

Degradation of surfactant waste of leather tanning using Fe_2O_3 /activated carbon catalyst

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ABSTRACT

The development of the tannery industry in addition to being beneficial for the economic growth of the community also has a negative impact on the environment due to the disposal of waste produced. Components of waste produced from the leather tanning industry include residual protein and fat, surfactants, anti-bacterial, anti-fungal, coloring and tanning agents. One component that is found in surfactants and often pollutes waters is alkyl benzene sulfonate and linear alkyl benzene sulfonate surfactants. Alkyl benzene sulfonate (ABS) is an anionic surfactant that has a very long and branched carbon chain that is difficult to degrade by microorganisms in nature. Characterization and testing of the activity of porous/activated carbon catalysts will be carried out. The type of porous activated carbon used is coconut shell carbon with microspores character. The stages of this research consisted of the process of impregnation of iron oxide on porous carbon, the surfactant waste degradation process and the characterization of the catalysts produced. Based on the research that has been done, it can be concluded that the catalyst Fe_2O_3 /coconut shell activated carbon is very effective to be applied for the degradation of surfactant waste. The degradation capacity of surfactant wastes increases with increasing concentration of active site Fe. The capacity of the surfactant waste degradation reaction using coconut shell catalyst at $t = 3$ hours for variations in the concentration of Fe 2%, 4% and 6% respectively 6.77 mmol/gram catalyst, 3.18 mmol/gram catalyst and 1.61 mmol/gram catalyst. The data show that the surfactant waste degradation reaction capacity increases with the increase in the composition of iron oxide added to the surface of the porous carbon support.

Keywords: degradation, fenton heterogen, surfactant waste, tannery industry.

INTRODUCTION

The tannery industry in Indonesia is currently developing very rapidly. Various products can be produced from the leather tanning industry such as shoes, bags, wallets and other accessories. The development of the tannery industry in addition to being beneficial for the economic growth of the community also has a negative impact on the environment due to the disposal of waste produced. Components of waste produced from the leather tanning industry include residual protein and fat, surfactants, anti-bacterial, anti-fungal, coloring and tanning agents. The component of waste produced from the tannery industry results in a higher toxicity of the tannery industrial wastewater compared to the textile and paper industry wastewater (Verma, 2011). Therefore we need a waste treatment unit in the leather tanning industry before the wastewater is discharged into the environment. The tannery industry wastewater treatment consists of primary treatment, secondary treatment and tertiary treatment. Tertiary waste treatment needs to be done to ensure that wastewater discharges meet the quality requirements of liquid waste because pollutants in the form of surfactants are generally stable enough compounds and difficult to

degrade biologically (Mall *et al.*, 2007). So it is feared that it can cause problems in the aquatic environment, such as the formation of foam that covers the surface of the water (Panizza *et al.*, 2013). One component that is found in surfactants and often pollutes waters is alkyl benzene sulfonate and linear alkyl benzene sulfonate surfactants. Alkyl Benzene Sulfonate (ABS) is an anionic type surfactant that has a very long and branched carbon chain making it difficult to be degraded by microorganisms in nature (Yu *et al.*, 2008).

Adsorption is a purification method that is widely used in various industries, one of which is to deal with waste containing ABS and LABS. Various materials have also been used as ABS and LABS adsorbents, such as synthetic clay, carbon nanotubes, resins, and soil/sediment (Orta *et al.*, 2018; Guan *et al.*, 2016; Mattaredona *et al.*, 2003; Yang *et al.*, 2006; Prieto *et al.*, 2013). However, the adsorption method only removes pollutants to other media, so it is feared that adsorbents that have saturated adsorbing waste can cause new problems regarding solid waste in the water. Other methods that can be used include Advance Oxidation Processes (AOPs). This method has the advantage of being able to degrade hazardous compounds

in waste through oxidative degradation (Malato *et al.*, 2003). However, the homogeneous Fenton reaction has a disadvantage in terms of catalyst separation from the system/mixture. This results in high operating costs. To overcome this, a heterogeneous catalytic reaction system can be used namely by developing an active catalyst of iron in a porous material, such as alumina, activated carbon, and zeolite.

