The influence of hydrogen peroxide concentration on catalytic activity of fenton catalyst@bacterial cellulose

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Abstract. Utilization of commercial Bacterial Celluloses (BCs) as catalyst support for preparation of heterogeneous fenton catalysts is attractive because catalytic activity of fenton catalyst can be increased by reducing their particles size. In this report, fenton catalyst@BC were prepared by sol gel method with fixed precursor concentration (0.5 M) and varied concentration of H2O2 (0.3, 0.6, 1.2 and 1.7 %v/v) to obtain optimum condition for fast degradation of Methylene Blue (MB). Scanning Electron Microscope (SEM) showed that micron-sized particles with particle sizes 1002.7 ± 511.5 nm has been successfully deposited on the surface of BC aerogel. Energy Dispersive Spectroscopy (EDS) results revealed that a small portion of iron oxide is observed in sample, even though the dominant elements in sample are sodium and chloride. UV-Vis spectroscopy unveiled that catalytic degradation profile of MB follows pseudo-first order reaction kinetics and the fastest degradation of MB was observed at 1.2 %v/v of H2O2 with Constanta of degradation rate (k) value is 2.65 x 10⁻² min⁻¹. Finding optimum condition for fastest degradation of MB is essential for the effort to completely remove dyes from clean water.

Keywords: advanced oxidation processes, bacterial celluloses, heterogeneous fenton catalyst, recalcitrant organic pollutant, waste water treatment

1. Introduction
Nowadays, textile industries are preferring to use synthetic dyes because they are cheaper and more efficient than natural ones. Unfortunately, utilization of huge amount of synthetic dyes without proper treatment process will be harmful for our ecosystem because synthetic dyes are mostly classified as recalcitrant pollutants and some of them are carcinogenic [1, 2]. To answer this problem, waste water treatment based on advanced oxidation processes (AOPs) are attractive because AOPs are able to completely degrade synthetic dyes and other organic pollutants into harmless chemicals such as CO2 and H2O [3-5].

One of appealing AOPs to degrade organic pollutants is fenton catalyst because of its general applicability and high degradation efficiency [3-5].Unfortunately, homogeneous classical fenton catalyst, a commonly used method in industries, have several limitations such as requires acidic condition (pH lower than 3) and an enormous amount of iron ion still remained in wastewater [3]. In this context, heterogeneous fenton catalysts are preferable than homogeneous ones because they are reusable and can be used at broad pH condition [3-6]. However, catalytic activity of current...
heterogeneous fenton catalysts are not high enough for practical use [5, 6]. Therefore, a strong effort should be performed to enhance their catalytic activity. Catalytic activity of catalyst can be improved by, for example, decreasing particle size of catalyst because it increases volume-to-surface ratio of catalyst. Previously, we are successfully reduced particle size of fenton catalyst by utilization of Bacterial Celluloses (BC) from fermentation of coconut water, namely Nata de Coco, as catalyst support. Even though catalytic activities of fenton catalyst have been enhanced using this techniques, but their catalytic performance might be further increased by optimization of various parameter in fenton process. In this report, concentration of hydrogen peroxide (H$_2$O$_2$) have been varied (0.3; 0.6; 1.2 and 1.7%) to know the influence of concentration of H$_2$O$_2$ to catalytic activity of obtained fenton catalyst@bacterial cellulose.

2. Materials and Methods

2.1. Materials
Pro analyst (p.a) grade chemicals from sigma Aldrich were used in all of experiments. Commercial Bacterial Cellulose (BC) hydrogels were obtained from store in Bandung. Sugar content in commercial BC hydrogels were removed by overnight immersion in demineralized water.

2.2. Fabrication of fenton catalyst@BC
Preparation procedure of fenton catalyst@BC were based on previous report with slightly modification [6, 7]. Fenton catalysts@BC were prepared by overnight immersion of BC hydrogels in precursor solution containing 0.05 M FeCl$_2$ and FeCl$_3$ with molar ratio between Fe$^{2+}$ and Fe$^{3+}$ ion is 1:2, followed by overnight immersion in 4M NaOH solution. Then, samples were freeze dried to conserve their interconnected structures.

2.3. Characterizations
Morphology and elemental analysis of obtained samples were performed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) method (SEM, Hitachi SU3500). Image J software was used to calculate average particle sizes of observed particles in SEM images. In this study, Methylene Blue (MB) was used as dyes model and catalytic activities of catalyst were performed at various concentration of H$_2$O$_2$ (0.3; 0.6; 1.2 and 1.7%) without light illumination. Degradation of dyes were followed by UV-VIS Spectrophotometer (Agilent 8453 G1103A) method to quantify concentration of MB in solution.

