High Adsorption Capacity of Activated Carbon from Rubber Seed Shells on Tofu (Soybean Whey) Wastewater

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Abstract. Rubber seed shells are the wastes of rubber plants containing active compounds in the form of lignin, so that this part is quite potential to be processed into activated carbon products. Activated carbon is a material that contains amorphous carbon which has an internal surface that has a high adsorption capacity and is often used as an adsorbent. This study aims to determine the effect of the size of the adsorbent, the adsorbent dose and the modified adsorbent from rubber shells on the adsorption process of BOD, COD and TSS in tofu (soybean whey) wastewater. Batch experimental adsorption using magnetic stirrer with a speed of 100 rpm during 6 hours, pH of 7.5±0.2 and room temperature showed the optimum dosage adsorbent were 10 g/L, 355 microns particle size, resulting in decrease in the concentration and levels of COD parameters from 8,287 mg/L to 504 mg/L and 93.92% percentage removal; BOD parameters from 1,300 mg/L to 109 mg/L and 91.61% percentage removal; and TSS from 382 mg/L to 95 mg/L and 75.13% percentage removal, respectively. Therefore, the adsorbent from rubber seed shells has a potential to be used as an adsorbent for water and wastewater treatment.

Keywords: activated carbon, adsorption, rubber seed shells, tofu wastewater

1. Introduction
Soybean is an important crop that has been used for a long period as a protein source of nutritional food production especially in Asia countries [1, 2]. Tofu is traditional food, processed soybean product from soymilk by addition of acidulants, calcium or magnesium salts [3]. Soy whey can be generated during process production of tofu from the soybean. Soybean whey from tofu production consists mainly of carbohydrates, proteins and minerals as well as causes high biological oxygen demand (BOD: 8000–9800 mg/L) and chemical oxygen demand (COD: 17,000–26,000 mg/L) [4, 5], even total suspended solid (TSS), making it essential to treating the tofu (soybean whey) wastewater before discharge into the water body. Hence, the effective and economical utilization of tofu (soybean whey) wastewater will be required to reduce the amount of soybean whey discarded or to reduce the BOD, COD and TSS below the standard prior to disposal. Some technologies was utilized to treat the tofu wastewater such as by conventional aerobic/anaerobic processes, membrane separation, and adsorption process [6]. Although many treatment processes have been utilized for tofu wastewater, adsorption process is more effective and economical process. However, it still requires the possibility of cost-effective and efficient treatment approach, while avoiding adverse effect on the treated system.
using natural adsorbent such as biomass waste, agricultural waste, naturally-occurring soil and mineral deposits, and other available waste materials.

Rubber seed shell (RSS) is a solid agricultural by-product obtained from the rubber tree (Hevea Brasiliensis) which mainly grows in the tropical region and cultivated wildly for use of its latex as source of natural rubber [7, 8]. Rubber seed shell compromise of around 97 wt% organic content [8], its means abundant amount of carbon as sources for producing activated carbon. Indonesia producing rubber seed in 2018 around 3,770,000 ton, then it is potentially and challenging used RSS as waste material to produce activated carbon as adsorbent for soybean wastewater. Conversion of RSS into activated carbon (AC) as adsorbent is promising material from economic point of view. Modified surface morphology and pore structure using KOH as activation agent is commonly used to enhancement large internal surface areas and similar pore structures that plays an important role in adsorption process [9, 10].

This present study focuses on the preparation, characterization and evaluation of adsorption properties of activated carbon from RSS for reducing COD, BOD and TSS of tofu wastewater.

2. Material and Methods
Rubber seeds were collected from Banjar District, South Kalimantan, Indonesia. The shells were separated manually and used for carbonization process to produce activated carbon. Before carbonization process, the shell was sun dried around 3 days, grinded, and then sieved to a particle size of less than 2 mm. Tofu wastewater was collected from a home industry located in Banjar District and was stored at temperature of 4°C in refrigerator. The chemicals, such as KOH and HCl, were pure grade analytical obtained from Aldrich and used without further purification.

