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SYNTHESIS AND CHARACTERIZATION OF ALGINATE-CARBOXYMETHIL CELLULOSE BEADS FROM CORN STALK (*Zea mays*) WITH CROSSLINK VARIATION $C_4H_6O_4Zn$

Annazmil Fayros Latifah[1], Eny Yulianti[2*], Lilik Miftahul Khoiroh[1]

[1]*Department of Chemistry, Faculty of Science and Technology, UIN Maulana Malik Ibrahim Malang Jalan Gajayana 50, Malang 65144, East Java, Indonesia*
[2]*Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science and Technology, UIN Maulana Malik Ibrahim Malang, Jalan Gajayana 50, Malang 65144, East Java, Indonesia*

*Corresponding author: enyyulianti@kim.uin-malang.ac.id

ABSTRACT

Corn stalk has a high cellulose content, so that it is potential to be used as a composition for making alginate-carboxymethyl cellulose beads. Alginate and cellulose are biodegradable, renewable and non-meltable polymers that have wide applications in various industrial sectors. The purpose of this study was to determine the effect of crosslinking agent $C_4H_6O_4Zn$ on the adsorption and shape of beads. The varied concentrations of $C_4H_6O_4Zn$ are 3%; 5% and 10%. Characterization of alginate-carboxymethyl cellulose beads composites using Fourier Transform InfraRed (FTIR), and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). Based on research, the highest swelling value is obtained at 5% $C_4H_6O_4Zn$ crosslink which is 59.68%. FTIR data shows the appearance of wave numbers at 1413 cm^{-1} which indicates the presence of C-O Na groups, while at wave number 458 cm^{-1} indicates the presence of Zn-O groups. SEM-EDX data with a 5% $C_4H_6O_4Zn$ crosslink has a round shape with a wrinkled surface, multiple grooves causing a non-homogeneous surface. Whereas in $C_4H_6O_4Zn$ 10% the surface is almost smooth.

Keywords: Alginate, Carboxymethil Cellulose, Corn Stalk

INTRODUCTION

Corn stalk waste contains 69% cellulose which has the ability to be an adsorbent, in natural and modified [1]. Carboxymethyl Cellulose (CMC) is a hydrophilic modification and can be processed into cellulose beads [2] while the process includes two steps, alkalization and carboxymethylation [3]. The purpose of alkalization is to activate hydroxyl groups on cellulose molecules and to be substituted by carboxymethyl with add sodium monochloroacetate [4].

The degree of substitution (DS) is substituted hydroxyl groups [5]. DS is a main factor in CMC solubility in solvents and has a commercial degree of substitution from 0.4 to 0.8 [6]. Adsorbent in the form of gel beads is more effective than powder, because in the form of powder there is a small hydrodynamic (water movement) barrier which causes it to dissolve easily [7].

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Adsorption beads can be improved with making composite alginate beads. The optimal of sodium alginate / CMC composition for beads formation is 1: 2 because it produces optimum swelling power [8]. The ionic gelation is a method used with the working principle of the dropping technique [9]. In the ionic gelation method the crosslink agent is used as a solution which is dripped with alginate-carboxymethyl cellulose to form a hydrogel [10].

Ions that can be used as crosslinking are Ca^{2+}, Zn^{2+}, and Fe^{3+} [11]. Zinc acetate ($C_4H_6O_4Zn$) can produce a uniform size between beads and pores, because Zn^{2+} has stable and electronegative character [12] This is make the carboxylic acid (COOH) of alginate ionized to COO^- resulting in electrostatic repulsion that disturb the unity of beads by stretching the structure so that swelling power more maximum [13].

Beads with 3% zinc acetate solution are flat and sticky. While beads with 5% and 10% zinc acetate solution produce beads with round shape and harder not sticky [14]. However, cellulose alginate beads with crosslinks of $CaCl_2$ 3% and 5% produce greater swelling power than the concentration of 10%, with a percentage of 791, 651 and 276 [15]. This is because the higher crosslink concentration can induce the higher the crystallinity value, so the adsorption ability is lower.

Based on this background, it is necessary to develop research on the synthesis of CMC alginate beads from corn stalk with the addition of sodium alginate: CMC 1: 2 and variations concentration of crosslinks $C_4H_6O_4Zn$ 3%, 5% and 10% to obtain a rounded beads shape and optimal adsorption. The determination of CMC synthesis by the value of the degree of substitution and the determination of the best variation of crosslink concentration with swelling both gravimetrically and optical microscope. SEM-EDX to determine the morphology of beads and FTIR to determine the functional group.