The impregnation method is a method of making catalysts in the form of filling metals into the pore cavity by bringing solids dissolved in the solvent into the pore cavity so that it can be bound to the supporting surface such as zeolite, silica gel, carbon, etc. There are several types of impregnation methods, one of them is the wet impregnation method. This method is the process of making a catalyst in which the volume of the solution used is greater than the volume of the pore buffer (Haber *et al.*, 1995). The first step is to contact the metal salt solution on the carbon surface. The process is followed by drying and calcination to evaporate volatile components so that the metal as an active site will be bound to the supporting surface. Metal oxide is a catalyst that can be used in the ABS/LABS waste degradation process. Metal oxides that can be used are Fe_2O_3 and Ce_2O_3 (Castro *et al.*, 2009). In its use metal oxides can be used in the form of nanoparticles or embodied in support material. In terms of ease of separation of metal oxides embedded in porous material has advantages. Porous carbon is an excellent candidate as a carrier because of its high surface area and excellent chemical stability (Hameed *et al.*, 2007).

The novelty of this research is to do degradation of surfactant waste by the simultaneous heterogeneous Fenton method with the adsorption process. The activated carbon used comes from a coconut shell which has a micropore size. Before it is used, activated carbon is first treated with iron oxide. The resulting iron oxide acts as a catalyst that will help the process of decomposition of hydrogen peroxide (H_2O_2) so that it produces hydroxyl groups ($\cdot\text{OH}$) that will degrade ABS and LABS while activated carbon as a carrier becomes a provider of surface area to adsorb ABS and LABS to be degraded. So that the system occurs simultaneously between the adsorption of activated carbon with the degradation of surfactant waste by heterogeneous Fenton reaction.

MATERIALS AND METHODS

Materials

The materials used in this study were coconut shell carbon, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Merk) and isopropanol (97% analytical grade, Bratacem) each used as a catalyst carrier, iron precursor and solvent. In the Fenton reaction, synthetic ABS/LABS (95% analytical grade, Sigma Aldrich) is used as simulated waste while H_2O_2 as an initiator hydroxyl ions. The pore structure of carbon is characterized by using an N_2 -sorption analyzer (Nova 2000, Quantachrome). UV/Vis spectrophotometer (Shimadzu Mini 1240) was used to analyze surfactant waste concentration per unit time.

Impregnation of Iron Oxides on Porous Carbon Surfaces

A total of 5 grams of activated carbon that has been condensed were included in the sample bottle. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt that has been dissolved with isopropanol was added according to the variable Fe concentration (2%, 4%, or 6%) into a sample bottle that already contains activated carbon. The mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt solution with activated carbon was then stirred for 1 hour with an ultrasonicator. After the evaporation process at room temperature then the carbon was heated at 60°C . The calcination process was then carried out at a temperature of 300°C for 3 hours with an inert N_2 flow.

Adsorption Process and Fenton Reaction

200 ml of surfactant waste solution with a concentration of 20 ppm was prepared in a beaker glass. The solution was stirred with a magnetic stirrer at a constant speed of 450 rpm and a room temperature of 30°C . Then 5 ml of H_2O_2 was put into a glass beaker that contains a surfactant waste solution. Furthermore, 0.025 grams of Fe_2O_3 /activated carbon adsorbent with each variable loading were put into a glass beaker that contained a surfactant waste solution. A total of 2 ml of the sample solution was taken at intervals for 3 hours. Furthermore, the concentration of surfactant waste in solution (C) at any given time interval was analyzed with a UV-VIS spectrophotometer at a wavelength of 223 nm.