2.1. Preparation of the rubber seed shell using carbonization process
The shells were separated from the rubber seed, washing using deionized (DI) water, dried and grinded into small sizes around 2 mm. The sample of 250 g was weighed and heated at temperatures of 400±5°C for 3 hours using the muffle furnace. The carbonized shells were then milled to the fine powder and sieved through a 25 mesh (around 710 µm) and 45 mesh (around 355 µm). 50 grams (+1%) of activated carbon was immersed into 0.1 N KOH solution with certain concentration. The activated carbon slurry was then stirred for 24 hours at room temperature. The slurry was dried in oven at 105 ºC overnight, and was then cooled in the desiccator. The product was then quickly rinsed once with ethanol followed by subsequent washing with DI water several times until pH of the water after washing was constant. Washed carbon was dried again in oven at 105°C overnight. Dried activated carbon was cooled in the desiccator and sieved until the particles were below 100 mesh.

2.2. Batch Adsorption process of tofu wastewater
Batch adsorption experiments were carried out by putting 100 mL of tofu wastewater into 250 mL plastic bottles and adjusting its pH values with sodium hydroxide (NaOH, 1M) and hydrochloric acid (HCl, 1M). A weighted amount of the adsorbent (Activated Carbon and Modified Activated Carbon) was then added into plastic bottle. The mixture was placed in a shaker with water bath at pre-determined temperature for certain time (15 to 1440 minutes). At the end of the experiment the solution was centrifuged and filtered by using a 0.2 µm PVDF membrane. Finally, the filtrates were analysed for COD, BOD and TSS. The COD was analyzed by open reflux method (APPHA 5520B), BOD determination as an empirical test in which standardized laboratory procedures by using 5-days period BOD test (APPHA 5210 B), and TSS values was measured by using standard method of 2540D (APPHA 2540D) [11]. Adsorbed COD, BOD and TSS were calculated from the difference between the initial and equilibrium concentrations. The adsorption experiments were done in duplicate samples and the average value was taken. The data from experiment were fitting and figure out by Sigma Plot® version 10 of software.
3. Results and Discussion

| Parameters                                | Value       |
|-------------------------------------------|-------------|
| pH                                        | 4.65±0.2    |
| Chemical oxygen demand (COD, mg/L)        | 8.287±50    |
| Biological oxygen demand (BOD<sub>5</sub>, mg/L) | 1.300±50    |
| Total suspended solid (mg/L)              | 382±25      |

Table 1: Characteristics of the tofu (soybean whey) wastewater

Table 1 shows the characteristics of the tofu wastewater. COD, BOD and TSS ware above the permission standard for effluent water quality (i.e., 250 mg/L, 100 mg/L and 100 mg/L, respectively). These values indicated that the tofu wastewater must be treated before release to water body.

3.1. Characterization study of activated carbon from RSS

![SEM images of activated carbon from rubber seed shells](image)

Figure 1: SEM images of activated carbon from rubber seed shells (a) without modification (b) and with modification using KOH solution 1 N.

Generally, activated carbon formed from the carbonization process has a rough surface structure with a pore size that is not so large that it can affect the adsorption capacity (Figure 1). Particle size and surface area are important for adsorbents, because particle size affects the adsorption capacity. Shown in this figure that the pore size of activated carbon obtained from RSS carbonization process was around 50 µm without modification, and < 25 µm with modification using KOH solution 1 N. It indicated that impregnation of KOH plays important roles in formation of pores, and promotion more pore formation [12]. The total surface area affects the total adsorption capacity thereby increasing the effectiveness of the adsorbent in the removal of organic compounds in wastewater.
3.2. Batch adsorption experiment