MATERIAL AND METHOD

Materials

Corn Stalk waste obtained from Malang. The chemical used include sodium hydroxide (NaOH) p.a (Merck), hydrochloric acid (HCl) p.a (Merck), sodium monochloroacetate p.a, sodium chlorite ($NaClO_2$) p.a (Merck), sodium alginate $(C_6H_7O_6Na)_n$ p.a (Merck) and zinc acetate ($C_4H_6O_4Zn$) p.a (Merck).

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Extraction of Cellulose

Corn stalks were cleaned and sun-dried, dry samples were crushed into powder with a size of 100 mesh, then put into oven for 24 hours at 90ºC. 50 grams of corn stalk powder were immersed in 1000 mL NaOH 10% (w/v) at 80ºC for 90 minutes then washed several times with distilled water and squeezed. The pulp was treated with 200 mL $NaClO_2$ 1% (v/v) and added CH_3COOH 10% (v/v) to pH 5 at 75ºC for 1 hour. After that, it was washed with distilled water until the pH neutral and wrung. Cellulose pulp obtained was hydrolyzed with 5% (v/v) HCl (1:20) at 95ºC for 1 hour to obtain microfiber-dispersed [16]. The samples obtained were characterized by FTIR.

Synthesis of Carboxymethil Cellulosa

Five grams of corn stalk extract was added with 100 ml of distilled water in a 250 ml erlenmeyer. Then add 10 ml of 30% NaOH drops per drop for 1 hour. Then 6 grams of sodium monochloroacetate was added at a temperature of 60-70˚C. The mixture is soaked in residue using 100 mL of methanol for 24 hours. The resulting mixture was neutralized with glacial acetic acid, filtered and dried in an oven at 60˚C until a constant weight was obtained [17] after which it was characterized using FTIR and the degree of substitution was determined.

Variation of Crosslink $C_4H_6O_4Zn$

One gram of sodium alginate is dissolved in 25 mL aqua demin. Then, carboxymethyl was added with an alginate-cellulose ratio of 1: 2. Then the solution was dropped using an 18G syringe needle into $C_4H_6O_4Zn$ 3%, 5% and 10% 50 mL and allowed to stand for 24 hours. The formed beads are filtered and washed using aqua demin. BACMC is reacted in 50 mL of 10% CH_3COOH and placed on a hotplate until bubbles do not appear. The resulting BACMC was washed to neutral pH with aquademin. The wet BACMC produced was dried using 37ºC for 24 hours [16]

Determination of the Degree of Substitution

Two grams of carboxymethyl cellulose add 60 ml of 95% ethanol solution and stirred. Then 10 ml of 2 M nitric acid solution is added and the mixture is stirred again for 2 minutes. The mixture is heated for 5 minutes and stirred again for 15 minutes. After that, the mixture is filtered and the residue is washed using 30 ml of 95% ethanol solution which has been heated to 60ºC. The residue is then washed again using a methanol solution, and followed by drying in an oven at

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105oC for up to 3 hours. 0.5 g of residue is put in Erlenmeyer then 100 ml of distilled water is added while stirring. After that, add 25 ml of 0.5 N NaOH solution, and heat for 15 minutes. In hot conditions, the mixture is titrated with 0.3 N HCl solution and using the pp indicator.

Characterization of Functional Groups

The measurement is performed using Bruker-Alpha. The sample of 5 mg is pressed into a disk for FTIR measurement.

Swelling Beads

A total of ± 40 mg alginate beads: CMC is immersed in 10 mL aqua demineralization. BACMC was weighed after being soaked for 3, 5, 8, 24, 29 and 31 hours. Gravimetric swelling test is determined based on (Equation 3.1) and optical microscopy is processed using the Image-J based application (Equation 3.2) both before and after swelling.

$$\% \text{ Swelling} = \frac{Wt-Wo}{Wo} x\ 100\% \qquad (3.1)$$

$$\text{Diameter (D)} = \sqrt{((\text{LA} \times 4)/3{,}14)} \qquad (3.2)$$

where, W_0 and W_t are the masses of the dry and swollen beads, respectively, at a time (t).

Characterization of Surface Morphology

Surface morphology characterization with SEM-EDX was carried out at 40x and 5.000x.