Analysis Method

The adsorption data were analyzed using a UV VIS spectrometer with wavelength $\lambda = 223$ nm. The results of the analysis were used to calculate the concentration of surfactant in liquids per unit time (C_{AL}).

RESULTS AND DISCUSSION

Characterization of Fe_2O_3 /Activated Carbon Catalysts

The structure of coconut shell porous carbon which includes specific surface area, average pore diameter and pore volume are presented in Table 1. The table shows that commercial porous carbon from coconut shell is micropore carbon (IUPAC classification) with an average diameter of 1.82 nm. Furthermore, it can be seen from the surface area and micropore volume that is more dominant than the surface area and mesoporous volume, which is 92%. In addition, Table 1 also provides information that the pore structure of a coconut shell porous carbon is a micropore carbon (classification of IUPAC) with a specific surface area of coconut shell porous carbon which is equal to $1320 \text{ m}^2/\text{gram}$.

The procedure in making iron oxide catalysts with activated carbon carriers begins with the impregnation of the catalyst precursors on the surface of the carbon pore. In terms of the size of iron ions (194 pm, hydrate), these ions can enter the coconut shell carbon pores. The impregnation process begins by contacting the metal

Table 1. Characteristics of coconut shell carbon (Amelia *et al.*, 2019).

Characteristic	Value
Specific surface area (S_{BET}), m ² /gram	1320
Micropore area (S_{mic}), m ² /gram	1220
% S_{mic}	92
Total pore volume, cm ³ /gram	0.60
Micropore volume (V_{mic}), cm ³ /gram	0.45
% V_{mic}	75
Average pore diameter, nm	1.82

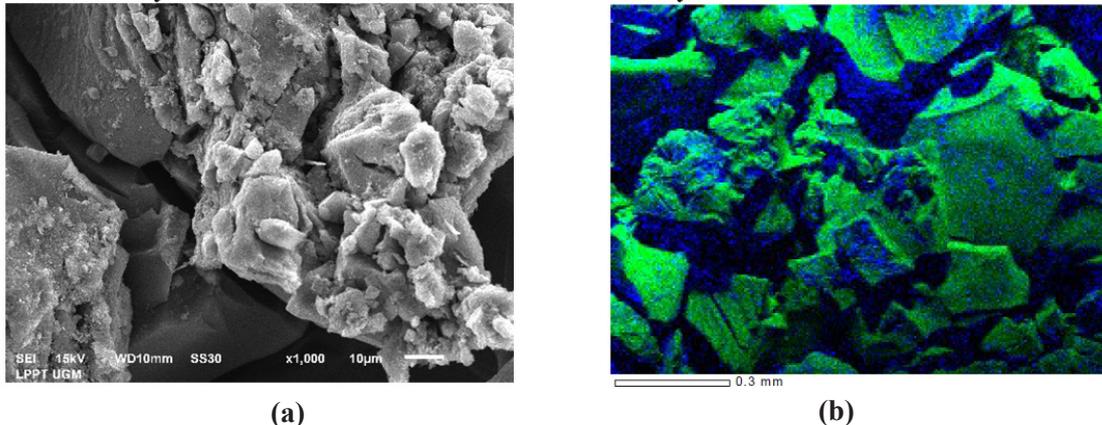
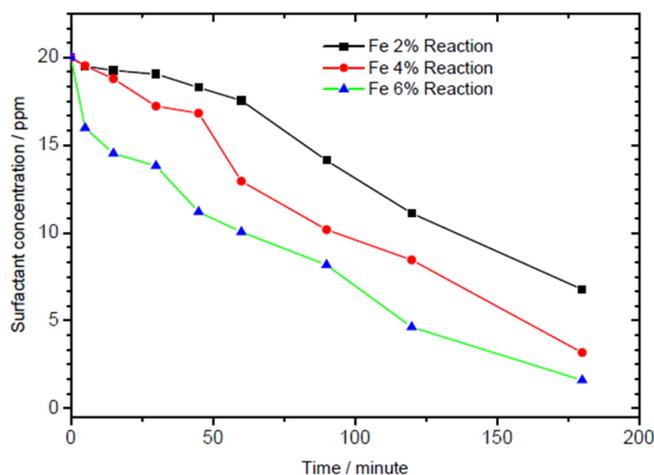
solution on the carbon surface. Then proceed with drying and calcination for the formation of iron oxide. The process of impregnation of the catalyst precursors into the surface of the carbon pore affects the decrease in surface area of activated carbon. That is because most of the surface area of activated carbon is covered by iron oxide as a catalyst precursor. The decrease in surface area does not have a significant effect on the surfactant degradation process (Han *et al.*, 2015).

