Development of Screen-Printed Conductive Ink Based on Biopolymers

Samar A. Abdelaziz[1], Nasser Y. Mostafa[1*] and Kholoud M. Abou El-Nour[1]

[1]Chemistry Department, Faculty of Science, Suez Canal University, Ismailia, Egypt

Received: *1/11/2023*

Abstract: Plant-derived biopolymers, also known as natural polymers, have been extensively studied for sustainable and eco-friendly technologies. This research paper explores the extraction, characterization, and application of biopolymer carrageenan in screen-printed conductive ink formulation. Carrageenan was extracted from red algae (Rhodophysea). Conductive inks fabricated from graphite as a conductive agent and carrageenan with carboxymethyl cellulose as adhesives. The use of carrageenan enhances the conductivity of the produced ink with respect to carboxymethyl cellulose. The high conductivity of carrageenan based conductive ink is due to the amorphous structure of carrageenan and the presence of sulfate groups in its chain structure.

Keywords: Conductive ink; carrageenan; electrical resistivity; extraction.

INTRODUCTION

In the rapidly evolving landscape of electronic devices and printed electronics, the development of sustainable and environmentally friendly conductive inks has emerged as a critical area of research and innovation (Bixler, Johndro et al. 2001, Ohfuji, Sato et al. 2004). Traditional conductive inks, often based on metallic nanoparticles, pose environmental concerns due to their non-biodegradable nature and energy-intensive manufacturing processes. In response to these challenges, researchers have been exploring alternative materials derived from renewable sources, such as biopolymers, to create conductive inks that are both eco-friendly and high-performing (Matsuura, Yamawaki et al. 2013). A wide range of polysaccharides, such as alginic acid and alginates, carrageenans and agar, laminarans, fucoidans, ulvans, and derivatives, make up the cell walls of algae. These polysaccharides may serve as the structure and the storage components in green, brown, and red seaweed (Arunkumar 2017). Additionally, oligosaccharides obtained by depolymerizing seaweed polysaccharides also induce protection against viral, fungal, and bacterial infections in plants (Boulho, Marty et al. 2017). Alginic acids have linear molecules built up of different blocks of two monomeric units, whereas some algal polysaccharides, such as sulfated galactans of red algae or ulvans of green algae, have linear backbones containing disaccharides repeating units. Sulfated polysaccharides include carrageenan and agar from red algae, alginate, fucan, and laminarinan from brown algae and cellulose and ulvan from green algae (Borlongan, Terada et al. 2020) . Red seaweed cell walls mostly consist of a group of molecules called carrageenan, which are linear polysaccharide chains with sulfate half-esters connected to their sugar unit. According to the level of sulfation, there are three general forms: kappa, lambda, and iota. While lambda carrageenan has three sulfate groups per disaccharide unit, kappa and iota carrageenan only have one or two sulfate groups per disaccharide unit and anhydrogalactose residue, respectively (Stortz and Cerezo 1993).

In the current paper, carrageenan was extracted from red algae (Rhodophysea) and used for the formulation of conductive inks for screen-printed electrodes. The extracted carrageenan biopolymer was elucidated with Fourier transform infrared (FTIR). This investigation study contributes to the ongoing discourse surrounding sustainable materials in the electronics industry, paving the way for a greener and more eco-conscious future.

MATERIALS AND METHODS

1.Extraction of carrageenan: Red algae, Rhodophysea, were collected from Hurgada, Red Sea, Egypt. The algae were cleaned with clean sea water to remove any impurities. Following delivery to lab, the algae soaked in tap water for 2 hours. A sample of 10g of previously dried algae was pulverized in a blender after being soaked in (800 mL) of deionized water for an hour. This mixture was then added to 1 L of deionized water, heated between 80 and 85°C for 2 hours, and coarser filtration was done using cotton clothes that had been washed several times in ethanol. The concentrated extract that resulted from this process was then precipitated with 95% ethanol (1:3 v/v) and filtered once more using filter paper. As seen in Fig. (1), the extracted carrageenan gel and the freeze-dried sample.

