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Physico-chemical properties and characterization of iron (II) electrochemical sensor based on carbon paste electrode modified with novel antimicrobial Carboxymethyl chitosan-*graft*-poly(1-cyanoethanoyl-4-acryloyl-thiosemcarbazide) copolymers

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ABSTRACT

Carbon paste electrode (MCPE) modified with novel Carboxymethyl chitosan/poly(1-cyanoethanoyl-4-acryloyl thiosemcarbazide) copolymers (CMCS-PCEATS) was prepared for determination of iron(II). The interaction between the modifier (CMCS-PCEATS) and iron(II) ions at the electrode surface was characterized using scanning electron microscope (SEM), the energy dispersive X-ray analyzer (EDX) and FTIR. Effect of different plasticizers (TCP, o-NPOE, FPNPE, DBP, DOP and DOS) and content of modifier were studied. The best performance was obtained with the electrodes plasticized with FPNPE (electrode I) and TCP (electrode II)·Under the optimized conditions, the electrodes reveal Nernstian slopes of 30.21 ± 0.31 and 30.17 ± 42 mV decade^{-1} over a wide concentration range from 1.0×10^{-7} to 1.0×10^{-1} mol L^{-1} with a detection limit of 1.0×10^{-7} mol L^{-1}at pH range from 3 to 8 for electrodes I and II. The paste is enough stable for 37 days without any measurable divergence in the potential. This method was successfully applied for potentiometric determination of iron (II) in pharmaceutical and water samples, and the results obtained agreed with those obtained with spectrophotometer and inductive coupled plasma (ICP). The thermal stability as well as the antimicrobial activity of the MCPE and MCPE-iron(II) were also studied. The results illustrated that MCPE-iron(II) was thermally stable over wide range of temperature than MCPE and it has higher antibacterial activity against *Streptococcus aureus*, *Salmonella SP.*, *Escherichia coli* and antifungal activity against *Candida albicans*.

1. Introduction

Iron is more distributed in nature, and it is one of the essential elements in biological and environmental systems. Iron plays an important role in diversity of cellular events and indeed no life form is possible without this element with a few possible exceptions in bacterial world [1,2], though it is a critical element for living systems. The gradual cumulation of iron leads to some diseases [3–6]. The increase of iron in body causes kidney and liver damage (hemochromatosis), but its deficiency leads to anemia [7–9]. Several methods for the determination of iron are available, including inductively coupled plasma–mass spectrometry [10,11], atomic absorption spectrometry [12,13] and emission spectrometry [14–16]. However, most of these methods require numerous time-consuming manipulation steps [17,18]. Potentiometric ion-selective electrodes (ISEs) have been extensively used in determination of ions in both pharmaceutical and water samples [19–22]. They also used in determination of anionic species such as dichromate, perchlorate, oxalate ions [23–25] and widely used for the direct potentiometric determination of ion concentrations or ion activities in various samples. Their advantages are low cost, simple design, low detection limit, high accuracy and adequate selectivity [26–29]. Recently, the attention of researchers was directed to use voltammetric sensors based on a graphene–carbon paste electrode modified with imprinted and non-printed polymers for electrochemical determination of many drugs and elements potentiometrically. Carbon paste electrodes provide a renewable surface, low ohmic resistance and stable response; also they can be modified by nano-materials [30–32].

The goal of this work is to prove the ability of a good ionophore in the construction of carbon paste electrodes and the use of these modified electrodes as electrochemical sensors for Fe (II) determination. The characteristics and analytical performance of MCPEs like influence of ionophore content, different plasticizers, pH range, effect of the interfering cations and temperature have been investigated. It is worth mention that we use novel Carboxymethyl chitosan-*graft*-poly(1-

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cyanoethanoyl-4-acryloyl thiosemcarbazide)*co*-polymers (CMCS-PCEATS) as an ionophore. Whereas Both CMCS and PCEATS separately have been reported as a better chelating agents towards several metal ions as Cu(II), Ni(II), Cd(II), Co(II), …etc. [33–36]. Grafting of CMCS with 1-Cyanoethanoyl-4-acryloyl thiosemcarbazide gives CMCS-PCEATS *co*-polymers as a novel co-polymers that characterized by a higher chelating capacity due to the presence of different kinds of function groups (OH, COOH, NH2, CONH, C=S, CN, …) with a polar and hydrophilic characters that facilitate the chelation with the metal ions. In addition they have wide biological application. Since thiosemicarbazides and thiosemicarbazones are considered have higher biological applications they exhibits potential activity in the field of anticancer, antitubercular, anti HIV, antidepressant, antiviral, antifungal, antibacterial and anticonvulsant. Also they have parasiticidal activity against Plasmodium, Trypanosoma cruzi … etc. [37,38]. These may be due to the presence of the S and N donors with its higher chelation interaction. On the other hand Carboxymethyl chitosan (CMCS) exceeds chitosan in its solubility in water and different organic solvents, in addition it is characterized by higher nontoxicity, biodegradability and biocompatibility it has antimicrobial activity towards different kinds of bacteria and fungi. Its antibacterial activity resulted from the ability to bind and disrupt the normal function of bacteria cell membrane thus promoting the leakage of intracellular components and prevent transportation of the nutrients into the cells [39–42] while, the inhibiting effect on fungi is due to the disturbance of the enzyme activities responsible for the growth criteria. Carboxymethyl chitosan and its derivatives were employed in many medical applications as artificial bone and skin, a moisture-retention agent, blood anticoagulant, wound dressing agent, and also in drug delivery systems, antioxidants [43]. In this work we prepared CMCS grafted with a monomer bearing thiosemicarbazide moiety as antimicrobial modifier for carbon paste electrode which can be used in determination of Iron (II) in pharmaceutical and water samples. The modified carbon paste electrode (MCPE) considered a promising as Iron (II) electrochemical sensor.

