

## Synthesis of Biodegradable Superabsorbent Polymers from Carboxymethyl Cellulose/Humic Acid

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### ABSTRACT

Superabsorbent polymer (SAP) blend has been synthesized from carboxymethyl cellulose (CMC), humic acid, and aluminum sulphate octadecahydrate cross-linker. SAP is hydrophilic networks that can absorb and retain huge amount of water within their structures. Humic acid as starting material of polymer, was isolated from subgrade Batujai Dam by using IHSS method. Water Absorption Capacity (WAC) measurement, FTIR analysis, and agitation tests to investigate the cross-linking process and which of  $Al^{3+}$  and  $SO_4^{2-}$  ions causes the crosslinking are carried out. Optimum cross-linking ratio of CMC and cross-linker appeared to be 2wt% corresponded to WAC determination. FTIR spectrum of CMC/humic acid blend and agitation test showed that CMC react with humic acid during polymerization process via  $Al^{3+}$  ion.

**Keywords:** carboxymethyl cellulose;  $Al^{3+}$  ion; humic acid; superabsorbent polymer.

### INTRODUCTION

Recently interest in developing superabsorbent from biopolymer such as starch [1], cellulose and its derivatives [2], and chitosan [3] has been increased due to their exceptional properties compared to petroleum-based polymers that is sustainable, biocompatible, biodegradable, renewable and nontoxic [4]. Owing to their three-dimensional polymeric networks that can absorb and retain large volumes of water, superabsorbents are widely used in many fields, such as hygienic products, drug-delivery systems, agriculture and horticulture [5].

Superabsorbent prepared through electrostatic complexing can be used for example crosslinking of CMC/HEC [2] and CMC/starch [1] with aluminium sulphate as cross-linking agents. Aluminium sulphate, with its cationic species in effective form of  $Al^{3+}$ ,  $Al(OH)^{2+}$  and oligomeric species in aqueous solution when  $pH < 5$ , provides multivalent positive charges and abundant sites for crosslinking with anionic groups [6] such as NaCMC that containing  $-COO^-$  groups to form hydrogel structures.

Application of humic acids (HA, one of the main fractions of humic substances) in agriculture as soil fertilizer and soil conditioner has been extensively discussed in the literature [7]. Containing of carboxylic and phenolic groups, humic acid provides favorable conditions for chemical reactions, biological activity and improves physical structure of soil, water holding capacity, pH buffering and accelerate transport of nutrients to plants [8]. Therefore, it was planned to synthesize a

biodegradable superabsorbent with suitable for soil water conservation by crosslinking CMC and humic acid with aluminum ions. Optimum cross-linker concentration, water absorption capacity and FTIR analysis were also studied.

### EXPERIMENTAL SECTION

#### Materials

Humic acid used in this study were isolated from subgrade Batujai Dam, Lombok Tengah, West Nusa Tenggara. Analytical quality materials (analytical grade) for humic acid isolation include: NaOH (sodium hydroxide), HCl (hydrogen chloride), HF (hydrogen fluoride),  $AgNO_3$  (silver nitrate), paper Whatman filter 42, pH indicator strip were obtained from Merck (Germany). Nitrogen gas, carboxymethyl cellulose sodium salt, aluminum sulphate octadecahydrate was used at reagent grade and could be available from commercial sources.

#### Instrumentation

Tomy LC-200 centrifuge, Memmert WNB 2214 shaker, BIOSAN/MSH 300 magnetic hot plate, Memmert u10 oven, Hanna pHmeter, Simadzu electrical balance, and Perkin Elmer Spectroscopy FTIR.

#### Procedure

##### *Isolation and Characterization of Humic Acid*

Humic acid isolated and purified by using recommended method of the International Humic

Substances Society [9]. Humic acid isolated then were characterized using FTIR spectroscopy.

### Preparation of Cross-Linked CMC/HA Blend

Carboxymethyl cellulose sodium salt (10 g) was mixed with 1.0 L of distilled water (DW) in a large beaker using a magnetic stirrer. The solution was agitated for 1 hour at 70°C. Then varying amounts of aluminum sulfate were added to the beaker to investigate the optimum crosslinkage, and the solution was allowed to mix for another 30 min. The solution was then spread on Teflon baking pans and dried at 50°C until a film is formed. The film was shredded with a blender and then ground into a powder with a mortar and pestle. Dried film of the cross-linked CMC, was crushed and dissolved in DW. Using magnetic hot plate, humic acid solution mixed with the cross-linked CMC gelatinized for 30 minute at 70°C. Result paste was dried overnight at 50°C, crushed, and tested.

