Makara Journal of Technology

Volume 24 | Issue 3 Article 2

12-3-2020

Influence of Lithium Bromide on Electrical Properties in Bio-based Polymer Electrolytes

Ahmad Faizrin Fuzlin
Ionic Materials Team, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Pahang 26300, Malaysia

Bouchta Sahraoui
Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, ANGERS cedex 49045, France

Ahmad Salihin Samsudin
Ionic Materials Team, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Pahang 26300, Malaysia, ahmadsalihin@ump.edu.my

Follow this and additional works at: https://scholarhub.ui.ac.id/mjt

Part of the Chemical Engineering Commons, Civil Engineering Commons, Computer Engineering Commons, Electrical and Electronics Commons, Metallurgy Commons, Ocean Engineering Commons, and the Structural Engineering Commons

Recommended Citation

Fuzlin, Ahmad Faizrin; Sahraoui, Bouchta; and Samsudin, Ahmad Salihin (2020) "Influence of Lithium Bromide on Electrical Properties in Bio-based Polymer Electrolytes," *Makara Journal of Technology*: Vol. 24: Iss. 3, Article 2.
DOI: 10.7454/mst.v24i3.3836
Available at: https://scholarhub.ui.ac.id/mjt/vol24/iss3/2

This Article is brought to you for free and open access by the Universitas Indonesia at UI Scholars Hub. It has been accepted for inclusion in Makara Journal of Technology by an authorized editor of UI Scholars Hub.

Makara J. Technol. 24/3 (2020), 106–110
doi: 10.7454/mst.v24i3.3836

Influence of Lithium Bromide on Electrical Properties in Bio-based Polymer Electrolytes

Ahmad Faizrin Fuzlin[1], Bouchta Sahraoui[2], and Ahmad Salihin Samsudin[1*]

1. Ionic Materials Team, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang,
Pahang 26300, Malaysia
2. Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, ANGERS cedex 49045, France

E-mail: ahmadsalihin@ump.edu.my

Abstract

This research presents the influence of lithium bromide (LiBr) on the electrical properties of alginate in bio-based polymer electrolytes (BBPEs) system. Bio-based alginate was prepared using the solution casting technique with various LiBr compositions. The ionic conductivity and electrical properties of the prepared BBPEs samples were studied using electrical impedance spectroscopy over a frequency range of 50 Hz–1 MHz. A maximum ionic conductivity of 7.46×10^{-5} S cm^{-1} was obtained for a sample containing 15 wt. % lithium bromide-doped alginate BBPEs at ambient temperature (303 K). The electrical analysis revealed that the most conductive sample based on alginate-LiBr BBPEs has optimum dielectric constant and loss, which significantly increases as temperature increases. The dielectric properties show that all alginate-LiBr BBPEs are in non-Debye behavior conditions, where no single relaxation occurs in the present system.

Abstrak

Pengaruh Litium Bromida pada Sifat-sifat Listrik di dalam Elektrolit Polimer Berbasis Hayati. Riset ini menampilkan pengaruh litium bromida (LiBr) pada sifat-sifat listrik alginat di dalam sistem elektrolit polimer berbasis hayati (BBPEs). Alginat berbasis hayati dibuat dengan menggunakan teknik penuangan larutan dengan berbagai komposisi LiBr. Konduktivitas ion dan sifat-sifat listrik dari sampel-sampel BBPEs yang dibuat dikaji dengan menggunakan spektroskopi impedansi listrik pada suatu kisaran frekuensi 50 Hz–1 MHz. Konduktivitas ion maksimum sebesar 7,46 × 10^{-5} S cm^{-1} diperoleh untuk suatu sampel yang mengandung 15% berat alginat BBPEs yang didoping dengan litium bromida pada temperatur lingkungan sekitar (303 K). Analisis listrik mengungkapkan bahwa sampel yang paling konduktif berdasarkan pada alginat-LiBr BBPEs memiliki konstanta dielektrik optimum dan kerugian, yang meningkat secara signifikan seiring dengan peningkatan temperatur. Sifat-sifat dielektrik menunjukkan bahwa semua alginat-LiBr BBPEs berada dalam kondisi perilaku non-Debye, di mana di dalam sistem ini tidak terjadi relaksasi sama sekali.

