

## Fourier Transform Infrared Spectroscopy of Porous Zinc with Different Concentration of Potassium Hydroxide in Agar Binder

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**ABSTRACT.** Fourier Transform Infrared (FTIR) is a method to identify the chemical bonding exists in materials. FTIR on porous Zn have been conducted with different concentration of potassium hydroxide solution. Bacto-agar and commercial agar were applied as binder in porous Zn. Both agars show the typical spectra of agar-like galactans under FTIR. The peaks in the range of 400 – 600  $\text{cm}^{-1}$  were attributed to the Zn molecules. Applying different concentration of KOH on porous Zn gave different intensities to the spectra of FTIR for both agars. As KOH concentration increased, the amount of  $\text{OH}^-$  increased resulting the increasing of peak belong to  $\text{OH}^-$  and Zn bonding. Besides, addition of Zn and KOH in agar might not affect the bare Zn.

**Keywords:** FTIR, Porous zinc, Polysaccharide, Agar binder;

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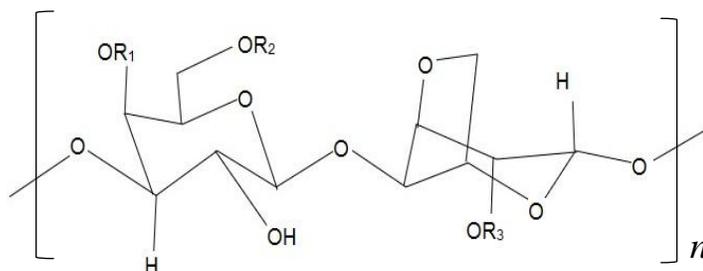
### 1. INTRODUCTION

Agar is one of polysaccharides mixture that is recently getting attention in various applications because of gel strength, gelling and melting temperature as well as having great capability in adhesion with other materials. Properties of good mechanical and steel adhesion that possessed by some polysaccharides lead to the materials being processed in the film form. Moreover, agar is a natural, abundance in raw material and biodegradable sources that makes it easy to reach and safe for environment [1, 2].

This polysaccharide composes of two major fractions, agarose and agaropectin extracted from cell wall from certain seaweeds of the Rhodophyceae class. Agarose is the gelling fraction, composed of repeating alternate units of  $\beta$ -1,3-linked- D-galactose and  $\alpha$ -1,4-linked 3,6-anhydro-L-galactose [3]. Other than that, agaropectin is non-gelling fraction, composed of agarose within range 5% to 8% of sulphate, D-glucuronic acid and small quantities of pyruvic acid. Agarose normally represents bigger fraction than agaropectinin the natural agar.

The processes of polysaccharides modification through chemical reactions, such as etherification, esterification, cross-linking and grafting or physical modification has led to alteration of its gelatinization and pasting behaviour due to introduction of functional group into the polysaccharides molecules [4]. The structural differences between agarose and agaropectin are indicated by substitutions with various functional groups which polymerize into a long chain as Fig. 1 [5]. This situation has interrupted the molecular forces of hydrogen bonds, hence weakening the semi crystalline structure of materials. Besides, the motional freedom of polysaccharides chains in amorphous regions also increases due to poor inter and intra molecular reaction of hydrogen bonds. Previous study stated the morphological and structural properties of porous Zn in agar binder and additives but there is no study on chemical bonding exists after the materials corporation [6, 7]. In this study, porous zinc (Zn) mixed with two different agar (Bacto-agar and commercial agar) binder in

various concentration of potassium hydroxide (KOH) were analysed using FTIR to identify chemical bonds and molecular compositions presence in that materials.



**Fig.1** Structure of agarose and agarpectin are indicated by substitutions with various functional groups at R1, R2 and R3

## 2. MATERIALS AND METHODS

Bacto-agar (Becton Dickinson, USA) commercial agar (BintangEmas), Zn powder (65.38 g/mol, Bendosen) and KOH pellets (ChemAR, System) are the main materials used. 0.3 g of agar was heated in 20 ml of distilled water at 90°C for 10 minutes. Then, the KOH pellets were balanced to get desired concentration as referred in Table 1 and the KOH solution was poured into the cool agar paste. 4.5 g of Zn powder were added into the agar paste. The preparation of porous Zn in agar binder with different concentration of KOH was following the composition as shown as Table 1.