Activity as adsorbent for Methylene Blue

About 5 mg of methylene blue was dissolved into 100 mL of distilled water, then pipetted 10 mL and placed into a test tube based on variations in crosslink concentration. Then, as many as 3 beads based on variations of crosslinks were placed into a blue methylene solution and absorbance was measured using UV-Vis at 664 nm [18]. The beads activity test was carried out for 168 hours [12] by observing the decrease in absorbance of the beads for each variation of crosslink concentration. The determination of adsorption capacity is based on (Equation 3.3).

$$q_t = \frac{\text{Co}-\text{Ct}}{m} \times \text{V} \qquad (3.3)$$

RESULT AND DISCUSSION

Extraction of Cellulose

In this process NaOH base compounds are used and a cellulose extract yield of 93.5% with a moisture content of 6.3% is obtained, the yield indicates the value of the extract produced

a lot. After delignification, the particles turn blackish brown, which indicates that lignin is still present. Then the next stage is soaking using sodium chlorite ($NaClO_2$) to whiten the remaining lignin remaining. According to [19], sodium chlorite is a powerful oxidizer that can degrade lignin without damaging cellulose.

Synthesis of Carboxymethil Cellulosa

CMC synthesis process include two main stages, alkalization and carboxymethylation. Alkalization is carried out to develop cellulose structure so as to facilitate the substitution of carboxylation reagents into cellulose structure. The carboxymethylation is carried out to substitute the anhydroxyl group in the anhydroglucose unit using a carboxymethylation reagent

Table 1 is a DS result of 0.7264 if 5 grams of NaMCA is added, while the addition of 6 grams of NaMCA produces a DS of 0.604. The amount of sodium monochloroacetate used affects the substitution of the anhydroglucose unit in cellulose. According to [20], the amount of alkali used can increase the amount of dissolved monochloroacetic salt, making it easier and accelerating the diffusion of monochloroacetic salt into the hydroxy group. However, according to [21], the purity of CMC will decrease if more NaMCAs are added, this is due to the formation of NaCl by products and a decrease in the degree of substitution.

Based on research conducted by [22] an increase in the value of DS to 0.7 can increase the value of swelling by 144.6%. Addition of carboxymethyl groups in cellulose expressed as the degree of substitution can change the nature of cellulose which was originally hydrophilic to hydrophobic, there by reducing the level of carboxymethyl cellulose solubility in water.

From Figure 2, a graph sample spectra of cornstalk powder, delignification, bleaching, cellulose after hydrolysis and CMC were obtained. In the IR spectra of cornstarch powder there was a peak in the region of 3409 cm^{-1} which showed strain O-H bonds and in the area of 2920 cm^{-1} showed the strain of C-H saturated bonds in cellulose and hemicellulose. The C = O ester bond in hemicellulose is shown in the region of 1733 cm^{-1} whereas the C = O carboxylic bond that is in cellulose, lignin and hemicellulose is shown in the region 1634 cm^{-1}. 1513 cm^{-1} and 1457 cm^{-1} indicate aromatic C = C compounds in lignin. The C-O-C (aryl-alkyl ether) bond appears in the 1250 cm^{-1} region, where this region indicates the presence of lignin polymers due to ether bonds [23].

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The IR cellulose spectra with CMC there are wave numbers in the area of 3436 cm-1 which shows the presence of OH groups and is a characteristic of cellulose. According to [24], OH functional groups are very strong at wave number 3427 cm-1. In CMC IR spectra there is a wave number of 1596 cm-1 indicating the presence of a carboxyl group (COO-) and a wave number of 1413 cm-1 indicating the presence of a carboxyl group as a salt. According to [25], CMC was identified to have a carboxyl group in the area of 1600 cm-1 and according to [26] the presence of a carboxyl group as a salt was shown in an area of around 1423 cm-1. In the area of 1334 cm-1 and 1063 cm-1 each showed the -OH and ether bonds, namely the C-O-C group. According to [25], the ether group (-O-) in the area of 1068 cm-1. From the results of the functional groups measured in the IR spectrum with each absorption at a certain wavelength region shows conformity to the carboxymethyl cellulose structure. This is indicated by the vibration of -OH, the carboxyl group (COO-), and the ether group (-O-).

Swelling Power, Optical Microscope Measurement Diameter and Beads Mechanical Strength.

The difference in the concentration of zinc acetate solution 3%, 5%, and 10% affects the shape of the beads produced. Beads made with 3% zinc acetate solution are slightly flat, not round with jagged and caudal edges, while beads made with 5% and 10% zinc acetate solution produce round shapes with more regular edges. The physical differences of the three crosslink concentrations used are shown in Figure 3

Of the three different crosslink concentrations above, beads with a harder texture are produced by the highest concentration of 10%, as tested by the hardness test shown in Figure 4. This is because the more the amount of zinc ions that bind to alginates, the greater the cross links that are formed and the resulting beads are getting rounder and harder [14]. According to [27], the higher concentration of crosslinkers can increase the value of crystallinity. So that the stiffness of beads is also increasing [28].

