The Effect of Crosslinker and Pore Generated on Selective Adsorbent (Cu$^{2+)}$ based on Grafting of Acrylic Acid onto Cassava Starch

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Abstract

The technology development in many industries nowadays, such as electronic industry produces heavy metal wastes which may pollute our environment. The use of adsorbent as a heavy metal removal from soil and water is one of the efficient process which can be considered to be used. In addition the release of the adsorbate becomes an important way as well because usually those heavy metals still have a high value. The objective of this research is to develop adsorbent based on cassava starch. So, the release process will become easier and will not produce another waste. The adsorbent was produced through the grafting of acrylic acid onto cassava starch by using Fenton initiator. To construct a stable 3-D network, the crosslinker (CL) N,N'- methylenebisacrylamide was added. The variable observed were the amount of CL added (0.5%; 1.5%; 2.5% and 3.5%) and the treatment of generating more pores on starch copolymer. The treatments on starch copolymer observed were single freezing, second freezing, and citric acid modification and carbonization methods. Analysis performed on the adsorbent was % add-on, water absorption and metal adsorption (especially Cu^{2+} ion) capacity. The result showed that the used of 2.5% CL produced the highest add-on (47.66 %), the highest water absorption capacity and the highest metal adsorption capacity (0.29g Cu^{2+}/g adsorbent) The citric acid modification also produced the highest pores on the adsorbent.

Keywords: adorbent, carbonization, cassava starch, crosslinker, freezing, heavy metal

1. Introduction

The adsorbent used nowadays in waste water treatment become more popular, since many industries produce a heavy metal disposal which most of time still has a high value. Petroleum-based adsorbent start to be replaced by biomass-based adsorbent like from orange waste (Pérez-Marín, A.B. et al. 2010), banana stem (Anirudhan, T.S. et al. 2012), sawdust (Naiya, T.K. et al. 2008) and other biomass (Arief, V.O. et al. 2008) which is known as biosoption. The basic mechanisms production of this adsorbent is through carbonization. The disadvantage using this type of adsorbent is the small size of the adsorbent which create a separation problem on the operation.

On the other side the use of natural product including biomass for the based-material of many products is an interesting aspect that should be considered in the near future. Indonesia is one of the country which produce a lots of natural resources whicharenotonly usefulas a foodbutalsoas anindustrial rawmaterial. One of the natural resources which has a unique properties as a natural polymer is starch. It can be disintegrated, assembly or modified into many kind of products. Starch can be found in almost every plant as seed, grain, cereal, tuber, root and legume. One of the starch resources which is easy to grow without intensive cultivation and also in dry area is cassava roots.

The degree of hydrolysis may control the pore size in the starch granule as have been done by Chen, G., et al. (2012) and Zhang, B., et al. (2012) using α-amylase and glucoamylase. And Qian, J., et al. (2011) combined ultrasonic and enzymatic hydrolysis in an attempt to enlarge the pores. The problem on this treatment is on the determination of the optimum degree of enzymatic hydrolisis and also sometimes the adsorbent dissolves in the mixture creating an additional waste.

In this work, the adsorbent is produced by attaching the acrylic acid monomer onto the macromolecule starch backbone and together with the crosslinker which is integrated inside the network creates a strong 3-D network

(Witono, J. R., et al., 2014). The variation amount of crosslinker added is observed in related to the ability of copolymer to adsorp heavy metal in the solution (waste water). This copolymer will be used as a template for the heavy metal adsorption. In order to create more porous structure or higher surface area, the further treatment is applied to the copolymer. Qian, D., et al. (2011) observed by freezing the starch gel, the ice crystal inside will expand the porous size. And then it was used citric acid to activate the surface. Finally, the activated copolymer was freezing once more. Those treatment, which is usually used in the gelatinized starch, is integrated into the copolymer.

The goal of this research is to develop a heavy metal adsorbent based on cassava starch copolymer , which is cheap, stable and easy to regenerate.

2. Method

2.1 Materials

The cassava starch used in this experiment was supplied by PT. AVEBE Indonesiawith a purity of 98%. Acrylic acid was kindly supplied by BASF PETRONAS Chemicals, Sdn. Bhd., and Malaysia and used without further purification. Ferro ammonium sulphate (FAS), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), N,N'-methylene-bisacrylamide (MBAM), hydroquinone (HQ), acetone, ethanol, citric acid and $CuSO_4.5H_2O$ were reagent grade chemicals, purchased from Sigma Aldrich, Singapore and used as received. All solutions were prepared with distilled water.