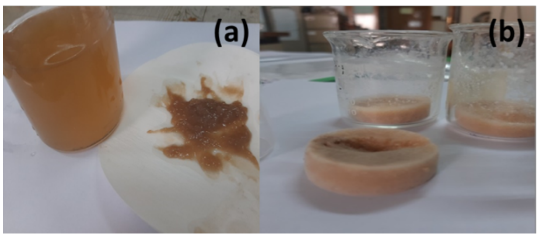

Fig. (1): Extracted carrageenan gel and freeze-dried sample

2.Preparation of carrageenan-based carbon inks: Carrageenan was employed as the polymeric base in the formulation procedure. To find the best ink formulation, we systematically varied the graphite/carrageenan ratios. We found that ink with graphite: carrageenan (80:20) is the best one with respect to low resistivity. Carboxymethyl cellulose is commonly used in the formulation of commercial conductive inks. Thus, carrageenan ink was compared to carboxymethyl cellulose based ink.

*Corresponding author e-mail: nmost69@yahoo.com

3. Fabrication of screen-printed electrode: Using a piece of plastic with dimensions of 3 to 4 cm in height and 1 cm in diameter for the working electrode stamp, a hand-made stamp was created for the working electrode to produce the screen-printed electrode on glass slide, as shown in Fig. (2).

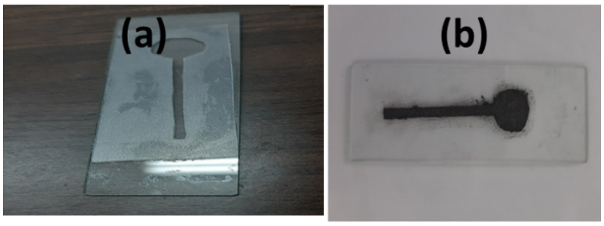

Fig. (2): Fabrication of screen-printed electrode

4. Characterization: Sheet resistance of the carbon ink was measured using the four-point method, as shown in Fig. 3. The 4-point probe with tip distance of 1.2 mm was used with a digital multimeter. Sheet resistances are shown as measured and, to better indicate the relative performance of the inks, resistivities were calculated as the product of sheet resistance and ink film thickness. A total of 5 measurements were taken for each ink type. Calculate the electrical resistivity (ρ) of the carbon ink using the following formula:

$$\rho = 2\pi s \frac{V}{I} \ (\Omega.cm)$$

where V is the measured voltage drop between the two inner probes, I is the current flowing through the outer pair of probes and s is the probe spacing between the two probes.

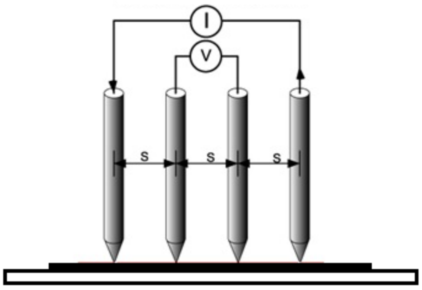

Fig. (3): The 4-point probe with tip

ATR- FTIR measurements were carried out using attenuated total reflection Fourier transform infrared (ATR-FTIR) Spectrometer (Bruker, Germany, Alpha-P). Each of the spectra was collected in the range 4,000-400 cm-1 at 2 cm-1 resolution.

RESULTS AND DISCUSSION

1. Carrageenan extraction characterization: The quantity of carrageenan extract and the carrageenan yields (%) were determined according to the formula: **(**Yield = (Wc/Wds).100 **)** Where, Wc is the carrageenan extract weight in grams and Wds is dry algae weight (g) used for extraction. The carrageenan yield from Rhodophysea species was 26% of the total weight of the algae. The extraction process involves the separation of carrageenan from other components of seaweed, such as cellulose, proteins, and salts. We notice that water extracted carrageenan has higher gel strength and better than alkaline extracted carrageenan in paste formation and smoother. So based on carrageenan yield and gel strength, water extracted carrageenan was selected for carbon paste formulations.