Between concentrations of 5% and 10% produce a difference of hardness of 0.98 Kgf. Meanwhile, based on research conducted by [32], an increase in CaCl2 crosslink concentration by 5% can increase the hardness of beads formed by a difference of 0.6 kg. This is because the affinity between COO- with Zn^{2+} ions is greater than with Ca^{2+} ions [33].

The ability of beads to expand was observed in aquademin media at room temperature for several hours and repeated three times (triplo). The difference in immersion time (5, 24, 29 and 31 hours) results in a different maximum swelling value, where the concentration of 3% at 29 hours, while the concentration of 5% and 10% at 24 hours. From the variation of concentration and immersion obtained maximum swelling power data produced by a concentration of 5% with a value of 59.68% while a minimum swelling power produced by a concentration of 10% with a value of 35.7%. The highest swelling value shows that the conversion of polymer into the gel matrix has been optimum [28]. After passing the optimum time, the matrix beads are diffused causing swelling to decrease. Diffusion occurs when the entrained substance flows through the pores of the polymer or through the space between the polymer chains, as shown in Figure 5.

In this study, the decrease in swelling power along with the increase in concentration in accordance with research conducted by [27], where with increasing crosslink concentration, the number of Zn^{2+} ions in liquid volume units will increase and more Zn^{2+} ions bound to the sodium alginate chain. This results in less space so less water can get into the beads. On the other hand, the number of COO-ion groups will decrease because there is a bond between the Zn^{2+} and COOH ions present in sodium alginate. Thus, the electrostatic repulsion between COO^- ions becomes weak and causes a decrease in the swelling power of the beads.

Based on research conducted by [29], making beads with variations in the concentration of zinc acetate 1%, 2.5%, 5% and 10% produces an optimal concentration of 5% for the next optimization process. This is because if the lowest concentration of 1% produces the highest swelling power, it is followed by rapid erosion of the beads. Whereas if the highest concentration of 10% results in the lowest swelling power, the strength of the high cross-linking causes aggregation.

The diameter after immersion increases with the weight of the beads and begins to shrink when it reaches maximum swelling. According to [14], this is caused by the occurrence of syneresis on beads which causes fluid in the beads to come out and evaporate, so the diameter size also shrinks. The percent diameter chart results are shown in Figure 6

In Figure the emergence of new uptake at the addition of zinc acetate concentrations of 3%, 5% and 10% in the wave numbers 458 and 460 cm-1 indicates the presence of Zn-O groups. Based on research conducted by [30], the presence of ZnO in the photocatalyst results of

synthesis is shown by the presence of a sharp characteristic peak at the wave number 468.24 cm-1. According to [31], the peak of Zn-O vibrational uptake was shown at wave number 590-400 cm-1, so that the appearance of uptake in the area of 458 and 460 cm-1 indicated the existence of cross links on beads. However, there is a difference in absorption at variations in concentration of 3%, 5% and 10%, where the peak characteristic concentration is 10% sharper and wider than other variations, this is because the greater the concentration the sharper peak produced.

SEM-EDX analysis

Beads morphology were analyzed by SEM-EDX (Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy) to analyze the material components both quantitatively and qualitatively. Morphology of zinc alginate gels formed at concentrations of 5% and 10% is shown in Figure 8.

In the picture above it can be seen that the zinc alginate gel formed at a concentration of 5% has a round shape with a wrinkled surface, multiple grooves that prove the surface is not homogeneous. Whereas at a concentration of 10%, visible wrinkles disappear and the surface is almost smooth. According to [34], an increase in crosslink concentration causes crosslinking to increase and make the gel stronger so that it can produce a homogeneous surface.

Based on the EDX in table 2 results above, obtained elements contained in BACMC with 5% zinc acetate concentration are elements C, O, Zn, Na and Cl, with Zn content of 3.9. Whereas at a concentration of 10%, it was found that Zn content was higher than before, which was 7.5%. This indicates that the higher the crosslink concentration, the Zn^{2+} cation ion contained in the beads is getting bigger, but at a concentration of 10% there is no Cl element. Based on research conducted by [35], the presence of salt (NaCl) can cause a higher swelling power value than if there is no salt. According to [36], the swelling of polymers in the presence of salt is due to the osmotic swelling process, which is the pressure on ionic contributions.

Beads Activity as adsorbent Methylene

Figure 9 shows the results of the bead activity test graph on adsorption of methylene blue. The Activity Test was studied by soaking beads with varying concentration in duplicate over several days. The absorption capacity of the three beads increased sharply on the 7th day to the 16th day, then increased more slowly on the 22nd day and decreased on the 28th day. This shows the optimum time to absorb methylene blue is on the 22nd day.