2.2 Starch Grafted Synthesis

7.5% starch was suspended in 500 ml aquadestin the jacketed stainless steel reactor (the reactor set up can be seen in Figure 1). Then starch slurry was heated up to its gelatinized temperature ~ 70^0C and kept at this temperature for 25 min. The gelatinized starch was cooled up to 40^0C (grafting temperature). And the monomer (acrylic acid), initiator I–FAS, initiator II–H_2O_2 was added, respectively. After the copolymerization reaction was carried out for 2 hours, the crosslinkerwith variation 0,5%; 1,5%; 2,5%and 3,5% was added.Finally, NaOHwith the degree of netralization 50% was added. The reaction was ceased by adding 2ml 0,1M hydroquinone.

1. Stainless steel (jacketed) isothermal reactor with turbin blade stirrer
2. Nitrogen gas tank
3. Overhead stirrer
4. Gas outlet / reactant inlet
5. Thermocouple connected to the temperature control
6. Thermometer
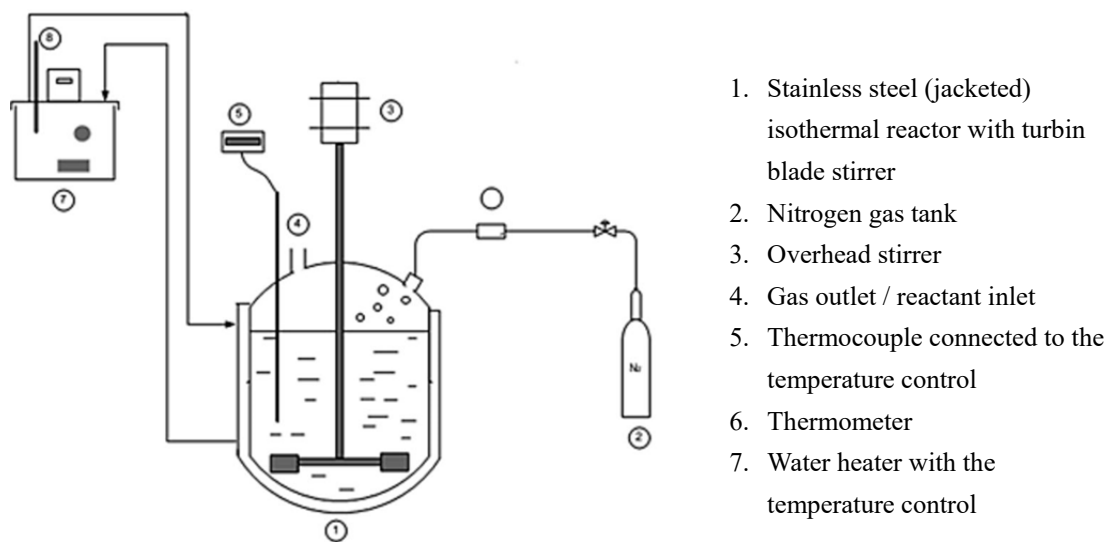7. Water heater with the temperature control

Figure 1. Reactor set up

2.3 Adsorbent Preparation

Before the copolymer produced by grafting reaction was treated further to be an adsorbent, it should be separated from its side product like homopolymer, salts and unreacted monomer. The separation process was done by washing the copolymer gel with acetone 3 times. It is followed by drying the cleaned copolymer at 60^0C in oven until its weight constant.

The pores formation in thecopolymerwere propagatedbyvarious treatment (Qian, D., et al., 2011). Firstly, the freezing process. The starch copolymer gel was cut into cubes and frozen in freezer. The frozen cubes were soaking in ethanol for 3 h. Then the cubes were dried at $50^0C$for 6 h. Secondly, the copolymer activation by citric acid. The starch copolymer dry were immersed in CA solution and conditioned for 12 h at room temperature.

CAsolution was prepared by disolving 0.09 g citric acid into 10 ml95% ethanol. The weight ratio of CA and copolymer starch was 15:100. Then it washeated at 130^0C for 2 h in the oven followed by washing with ethanol three times or until all unreacted citirc acid removed. Thirdly, the second freezing process. Starch (+ citricacid) copolymer cubes were immersed into the starch pastes using ultra sonication until no bubbles appeared again. Then the cubes were taken and frozen. The cubes were immersed three times in ethanol. The cubes were dried in at 50^0C for 4 h.

As a comparison the carbonization method was applied into the copolymer by pyrolizing it at 400^0C for 15 h.