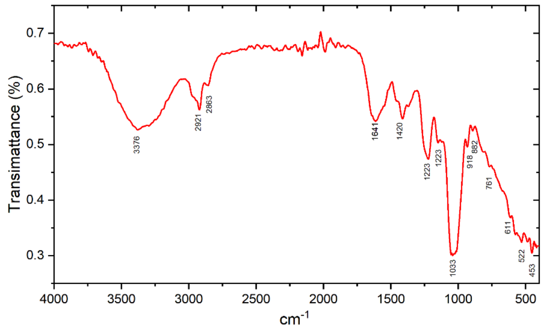

Fig. (4): FTIR spectra of carrageenan

FTIR spectroscopy is a valuable tool for biopolymer analysis elucidating the function groups. The FTIR spectra of water extracted carrageenan is shown in Fig. 4. The peaks observed at 840 to 850 cm^{-1} indicated that the carrageenan is k-type [8], which is assigned to d-galactose-4-sulfphate. A broad absorption peak showed at 3283 cm^{-1}, indicating the OH stretching mode. Absorption peaks observed at 1223 cm^{-1} at all types of carrageenan indicated the presence of sulfate ester. The broad band around 3375 cm^{-1} is attributed to the stretching vibration of hydroxyl (OH) groups, which are abundant in Carrageenan due to its polysaccharide structure. The band around 2921 and 2863 cm^{-1} is attributed to the stretching vibration of aliphatic CH groups, which are primarily found in the galactose and 3,6-anhydrogalactose components of Carrageenan. The bands around 1632-1614 cm^{-1} are attributed to the stretching vibration of carbonyl (C=O) groups, which are present in the galactose and 3,6-anhydrogalactose rings. The band around 1420 – 1413 cm^{-1} is attributed to the bending vibration of CH_2 groups, which are found in the galactose and 3,6-anhydrogalactose components. The band around 1223 cm^{-1} is attributed to the stretching vibration of C-O-C groups. Fig. (5) shows SEM microstructure of water extracted carrageenan and calcium hydroxide extracted carrageenan. The microstructure of water extracted carrageenan shows fibers with cotton-like shape and high porosity.

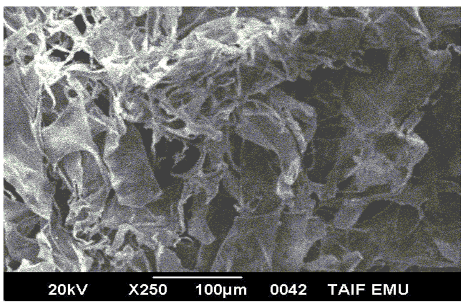

Fig. (5): SEM micrographs of lyophilized extracted carrageenan

2.Conductive inks formulation: Table (1) shows various inks with 80% graphite and 20% biopolymers (carboxymethyl cellulose or carrageenan). According to Table 1, when carrageenan content increased, the adhesion to the glass substrate increases. Ink prepared with carboxymethyl cellulose as biopolymer (Ink1) shows electrical resistivity of 0.052 Ω.cm. The electrical resistivity decreases to 0.034 Ω.cm by replacing half the carboxymethyl cellulose with carrageenan (Ink2) and decreases to 0.012 Ω.cm with complete replacement of carboxymethyl cellulose with carrageenan (Ink3). The high conductivity of carrageenan conductive ink is due to the amorphous structure of carrageenan and the presence of sulfate groups in its chain structure (Raman, Gurikov et al. 2017)]. These results demonstrated that the third ink (Ink3), which included 80:20 ratio of graphite to carrageenan, was the best for printing since it had the best conductivity, the highest adherence, and the best distribution on the glass slide. Therefore, screen-printed electrodes were successively printed using Ink3 as shown Fig. (6).

Table (1): Physical properties of inks based on carrageenan and carboxymethyl cellulose

Ink	Formulation %			Adhesion	Spread	Resistivity.
	Graphite	CMC	CAR			(Ω cm)
Ink1	80	20	0	Weak	good	0.052
Ink2	80	10	10	Good	good	0.034
Ink3	80	0	20	Best	Best	0.012

*CMC; carboxymethyl cellulose, CAR; carrageenan

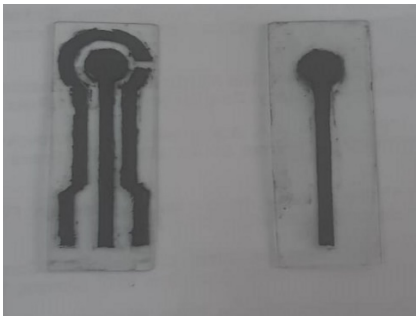

Fig. (6): Different screen-printed electrode based on carrageenan biopolymer

CONCLUSION

In this work, we have demonstrated the potential use of carrageenan to produce water-based conductive inks with a low electrical resistivity (0.012 Ω.cm). This ink is useful for the fabrication of screen-printed electrodes. Conductive inks fabricated from graphite as a conductive agent and Carrageenan with carboxymethyl cellulose as adhesives. The use of Carrageenan enhances the conductivity of the produced ink with respect to carboxymethyl cellulose. The high conductivity of Carrageenan based conductive ink is due to the amorphous structure of Carrageenan and the presence of sulfate groups in its chain structure. Conductive ink fabricated using Carrageenan can open new opportunities to develop the future generation of green materials for printed electronics and sensors.