FTIR spectra were evaluated by Thermo Fisher Scientific iZ10 FTIR Spectrometer. The spectrum was recorded between the wave number ranging from 4000 – 400 cm<sup>-1</sup> using 16 scans at a resolution of 4 cm<sup>-1</sup>. The samples were tested by the transmission method. Then the spectra were analysed by using OMNIC software.

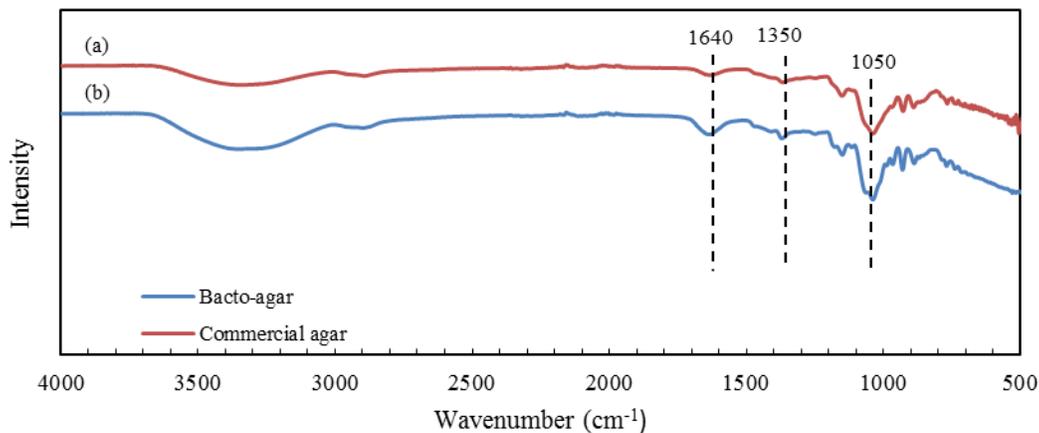
**Table 1** Materials compositions of Zn paste

| KOH, [M] | KOH, [g] | Agar, [g] | Zn powder, [g] | Distilled water, [mL] |
|----------|----------|-----------|----------------|-----------------------|
| 0.01     | 0.01     | 0.30      | 4.50           | 20                    |
| 0.05     | 0.06     | 0.30      | 4.50           | 20                    |
| 0.10     | 0.11     | 0.30      | 4.50           | 20                    |
| 0.15     | 0.17     | 0.30      | 4.50           | 20                    |
| 0.20     | 0.22     | 0.30      | 4.50           | 20                    |

## 3. RESULTS AND DISCUSSION

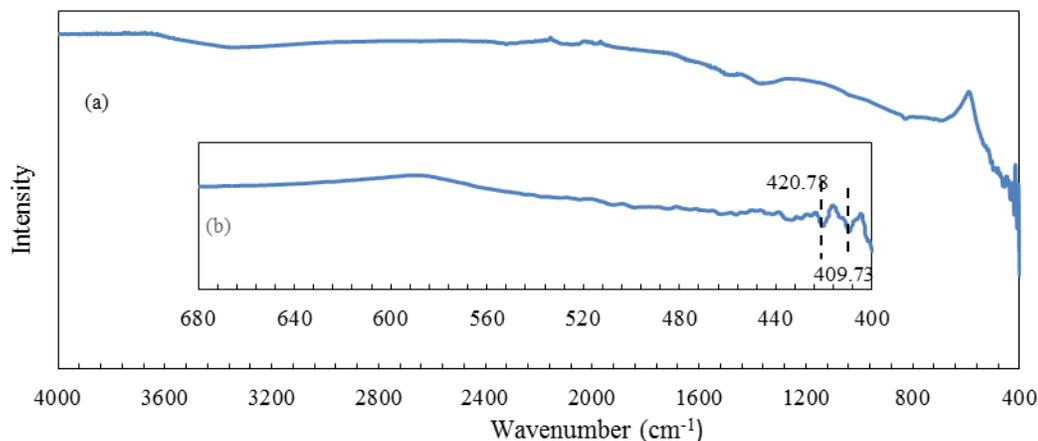
Fig. 2 displays the spectra of commercial agar and Bacto-agar. Fig. 2(a) shows the FTIR spectrum for commercial agar powder. Broad band was observed at 3600 to 3050 cm<sup>-1</sup>. Besides, the obvious sharp peak was indicated at signal 1040 cm<sup>-1</sup>. These peaks are similar to the peaks of Bacto-agar spectrum in Fig. 2(b). The dominant bands appeared at 3600 to 3050 cm<sup>-1</sup> are attributed to stretching of hydroxyl (OH groups). There was a bump at 2925 cm<sup>-1</sup> is associated to chains of C-H bonding and 1350 cm<sup>-1</sup> are assigned to ester sulphate in both polysaccharide [8]. Sharp peak at 1050 cm<sup>-1</sup> of Bacto-agar spectrum also indicates the C-O

stretching group of 3,6-anhydro-galactose [9]. From these finding, both agar show the typical spectra of agar-like galactans [10].



