Modification Charcoal Eceng Gondok (*Eichornia Crassipes*) Toward Chitosan-Epichlorohydrin and its Solubility Test

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Abstract. The research has been conducted entitled "Modification of Eceng Gondok (*Eichornia Crassipes*) to Chitosan-Epichlorohydrin". The aim of this research is to determine the solubility test of water hyacinth composite on chitosan-epichlorohydrin. This research begins with sample preparation covering the manufacture of eceng gondok and charcoal activation and testing the quality of activated charcoal of Eceng Gondok. After that, it is continued by making the composite through the initial stages of chitosan charcoal production and chitosan modified chitosan test and chitosan-epichlorohydrin modified chitosan test. The result of the research shows that 3 standard of active charcoal quality test fulfill SNI requirement except fly content. And chitosan charcoal solubility test showed that the solubility level of charcoal: the lowest chitosan was found on charcoal ratio: chitosan 5:7. While chitosan-epichlorohydrin modified chitosan test showed that the lowest solubility rate occurred at a concentration of 1% epichlorohydrin.

Keywords: *Eichornia crassipes*, hyacinth, chitosan, epichlorohydrin

INTRODUCTION

Activated carbon, also called activated charcoal, is charcoal with the configuration of carbon atoms liberated from bonding with other elements and the pores are cleared of dirt or other compounds so that the surface and the active center become large, and the adsorption capacity of liquids and gases increases [1]. Raw materials derived from animals, plants, and waste containing carbon can be activated charcoal. One of the raw materials that can be used to make activated charcoal is eceng gondok (*Eichornia Crassipes*) or water hyacinth plant. Water hyacinth gondok is underutilized as it is considered a weed that destroys the aquatic environment, but it has the advantage of being able to absorb organic, inorganic, and other heavy metals that are pollutants [2].
The addition of chitosan to activated charcoal aims to obtain materials with better physical and mechanical properties than the properties of each of the original constituent components. Chitosan is non-toxic, biocompatibility, high chemical reactivity, anti-bacterial, chelation, and adsorption properties. Chitosan is a very good natural adsorbent because it has amine (-NH$_2$) and hydroxyl (-OH) groups that can function as a coordination place to form complex with other substances [3]. However, chitosan is easily soluble in acid, so modification is required by adding a crosslinking agent such as epichlorohydrin. The addition of epichlorohydrin can optimize bond strength in beads and resistant to acids. Therefore, in the preparation of charcoal beads of eceng gondok modified chitosan-epichlorhydrin, need to be tested the quality of activated charcoal from eceng gondok, chitosan modified charcoal solubility, and chitosan-epichlorhydrin modified charcoal solubility.

MATERIAL AND METHODS

Materials
Eceng gondok, HCl p.a (Merck), 10% oxalic acid (Merck), NaOH p.a (Merck), and 99% epichlorohydrin (E.Merck), chitosan powder (DD = 85.89%).

Instrumentation
Laboratory standard glass equipment (Pyrex), oven (Carbolite), porcelain cup, pH meter (Tenway 3040 ion analyzer), desiccator, analytical balance (OHAUSS galaxy TM 160 model), 60-230 mesh filter (Retsch), Whatman 42 filter paper, hot plate (Cimaec), magnetic stirrer, furnace, shaker GKL 300.

Procedure

Sample preparation
Eceng gondok of 2.70 kg washed with running water, then cut into pieces and dried. Dried eceng gondok is put into prepared containers. The combustion process is carried out with a moderate flame. Burning containers are given holes first before the combustion process. The process of making charcoal is stopped until the resulting smoke gets smaller and is blue.

Charcoal preparation
Eceng gondok that has been obtained is then be mashed with mortar and filtered with 60 mesh sieve, then boiling for ± 3 hours. After that it is filtered and dried in the oven for ± 1 hour at 100°C.

Charcoal activation process
25 g of water hyacinth then washed 2 times with 20 mL of 0.1 M HCl followed by centrifugation at 2800 rpm, then washed with distilled water until neutral. A total of 150 mL of 0.1 M NaOH was added to charcoal and allowed to stand for 24 hours. Then dried in the oven for 1 day at 60-70°C and then be mashed and filtered using a 60 mesh filter and stored at room temperature.

