

# Study of Cellulose-N,N'-Methylenebisacrylamide-Acrylic Acid as Pb<sup>2+</sup> Ion Adsorbent

M. Suhartini<sup>1\*</sup>, J. Ginting<sup>2</sup>, Sudirman<sup>2</sup>, A.D. Putri<sup>3</sup> and Z.R. Mubarak<sup>4</sup>

<sup>1</sup>Center for Isotopes and Radiation Application, National Nuclear Energy Agency,  
Jl. Lebak Bulus Raya No.49, Jakarta 12440, Indonesia

<sup>2</sup>Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency,  
Puspiptek Area, Serpong, Tangerang Selatan 15314, Indonesia

<sup>3</sup>Pancasila University, Jl. Raya Lenteng Agung No.56-80, Srengseng Sawah, Jagakarsa, Jakarta Selatan 12640, Indonesia

<sup>4</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Indonesia, Depok 16424, Indonesia

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## ABSTRACT

Cellulose can be used as a metal ion adsorbent. However, it is specific to certain metal ions and has some drawbacks. To increase the capture of certain metal ions, cellulose needs to be modified. Cellulose modification was carried out using N, N'-methylenebisacrylamide (MBA) as crosslinking agent and acrylic acid (AA) as grafting agent. Gamma rays from Cobalt-60 was used as the initiator by simultaneous irradiation method. The aim of this study is to improve and observe the capture ability of cellulose as Pb<sup>2+</sup> metal ion adsorbent. The characterization was performed by FTIR, DSC, SEM, and EDX. The thermal analysis and ion exchange capacity measurement showed that the resulting copolymer has a better thermal stability and ion exchange ability than pure cellulose. The applications of the copolymer on Pb<sup>2+</sup> ion adsorption indicated that the maximum adsorption is 99.8 % of 3 ppm Pb<sup>2+</sup> ion sorbent at pH ≈ 7. SEM analysis showed that the copolymer is porous while pure cellulose appears fibrous. EDX Analysis showed Pb<sup>2+</sup> metal ion adsorption by cellulose-MBA-AA.

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## INTRODUCTION

Cellulose is the most abundant polymeric material on earth and it possesses several valuable physicochemical properties such as a fine cross section, good biocompatibility, high durability and thermal stability, and good mechanical properties. Cellulose is a reactive chemical due to the presence of three hydroxy groups in each glucose residue, which are mainly responsible for the reactions of cellulose. Cellulose contained in rice straw can be modified to obtain the chemical or physical characteristics that are suitable for use. Modified cellulose is also a practical raw material in the manufacture of membranes for various separation techniques such as osmosis, dialysis, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation, and electrodialysis [1].

Radiation graft polymerization is a method for modifying the physical and chemical properties

of polymers. Polymer radicals formed by irradiation of polymer can react with monomers, resulting in graft chains. Radiation-induced graft polymerization techniques can be classified into the following two groups:

- a. Direct or simultaneous irradiation method, irradiation of mixture of a trunk polymer and monomers.
- b. Pre-irradiation method-grafting initiated by trapped radicals, pre-irradiation of a trunk polymer, post-contact with monomers [2].

Modification of cellulose lately utilizes copolymer-forming grafting techniques that are commonly called graft copolymerization. Graft copolymerization can be implemented through various means such as chemical, photochemical, enzymatic, induction, or induction plasma radiation techniques [1].

Cellulose is highly crystalline and generally insoluble, due to the intramolecular hydrogen bond networks extending from the O(30)-H hydroxy to the O(5) ring oxygen of the next unit across the

\*Corresponding author.

E-mail address: [meri@batan.go.id](mailto:meri@batan.go.id)

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glycosidic linkage and from the O(2)-H hydroxy to the O(6O) hydroxy of the next residue. Presently the main uses of cellulose are for paper or cardboards, membranes, tissues, explosives, textiles and construction materials. The scope of applications of cellulose is limited by insolubility in common solvents and lack of properties inherent to synthetic polymers. Significant efforts have been paid to the chemical modification of cellulose [3] to improve resistance to heat or abrasion, mechanical strength [4-6], water or oil repellency [7], or antibacterial activity [8]. Poly(glycidyl methacrylate)-grafted cellulose has been efficiently modified with iminodiacetic acid in aqueous solution under mild conditions, resulting in an effective natural material-based porous adsorbent [9]. One convenient route to introducing new chemical and physical properties to cellulose is the graft modification. Three approaches are generally used for synthesis graft copolymers. "Grafting onto" involves the reaction between functional groups on two different polymers. "Grafting from" involves a polymers with functional groups (macro-initiators) that initiate the polymerization of vinyl monomers. "Grafting through" involves (co)polymerization of macromonomer(s) [10]. Modification of cellulose by grafting copolymerization techniques is the most efficient way for modifying cellulosic properties. The modified cellulose can be used in various fields [3,11]. The chemical contamination of water by various derivatives that are potentially toxic to humans, particularly heavy metals, aromatic molecules, and dyes, is a serious environmental problem [12]. Currently, many industries use lead as one of the important additional material. However, lead carried by waste water is very hazardous for health. The maximum permissible limit of  $Pb^{2+}$  content in potable water is 0.01 mg/L [13]. In this study, cellulose isolated from rice straw is used as polymers, and monomers as functional substance (copolymer formation) is grafted by copolymerization technique. Simultaneous copolymerization techniques induced by gamma radiation was used to polymerize N,N'-methylenebisacrylamide (MBA) and acrylic acid (AA). The use of MBA as a crosslinking agent can lead to increase molecular weight and degree of polymerization. It can be predicted that MBA prevents degradation in the reaction of radical formation caused by radiation [14]. On the other hand, AA as a grafting agent has carboxyl groups that plays a role in supporting the ion exchange ability as an adsorbent metal cations. Rahmawati has managed to modify cellulose as fiber ion exchanger with grafted acrylic acid (monomer) on cellulose, using the technique of pre-irradiation graft copolymerization. In her research the modified cellulose has a  $Cu^{2+}$  ion adsorption capacity of