**Fig. 2** FTIR spectra of (a) commercial and (b) Bacto-agar

In comparison between spectrum band  $1040\text{ cm}^{-1}$  of commercial agar and Bacto-agar, commercial agar displays lower intensity than Bacto-agar which indicates that C-O bonding in commercial agar is weaker than Bacto-agar. The spectra appeared at  $1640\text{ cm}^{-1}$  is due to the stretching vibration of the conjugated peptide bond formation by amide (NH) and acetone groups. In this wavelength, commercial agar gave lower intensity than Bacto-agar. On the other hand, the absorption band at  $886\text{ cm}^{-1}$  is due to C-H stretching residual carbon of  $\beta$ -galactose [8]. There were difference in intensity as Bacto-agar demonstrated higher intensity than commercial agar at peaks of  $3600 - 3050$ ,  $2925$ ,  $1640$  and  $1040\text{ cm}^{-1}$  that indicates a Bacto-agar as having stronger chemical bond. However, the spectra pattern of FTIR for commercial agar almost similar to the Bacto-agar suggesting that there is no significant chemical bond formed between commercial agar powders.

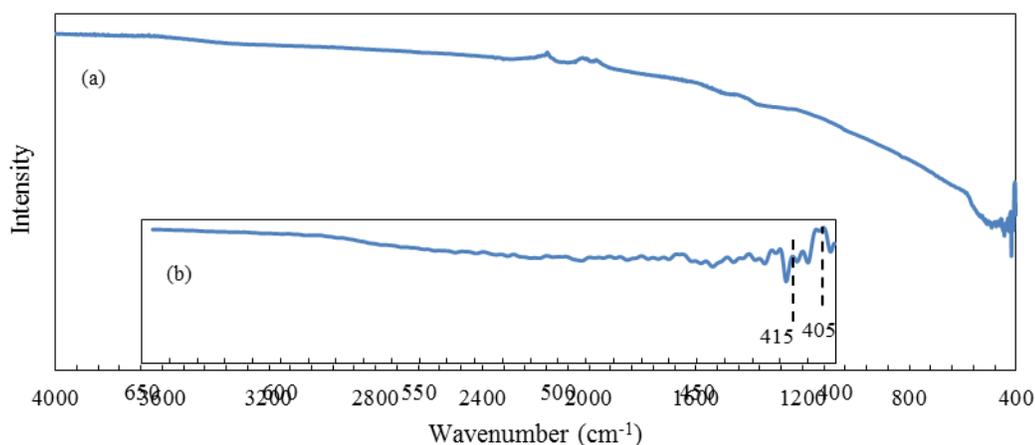


**Fig. 3** FTIR spectrum of Bacto-agar containing Zn (a)  $4000 - 400\text{ cm}^{-1}$  and (b) enlargement in range of  $680 - 400\text{ cm}^{-1}$

Bacto agar was mixed with Zn powder followed by the alteration of chemical bonding were performed on the spectra as Fig. 3. Based on Fig. 3(a), the broad peaks appear on wavenumbers of  $3348.98$ ,  $2089.62$  and  $1489.13\text{ cm}^{-1}$ . While, the small peaks detected on wavenumbers of  $832.71\text{ cm}^{-1}$  and  $687.12\text{ cm}^{-1}$ . In addition,

the sharp peaks were also detected on wavenumber in range of 400-500  $\text{cm}^{-1}$ . The most noticeable peaks in this range laid on 420.78 and 409.73  $\text{cm}^{-1}$ . The functional group possess on this spectrum are inorganic phosphates and aliphatic amino acids. The inorganic phosphates laid on wavenumber 1100- 1000, 1500- 1400, 3300- 2600  $\text{cm}^{-1}$  whereas aliphatic amino acids recorded at 1600  $\text{cm}^{-1}$  and between 3200- 2500  $\text{cm}^{-1}$ .