### Investigation of the Active Ion

When aluminum sulfate octadecahydrate dissolve in water, the material dissociates into  $Al^{3+}$  and  $SO_4^{2-}$ . Investigating the ions which enters the cross-linking reaction has done by adopting following procedure: pieces of the cross-linked CMC/starch blend immersed in hot water 70°C for 30 minutes and then filtered. The extraction then divided into two parts. The first part is tested for sulfate group using  $BaCl_2$  solution, while the second part is tested for  $Al^{3+}$  ion using NaOH solution.

### Water Absorption Capacity Measurement at Various Cross-linker Concentration

The accurately weighed CMC/HA superabsorbent powder in various amount of  $Al^{3+}$  ( $0.1 \pm 0.0001$  g) was immersed in 500 mL DW for 2 h to reach swelling equilibrium. The swollen sample

were then separated from the unabsorbed water by being filtered over 100-mesh nylon screen. The weight of the swollen sample was measured. The water absorption capacity (WAC) was calculated by the following equation,

$$W_{AC} = \frac{W_1 - W_0}{W_0} \quad (1)$$

Where  $W_0$  is dried sample weight (g) and  $W_1$  is swollen sample weight (g) and  $W_{AC}$  is water absorption capacity per gram of dried sample (g/g).

## RESULTS AND DISCUSSION

### Isolation and Characterization of Humic Acid

HA was obtained from subgrade Batujai Dam after separating its humin and fulvic acid then purifying by using mixed HCl/HF solution to dissolves silica oxide mineral. Based on interpretation of the FTIR spectra of crude and pure HA in Table 1 can be seen that purification decreased the ash content, from 5.3 % to 1.3 %, indicated by decrease of SiO stretching in  $914\text{ cm}^{-1}$ . Peak at  $1388\text{ cm}^{-1}$  coupled with  $1659\text{ cm}^{-1}$  peak suggests that crude HA has carboxylate groups, presumably because of the ash content [10][11]. The peak was shifted to 1381 and  $1653\text{ cm}^{-1}$  respectively after purification of HA. Intensity of this peak was decreased, while peak intensity around  $1722\text{ cm}^{-1}$  increased at pure HA spectra due to carboxylate to carboxylic changes in HA. This is supported by result of ash content determination that purification decreased ash content from 5.60% to 1.13%. Based on FTIR spectra, HA isolated containing functional groups of COOH, phenolic -OH, aliphatic hydrocarbon and aromatic ring.

**Table 1** Interpretation of the FTIR spectra of HA

| HA before purification ( $\text{cm}^{-1}$ ) | HA after purification ( $\text{cm}^{-1}$ ) | Vibration Type  |
|---|--|---|
| 3425  | 3408                                       | OH stretching of alcohols or phenols                            |
| 2927  | 2927                                       | asymmetric stretching of aliphatic C-H in $-CH_2-$ groups       |
| 2851  | 2851                                       | symmetric stretching of aliphatic C-H in $-CH_2-$ groups        |
| 1728  | 1722                                       | C=O stretching (carboxylic and carbonyl group)                  |
| 1659  | 1653                                       | aromatic C=C and asymmetric C=O stretching in $COO^-$ groups    |
| 1564  | 1552                                       | nitro groups  |
| 1463  | 1457                                       | methyl asymmetric C-H bending                                   |
| 1388  | 1381                                       | OH deformation and C-O stretching in phenols and $COO^-$ groups |
| 1255  | 1236                                       | C-O stretching of aryl ethers and OH deformation of COOH groups |
| 1035  | 1035                                       | C-O stretching (alcohols and polysaccharide)                    |
| 914   | 914  | SiO stretching  |
| 700   | 700  | ortho disubstituted out-of-plane = C-H bending vibration        |
| 529-473                                     | 524-466                                    | metal-humic acid interaction                                    |

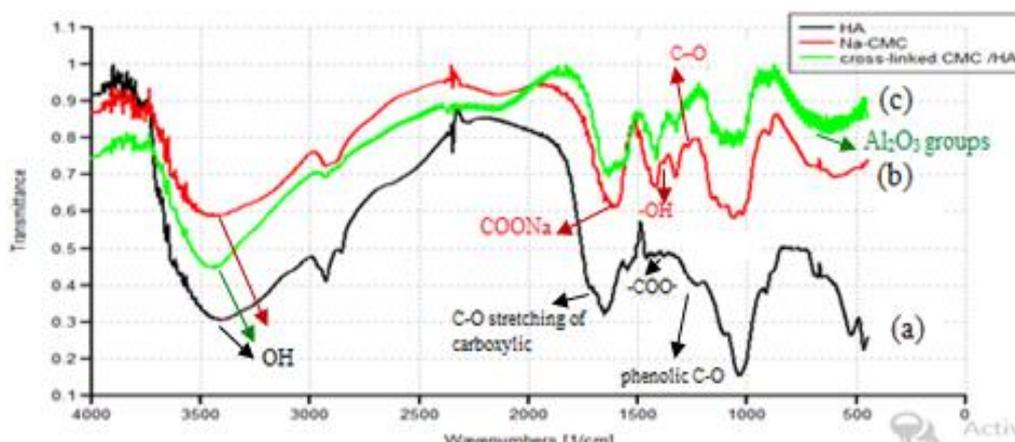


Figure 1 FTIR spectra of, CMC (b), and CMC/HA blend (c)