Keywords: bio-based polymer, ionic conductivity, electrical analysis, dielectric properties

1. Introduction

Lithium-ion batteries (LIBs) have been widely used and fabricated for commercial purposes in portable electronic devices such as cameras, smartphones, and laptops. Because of their high electrochemical properties, low cost, long life cycle, and good energy density [1]. LIBs are used as power sources. The electrolyte plays an important role in maintaining performance in LIBs. However, some drawbacks arise when the energy devices are constructed using conventional liquid electrolytes [2]. To overcome the problem of leakage, non-environmentally friendly, hazardous, and harmful bio-based polymer electrolytes (BBPEs) have been introduced.

Several bio-based materials such as carboxymethyl cellulose (CMC), chitosan, starch, and carrageenan [3] have been discovered in recent years. BBPEs act as solid-state electrolytes, which have been found to contain solvent-free and non-leakage elements. In this regard, researchers have been focusing on developing biopolymer electrolytes from a combination of polymers and suitable ionic dopants. In this study, alginate, which acts as a biopolymer (host), has been used. Alginate is an anionic polymer, extracted from the cell walls of brown seaweed, with linear binary copolymers of (1-4)-linked β-d-mannuronic acid (M) and α-l-guluronic acid (G) monomers, constituting M-, G-, and MG-sequential block structure [4]. Good adhesive properties and low toxicity make it suitable for industries such as the food industry, pharmaceutical, packaging, and textiles.

To enhance the potential of the alginate polymer for electrochemical cell applications, lithium bromide (LiBr) was introduced as a dopant system as it can enhance the performance of BBPEs. Lithium-based ionic salts are preferred owing to the small size of lithium ions (Li^+), which provides a high gravimetric coulombic density [5]. The weak coordination in the presence of salt LiBr makes the incorporation of the ion with the alginate polymer possible, which leads to an increase in ionic conduction [6]. The potential of LiBr was reported by Arockia Mary *et al*. [7]. They used K-carrageenan as a polymer host, achieving an optimum ionic conductivity of 3.43×10^{-3} S cm^{-1}.

In this work, BBPEs based on alginate (host) incorporated with lithium bromide (ionic dopant) using the solution casting technique have been used. This research aims to study the electrical properties of BBPEs systems. The prepared sample of the BBPEs system with various compositions of LiBr was investigated using Electrical Impedance Spectroscopy (EIS).

2. Methods

Preparation of the BBPEs system. In this study, alginate polymer (Shaanxi Orient Co.) and LiBr (Sigma Aldrich) have been used for synthesizing BBPEs. Using the solution casting technique, alginate was dissolved in distilled water (solvent), followed by the addition of LiBr (5–25 wt. %). The mixture was continuously stirred at ambient temperature until the homogenous solution was formed. The solution was cast into a petridish and left to dry in an oven at 60 ˚C for 24 hours until transparent films were attained. The film was further dried in desiccators filled with silica gel to remove trapped water in the BBPEs system. The composition of LiBr and sample classification for the BBPEs system are tabulated in Table 1.

Characterization of the BBPEs system. The ionic conductivity of the prepared BBPEs sample was analyzed using HIOKI 3532-50 LCR Hi-TESTER with frequencies ranging from 50 Hz to 1 MHz. The BBPEs film placed between two stainless steel current collectors and tested at a temperature range from 303 K to 343 K. The thickness of the BBPEs system was measured using a digital thickness gauge (DML3032). The ionic conductivity of the film-based alginate-LiBr BBPEs system was calculated using the following equation:

$$\sigma = \frac{d}{R_b A} \tag{1}$$

where d is the thickness of the electrolytes, A is the contact area (cm^2), and R_b is the bulk resistance of the BBPEs system obtained from Cole-Cole plot.