ACKNOWLEDGMENTS

We acknowledgments Suez Canal University for support this research.

REFERENCES

Arunkumar, K. (2017). Extraction, isolation, and characterization of alginate. Industrial Applications of Marine Biopolymers: 19-36.

Bixler, H. J., K. Johndro and R. Falshaw (2001). "Kappa-2 carrageenan: Structure and performance of commercial extracts II. Performance in two simulated dairy applications." Food Hydrocolloids 15(4-6): 619-630.

Borlongan, I. A., R. Terada and A. Hurtado (2020). "Concise review of the genus Meristotheca (Rhodophyta: Solieriaceae)." Journal of Applied Phycology.

Boulho, R., C. Marty, Y. Freile-Pelegrín, D. Robledo, N. Bourgougnon and G. Bedoux (2017). "Antiherpetic (HSV-1) activity of carrageenans from the red seaweed Solieria chordalis (Rhodophyta, Gigartinales) extracted by microwave-assisted extraction (MAE)." Journal of Applied Phycology 29(5): 2219-2228.

Matsuura, H., Y. Yamawaki, K. Sasaki and S. Uchiyama (2013). "Coulometric determination of dissolved hydrogen with a multielectrolytic modified carbon felt electrode-based sensor." Journal of Environmental Sciences (China) 25(6): 1077-1082.

Ohfuji, K., N. Sato, N. Hamada-Sato, T. Kobayashi, C. Imada, H. Okuma and E. Watanabe (2004). "Construction of a glucose sensor based on a screen-printed electrode and a novel mediator pyocyanin from Pseudomonas aeruginosa." Biosensors and Bioelectronics 19(10): 1237-1244.

Raman, S. P., P. Gurikov and I. Smirnova (2017). "Hybrid alginate based aerogels by carbon dioxide induced gelation: Novel technique for multiple applications." Journal of Supercritical Fluids 106.

Setijawati, D., H. Nursyam and H. Salis (2018). Carrageenan :the difference between PNG and KCL gel precipitation method as Lactobacillus acidophilus encapsulation material. IOP Conference Series: Earth and Environmental Science.

Stortz, C. A. and A. S. Cerezo (1993). "The systems of carrageenans from cystocarpic and tetrasporic stages from Iridaea undulosa: fractionation with potassium chloride and methylation analysis of the fractions." Carbohydrate Research 242(C): 217-227.

تطوير حبر موصل مطبوع معتمد على بوليمرات حيويه

[1] سمر أ. عبد العزيز, [1*] ناصر مصطفى و [1] خلود ابو النور

[1] قسم الكيمياء, كليه العلوم, جامعه قناه السويس, الاسماعيليه , مصر

تعتبر البوليمرات الحيويه المشتقه من النباتات مصدر مهم للتكنولوجيا الصديقه للبيئه , فى هذا البحث تم دراسه استخلاص، تحليل خصائص وتطبيقات الكارجينان فى عمل حبر موصل مطبوع . تم استخلاص الكارجينان من الطحالب الحمراء , ولعمل الحبر الموصل تم استخدام الجرافيت كعامل موصل واستخدام الكارجينان ذو التوصيليه العاليه بسبب هيكله الغير متبلور ووجود مجموعات الكبريتات فى تركيبه الكيميائى. بعد استخلاص ماده الكارجينان من الطحالب الحمراء بأكثر من طريقه , تم عمل أحبار بمعدلات مختلفه من الكارجينان والجرافيت ومقارنه خصائص كل حبر على حدى . بعد معرفه افضل معدل لعمل الحبر من الكارجينان والجرافيت والذى هو 80:20 على التوالى والذى كان يتميز بأقل مقاومه وافضل توصيليه ، تم استخدام هذا الحبر لطباعه الكترود عامل على سطح البلاستيك. تم استخدام ورقه من البلاستيك فى طباعه الحبر يدويا بارتفاع من 3 الى 4 سم وقطر 1 سم فى القطب العامل. بعد طباعه الحبر على البلاستيك تم دراسه خصائص الحبر المطبوع باستخدام الاشعه تحت الحمراء والتى من خلالها تم معرفه نوع الكارجينان المستخدم والذى كان من النوع كابا ، ايضا تم استخدام المجهر الالكترونى الماسح والذى اوضح التركيب النفاذى الشبيه بالقطن للكارجينان .

الكلمات المفتاحية: حبر موصل ، كارجينان ، المقاومه الكهربيه ،الاستخلاص