The distribution of iron oxide on the surface of carbon is an important aspect in the process of impregnation of iron oxide on the surface of carbon. The even distribution of metals on the carbon surface will maximize the surfactant waste degradation process. For the same amount of iron composition, if agglomeration occurs on the carbon surface, the amount of degraded surfactant waste will be reduced compared to if the Fe metal can be spread evenly on the carbon surface. This is because the active site that

is used to degrade surfactant waste will be reduced so that the decolorization process becomes less effective which results in a smaller amount of degraded surfactant waste. Therefore the distribution of metals on the carbon surface is important to know. To see the mapping of Fe metals on carbon surfaces, an analysis was carried out using SEM-EDX analysis. The results of the SEM-EDX analysis can be seen in Figure 1.

Effect of Active Site (Fe) Concentration on Surfactant Waste Degradation

The active site (Fe) concentration used has an effect on the surfactant waste degradation reaction capacity. This is because the amount of iron oxide distributed on the porous carbon surface as an active site catalyst will vary. In this research, variations in% loading Fe are used, namely 2%, 4% and 6% (% w). The difference in surfactant waste degradation reaction capacity can be seen in Figure 2.

**Figure 1.** (a) SEM for Fe₂O₃/activated carbon catalyst, (b) elemental mapping C-Fe (Amelia *et al.*, 2018).**Figure 2.** Surfactant waste degradation reaction capacity with Fe₂O₃/activated carbon catalyst.

From Figure 2 above the data obtained by the surfactant waste degradation reaction capacity using a coconut shell catalyst at time $t = 3$ hours for the active site variation Fe 2%, 4% and 6% respectively 6.77 mmol/gram catalyst, 3.18 mmol/gram catalyst and 1.61 mmol/gram catalyst. The data shows that the surfactant waste degradation reaction capacity is increasing with the increasing composition of iron oxide added to the porous carbon support surface. Because the greater the active site concentration that is developed, the surfactant waste degradation reaction will be faster and result in the surfactant waste degradation reaction capacity will increase. With the increasing concentration of Fe ions, the oxidation process against pollutants gets higher. The speed of the degradation process will affect the COD reduction in the tannery industry wastewater so that it can reduce COD levels below the quality standard (Sholeh, M., *et al.*, 2013). In addition, the effect of the Fenton reaction that occurs due to an increase in Fe ions also causes more hydroxyl radicals to form (Achile and Yilian, 2010). This was also found in research conducted by Mousavi *et al.*, 2011, Masomboon *et al.*, 2011 and Hashemian *et al.*, 2013.

CONCLUSION

Based on the results of this research can be concluded that the Fe_2O_3 /Coconut shell activated carbon catalyst is very effectively applied to surfactant waste entrapment. The surfactant waste degradation reaction increased with increasing Fe loading concentration and the result of the surfactant waste degradation reaction capacity using a coconut shell catalyst at time $t = 3$ hours for the active site variation of Fe 2%, 4% and 6% respectively at 6.77 mmol/gram catalyst, 3.18 mmol/gram catalyst and 1.61 mmol/gram catalyst. The data shows that the surfactant waste degradation reaction capacity is increasing with the increasing composition of iron oxide added to the porous carbon support surface.

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