Table 1. Designation for Alginate-LiBr of BBPEs System

Designation	LiBr composition (wt. %)
ALiB -1	5
ALiB -2	10
ALiB -3	15
ALiB -4	20
ALiB -5	25

Electrical study. Electrical analysis, comprising dielectric constant and loss, provides important insights on the conduction behavior of BBPEs systems. Dielectric constant is a measure of the accumulated charge in biopolymer-salts complexes whereas dielectric loss represents the energy losses caused by the movement of ions when the polarity of the electric field reverses rapidly. The dielectric constant ε_r (real part of complex permittivity) and dielectric loss ε_i (imaginary part of complex permittivity) can be calculated using the following equation:

$$\varepsilon_r = \frac{Z_i}{\omega C_o({Z_r}^2 + {Z_i}^2)} \tag{2}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o({Z_r}^2 + {Z_i}^2)} \tag{3}$$

where Z_r and Z_i are the real and imaginary impedances, respectively, obtained from Cole-Cole plot; C_o is the vacuum capacitance ($C_o = \varepsilon_o A/d$); d is the thickness of the BBPEs film; A is the surface area of sample in contact; ε_o is the vacuum permittivity; and ω is the angular frequency ($\omega = 2\pi f$).

Modulus study. Electrical modulus study was used to determine the relaxation and capacitive mechanism by suppressing the polarization effect of the electrode polarization. The real part M_r and the imaginary part M_i of electrical modulus were calculated using the following equation:

$$M_r = \frac{\varepsilon_r}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{5}$$

$$M_i = \frac{\varepsilon_i}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{6}$$

3. Results and Discussion

Conductivity study. The ionic conductivity derived from the EIS data was plotted against the frequency

(Figure 1). The incorporation of LiBr dopants into the alginate improved the ionic conductivity of BBPEs. Generally, a typical ionic conductivity spectrum as a function of frequency has three regions: (i) low frequency dependent region, (ii) medium frequency plateau, and (iii) high frequency dependent region [8]. It can be observed that the conductance spectra for present alginate-LiBr BBPEs comprise three regions. The low-frequency dispersion region (where an increase in conductivity is observed with increase in frequency) is attributed to space charge polarization at the electrode–electrolyte interface [9]. The intermediate frequency independent plateau region corresponds to the bulk conductivity or *dc* conductivity σ_{dc} of the complex BBPEs system [10]. In contrast, the higher frequency dispersion region (above log 6 Hz), corresponding to the bulk relaxation process, is formed due to the coulombic interaction of the charge carrier and disorder within the structure; hence, all the samples exhibited different patterns [11]. This could be attributed to the non-Debye behavior observed in the BBPEs samples.

The calculated *dc* conductivity value from the conductance spectra showed good agreement, where ALiB-3 achieved the optimum conductivity value at 7.46 x 10^{-5} S cm^{-1} for a sample containing 15 wt. % of LiBr (ALiB-3). Upon addition of LiBr above 15 wt. %, it shows a decrease in ionic conductivity, which could be due to the neutral aggregation of the ions re-associated, thus leading to the formation of ion clusters, as reported other researchers [12], [13].

Electrical study. Dielectric properties can vary in different types of polymer electrolyte systems due to several factors, including frequency of applied electrical field, temperature, structural characteristics, and other external factors [14]. It is clear from Figures 2 that the values of ε_r and ε_i are very high in the low-frequency region due to the polarization effect, which confirms non-Debye dependence [15], [16]. At high frequencies, the high periodic reversal of the applied field explained that there is no charge build-up at the interface between the sample and the electrode (space charge) and also no excess ion diffusion in the field path, which decreases the values of ε_r and ε_i due to reduction in the polarization effect by the charge accumulated [17], [18]. The value for both dielectrics has been experimentally found to be higher for ALiB-3, which can be attributed to the increment in the charge carrier concentration that lead to the increase in conductivity. Thus, it is found to be similar with previous studies that have used $LiNO_3$ as dopants in polymer electrolytes [5].