2. Experimental

2.1. Instrumentation and chemicals

All potentiometric measurements were performed at 25 ± 1 °C using a digital Hanna pH/mV meter (model 211), scanning electron microscope (SEM) and the energy dispersive X-ray analyzer (EDX), were made in National research center, Egypt. The microanalysis were completed using FT-IR spectra were recorded on a Perkin-Elmer 1650 spectrometer (4000–400 cm^{-1}) in KBr pellets at the Micro analytical Center, Cairo University, Egypt. Silver-silver chloride double-junction reference electrode in conjugation with different ion selective electrodes were used, concentration of iron(II) determined using analytika Jena spectrophotometer (Germany)and ICP–OES PerkinElmer optima 7300DV American.

Graphite fine powder extra pure, Ammonium iron (II) sulfate $[[NH_4]_2Fe\ (SO_4)_2.6H_2O]$ were of analytical grade and purchased from Merck (Germany),o-nitro phenyl-octylether (o-NPOE) was supplied from Fluka. Dioctylphthalate (DOP), 2-florophenyl 2-nitrophenylether (FPNPE), Tricresylphosphate (TCP), dibutylphthalate (DBP) and dioctylsebacate (DOS) were supplied from BDH. Chloride salts of sodium, potassium, zinc, cadmium, cobalt, chromium, manganese, nickel and copper were used as interfering materials which were supplied from El Nasr Company.

Chitosan with a degree of deacetylation of 88% and molecular weight of 2.0 × 105 was purchased from Acros Organics, New Jersey, USA. Potassium persulfate was of analytical grade and was supplied from Merck Chemicals. Other reagents and solvents were of analytical grades from Aldrich and were used as received. 1-Cyanoethanoyl-4-acryloyl thiosemcarbazide (CEATS) was synthesized according to the method described previously [36]. Carboxymethyl chitosan (CMCS) was prepared following the method reported in literatures [44,45].

Table 1
Water samples location.

No. of sample	Type	Location
1	Drinking water	Elhager plant
2	Drinking water	Embaba plant
3	Drinking water	Nekla plant
4	Drinking water	Gziretelwrak plant

2.2. Water and pharmaceutical samples

Water samples from different sources were collected and acidified by nitric acid, and analyzed for Fe(II) ions content by the MCPE and ICP method (Table 1).

Drug samples:

1. Marvit (syrup), each 5 mL contains 9 mg ferrous gluconate, manufactured by Marcyrl Pharmaceutical Industries–ElObour City Cairo-Egypt.
2. Pharovit (syrup), each 100 mL contains 1.04 g ferrous gluconate (equivalent to 120 mg iron), manufactured by Pharaonia pharmaceutical spharopharma new Borg El Arab city Alexandria-A.R.E.

2.3. Preparation of carboxymethyl chitosan-graft-poly(1-cyanoethanoyl-4-acryloyl thiosemcarbazide) copolymers (CMCS-PCEATS)

Calculated amount (0.5 g) of dry carboxymethyl chitosan was dissolved in double-distilled water in a three-necked round-bottom flask, with a 1:50 liquor ratio, followed by the addition of 2.64 g (0.25 mol L^{-1}) of the prepared 1-Cyanoethanoyl-4-acryloyl thiosemicarbazide (monomer). The flask was placed in a thermostat bath at 60 °C. Nitrogen gas was passed for 30 min under stirring to remove the dissolved oxygen. Then 0.4 g ($3 \times 10^{-2}\ \text{mol L}^{-1}$) of potassium persulfate (initiator) was slowly added to the flask to initiate graft copolymerization. After 2 h, the reaction mixture was poured on cold methanol to precipitate the grafted *co*-polymers, Carboxymethyl chitosan-*graft*-poly(1-cyanoethanoyl-4-acryloyl thiosemicarbazide), designated as (CMCS-PCEATS) (Scheme 1). After that, the grafted copolymers were separated by filtration and dried under vacuum at 50 °C until constant weight was reached. Purification of the grafted copolymers from the homopolymer was achieved by extraction of the products with methanol using a soxhlet for 10 h [46]. The grafting percentage was determined from the equation %G = [(W2 − W1)/W1] × 100 where W1 denote the weight of initial carboxymethyl chitosan and W2 denote the grafted copolymers after extraction with methanol, the calculated %G was 20%.

2.4. Preparation of the modified carbon paste electrodes (MCEPs)

Modified carbon paste electrodes (MCPEs) were prepared by thoroughly mixing different amounts of CMCS-PCEATS (5–15 mg), carbon powder (250 mg) and 100 μL plasticizer (TCP, DBP, DOP, DOS, 0-NPOE or FPNPE) in a mortar and the resulted paste was used to fill the electrode body [47]. These sensors were used directly for potentiometric measurements without any preconditioning [48]. A new surface of the paste was obtained by squeezing more out, the surplus paste was wiped out and the freshly exposed surface was polished on a paper until the surface showed shiny appearance.

2.5. Potential measurement

All Electromotive force (EMF) measurements were carried out with the following assembly cell: Ag | AgCl | satd. KCl || sample solution |