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Towards analytical stripes for detection of iron III cations in domestic water using proteinic biopolymers

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ABSTRACT

Two renewable proteinic biopolymers; namely keratin and sericin, were blended, each separately, with poly acrylonitrile (PAN) as a supporter for film formation. The said protein/PAN composite was reacted with potassium thiocyanate in a way which directs the reaction away from thiohydnation mechanism. The resulted proteinium thiocyanate salt was utilized in detection of iron III ion in water through formation of the colored iron III thiocyanate complex which can be detected calorimetrically. The obtained colour depends on the concentration of iron III ion in the tested water sample. Results of this investigation proved that the said protein/PAN composite is an appropriate candidate for detection of iron III ion in water. The mode of interaction between the starting materials after being processed with PAN was monitored by using amino acid analysis, infrared spectroscopy, mass spectrometry, gel electrophoresis, and protein content. Scanning electron microscopy was used to study the surface characteristics of keratin/PAN/KSCN and sericin/PAN/KSCN films as well as their cross sections.

1. Introduction

Typical domestic water contains sensible amounts of pollutants depending primarily on the concentration of the following ions/elements: chlorine, nitrates, iron III, calcium, magnesium, and copper I. Among those species, iron III ion is the most dangerous ones.

European legislation has established a maximum contaminant level at 200 μg/l for iron content in drinking water (The quality of water inte, 1998), and the World Health Organization has fixed a sanitary security limit for iron at 2 ppm (Davison et al., 2005). These values originated from aesthetic reasons for iron (coloration of water).

Iron III ions present in domestic water is usually formed as a result of corrosion of non-galvanized metal pipe lines assisted by acidity of the water, measured as pH, is below 6.5. Moreover, use of Fe III salts as coagulants in water treatment may lead to increased concentrations of iron III ions in treated water.

Excess iron species in drinking water may cause increase in iron content inside blood resulting in damage cells of gastrointestinal tract, preventing them from regulating iron absorption. Humans experience iron toxicity above 20 and 60 ppm is a lethal dose (El-Harbawi et al., 2010).

The need of domestic easily used stripes for detection of iron III ions in tap water necessitates investigations towards this target. Utilization of polluting waste proteinic materials in manufacture of stripes using environmentally acceptable methods is of prime importance from the environmental and economic point of views. Prevention of some diseases which may arise from the presence of pollutants in water is a social demand.

It has been reported recently that proteinic biopolymers; namely keratin and sericin, can be regenerated from waste or invaluable natural materials; viz. coarse wool, feather, hair and degumming effluent (Abou El-Kheir et al., 2016; Mowafi et al., 2013). These biopolymers have many applications in textile and non-textile fields by virtue of their structures which are rich in active niches able to bind with any substrates (Karithikeyan et al., 2007; Allam et al., 2009; Haggag et al., 2009; Padamwar and Pawar, 2004; Kantouch et al., 2012; El-Gabry et al., 2016; Abou Taleb et al., 2018; Abou El-Kheir et al., 2012). The said regenerated proteinic materials, in acidic medium, have the active niches necessary to form salt links with the reagents to be utilized in detection of iron III ions in tap water as shown in the following equations ("P" denotes protein; namely keratin or sericin).

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$$P\_NH_3^+Cl^- + KCSN \rightarrow P\_NH_3^+CNS^- + KCl$$
$$3P\_NH_3^+CNS^- + FeCl_3 \rightarrow 3P - NH_3^+Cl^- + Fe(CNS)_3$$
(Red Colour)

Therefore, the aim of this research work is to develop analytical stripes based on the regenerated proteinic material for detection of iron III ions in domestic tap water. Utilization of polluting waste proteinic materials in manufacture of analytical stripes using environmentally acceptable methods is an ecological demand. This work would have also a social impact by virtue of minimizing the harmful effect that may arise from using tap water containing the aforementioned pollutants.

2. Experimental

2.1. Materials and reagents

Raw silk yarns from Chinese silkworm *Bombyx mori* were used in this study. Coarse wool waste was collected from a local small enterprise. All chemical used in this study were of laboratory grade and used without further purification.

2.2. Methods

2.2.1. Extraction of sericin

Sericin powder was obtained from degumming effluent of raw silk by adjusting the pH of the solution around the isoelectric point of sericin (Abou El-Kheir et al., 2016).