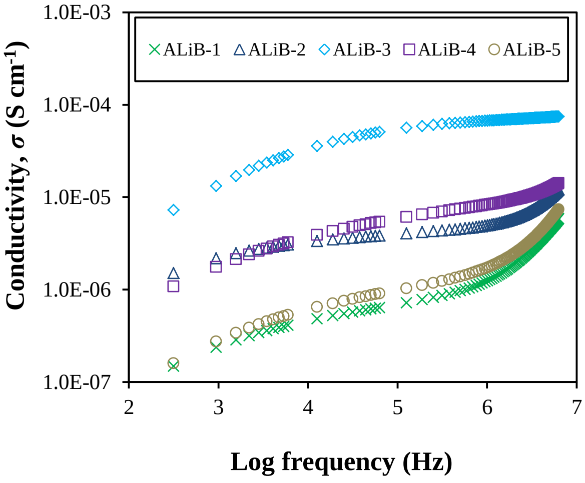
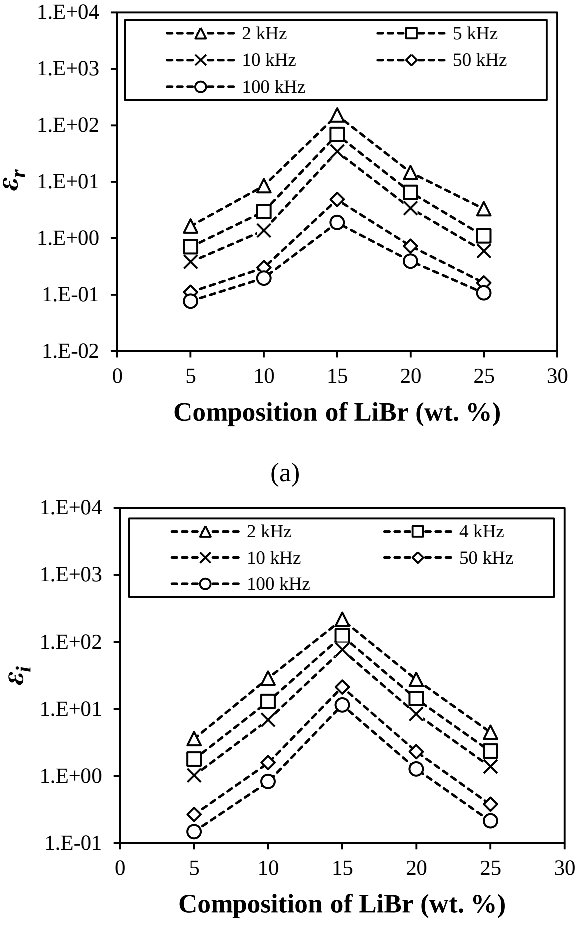


Figure 1. **Frequency Dependence Conductivity for the samples at the different composition of LiBr**

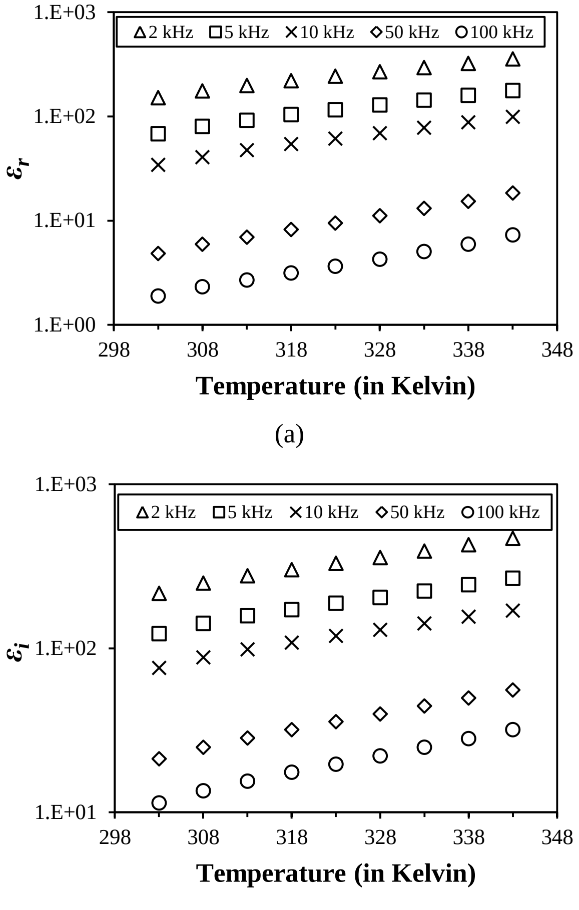
Figures 3 (a) and (b) depict the temperature dependence of ε_r and ε_i for the most conductive sample in the BBPEs system (ALiB-3). It can be observed that both ε_r and ε_i for the most conductive sample increased with increasing temperature, which can be attributed to the migration polarization of the mobile ions. As the temperature increased, the degree of LiBr dissociation



(a)

(b)