14.6 mg/g as determined by atomic absorption spectroscopy (AAS) and 3.54 meq/g as determined by titration [10]. Modification of cellulose is frequently called biopolymer engineering. In this study, biopolymer engineering of rice straw cellulose was performed by graft copolymerization of acrylic acid using MBA as crosslinking agent with gamma ray irradiation as reaction initiator. The novelty of this work is that the modified cellulose (cellulose-MBA-AA) has a better thermal stability, which means that the sample can be used in hot waste water. Furthermore, cellulose-MBA-AA has a porous and compiler structure that improve the adsorption of  $Pb^{2+}$  ion.

## EXPERIMENTAL METHODS

### Materials

Rice straw was obtained from agricultural lands in Cigombong, Bogor. Other materials were N-N'-methylene bisacrylamide practical grade (p.a.), acrylic acid p.a., NaOH,  $H_2O_2$ , HCl, and copper nitrate.

### Procedure

#### *Cellulose isolation from rice straw*

Cellulose was isolated from rice straw following procedure which as described elsewhere [10]. Dry rice straw was macerated using a 2:1 toluene-methanol mixture for 48 hours then filtered to remove fat. Furthermore, to remove minerals, 600 mL of 3 % hydrochloric acid was added, followed by heating at 70 °C for 1 hour and washing with distilled water until the filtrate was neutral. The sample was then mixed with 700 mL of 20 % sodium hydroxide and heated to 80 °C for 3 hours. It was then washed with distilled water until the filtrate was neutral. Delignification was carried out by adding 500 ml of 1.5 % hydrogen peroxide and heating in a water bath at 80 °C for 3 hours, then filtered. Treatment with hydrogen peroxide was performed twice with a subsequent heating time of 2 hours. The resulting slurry (pulp) was then flattened and dried to obtain a thin sheet of cellulose. Drying was done in an oven at 90 °C to a fixed weight.

#### *Copolymerization*

Copolymerization was performed following the steps outlined in [15]. Basically, two different copolymers, henceforth referred to as copolymer A (which was prepared with high AA concentration) and copolymer B (with low AA concentration), were prepared.

To perform the copolymerization, the cellulose was first put into polyethylene plastic bags, to which 1.0 mL of N-N'-methylenebisacrylamide p.a. 1 % (w/v) was added. Afterward, 0.75 mL of 99 % acrylic acid was added for copolymer A, and 0.75 mL of acrylic acid 19.8 % for copolymer B. The bags were irradiated with gamma rays at a doses of 10, 20, 30, and 40 kGy at a dose rate of 5 kGy/hour. The samples were then washed with distilled water and dried in an oven until the weight remains. The results were analyzed for their percentage of grafting copolymerization (grafting, %G). Using the weight of initial cellulose ( $W_0$ ) and after grafting ( $W_1$ ), the %G were calculated by formula (1).

$$\%G = \frac{W_1 - W_0}{W_0} \times 100 \% \quad (1)$$

### Characterization of copolymer

#### Analysis of functional groups of copolymer using fourier transform infrared (FTIR)

Copolymers of cellulose-MBA-AA were measured for their absorption of infrared light absorption for wave numbers ranging from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

#### Thermal analysis by differential scanning calorimetry (DSC)

The thermal properties of the copolymer was analyzed at the temperature range of 60-600 °C at a rate of 10 °C/min [4].

#### Surface morphology analysis using scanning electron microscope (SEM)

The morphology of cellulose before and after copolymerization were characterized using SEM. The characterization was carried out at a magnification of 4000 $\times$ .

#### Elemental composition analysis using energy dispersive x-ray (EDX)

The position of the peaks led to the identification of the elements and the peak height helped in the quantification of each element's concentration in the sample.