2.4 Analysis

2.4.1 Water Absorption Capacity

0.1 g dry sample was immersed in 100 mL aquadest at room temperature. After ... minutes the swollen sample was separated using Whatman filter paper and weighed. Water absorption capacity was calculated using equation (1):

$$Q = \frac{m_2 - m_1}{m_2} \tag{1}$$

Where m_2= weight of sample after immersed (g)

m_1= weight of initial dry sample(g)

2.4.2 Metal Adsorption Capacity

50 mg sample were immersed in $CuSO_4.5H_2O$ solution for 24 h. Adsorbent were separated from heavy metal solution and theunadsorped metal ions concentration determined using UV-VIS spectrophotometer. The Cu^{2+} adsorption capacity was calculated using equation (2):

$$qe = \frac{C_o - C_e}{m} \times V \tag{2}$$

Where   Co = initial concentration of $CuSO_4.5H_2O$ solution (g/l)

Ce = concentration of $CuSO_4.5H_2O$solution (g/l)

m = weight of adsorbent (g)

V = volume of $CuSO_4.5H_2O$ solution (l)

2.4.3 Carboxyl Content

1 g dry sample was added HCl 0.1 N and stirred for 30 min. Then the filter cake was separated and flushed with aquadest until the filtrate is free of chloride. 60 mL aquadest was added intothe filter cake and heated for 15 m. Phenolpthalein(pp)indicator was added to slurry filter cake and titrated with 0.1 N NaOH. %COOH (carboxyl contnet) was calculated using equation (3):

$$Carboxyl\ content\ (\%) = \frac{ml\ 0.1\ N\ NaOH \times 0.0045 \times 100}{sample\ weight\ (g)} \tag{3}$$

3. Results

3.1 %add-on

% add-on shows the ratio of the amount amount grafted monomer onto the copolymer. It can inform also the conversion level of the copolymerization. % add-on can be calculated by measuring the carboxyl content in the coplymer,. Based on the data observed, as it's shown in Figure 2, the highest % add-on is obtained at around 2 – 2.5% crosslinker added and after that tends to go down. It may cause of the properties of the crosslinker (N,N'-methylenebisacrylamide) itself which in the high concentration can be autopolymerized especially if there is an oxidizing agent (Witono, J. R., et al., 2014). So, the effect of the crosslinker goes down.
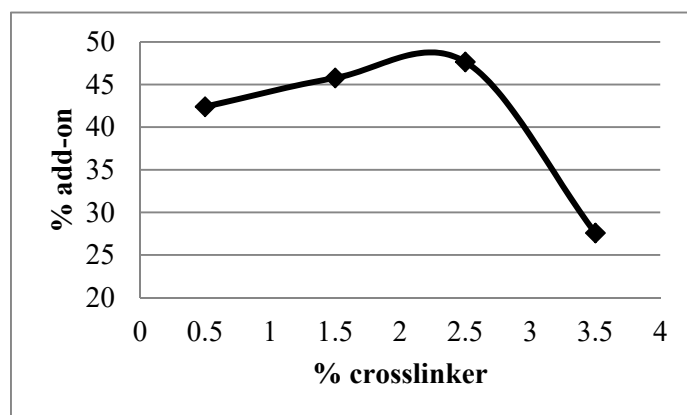
Figure 2. % add-on of the coplymer in the various amount of crosslinker added

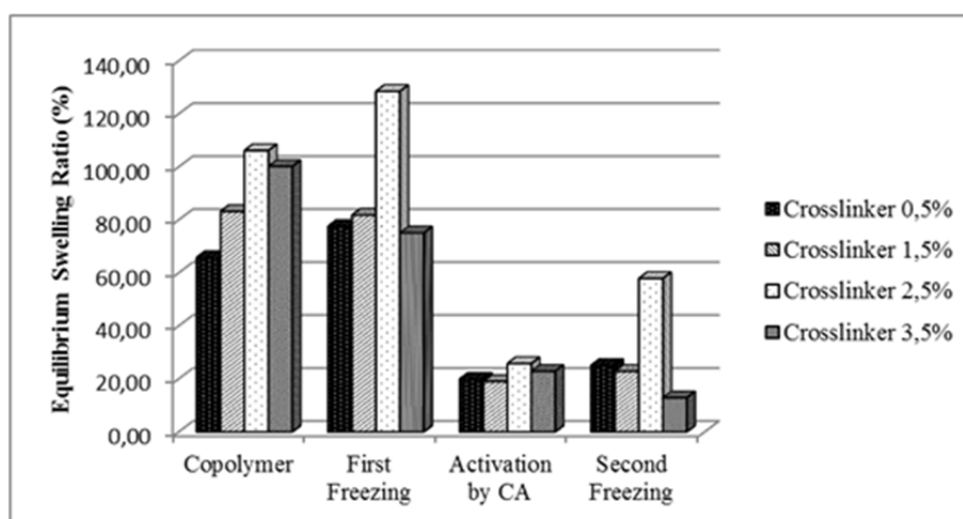*3.2 Water Absorbancy Capacity*

Figure 3. Water absorbency capacity in the various amount of crosslinker added and pore enlargement treatment