3. Results and Discussions
SEM images of bare BC aerogels and fenton catalyst@BC were presented in Fig. 1a and 1b respectively. Interconnected network that was observed in SEM images of bare BC aerogels sample (Fig. 1a) might be helpful for nucleation growth of catalyst particles and prevent agglomeration. Thus, utilization of BC aerogels as catalyst support for preparation of heterogeneous fenton catalyst might initiate formation of catalyst particles in the surface of BC aerogel with particles size 1002.7 ± 511.5 nm (Fig. 1b). This result is consistent with our previous result that the presence of BC aerogel might drive formation of micron-sized particles in the surface of BC aerogel.
Figure 1. SEM images of a) bare bacterial cellulose (BC) and b) fenton catalyst@BC.

Further characterization using Energy Dispersive Spectroscopy (EDS) method was used to know elemental composition of particles in sample of catalyst@BC. EDS result of sample can be seen in Fig. 2 and summary of elemental composition of sample was presented in Table 1. Based on EDS results, a small portion of iron oxide were formed in the surface of BC aerogel. However, main elements that were observed in sample are sodium (Na) and Chloride (Cl) which is considered as impurities in this sample. Concentration of Na⁺ in 4M of NaOH solution during sample fabrication might be high enough to stimulate formation of NaCl in sample [6].

Figure 2. Representative of EDS result of catalyst@BC sample.

Table 1. Summary of elemental analysis of catalyst@BC sample.

| Element | EDS results (mass %) |
|---------|-----------------------|
|         | 1ˢᵗ area | 2ⁿᵈ area | Average |
| C       | 13.0      | 19.4      | 16.2 ± 4.5 |
| O       | 15.2      | 25.2      | 20.2 ± 7.1 |
| Na      | 44.6      | 32.2      | 38.4 ± 8.8 |
| Cl      | 24.9      | 16.4      | 20.7 ± 6.0 |
| Fe      | 2.3       | 6.8       | 4.6 ± 3.2 |
The influence of H$_2$O$_2$ concentration on catalytic activity of fenton catalyst@BC was studied by varying concentration of H$_2$O$_2$ and determination of concentration of MB as a function of time were performed by UV-VIS spectroscopy method. Among other synthetic dyes, MB has the lowest absorption to catalyst. Thus, decreasing concentration of MB in this study can be only considered as degradation process driven by catalytic activity of fenton catalyst [8]. Percentage value of degradation profile of MB as a function of time (Fig. 3.a) showed that degradation profile of MB look similar regardless H$_2$O$_2$ concentration. Detailed interpretation of degradation profile of MB using logarithmic value (Fig. 3.b) showed that all of reactions follow typical equation for pseudo-first order reaction kinetics (Eq. 1) [9].

\[
\ln \frac{c_0}{c} = kt
\]  

(1)

Figure 3. a) Percentage and b) logarithmic value of catalytic degradation profile of methylene blue (MB) in the presence of catalyst@BC with various H$_2$O$_2$ concentration (0.3, 0.6, 1.2 and 1.7%).

Since all of reactions follow pseudo-first order reaction kinetics, their degradation rate depends on concentration of H$_2$O$_2$. Summary of Constanta value of degradation rate ($k$) of MB at various concentration of H$_2$O$_2$ (Table 2) showed that the highest $k$ value can be obtained at 1.2% v/v of H$_2$O$_2$. Interestingly, after normalization of $k$ value with concentration of H$_2$O$_2$, it can be seen that normalized $k$ value increase as concentration of H$_2$O$_2$ decreased.

| H$_2$O$_2$ (%) v/v | $k$ ($x$ 10$^{-2}$ min$^{-1}$) | Normalized $k$ ($x$ 10$^{-2}$ min$^{-1}$) |
|--------------------|----------------------------|----------------------------------------|
| 0.3                | 2.26                       | 7.53                                   |
| 0.6                | 1.81                       | 3.02                                   |
| 1.2                | 2.65                       | 2.21                                   |
| 1.7                | 2.16                       | 1.27                                   |

4. Conclusions
Deposition of fenton catalyst on the surface of BC aerogel has been successfully prepared using sol gel method. By varying concentration of H$_2$O$_2$, it was found that 1.2% (v/v) of H$_2$O$_2$ is the optimum condition to degrade MB with Constanta of degradation rate ($k$) value 2.65 x 10$^{-2}$ min$^{-1}$. Optimization of degradation process using fenton catalyst@BC is important for finding the best and the fastest condition to remove recalcitrant pollutant such as textile dyes in our environment.
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