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From the three variations of beads concentration, the most data that absorbs methylene blue is 3% concentration which is 42.75 ppm. However, concentrations of 5% and 10% also absorb the maximum with a difference not far from 5% which is only 1.45 and 4.32 ppm. This is because according to [37], hydrogels with a porous tissue structure, high surface area, and lots of phenolic hydroxyl are proven to be effective adsorbents for removing methylene blue dyes from aqueous solutions.

CONCLUSION

Variation in crosslink concentration on beads affects the shape and mechanical strength (hardness), where the higher the concentration, the more round and harder the beads. This variation also affects the swelling power and the increase in diameter of beads, where the higher the concentration, the swelling power and the increase in diameter are smaller. However, the maximum swelling power is produced by a concentration of 5%, which is equal to 59.68%. Based on FTIR analysis, the carboxymethyl cellulose character produces a new absorption at the wave number 1418 cm^{-1} which indicates the presence of C-ONa groups. Whereas the addition of $C_4H_6O_4Zn$ crosslink variations resulted in new absorption at 458 and 460 cm^{-1} which indicated the presence of Zn-O cross links. Character of carboxymethyl cellulose alginate beads with a crosslink concentration of 10% based on SEM-EDX analysis has a finer surface shape than a concentration of 5%.

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Table 1. Degree of Substitution (DS)

NaMCA: Cellulosa	DS
5:5	0,726
6:5	0,604

Table 2. Percent weight of each element of BACMC with varying concentrations of zinc acetate 5% and 10%

Sample	Percent weight of each element (%)				
	C	**O**	**Zn**	**Na**	**Cl**
$C_4H_6O_4Zn$ 5%	50	44.42	3.9	1.46	0.22
$C_4H_6O_4Zn$ 10%	49.65	40.75	7.5	2.1	-

Figure 1. a) Corn stalk powder b) Cellulose extract c) CMC

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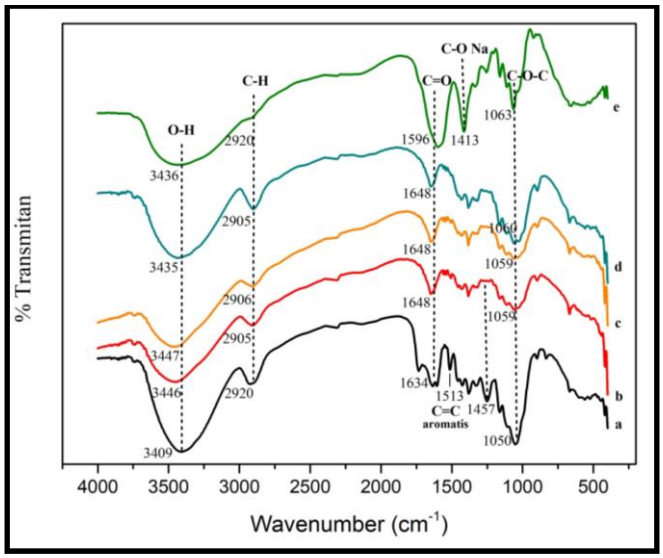

Figure 2. IR spectra (a) corn stalk powder, (b) delignification, (c) bleaching, (d) extraction of cellulose, and (e) CMC

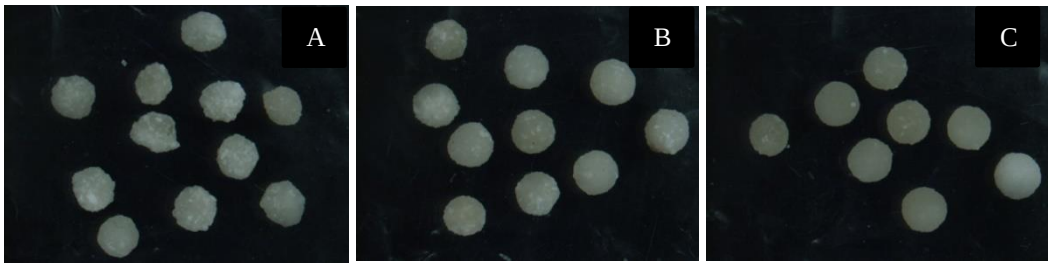

Figure 3. Physical differences in beads with concentrations of 3%, 5%, and 10%.