3.2.1. Effect of contact time on removal of COD, BOD and TSS of the tofu wastewater

Figure 2 showed the effect of contact time on the adsorption of COD, BOD and TSS during adsorption process using activated carbon from RSS as adsorbent. The first 30 minute, adsorbents gained higher adsorption uptake capacity, then reached maximum saturation at hour 6. The adsorption time of 6 hours has been fixed as the contact time for further experiments in the adsorption process. In the beginning, the rates COD, BOD absorption and TSS removal increased with increasing contact time. This may be explained by presence of vacant site on the adsorbents. The results also showed that the adsorption process was going up to equilibrium point. Beyond 6 hours, no significant change was observed in the adsorption uptake capacity and this may because the surface of adsorbent was saturated. The uptake capacity of activated carbon adsorbent was found to be more than 90% for COD and BOD removal, and around 75% for TSS removal, whereas the remaining of COD concentration of 504 mg/L, BOD of 109 mg/L and TSS of 95 mg/L in the solution.

3.2.2. Effect of adsorbent dosage on removal of COD, BOD and TSS of the tofu wastewater

Figure 3 shows the effect of adsorbent dosage on COD, BOD, and TSS. It is indicated the uptake capacity increase by increasing the doses and reached more than 90% at doses of 10 g/L, whereas the remaining of COD concentration of 504 mg/L, BOD of 109 mg/L and TSS of 95 mg/L in the solution. The increasing uptake capacity by increased the adsorbent doses because when the adsorbent dosage
increases, its surface area and the number of active sites of the adsorbent also increase which leads to increase uptake capacity of COD, BOD and TSS in this batch adsorption experimental [13].

3.2.3. Effect of adsorbent particle size on removal of COD, BOD and TSS of the tofu wastewater

![Figure 3: Adsorption uptake capacity of COD (C₀ = 8,287±50 mg/L), BOD (C₀ = 1,300±50 mg/L), and TSS (C₀ = 382±25 mg/L) at room temperature various adsorbent dose, stirring rate of 150 rpm.](image)

![Figure 4: Uptake capacity of COD (C₀ = 8,287±50 mg/L), BOD (C₀ = 1,300±50 mg/L), and TSS (C₀ = 382±25 mg/L) at room temperature, adsorbent dose of 10 g/L, stirring rate of 150 rpm at various particle size adsorbent](image)
Figure 4 indicated that the uptake capacity increased by decreasing the particle size and reached more than 90% removal for COD and BOD at doses of 10 g/L, and 75% removal for TSS in the final solution after adsorption process. The changes in uptake capacity were probably because of the changes in surface area, the number of active sites, and pores of the adsorbent.

3.2.4. Effect of impregnation of KOH on adsorbent removal of COD, BOD and TSS of the tofu wastewater

![Graph showing COD, BOD, and TSS uptake](image)

Figure 5: Uptake capacity of COD ($C_0 = 8,287\pm50$ mg/L), BOD ($C_0 = 1,300\pm50$ mg/L), and TSS ($C_0 = 382\pm25$ mg/L) at room temperature, adsorbent dose of 10 g/L, stirring rate of 150 rpm as affected by modified or unmodified adsorbent.

Figure 5 indicated that the oxygen and suspended solid were uptakes more by modified absorbent as compared to unmodified adsorbent in batch adsorption process. Increasing surface area and number of active sites in modified absorbent leads to the increase in uptake capacity of COD, BOD and TSS. The nonpolar properties of carbonaceous adsorbent result in their hydrophobic character [9]. Hydroxides ion also adsorb the organic anionic particle surface [14) and enhanced the COD, BOD and TSS adsorption.

4. Conclusions
Rubber seed shells can be used as an alternative and promising adsorbent for tofu wastewater treatment. This is proven by decreasing the BOD, COD, and TSS parameters in the wastewater. Adsorbent dosage and adsorbent particle size have significant effect on adsorption process for COD, BOD and TSS removal of tofu wastewater. The surface modified of activated carbon as adsorbent has a greater adsorbent capacity than the unmodified. Activated carbon formed from the carbonization process of RSS has a rough surface structure with a pore particle size, then impregnation of KOH plays important roles in formation of pores, and promotion more pore formation.

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