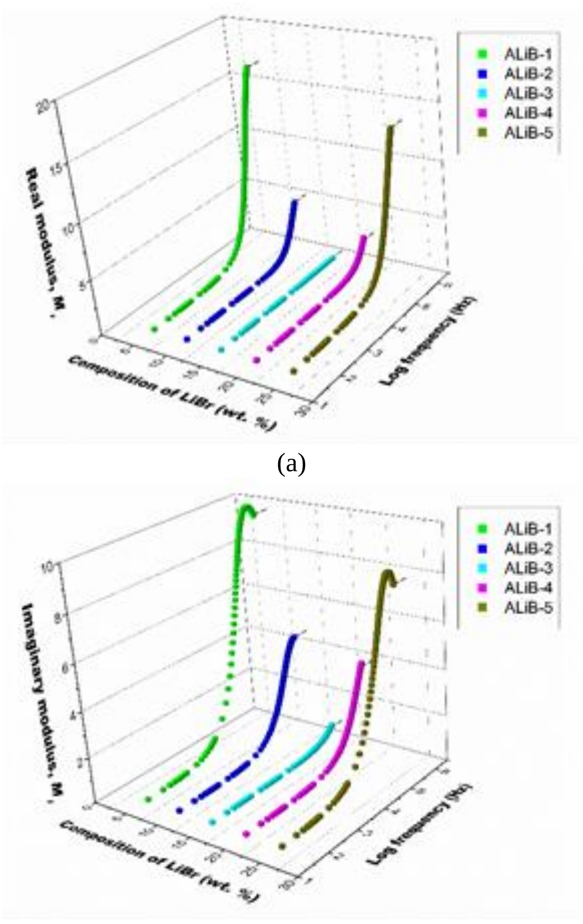
Figure 2. **Dielectric (a) Constant and (b) Loss of Alginate-LiBr BBPEs System at Ambient Temperature**



(a)

(b)

Figure 3. Dielectric (a) Constant (b) for ALiB-3 BBPEs System at Various Temperature



(a)

(b)

Figure 4. Frequency Dependence of (a) Real Modulus and (b) Imaginary Modulus for Alginate-LiBr of BBPEs System at Ambient Temperature

and re-dissociation of ion aggregates increased due to the greater number of free ions or higher charge carrier density, thus enhancing the ionic conductivity to the optimum value in the BBPEs system [17]. A further, more accurate investigation of the dielectric behavior can be achieved using a modulus formalism analysis.

Modulus study. The real and imaginary parts of electrical modulus for the BBPEs at ambient temperature were plotted (Figure 3). Based on Figure 3, both modulus, M_r and M_i increase towards higher frequencies due to the electrode polarization phenomenon [19]. A long tail at low frequencies indicates that a large capacitance may be associated with the electrodes polarization effects used in impedance measurement, which further confirms with the non-Debye behavior in the present sample [20,21]. However, at a higher frequency, ALiB-3 obtained lower M_r and M_i curve due to higher dissociation of LiBr, which lead to an increase in ionic conductivity of the present samples. The curves at higher frequencies may be caused by the bulk effect and decrease in the curve height with the ionic dopant, indicating a plurality of relaxation mechanism [22]. According to Bakar *et al.* (2015) [23], as frequency increases, the modulus part increases due to bulk polarization, which can be differentiated into two elements: (i) electron transfer, (ii) avalanche transit-time. In the present system, bulk effects appeared in the complexes due to electron transfer between host polymer and dopant system. Figure 4(b), shows that the presence of peaks for ALiB-1 and ALiB-5 in the imaginary part of the electrical modulus spectra, believed to be caused by the capacitance behavior and segmental movement, are coupled and build up a peak in the modulus spectra [24]. A similar trend was obtained by Vijaya [25] where the existent peak in M_i spectra was attributed to the long-range ionic movement of ammonium halide in the polymer matrix. The disappearance of the peak for other BBPEs is due to frequency limitation [26].

4. Conclusion

In this work, the electrical properties of BBPEs systems, which are based on alginate doped with various compositions of LiBr prepared using the solution casting method, has been studied. The ionic conductivity of the BBPEs system at ambient temperature proved that LiBr influences the complex ionic conductivity and exhibits an optimum value at 7.46 × 10^{-5} S cm^{-1} for 15 wt. % of LiBr (ALiB-3). The dielectric behavior of the BBPEs system was characterized using complex permittivity (ε^*) and complex electrical modulus (M^*) and exhibits non-Debye behavior, where non-single relaxation of ions was observed in the present work.