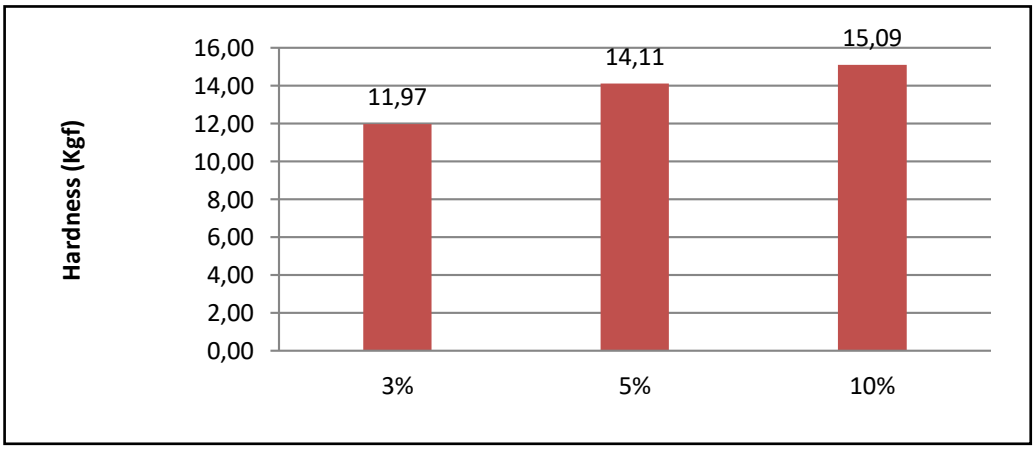

Figure 4. Hardness Test Results from 3 variations of crosslink concentrations

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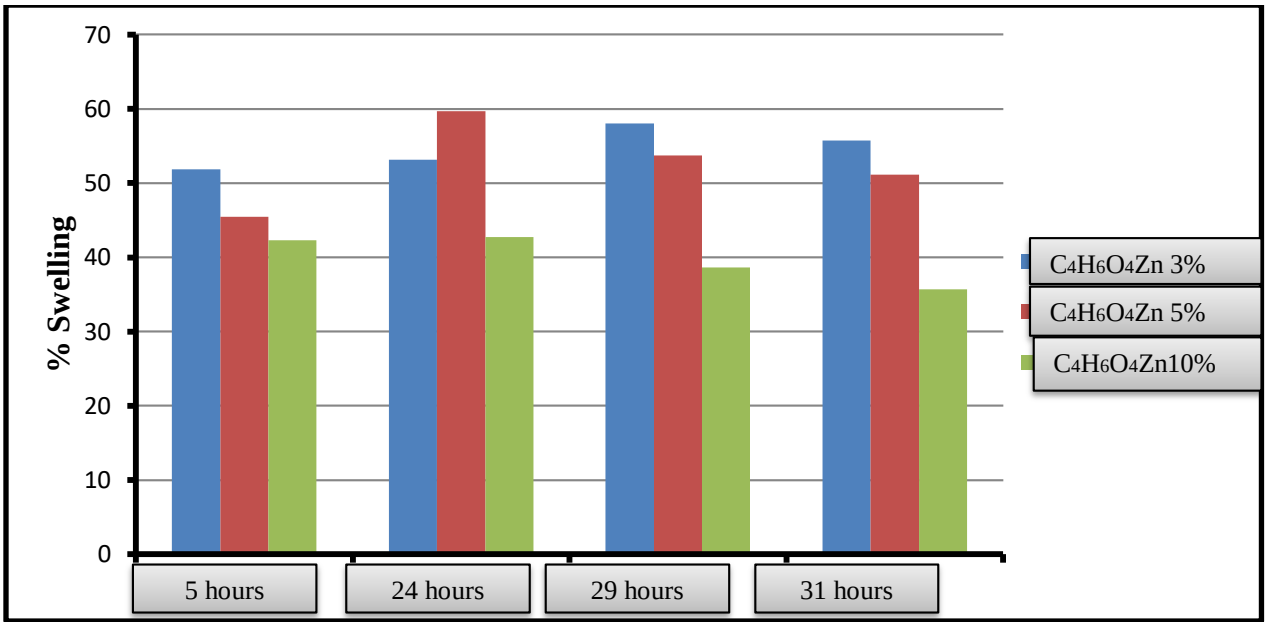