Active charcoal quality test
Activated charcoal quality test is done based on SNI No. 06-3730-1995 with water content test parameters, ash content, airborne content and absorption to solution of I$_2$. In the determination of moisture content, 1 g of charcoal samples were dried at 105°C for 3 hours then cooled and weighed to a constant weight. In the determination of ash content, 1 g of charcoal samples were placed in a furnace at 700°C for 6 hours then cooled and weighed to a constant weight. In the determination of the content of the fly substances, 1 g of charcoal samples were placed in the furnace at 950°C for 10 minutes and then
cooled and weighed to a constant weight. In the absorption test I, 0.25 g of charcoal samples were added with 0.1 N iodine solution. The suspension was filtered and the filtrate was titrated with 0.1 N sodium thiosulfate solution.

**The making of chitosan modified charcoal**
Charcoal and chitosan are made with a ratio of 5:5, 5:6, 5:7, 5:8, and 5:9 (w/w). In each chitosan variation dissolved in 100 mL 10% oxalic acid, stirred and heated at 40-50°C until dissolved, then 5 g of activated charcoal was added and stirred until homogeneous. The chitosan-coated charcoal is then dripped and immersed into 2 M NaOH until it forms a bead. The formed bead is then washed with distilled water until it is neutral and then dried.

**Solubility Test of Chitosan-modified charcoal**
Bead with a ratio of 5:5, 5:6, 5:7, 5:8, and 5:9 (w/w) were prepared to be added with 25 mL distilled water and the pH was adjusted from 2, 3, 4, 5, 6, and 7 with 0.1 M HCl solution and stirred constant for 24 hours, and then filtered, dried, and the bead is weighed back until the weight is constant. The amount of chitosan-modified charcoal solubility can be determined by looking at the initial weight minus the final weight.

**The making chitosan-epichlorohydrin-modified charcoal**
A total of 0.5 g of charcoal-chitosan beads were introduced into 2 ml of 99% epichlorohydrin with a concentration variation of 0.4; 0.6; 0.8; 1.0; and 1.2%. Then shake for 1 hour and stand for 24 hours. The bead is then filtered, washed with aquades until neutral and dried.

**Solubility test of Chitosan-epichlorohydrin-modified charcoal**
Bead with a ratio of 5:5, 5:6, 5:7, 5:8, and 5:9 (w/w) were prepared to be added with 25 mL distilled water and the pH was adjusted from 2, 3, 4, 5, 6, and 7 with 0.1 M HCl solution and stirred constant for 24 hours, and then filtered, dried, and the bead is weighed back until the weight is constant. The amount of chitosan-epichlorohydrin modified charcoal solubility can be determined by looking at the initial weight minus the final weight.

**RESULTS AND DISCUSSION**

**Preparation & Quality Test of Activated Charcoal from Eceng Gondok**
The activated charcoal preparation of eceng gondok (Eichornia crassipes) biomass begins with cleaning, cutting to become a smaller parts, and drying it out. The wet weight of biomass is 2.70 kg and after drying weighs 2.15 kg. After that done the process of making charcoal with a moderate flame. Charcoal is then mashed and filtered with a size of 60 mesh to increase the surface area. The charcoal obtained was activated by 0.1 M HCl and 0.1 M NaOH and dried for 1 day and heated at 60-70°C. This heating is done to stretch the space between the pores so that the activator can penetrate the small pores and urged dirt and residual organic substances that are still attached to get out of the pore [4]. The activation process is carried out to enlarge the pores and increase the adsorption capacity of the charcoal. The activated charcoal obtained is 310.77 g. The resulting charcoal is black dan shiny

The activated charcoal obtained is tested its quality with the parameters in accordance with SNI No.06-3730-1995 requirement of activated charcoal technical. The results of the analysis can be seen in Table 1.
Table 1. Results of Quality Test of Activated Charcoal from Eceng gondok

| Test Parameter          | unit | Test Result | SNI No.06-3730-1995 |
|------------------------|------|-------------|---------------------|
| Water content          | %    | 9           | Max 15 %            |
| Ash content            | %    | 7           | Max 10 %            |
| Fly substances content | %    | 23          | Max 25 %            |
| Absorption capacity of solution of I₂ | mg/g | 875.82 | Max 750 mg/g |

Based on the test results in Table 1, the activated charcoal from eceng gondok meets the requirements of SNI No.06-3730-1995.