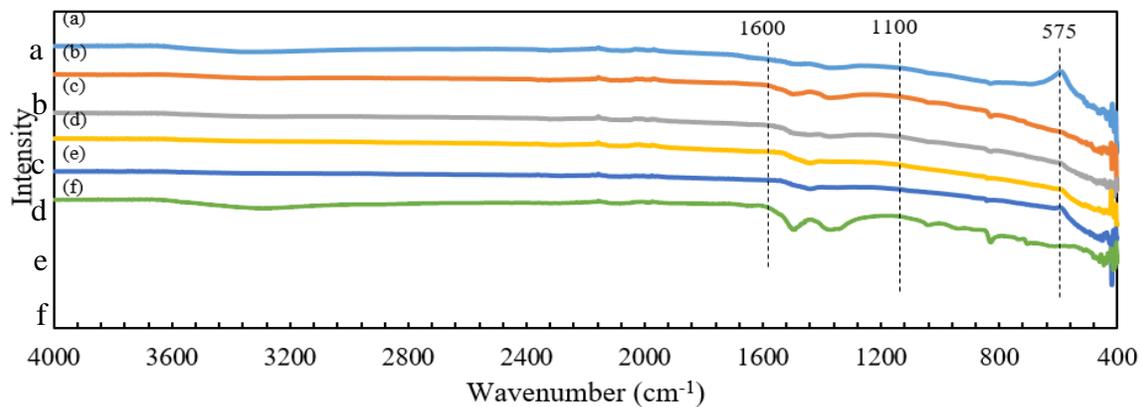
After the addition of Zn into Bacto-agar, the spectrum absorption changed, indicating the changes in structure and intermolecular interaction [11]. Changes of agar spectrum with the presence of Zn proved that the  $\text{Zn}^{2+}$  ions were successfully incorporated with the structure of agar [12]. The structures of Zn were always found in the range of 400  $\text{cm}^{-1}$  - 600  $\text{cm}^{-1}$  [11, 13]. The addition of Zn into Bacto-agar breakdown the O-H bonding then the  $\text{Zn}^{2+}$  replaced the  $\text{H}^+$  to make formation of ZnO bonding.



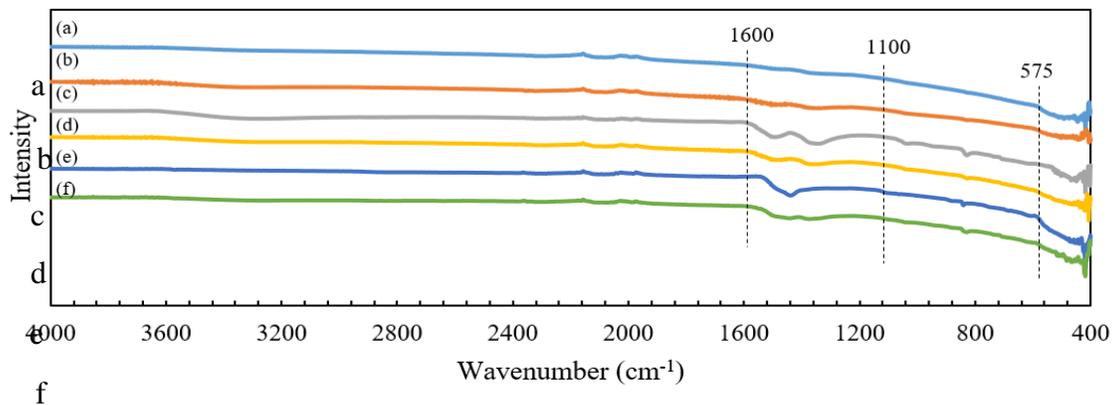
**Fig. 4** FTIR spectrum of commercial agar with Zn at (a) 4000- 400  $\text{cm}^{-1}$  and (b) enlargement in range of 650- 400  $\text{cm}^{-1}$

The spectra of commercial agar with addition of Zn powder is shown in Fig. 4. There was a hump peak calculated at 2098.45  $\text{cm}^{-1}$  as Fig. 4(a). The rest of the peaks were laid between ranges 500- 400  $\text{cm}^{-1}$  due to ZnO existence. The sharpest peaks of ZnO detected at 417.82 and 410.03  $\text{cm}^{-1}$  as Fig. 4(b). Similar pattern was observed on commercial agar and Bacto-agar with the presence of Zn. The peaks belong to aliphatic alcohol groups at 3358.30 and 1038.76  $\text{cm}^{-1}$  decreased in intensity after the addition of Zn. These peaks experienced the weak molecular bonding between oxygen and hydrogen molecules due to the replacement of Zn.