Figure 5. Results of BACMC $C_4H_6O_4Zn$ Swelling Power Analysis

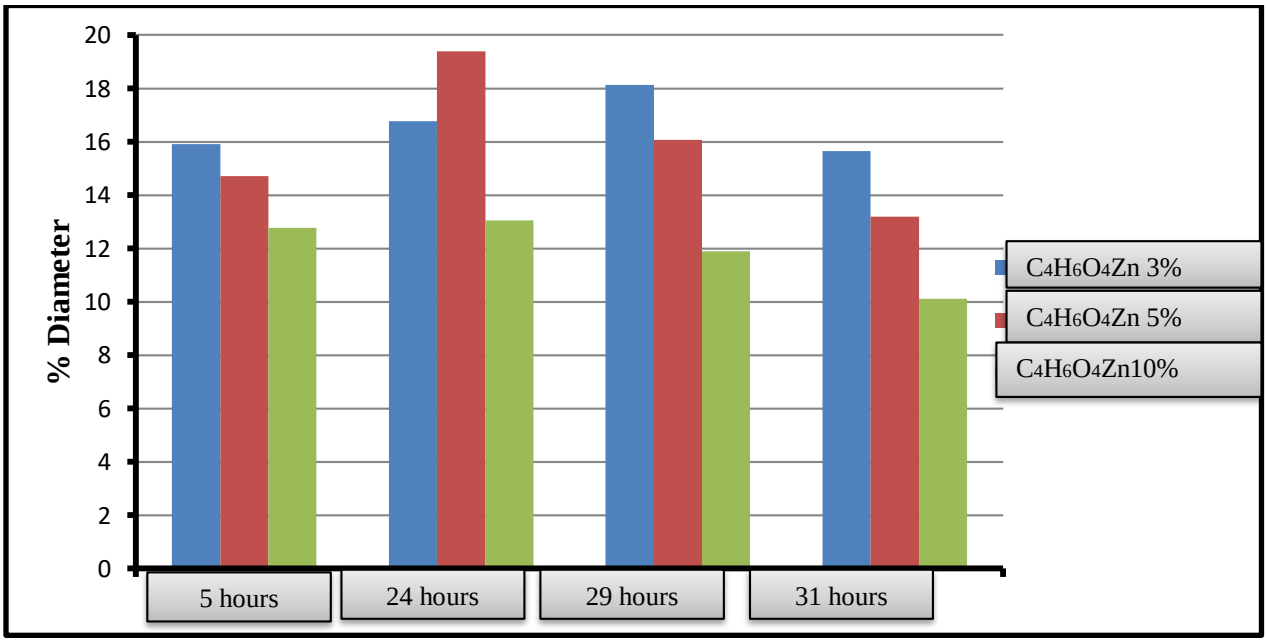

Figure 6. Graph of average beads diameter

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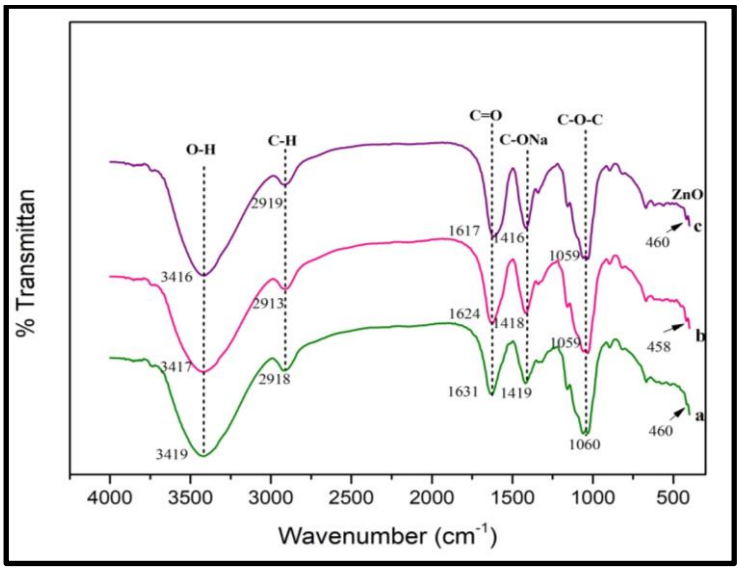