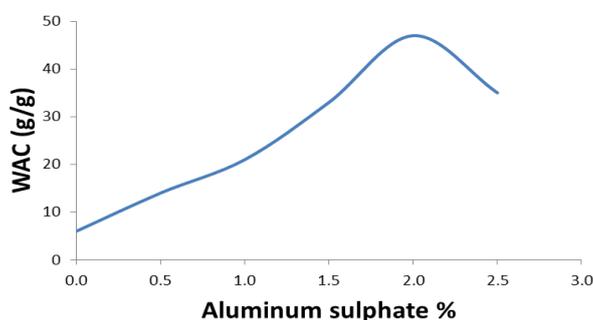


Figure 2 Optimum percent of aluminum sulphate octaahydrate cross-linker

### Proposed Interaction of cross-linked CMC/HA- $\text{Al}^{3+}$

The IR spectra of the HA, CMC, and CMC/HA blend are shown in Fig. 1 (a–c), respectively. Comparing with the IR spectrum of CMC (Fig. 1(b)), the absorption bands at  $1608\text{ cm}^{-1}$  for the  $-\text{COONa}$  group shift to  $1634\text{ cm}^{-1}$ , and the absorption bands at  $1381$  (OH bending vibration) and  $1268\text{ cm}^{-1}$  (C–O HA(a stretching)) disappeared in the IR spectrum of cross-linked CMC/HA (Fig. 1(c)). Comparing with the IR spectrum of HA (Fig. 1(a)), the absorption bands at  $3413$  and  $1653\text{ cm}^{-1}$  for the  $-\text{OH}$  stretching of alcohols or phenols group and C=O stretching in  $\text{COO}^-$  groups shift to  $3451$  and  $1634\text{ cm}^{-1}$  respectively and the absorption bands at  $1722\text{ cm}^{-1}$  (C–O stretching of carboxylic group of HA),  $1381\text{ cm}^{-1}$  ( $-\text{COO}^-$  asymmetric stretching of HA) and  $1255\text{ cm}^{-1}$  (phenolic C–O stretching of HA) disappeared in the spectrum of cross-linked CMC/HA superabsorbent (Fig. 1(c)). The results obtained from IR analysis showed that the reaction of both CMC and HA occurs in carboxylic and phenolic groups of HA and  $-\text{COO}^-$  groups of CMC via cross-linker.

### Investigation of the Active Ion

In order to suggest a reasonable interaction, knowing which ions enters the cross-linking reaction ( $\text{Al}^{3+}$  or  $\text{SO}_4^{2-}$ ) is needed. Tested for sulfate group using  $\text{BaCl}_2$  solution on extraction of cross-linked

CMC/HA, shows dense white precipitate indicated that the sulphate group not share for blend formation. While, tested for  $\text{Al}^{3+}$  ion using NaOH solution on extraction of cross-linked CMC/HA, shows the absence of  $\text{Al}^{3+}$  ion. It was confirmed with FTIR analysis that the  $\text{Al}^{3+}$  ion share in the blend structure as cross-linker that bind the carboxylic or phenolic groups of HA with  $-\text{COO}^-$  groups of CMC.

### Water Absorption Capacity Measurement at Various Cross-linker Concentration

The effect of the amount of  $\text{Al}^{3+}$  ion on WAC was shown in Fig. 2. The max. of absorbency was at 2% of  $\text{Al}^{3+}$  ion. Increasing cross-linker could increase the nodes of network and the cross-linker density, which is favorable to the super-absorbent absorbing and retaining fluid [12]. Low concentration of the cross-linker leads to low degree of cross linking, and it is hard for network structure to form, so the water absorbency is low. However, when it is higher than the best value, there are more cross-linking points and the pores become smaller in the network, which causes the macroscopic decrease of the absorbency [13].

### CONCLUSION

A superabsorbent was successfully prepared using the cross-linking of CMC/HA with aluminum ions. The interaction was occurs in carboxylic and

phenolic groups of HA and – COO<sup>-</sup> groups of CMC via Al<sup>3+</sup> ion as cross-linker. The mass ratio of Al<sup>3+</sup> ion to CMC could affect its water absorption capacity.

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