#### Determination of swelling ratio (%S) in water

A total of 50 mg ( $W_1$ ) copolymer was put in a plastic cup container. Then, 50 ml of water was added at a temperature of 60 °C and it was allowed to stand for 24 hours. Afterward, the copolymer was

filtered with 120 mesh stainless steel strainer, drained for 30 minutes, and weighed to obtain  $W_2$  [9]. The value of %S can be calculated from formula (2).

$$\%S = \frac{W_2 - W_1}{W_1} \times 100 \% \quad (2)$$

### Determination of ion exchange capacity

A total of 25 mg copolymers that had the highest percentage of grafting (%G) was put into an Erlenmeyer flask. Then, 25.0 mL NaOH 0.1 N was added and the mixture was stirred with a magnetic stirrer for 15 minutes and filtered. Afterward, 5.0 mL was taken with a pipette and 2-3 drops of phenolphthalein indicator (pp) was added to the filtrate. Finally, the filtrate was titrated with a 0.05 N HCl solution until the color changed to pink [10]. The ion exchange capacity was then calculated by formula (3), with  $V$  representing solution volume and  $N$  representing normality.

$$\text{Capacity (meq/g)} =$$

$$\{(V_{\text{NaOH}} \times N_{\text{NaOH}}) - (V_{\text{HCl}} \times N_{\text{HCl}})\} / \text{sample weight} \quad (3)$$

### Application

Cellulose-MBA-AA (copolymer A) was used as an adsorbent of heavy metal ions. The metal used in this study was  $\text{Pb}^{2+}$  with concentrations of 3 ppm, 5 ppm, and 10 ppm.

## RESULTS AND DISCUSSION

### Copolymerization of cellulose-MBA-AA

The percentage of copolymerization was determined by gravimetric method. The measurement was intended to observe the success or failure of grafting copolymerization or how much AA monomer was grafted on cellulose by increasing the irradiation dose. A graph of grafting percentage versus the irradiation dose is presented in Fig. 1.

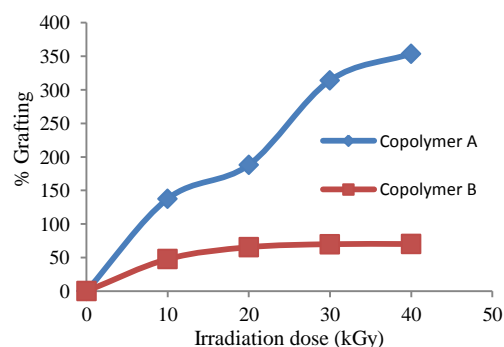


Fig. 1. Effect of irradiation dose on percentage of grafting (%G) in cellulose-MBA-AA (copolymer).

Figure 1 shows that copolymers A and B had the same linear pattern where the percentage of copolymer grafting %G increased with increasing irradiation doses in the 10-40 kGy range.

The grafting percentage of copolymer A was 137.61 % at irradiation dose of 10 kGy and 353.82 % at 40 kGy which were higher than that of copolymer B which attained a grafting percentage of 47.79 % at 10 kGy and 70.21 % at 40 kGy. The results occurred due to the higher monomer concentration in copolymer A than in copolymer B. A higher monomer concentration produces more radicals on monomer which react with cellulose, and while cellulose exhibits a high degree of crystallinity, grafting occurs mainly on amorphous phase and the topmost surface layers rather than in the bulk [3,16]. The effect of irradiation dose on the percentage of grafting for some variation of the concentration of acrylic acid largely follows logarithmic equation; the percentage of grafting copolymer increases and reaches the optimum grafting limit with the increasing irradiation doses. The grafting yield of copolymer A was higher than that of copolymer B because of the amount of radicals formed, radical position, availability and diffusion of monomers, and gel formation [1]. The best grafting yield (grafting percentage) occurred at an irradiation dose of 40 kGy. In addition, the grafting percentage for high-concentration acrylic acid (copolymer A) was higher than for low concentration (copolymer B).

## Characterization

Characterization is necessary to determine the cellulose-MBA-AA copolymer characteristics which formed optimal function group, thermal analysis, ion exchange capacity, and other physical and chemical properties.

## Thermal analysis

The thermal analysis aimed to determine the thermal stability of cellulose which has been modified. The thermal properties of the modified cellulose (copolymer) was found to be better than those of pure cellulose which was observed in the temperature range of 20-600 °C. At the temperature range of 300-600 °C, cellulose can generally be optimally degraded by heat. Based on thermal analysis, the cellulose-MBA-AA copolymer was found to have a higher percentage of grafting (A and B copolymer) than pure cellulose. The result of the DSC thermogram of cellulose-MBA-AA is presented in Fig. 2.