The spectra of Bacto-Zn without and with different concentrations of KOH are shown as Fig. 5. The concentrations of KOH were increased up to 0.2 M. Compare to Bacto-Zn in absence of KOH, spectrum of Bacto-Zn with addition of KOH indicated the significant changes at wavenumber 575  $\text{cm}^{-1}$ . The peak was getting flatter for 0.01 M KOH that presumably due to the presence of KOH which altered the strong chemical bonding of O-H with the ZnO molecules. The area under bands 1100 - 1600  $\text{cm}^{-1}$  can be explained by the Zn-OH bending mode. Some  $\text{Zn}^{2+}$  ions may be replaced with  $\text{P}^{5+}$  ions in inorganic phosphate or may distort  $\text{P}^{5+}$  ions and break the bonding between  $\text{P}^{5+}$  and  $\text{O}^{2-}$  in the range of 1100 - 1600  $\text{cm}^{-1}$ . As the concentration of KOH increased, the amount of  $\text{OH}^-$  also increased resulting the increasing of peak belong to  $\text{OH}^-$  and Zn bonding. However, the peaks refer to ZnO bonding were significant observed at range 450- 400  $\text{cm}^{-1}$ . The changes in the transmission spectra indicate the changes in structure, conformation and intermolecular interaction. The most significant peaks observed in range 500 - 400  $\text{cm}^{-1}$  indicated the presence of ZnO. Zn paste commercial agar-based with 0.01 M of KOH contains inorganic nitrites bonding associated at 1350 - 1200 and 850  $\text{cm}^{-1}$ . The peaks for Zn paste commercial agar-based in presence of 0.2 M of KOH was indicated at 1370.50  $\text{cm}^{-1}$ .



**Fig. 5** FTIR spectra of Bacto-Agar-Zn (a) without KOH, and with different concentration of KOH (b) 0.01, (c) 0.05, (d) 0.10, (e) 0.15 and (f) 0.20



**Fig. 6** FTIR spectra of Commercial-Agar-Zn (a) without KOH, and with different concentration of KOH (b) 0.01, (c) 0.05, (d) 0.10, (e) 0.15 and (f) 0.20

For spectrum in Fig. 5b, the hump peaks were recognized at 2092.56, 1370.50 and 826.82  $\text{cm}^{-1}$ . The paste contains inorganic nitrites stretching appeared at 1350–1200 and 850  $\text{cm}^{-1}$ . Among three Zn paste Bacto-agar, Bacto-agar in absence of KOH achieved the lowest intensity at peaks 1489.13 and 1391.99  $\text{cm}^{-1}$ . The decreasing of intensity for this spectrum are related to the weak chemical bonding for Bacto-agar and Zn until the existence of KOH strengthen the intermolecular bonding. Generally, almost all peaks showed increasing in intensity with the increases of concentration of KOH. This situation indicated the improvement in molecular strength with presence of potassium and hydroxyl molecules. All six spectra of commercial agar without KOH and different concentration of KOH as Fig. 6 show the similar pattern. In most cases, metal and its oxide can be observed by FTIR at lower wave number ranging from 400 to 800-  $\text{cm}^{-1}$ . Since the presence of oxygen and existence of KOH that supplied oxygen initiate the chemical reaction thus lead to formation ZnO usually laid on range 400 to 500-  $\text{cm}^{-1}$  [14].

#### 4. SUMMARY

Bacto-agar and commercial agar gave similar spectra to galactan-like spectra proving that both agars possess polysaccharides structures. However, the addition of Zn powder to agar has changed the spectra of agar. Several peaks between wavenumber of 400 – 500  $\text{cm}^{-1}$  attributed to the ZnO molecules. Then, various concentration of KOH were applied on porous Zn gave small alteration to the spectra of agar which indicated

the changes of intermolecular reaction. This situation indicates the incorporation of Zn and KOH in agar might not affect the bare Zn. Difference in the intensities and the area under bands was strongly related with the concentration of the functional groups.

#### ACKNOWLEDGEMENTS

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