**Solubility Test Of Chitosan-Modified Charcoal**

In this research, chitosan gel preparation was done by dissolving chitosan having deacetylation degree 74.30% in 10% oxalic acid, then heated at 40-50°C to form thick yellow gel. The activated charcoal from eceng gondok was mixed with chitosan gel, then made bead and put into 2 M NaOH solution. The solubility test of charcoal: chitosan was done on pH 2, 3, 4, 5, and 6 variations. 5 g of active charcoal was varied with weight chitosan as much as 5; 6; 7; 8; and 9 g. Solubility tests on pH variations were performed to determine whether chitosan is strongly bound and stable enough in charcoal. Based on Table 2, it can be stated that the level of solubility of charcoal: the lowest chitosan obtained in the comparison of charcoal:chitosan of 5:7.

Table 2. Solubility test of charcoal-chitosan bead at pH variations

| Charcoal:chitosan (b/b) | pH 2 | pH 3 | pH 4 | pH 5 | pH 6 |
|-------------------------|------|------|------|------|------|
| 5:5                     | 13.51% | 13.50% | 13.31% | 13.28% | 13.25% |
| 5:6                     | 13.21% | 13.13% | 12.91% | 12.65% | 12.21% |
| 5:7                     | **11.53%** | **11.48%** | **11.44%** | **11.38%** | **11.31%** |
| 5:8                     | 12.83% | 12.51% | 12.48% | 12.30% | 11.89% |
| 5:9                     | 13.71% | 13.53% | 13.01% | 12.95% | 12.72% |

**Solubility Test of Chitosan-Epichlorohydrin-Modified Charcoal**

Chitosan-modified charcoal beads with the lowest solubility then cross-linked with epichlorohydrin. The purpose of giving epichlorohydrin as a crosslinking agent is that the resulting bead has physical resistance to the acid, since chitosan has a soluble weakness in acidic conditions [5].
A total of 0.5 g of charcoal-chitosan beads with ratio 5:7 were introduced into 2 ml of 99% epichlorohydrin with a concentration variation of 0.4; 0.6; 0.8; 1; and 1.2%. Table 3 shows the solubility test of chitosan-epichlorohydrin-modified charcoal beads.

Table 3. Solubility test of charcoal:chitosan beads on epichlorohydrin concentration variation

| Epichlorohydrin concentration | pH 2  | pH 3  | pH 4  | pH 5  | pH 6  |
|-------------------------------|-------|-------|-------|-------|-------|
| 0.40%                         | 5.13% | 4.95% | 4.71% | 4.53% | 4.01% |
| 0.60%                         | 5.21% | 5.14% | 5.01% | 4.73% | 4.54% |
| 0.80%                         | 5.05% | 5.28% | 5.03% | 4.86% | 4.61% |
| 1.00%                         | **4.31%** | **4.20%** | **4.08%** | **3.82%** | **3.04%** |
| 1.20%                         | 6.58% | 6.38% | 6.21% | 6.43% | 6.67% |

According to Table 3, the lowest solubility rate occurred at 1% epichlorohydrin concentration. The addition of more and more crosslinkers to a certain concentration is required to enlarge the mechanical strength of the adsorbent as the number of cross-link points increases [6]. However, if the number of crosslinkers added too much, it is possible to reduce the active site of the charcoal-chitosan-epichlorohydrin beads itself.

**CONCLUSION**

The conclusions drawn from this experiment are:

1. Quality of activated charcoal of water hyacinth has fulfilled the requirement of SNI No.06-3730-1995 including water content, fly substances content, and absorption to solution of I2.

2. The solubility of charcoal-chitosan beads without the crosslinking agent is relatively high, the lowest solubility rate of charcoal-chitosan obtained on ratio 5:7.

3. The lowest solubility rate of charcoal-chitosan-epichlorohydrin occurs at a concentration of 1% epichlorohydrin.
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