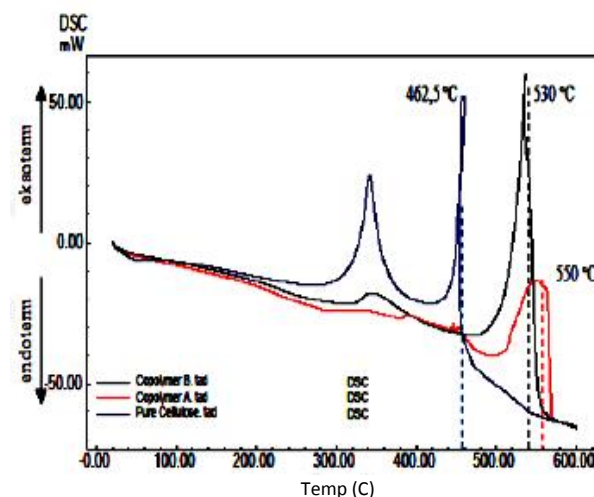


Fig. 2. DSC thermogram of the isolated rice straw cellulose and cellulose-MBA-AA copolymers.

Figure 2 shows that pure cellulose and B copolymers have similar calorimetric patterns; they both exhibit a low exothermic peak at point 340 °C before the peak in the highest exothermic ( $\geq 50$  mW). The exothermic peak temperature of pure cellulose (462.5 °C) is lower than that of copolymer B (530 °C). In the other words, the energy required to heat a sample of copolymer B is more than to do so for the pure cellulose. This is caused by the formation of grafting copolymer which increases the molecular weight and degree of polymerization of copolymer B, thus increasing the energy required to degrade copolymer B. This is consistent with the theory of bond energy where the greater the molecular weight of a substance, the greater the energy needed to break the bonds within the substance. In addition, the DSC thermogram of copolymer A shows a single exothermic peak at the temperature of 550 °C, indicating that its molecular weight and degree of polymerization are higher than that of copolymer B. Thus, it is indicated that the copolymers of cellulose-MBA-AA has a better thermal stability than pure cellulose, as reflected from the higher temperature needed to degrade it.

## Functional groups

Analysis of the functional groups was carried out to observe the change of functional groups. The FTIR spectrum of cellulose-MBA-AA copolymer with both a high concentration of acrylic acid (copolymer A) and a low concentration of acrylic acid (copolymer B) were compared with the FTIR spectrum of cellulose isolated from rice straw (pure cellulose). The comparison is presented in Fig. 3. The formation of copolymer is characterized with the emergence of the peak on FTIR spectra which cannot be seen on rice straw cellulose insulation yield. In general, shifting wave numbers can also describe that crosslinking occurred.

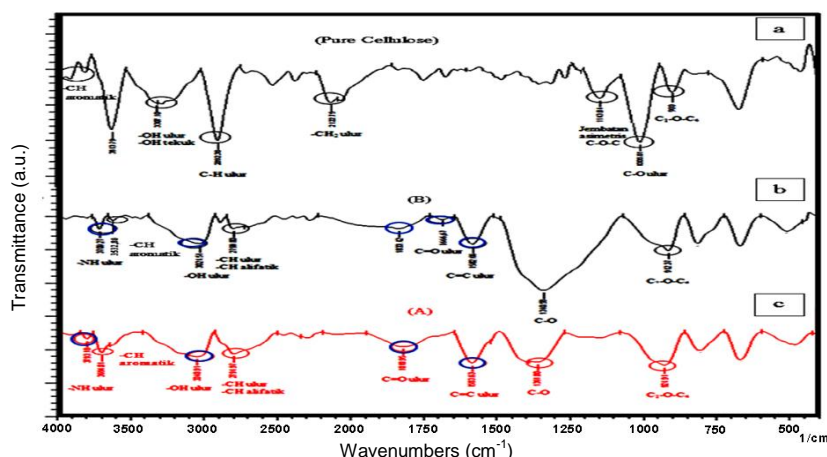


Fig. 3. FTIR spectra (a) Pure cellulose, (b) Copolymer B, (c) Copolymer A.

N,N'-methylenebisacrylamide (MBA) is a ketone compound and acrylic acid is a carboxylic acid compound. Carbonyl and carboxyl groups, which are part of ketones and carboxylate acids, respectively, show C = O peaks in the wave number range of 1820-1660 cm<sup>-1</sup> [17]. FTIR spectrum of cellulose-MBA-AA indicates the occurrence of crosslinking MBA and grafting of acrylic acid copolymer A has a weak C = O functional group peak at a wave number of 1818 cm<sup>-1</sup>, while copolymer B at 1666 cm<sup>-1</sup>. The emergence of the C = O functional group peak at 1818 cm<sup>-1</sup> that is accompanied by -OH peak at 3040 cm<sup>-1</sup> can be interpreted as an indication of the presence of carboxylic acid compounds in the copolymer or, in other words, that there has been a grafting of acrylic acid on cellulose, while the typical peak of the MBA monomer is characterized by -NH, indicating crosslinking peak at 3793 cm<sup>-1</sup> for copolymer A, and 3709 cm<sup>-1</sup> for copolymer B, with the wave numbers signifying that there has been MBA crosslinking on cellulose.