Figure 7. IR Spectra of crosslink Zn (a) 3%, (b) 5%, and (c) 10%

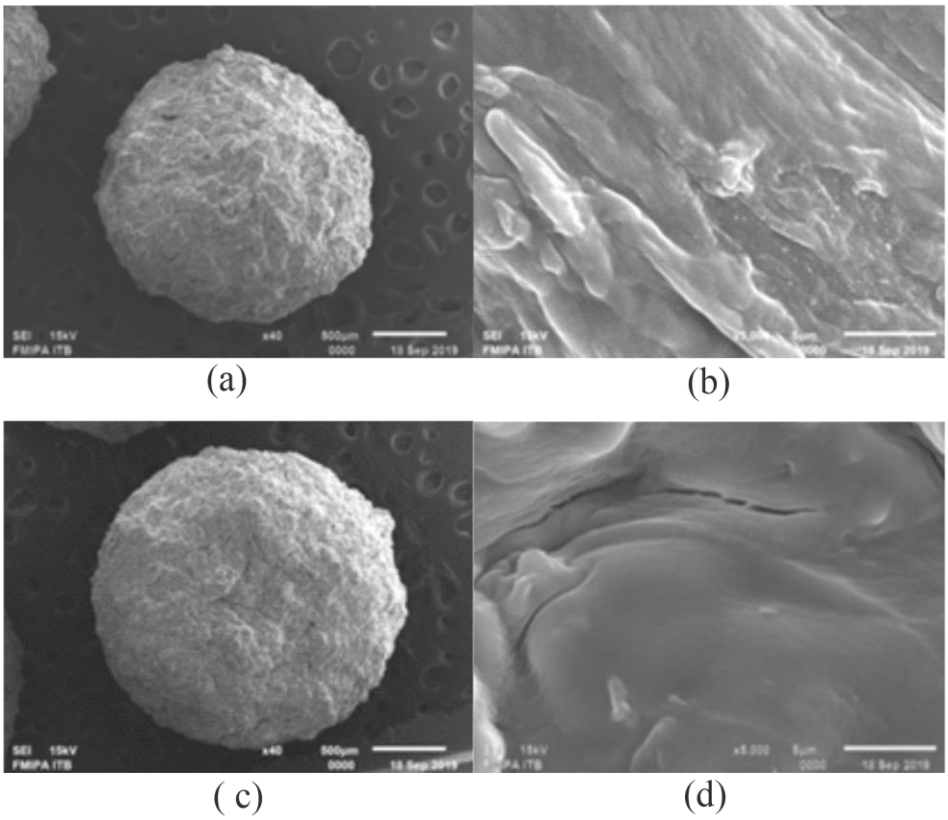

Figure 8. SEM characterization results (a) BACMC $C_4H_6O_4Zn$ 5% magnification 40x (b) 5000x magnification (c) BACMC $C_4H_6O_4Zn$ 10% 40x magnification and (d) 5000x magnification.

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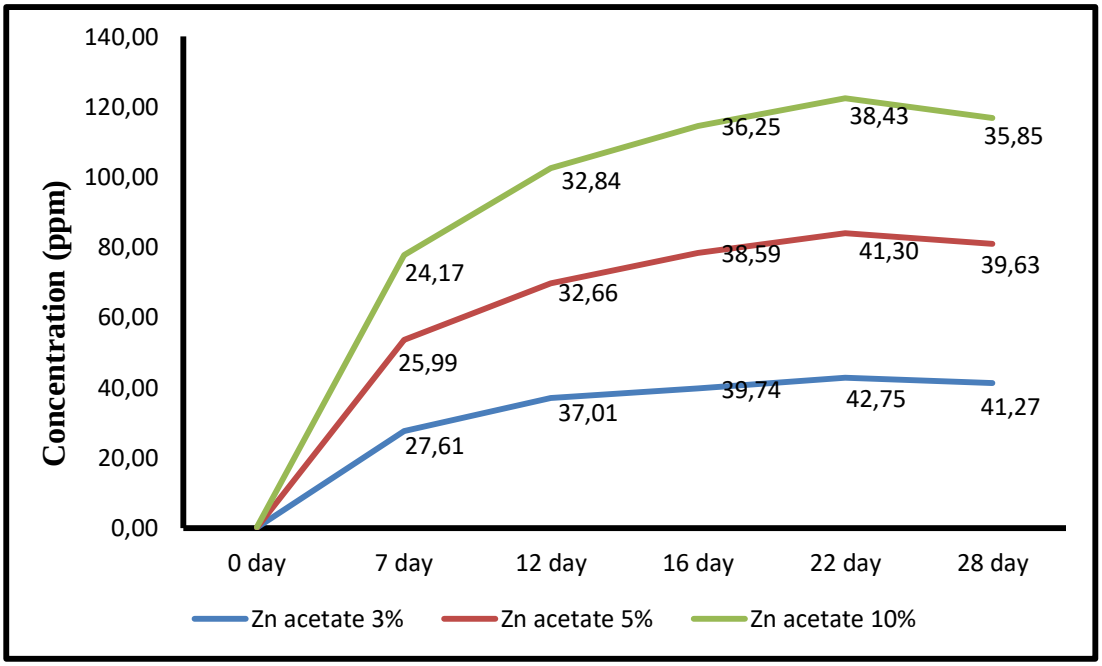

Figure 9. Test of beads activity on Methylene blue adsorption