There is a relation between % add-on and water absorbency capacity. The more monomer attached onto starch backbone, the more carboxyl groups attached onto copolymer. Carboxyl groups (–COOH) are capable to form hydrogen bonds with water. The highest %-add-on is obtained on the 2.5% crosslinker added, so the water absorbency capacity was reached at the 2.5% crosslinker added as well.

Some works (Varriano-Marston, E., et al., 1985; Freschi, J., et al., 2014) have observed that during (fast) freezing the size of cavities inside the starch gel can be enlarged depending on the gel matrix hardness. The problem arises from this situation is the reduced gel strength as a result of mechanical damage to the gel microstructure caused by ice crystal formation (Kalichevsky-Dong, M. T., et al., 2000). It can be seen from Figure 3 that after starch gel freezing the water absorbency capacity of coplymer increases. It means the capacity of copolymer to retain water increases because of the increasing of the pores size inside the copolymer. And since the gel matrix of the copolymer stronger than gelatinized starch this adsorbent is more stable.

3.3 Metal (ion Cu^{2+}) Adsorption Capacity

The metal adsorption capacity is tested on the ion Cu^{2+} in the solution. From Figure 4 can be seen that after freezing and activated by citric acid, the metal adsorption capacity of copolymer increases. The adsorption capacity in 2.5 % crosslinker added and after freezing and activated by citric acid gives the highest value i.e. 0.01063 mol Cu^{2+}/ gr adsorbent. The result is not fully paralel with the water absorbency capacity. But from this data, it can be assumed that the acid activation of coplymer has an important role to attract more metal ion.
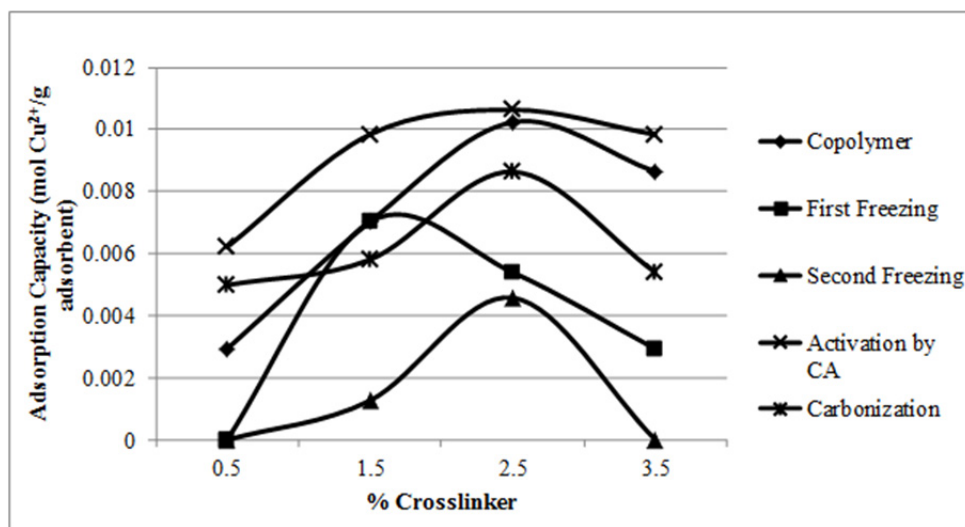
Figure 4. Metal ion adsorption capacity by copolymer after further treatment

Lu, Q., et al., (2013) who used grafted starch as an adsorbent template as well, obtained copper ions removal capacity is0.00256 mol Cu^{2+}/ gr adsorbent, lower than was gotten. This shows that the further treatment into the copolymer can increase its capacity in adsorbing metal.

Compared to the conventional method on adsorbent preparation i.e. carbonization, its metal adsorption capacity is higher. The other benefit of this adsorbent is saving a lots of energy in preparation and also regeneration.

4. Discussion

Grafted starch has a good prospect to be developed as a cheap, biodegradable and stable adsorbent. The metal adsorption capacity of this coplymer can be increased by further treatment. From this study can be seen freezing and activated by citric acid can improve its capacity. The maximum capacity is obtained 0.29g Cu^{2+}/g adsorbent. The further research is still going on.

Acknowledgments

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