References

[1] L. Sampathkumar, P.C. Selvin, S. Selvasekarapandian, P. Perumal, R. Chitra, M. Muthukrishnan, Ion. 25/3 (2019) 1067.

[2] H. Tan, S. Ramesh, C.-W. Liew, Ion. 25 (2019) 4861.

[3] N.M.J. Rasali, Y. Nagao, A.S. Samsudin, Ion. 25 (2019) 641.

[4] M. Fertah, A. Belfkira, M. Taourirte, F. Brouillette, Arab. J. Chem. 10 (2017) S3707.

[5] S. Monisha, T. Mathavan, S. Selvasekarapandian, A.M.F. Benial, Ion. 23/10 (2017) 2697.

[6] B. Chatterjee, N. Kulshrestha, P.N. Gupta, Int. J. Engine. Res. Appl. 5 (2015) 116.

[7] I.A. Mary, S. Selvanayagam, S. Selvasekarapandian, S.R. Srikumar, T. Ponraj, V. Moniha, Ion. (2019) 1.

[8] A. Pawlicka, F.C. Tavares, D.S. Dörr, C.M. Cholant, F. Ely, M.J.L. Santos, C.O. Avellaneda, Electrochim. Acta. 305 (2019) 232.

[9] V. Moniha, M. Alagar, S. Selvasekarapandian, B. Sundaresan, G. Boopathi, J. Non-Cryst. Solids. 481 (2018) 424.

[10] S. Patel,R. Kumar, J. Alloys Compd. 789 (2019) 6.

[11] M. Hema, S. Selvasekerapandian, A. Sakunthala, D. Arunkumar, H. Nithya, Phys. B Condens. Matter. 403/17 (2008) 2740.

[12] N.K. Zainuddin, M.A. Saadiah, A.P.P. Abdul Majeed, A.S. Samsudin, Int. J. Polym. Anal. Charact. 23/4 (2018) 321.

[13] N. Mazuki, Y. Nagao, A.S. Samsudin, Makara J. Tech. 22/3 (2019) 167.

[14] M.A. Saadiah, A.S. Samsudin, IOP Conference Series: Materials Science and Engineering, 2018, p.012045.

[15] V.S. Kumaran, H.M. Ng, S. Ramesh, K. Ramesh, B. Vengadaesvaran, A. Numan, Ion. 24 (2018) 1947.

[16] A.F.A. Fuzlin, N.S. Ismail, Y. Nagao, A.S. Samsudin, Makara J. Tech. 23/1 (2019) 48.

[17] M.S.A. Rani, N.S. Mohamed, M.I.N. Isa, Int. J. Polym. Anal. Charact. 20/6 (2015) 491.

[18] N.M.J. Rasali, S.K. Muzakir, A.S. Samsudin, Makara J. Tech. 21/2 (2017) 65.

[19] N.A.M. Noor, M.I.N. Isa, Adv. Mater. Res. 1107 (2015) 230.

[20] M.I.N. Isa, A.S. Samsudin, Int. J. Polym. Anal. Charact. 22/5 (2017) 447.

[21] A.F. Fuzlin, N.M.J. Rasali, A.S. Samsudin, IOP Conference Series: Materials Science and Engineering, 2018, p.012080.

[22] K.H. Kamarudin, M. Isa, M.I. Nizam, Adv. Mater. Res. 1107 (2015) 236.

[23] N.Y. Bakar, M.N. Hafiza, A.N.A. Bashirah, M.I.N. Isa, Amer. J. Appl. Sci. 12/1 (2015) 40.

[24] H.J. Woo, S.R. Majid, A.K. Arof, Mater. Chem. Phys. 134/2-3 (2012) 755.

[25] N. Vijaya, S. Selvasekarapandian, M. Sornalatha, K.S. Sujithra, S. Monisha, Ion. 23/10 (2017) 2799.

[26] M.H. Hamsan, M.F.Z. Kadir, S.B. Aziz, M.A.S. Azha, S.K. Muzakir, Makara J. Tech. 23/3 (2020) 131.