulation is not effective for a second potential scan and for the standard electrode carbon paste (ECP).

Figure 3 shows the cyclic voltammograms for 5×10^{-5} M Γ in HCl, pH 3.07. In this case, MCPE-polyacrylonitrile-grafted chitosan is again the most effective.

The results obtained for 4.0×10^{-5} M $[\text{Fe}(\text{CN})_6]^{3-}$ in 0.01 M KCl + HCl (pH 3.0) at electrodes polarized at +0.8V for 15 min before the potential scan are showed in the Figure 4. We observed well-defined reduction-oxidation waves in which the cathodic and anodic peaks gradually increased as the cyclic scans were repeated many times. The anodic and cathodic peaks are attributed to $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions respectively; once accumulated on the electrode they were not removed during the cyclic scans. These results were observed for all the polymers, even for the standard electrode carbon paste (ECP). It was also observed that MCPE-polyacrylonitrile-grafted chitosan is the most effective. In this case, it is worthwhile to remark that the accumulated anions remain adsorbed for a second scan potential and so on.

Conclusions

The MCPE-polyacrylonitrile-grafted chitosan proved to be very efficient at anion accumulation, due to the presence of significant number of active centers, which are protonated on amine nitrogen, and that probably undergo influence of the positive dipole of a nitrile group ($\text{R}-(\text{CH}_2)_3\text{-CN}$). The degree of polarity of the groups introduced, is factor determining in a change of the conformation of the polymeric chains, resulting a polymer less flexible. However, being polar, the graft copolymer is also capable of swelling in an aqueous medium, increasing the electrostatic anion accumulation¹¹.

MCPE-chitosan was efficient in accumulation of nitrite, ferricyanide, permanganate and iodide ions, due to a presence of a greater number of R-NH₂ groups (deacetylated polymer). Nevertheless, chitosan cannot be used for the accumulation of permanganate ion because of chemical oxidation of the polymer chitosan.

As shown by Bai *et alii*⁶, chitin has the capacity to accumulate anions, but, due to the presence of acetyl groups, its efficiency is lower than that of modified chitin.

Acetylated chitosan (100%), despite having a greater number of acetylated groups in comparison with chitin, is less efficient at anion accumulation.

Acknowledgments

The authors thank to Dr. W. F. Jardim and Dr. L. M. Aleixo and CNPq-RHAE for fellowship support of C.A. Rodrigues.

References

1. R. A. A. Muzzarelli, *Chitin*, (Pergamon Press London 5, 1977).
2. E. Agullo, B. Jeanneret, S. Sadi and L. Popovich, *An. Asoc. Quim. Argent.* **76**, 347 (1988).
3. V. T. Fávere, and M. C. M. Laranjeira, *VII Simp. Bras. Electroquim. e Eletroanal.* II, 415 (1990).

4. V. T. Fávere, I. G. Souza, M. C. M. Laranjeira and W.R. Senff, *Química Nova* **14**, 106 (1991).
5. V. T. Fávere and M. C. M. Laranjeira, *Química Nova* **14**, 111 (1991).
6. Z. Bai, T. Nakamura and K. Izutsu, *Anal. Sci.* **6**, 443 (1989).
7. O. C. Baggio, *MSc. Thesis*, Universidade Federal de Santa Catarina, Florianópolis (1988) p 28.
8. O. C. Baggio, E. Stadler, and M. C. M. Laranjeira, *Revista Química Industrial* **672**, 9 (1989).
9. E. H. S. Moecke, *MSc. Thesis*, Universidade Federal de Santa Catarina, Florianópolis, (1990), p 31.
10. J. Koshugi, *European Patent Application*, (1980) N°0021 750 A1.
11. A. Tager, *Physical Chemistry of Polymers*, MIR Publishers, Moscow, (1972) p. 91-93, 530-532.