Table 1. Functional groups and wave numbers of peaks of the isolated rice straw (pure cellulose) and cellulose-MBA-AA in the FTIR spectra.

Functional groups	Wave Number (cm <sup>-1</sup> )		
	cellulose from isolated rice straw	Copolymer A (Cellulosa-MBA-AA with high concentration of AA)	Copolymer B (Cellulosa-MBA-AA with low concentration of AA)
-OH	3307	3040	3024
C=O	1008	1361	1340
C <sub>1</sub> -O-C <sub>4</sub>	900	924	912
-CH aliphatic	2892	2794	2799
-CH	3613	3694	3532
aromatic	-	1583	1582
C=C	-	3793	3709
-NH	-	1818	1666

The differences of functional groups contained in the polymer can be seen in Table 1. From the table, it can be seen that the functional groups of aromatic, C = C and -NH can not be found in Cellulose but they appear in copolymer A and B which proved that crosslinking and grafting have been formed.

### Degree of swelling (%S) in water

From the degree of swelling test to find the swelling percentage (%S), it was found that the swelling percentage of pure cellulose was significantly higher (544.49 %) than that of copolymer cellulose-MBA-AA (144.15 % and 259.05 %).

The swelling percentages of copolymer A at doses of 10, 20, 30, and 40 kGy were 213.08 %, 187.04 %, 146.97 %, and 144.15 %, respectively, while for copolymer B they were 331.17 %, 301.95 %, 266.01 %, and 259.05 %, as presented in Fig. 4.

The decrease of %S with increasing dose starting from 10 kGy through 40 kGy indicates that there was a reduction of the hydroxy groups of the chains due to substitution of a number of monomers to -OH groups. The more substituted monomers would increase the ability to adsorb heavy metals. The copolymer with the lowest %S can be used as adsorbent. The %S value in the lowest water fraction on acrylic acid copolymer with a high AA concentration (copolymer A) and low AA concentration (copolymer B) occurred at a dose of 40 kGy with a value of 144.15 % and 259.05 %, respectively. Figure 4 shows that the percentage of copolymer swelling in water decreased with increasing irradiation dose. This decrease occurred because the radiation can increase the density of the bonds between the molecules in copolymers that were formed in the presence of crosslinking agent,

thus decreasing water adsorption. In addition, the copolymers with high concentrations of acrylic acid had a relatively small swelling percentage compared to those with low concentrations of acrylic acid. The greater number of grafted monomers in cellulose reduced %S as well.

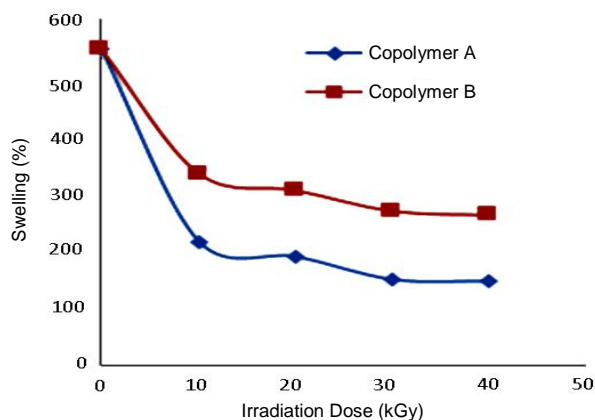


Fig. 4. Effect of irradiation dose to degree of swelling (%S) on cellulose MBA-AA.

### **Ion exchange capacity**

To determine the copolymers' capability of metal ion adsorption, the ion exchange capacity was measured. The principle of ion exchange capacity is neutralizing residual NaOH (from mixing with cellulose MBA-AA) with HCl until an equivalence point is reached. The effect of irradiation dose on ion exchange capacity of cellulose-MBA-AA is presented in Fig. 5.

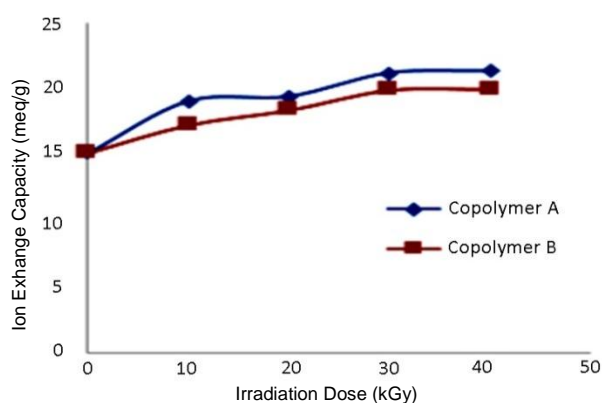


Fig. 5. Effect of the irradiation dose on ion exchange capacity of cellulose-MBA-AA.

Figure 5 shows that ion exchange capacity increased with increasing irradiation dose. The highest value of ion exchange capacity occurred at a dose of 40 kGy, where the ion exchange capacity value for copolymer A was 22.73 meq/g and for copolymer B it was 18.3 meq/g.