2.2.2. Extraction of keratin

Keratin was extracted from coarse wool waste (5%, w/v) according to the method reported by El-Sayed*et. al* (Abou El-Kheir et al., 2012). The obtained soluble keratin (40% of the starting wool mass) was filtered to remove any insoluble matters.

2.2.3. Preparation of keratin/PAN/KCNS composite

- A solution of poly acrylonitrile (PAN) was prepared by dissolving 7 g PAN in 100 ml dimethyl formamide at 70 °C for 15 min.
- A 50% (w/v) potassium thiocyanate solution was added to the keratin solution and stirred well to ensure complete and homogenous mixing.
- After that keratin/potassium thiocyanate solution was spread into Petri dish containing the soluble poly acrylonitrile PAN (which acts as a coagulating bath for PAN) with a ratio (2:1; respectively). Poly acrylonitrile was used as a supporter for keratin film.
- Keratin/KCNS/PAN film was formed through continuous shacking for 1 h to assure complete homogeneity between the film ingredients.
- Finally, the formed composite film was washed thoroughly with running water to ensure removal of any residual chemicals from the surface of the formed film, and air-dried overnight.

2.2.4. Preparation of sericin/PAN/KCNS composite

Sericin/PAN/KSCN film was prepared in a similar way to that of keratin/PAN/KSCN one using a sericin solution (5% w/v) obtained from degumming process.

2.3. Analyses

2.3.1. Colorimetric determination of iron III ions

Aqueous solutions of different concentrations of Fe^{+3} ions (5–100 ppm) were prepared. A stripe of the prepared films (about 1×4 cm) was immersed in each solution of iron III ion and left for 2 min. The obtained red colour of $Fe(SCN)_3$was determined by measuring its absorbance at λ_{max} 540 nm.

2.3.2. Amino acid analysis (AAA)

Wool fleece, sericin, keratin/PAN/KSCN, and sericin/PAN/KSCN composite were prepared for amino acid analysis by hydrolysis in 6 N hydrochloric acid. The amino acid composition of the dry hydrolysate was then determined on an SYKAM (S 7130 Amino Acid Reagent Organizer), Germany, (test method AOAC, 2012).

2.3.3. Infrared spectroscopy

Infrared spectroscopy was carried out for keratin, sericin, as well as their composite with PAN in presence of potassium thiocyanate on Nexus 670 Fourier transform infrared spectrometer (Nicolet, USA).

2.3.4. Liquid chromatography mass spectrometry

The molecular mass of the extracted soluble keratin was determined by electro spray ionization (ESI) on the negative mode, LC MS, LCQ Advantage MAX (Thermo electron Corporation, USA).

2.3.5. Gel filtration chromatography

In a typical experiment, the molecular mass of sericin obtained by degumming of raw natural silk as well as keratin extracted from wool fleece, was determined by gel filtration chromatography according to Andrews' method (Andrews, 1964).

2.3.6. Protein contents

The protein content in the extracted keratin and sercin was determined using Bradford reagent according to the method described elsewhere (Bradford, 1974).

2.3.7. Scanning electron microscopy

The scanning electron microscopy was used to study the topographical features of keratin/PAN/KSCN as well as sericin/PAN/KSCN films. The samples were mounted on aluminium stubs, and sputter coated with gold in an S150A sputter (coated Edward, UK), and examined by ZEISS LEO 1530 Gemini Optics Lens Scanning Electron Microscope (SEM) with 30 KV scanning voltage.

3. Results and discussion

In our previous studies, keratin-based composites were supported by polyvinyl alcohol (PAV) to be appropriately casted into film (Mowafi et al., 2013; Abou El-Kheir et al., 2012). However, the hygroscopic nature of potassium thiocyanate makes sericin/PVA/KSCN or keratin/PVA/KSCN composite deliquescent and impossible to be casted into film with a considerable shelf time (Figs. 1 and 2).

3.1. Colorimetric determination of iron III ions

Water samples containing various concentrations of aqueous solutions of iron III ion (5, 10, 50, and 100 ppm) were prepared. Keratin/PAN/KSCN or sericin/PAN/KSCN film was used to detect iron III ion in the prepared samples to assign the minimum detectable Fe^{+3}ion concentration by the said composites. Due to the stability of the formed red colour on the film for only few seconds, we adopt measuring the absorbance of the colored solution instead of measuring the colour intensity of the colored film because the latter method is more technically feasible.

Results of this investigation, summarized in Table 1, revealed that as the concentration of iron III cation in the tested samples increases from 5 to 100 ppm, the colour intensity of iron III