These values are higher than that of pure cellulose (14.46 meq/g). This is caused by the high degree of polymerization of the copolymer A. The functional groups of -OH, -COOH, and -NH (derived from AA and MBA monomers polymerized) were grafted in cellulose. These groups can perform ion exchange in excess NaOH solution such as Na<sup>+</sup> into -ONa and -COONa, so the concentration of NaOH solution will decrease [18].

### **Application**

#### **Effect of Pb<sup>2+</sup> sorbent concentration on adsorption**

One of the factors that may affect the ability of the adsorbent to adsorb metal ions is concentration [18]. The percentages of adsorption of pure cellulose and copolymer A are shown in Fig. 6.

Figure 6 indicates that cellulose-MBA-AA adsorbed better than pure cellulose. Increasing sorbent concentration tends to decrease adsorption percentage on both cellulose-MBA-AA (from 99.87 % on 3 ppm sorbent to 90.28 % on 10 ppm sorbent) or the pure cellulose (from 64.33 % on 3 ppm sorbent to 54.43 % on 10 ppm sorbent). The adsorption percentage of cellulose-MBA-AA copolymer was higher than that of pure cellulose due to the monomer of AA and MBA adding active groups on the cellulose-MBA-AA as -COOH, -C=O, -OH, and -NH that can adsorb metal ions (ion exchange). However, at the concentration of 10 ppm, the metal ion adsorption percentage on the cellulose-MBA-AA or pure cellulose decreased due to the bonding of Pb<sup>2+</sup> and active group such as -COOH or -C=O) being stronger than that between Pb<sup>2+</sup> and -OH, causing slower desorption and decreasing the percentage of adsorption.

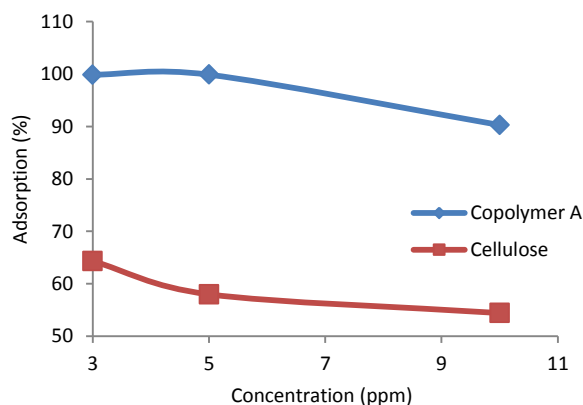


Fig. 6. Effect of Pb concentration on adsorption (pH≈7).

### Effect of $Pb^{2+}$ concentration on adsorption capacity

In addition to the percentage of adsorption, the adsorption capacity also needs to be calculated to determine the amount of metal ions which can be adsorbed [16]. The adsorption capacity measurement results for cellulose and cellulose-MBA-AA are shown in Fig. 7.

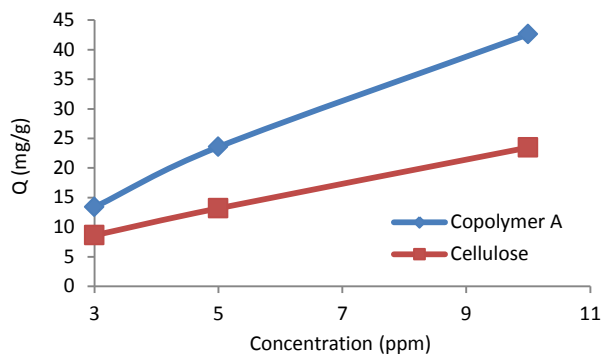


Fig. 7. Effect of  $Pb^{2+}$  concentration on adsorption capacity (Q).

Figure 7 shows that the value of the adsorption capacity increased with increasing  $Pb^{2+}$  concentration.

In addition, the adsorption capacities of pure cellulose and cellulose-MBA-AA are not extremely different at 46.21 mg/g for cellulose-MBA-AA and 42.42 mg/g for pure cellulose at a concentration of 10 ppm.

### Effect of pH on adsorption percentage

In the use of cellulose-MBA-AA as an adsorbent, it is also important to consider the effect of pH on the adsorption of the  $Pb^{2+}$  ion. Here, the pH variation used was 5 (acidic), 7 (neutral), and 9 (alkaline). The effect of pH on the adsorption of  $Pb^{2+}$  is presented in Fig. 8.

Figure 8 indicates that the optimum adsorption of  $Pb^{2+}$  was 90.28 % at neutral sorbent pH (pH≈7). For alkaline sorbent (pH=9), the percentage of adsorption decreases (58.40 %). This is because at the neutral sorbent pH, the coordinate bond between the metal and the adsorbent occurs through nitrogen or sulfur atom. In this condition, the nitrogen atom starts to remove proton and becomes negative charged. It effects a stronger interaction between metal ions and adsorbent, increasing the amount of metal ions adsorbed [18].

On the other hand, at acidic sorbent pH values (pH 1-5), nitrogen atoms in organic ligands as active sites of adsorbent are protonated and become positively charged. It effects a

reduction of metal ion adsorption capacity due to repulsion between adsorbent surface and metal ions. The number of -OH ions in solution in reactions between  $Pb^{2+}$  (positively charged) with -OH ions are characterized by formation of deposits that could potentially cover the surface and pores of cellulose-MBA-AA [18].

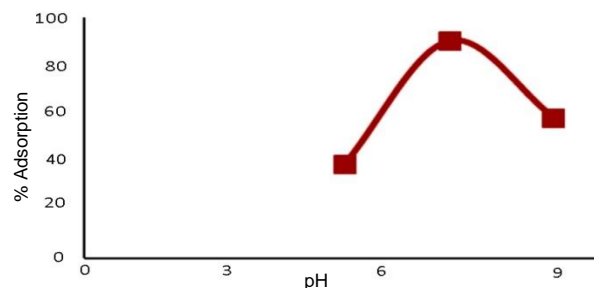


Fig. 8. Effect of pH on  $Pb^{2+}$  metal ion adsorption.

### Adsorption isotherms

Several types of adsorption isotherms can be used to study the mechanism of adsorption. In modeling adsorption equilibrium in solid-liquid phases, two types of adsorption isotherms, namely the Freundlich and Langmuir isotherms, are generally adopted. The adsorption isotherm and adsorption equilibrium can be shown on the  $Pb^{2+}$  ions in a solution by using the adsorbent (cellulose-MBA-AA).

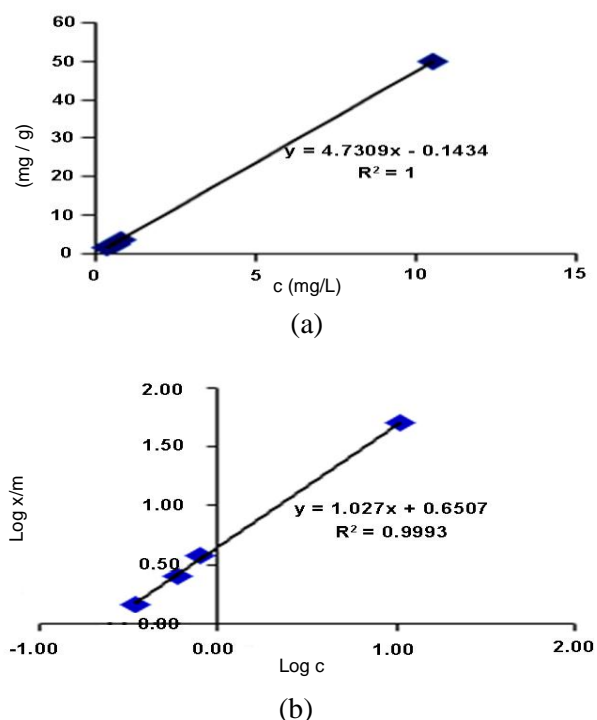


Fig. 9. (a) Langmuir isotherm and (b) Freundlich isotherms for Cellulose-MBA-AA.

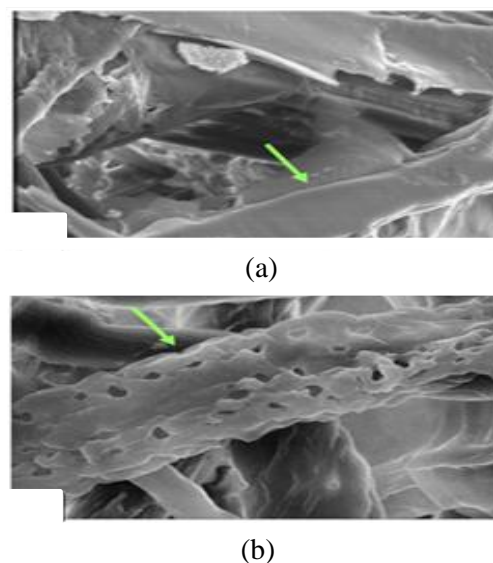
The selection of equilibrium models between the aforementioned two isotherms is based on the determination coefficient ( $R^2$ ). From the adsorption isotherm, the adsorption mechanism that occurred between the adsorbate molecules and the surface of the adsorbent can be determined. Figure 9 shows that the Langmuir isotherm type has a high linearity as indicated by its optimum  $R^2$  value (1) while for Freundlich isotherm it is marginally lower. The linearity of  $Pb^{2+}$  adsorption results showed that it tends to predominantly follow the Langmuir isotherm. Langmuir isotherm is a chemical adsorption that occurs because of the chemical bonding between the adsorbate and adsorbent surface. Due to the strong chemical bonding occurring when the adsorbent surface is covered by adsorbate, the adsorbate is adsorbed by adsorbent within one layer, Langmuir obtained the model by assuming that the adsorption occurs in a homogeneous surface of the adsorbent. The shortcoming of an adsorbent following this reaction model could be explained as follows. Langmuir isotherm involves the smaller regeneration of adsorbent, due to strong chemical bonding. Consequently, metal ions that have been adsorbed by adsorbent are difficult to release and some reagents are needed to remove them.

### Surface analysis

Surface analysis was carried out by SEM to determine the morphology of the surface of adsorbent from pure cellulose and cellulose-MBA-AA. Surface analysis was carried out on cellulose-MBA-AA copolymer before  $Pb^{2+}$  ion adsorption.

The surface analysis was based on the adsorbent surface characteristic X-rays generated from the transition between the electrons of a particular energy levels within an atom. The analysis of the surface of cellulose and cellulose-MBA-AA used a scanning electron microscope with a magnification of 4000 $\times$ . Before analyzed, pure cellulose and cellulose-MBA-AA were coated with particles of platinum (Pt) to aid the conductivity of the analysis. The comparison of analysis results of pure cellulose surface and cellulose-MBA-AA is presented in Fig. 10.

Figure 10 shows that on pure cellulose, fibers (fibrils), which are characteristic of pure cellulose, still appeared, while cellulose-MBA-AA appeared porous and showed a functional substance structure, due to the occurrence of MBA and AA.



**Fig. 10.** SEM micrographs with 4000 $\times$  magnification of surface of adsorbent from (a) pure cellulose and (b) cellulose-MBA-AA

### Elemental composition analysis by EDX

Scanning electron microscope (SEM) which is equipped with energy dispersive X-ray spectroscopy (EDX) can be used to determine the elemental composition of a sample. When a sample is photographed by SEM and then forwarded to the EDX, the EDX is able to identify each element in the sample. EDX analysis was carried out to observe and ensure that the copolymer can adsorb  $Pb^{2+}$  ions as shown in Fig. 11.

Figure 11 indicates that the predominant metal ion on the cellulose-MBA-AA was  $Pb^{2+}$ . This indicates that  $Pb^{2+}$  ions could be adsorbed by cellulose-AA-MBA with a concentration as shown in Table 2.

Table 2 shows that the amount of  $Pb^{2+}$  adsorbed by cellulose-MBA-AA reached 1.24 % (wt%) indicating that there had been a process of adsorption. However, some other metals such as Zn (0.5 %), sodium (1.4 %), and magnesium (0.01 %) probably came from the content of the straw in which they were contained (bonded) when the pure cellulose was isolated.

**Table 2.** Composition of cellulose-MBA-AA after  $Pb^{2+}$  adsorption

Element	Wt (%)
Carbon	43.83
Oxygen	52.40
Sodium	1.4
Magnesium	0.01
Silicon	0.01
Phosphorus	0.3
Chlorine	0.17
Zinc	0.5
Lead	1.24
Total	100



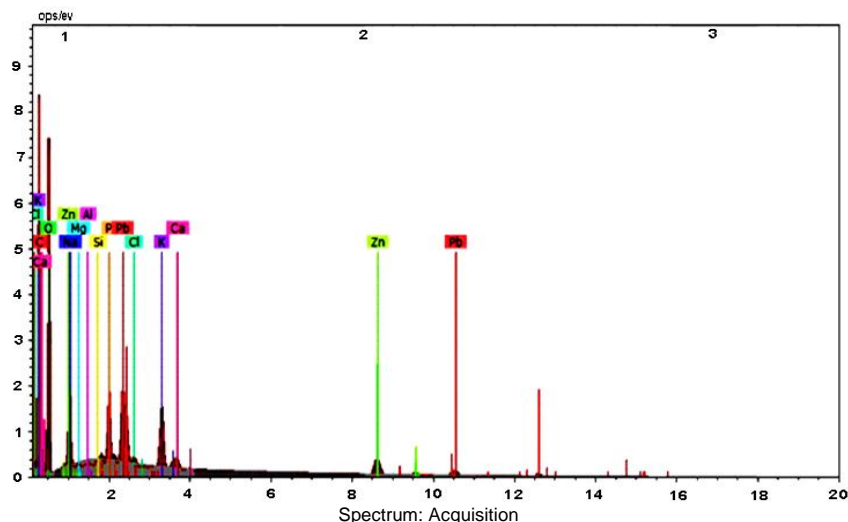


Fig. 11. Spectrum of cellulose-MBA-AA in adsorbing  $Pb^{2+}$  ion.

## CONCLUSION

Modification of cellulose by copolymerization using 40 kGy irradiation dose in the presence of MBA and AA has been successfully carried out. The copolymerization degree attained was 353 %.

The application of the modified cellulose on  $Pb^{2+}$  ion adsorption indicated that the adsorption reached 99.8 % for  $Pb^{2+}$  concentration of 3 ppm at a pH of around 7.

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