Oxalic Acid from Corn Stalk for Photocatalytic Reduction of Cr(VI)

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Abstract. Cr(VI) is toxic species of chromium in the aquatic environment. The reduced species, Cr (III), has lower toxicity than Cr(VI). The change of Cr(VI) species to Cr(III) can be conducted by photocatalytic reduction using oxalic acid as an oxidant with the aid of Fe(III) as a catalyst. Oxalic acid can be isolated from the biomass waste of corn stalk. This research aimed to isolate oxalic acid from corn stalk biomass as an oxidator for Cr(VI) photocatalytic reduction. The oxalic acid was isolated from corn stalks powder using NaOH, precipitated with the addition of CaCl₂, acidified with H₂SO₄, and then crystalized to form the oxalic acid crystals. The photocatalytic reduction was carried out in a closed reactor equipped with two of 30-watt UV lights. About 30 mg of oxalic acid was used to reduce 300 mg/L Cr(VI) with the presence of 4 ml Fe(III) 100 mg/L as a catalyst. The process was conducted for 120 minutes while stirring. The reduction efficiency was calculated from the differentiation of the initial Cr(VI) concentration to the final ones. Cr(VI) concentrations were measured as Cr(VI)-diphenylcarbazide complex compound at pH 2 that could be detected at 540 nm. The results showed that the isolated oxalic acid has hydroxyl and carbonyl groups at 3441 cm⁻¹ and 1627 cm⁻¹ respectively identical with the oxalic acid standard. The crystals have melting point at 103°C. It could be used effectively to reduced Cr(VI) up to 45.9 %.

1. Introduction
The concentration and toxicity of dissolved chromium and its mobilization in the environment depend on its oxidation state [1]. The toxicity level of Cr(VI) is about 100 times higher than the toxicity level of Cr(III). Hence, the reduction of Cr(VI) becomes one of the ways to reduce its toxicity. In the aqueous system, Cr(VI) is dissolved as divalent oxyanions of chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) while Cr(III) is deposited or absorbed by organic and inorganic compounds. Cr(VI) can cause many health problems. Direct contact with skin and eye causes irritation in the digestive and respiratory tract, characterized by a burning sensation, sneezing and coughing. Based on the Indonesian regulation (PP No. 82 of 2001), the maximum concentration of total chromium in drinking water and fishery water is 0.05 mg/L. Removal of Cr(VI) has been devoted through such process including ion exchange, adsorption using activated carbon, and reduction with the help of bacteria. However, such methods have disadvantages of the need for very high energy and/or chemicals. This weakness makes the photocatalytic method more prospective and superior for its application to reduce Cr(VI) compared to another methods [2].

The photocatalytic method can be applied to reduce Cr(VI) by the addition of Fe(III) catalysts in a homogeneous state. The catalysts have high activity and selectivity. Based on [3], the Fe catalyst can
reduce Cr(VI). Another study prove that using a catalyst Fe(III) with the addition of oxalic acid and citric acid can reduce Cr(VI) ions [2]. Fe(III) forms a complex compound with organic substances such as oxalic acid. This compound reduces Cr(VI) to Cr(III) while the organic substances are reduced to carboxyl radicals and start the new cycle. The oxalic acid is a derivative of carboxylic acid, which contains 2 carboxyl groups located at the ends of a straight carbon chain that has a molecular formula namely C$_2$H$_2$O$_4$.

Oxalic acid can be isolated from corn stalk biomass. Corn stalk contains cellulose in large enough quantities. Cellulose is a long chain carbon compound which can be cracked into simpler carbon compounds using strong alkali [4]. One of the carbon compounds produced in the cracking process is oxalic acid. According to previous studies, oxalic acid obtained from rice husk as much as 15% [5]. Therefore, the aims of this present research were to isolate oxalic acid from corn stalk biomass, determine its characteristics, and investigate the efficiency of photocatalytic reduction of Cr(VI) using the isolated oxalic acid.

2. Research Methods

2.1. Materials and Apparatus

The materials used in this study included corn stalk that obtained from Banyuwangi, sodium hydroxide (Emsure-Merck), calcium chloride (Merck), sulfuric acid (AR), nitric acid (Merck), diphenylcarbazide (Merck), acetone (AR), potassium dichromate (Merck).

The apparatus used in this study were a set of glassware, reactors, ovens, thermometers, UV-Vis (Genesys 10S VV-Vis Spectrophotometer). The photocatalytic reduction was conducted using a reactor (Figure 1) that has a size of 110 x 35 x 50 cm. The reactor box (1) was made from wood and was equipped with a magnetic stirrer (2), sample holder (3), beaker glass (4), and UV lights of 30 watts (5). The lights and magnetic stirrer were connected with electric power using a current connection (6).

2.2. Isolation of Oxalic Acid from Corn Stalk

Corn stalk was cleaned from dirt, dried, and then grinded. About 15 g corn stalk powder was put in a two neck flask and then added with 250 mL NaOH 2 M. The mixture was then heated at 90°C while stirring using magnetic stirrer for 3 hours. After heating was completed, the mixture was then cooled and filtered. The resulting filtrate was diluted to 400 mL [4].

As much as 25 mL of the filtrate was added with 25 mL of CaCl$_2$ 1M to form calcium oxalate deposits. The calcium oxalate was dissolved with 100 mL of H$_2$SO$_4$ 2M. Afterwards, the solution was heated to 70°C for 1 hour. After being cooled for 24 hours in the refrigerator, oxalic acid deposits were formed in the form of white needle crystals. The oxalic acid crystals were then separated from the liquid and dried at 70°C for 30 minutes. [4]. Afterwards, the functional groups and melting point of the oxalic acid crystals were characterized using FTIR spectroscopy and melting point apparatus. The yield of oxalic acid was calculated using equation (1).

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yield = \frac{\text{mass of oxalic acid}}{\text{mass of corn stalk}} \times 100\%
\]  

(1)

2.3. Photocatalytic reduction of Cr(VI)

As much as 30 mg of oxalic acid was mixed with 25 mL of Cr(VI) solution of 300 mg/L, 2 mL of Fe(III) 100 mg/L in a 50 ml flask. The mixture was then irradiated with 60 watts UV lights in the reactor for 120 minutes. The amount of Cr(VI) reduced can be determined from the difference between the initial and final concentration of Cr(VI). Cr(VI) concentrations can be determined spectrophotometrically through the formation of complex compounds with diphenyl carbazide. The complex compounds formed were measured at a wavelength of 540 nm.
3. Result And Discussion

3.1. Characteristic of Isolated Oxalic Acid

Oxalic acid could be isolated from cellulose of biomass such as corn stalk. Oxalic acid produced from the cellulose of Banyuwangi corn stalk was about 30% (calculated using Eq.1). Characterization of the isolated oxalic acid was carried out for its functional groups and melting point. The functional groups of the oxalic acid crystal were characterized using FTIR spectrophotometry with the spectra as shown in Figure 2. It can be seen from Figure 2 that the spectra of isolated oxalic acid from corn stalk was identical with the spectra of oxalic acid standard although there is a slightly shifted in the wave numbers. The standard of oxalic acid spectra has strong and sharp absorption of hydroxyl group at 3441.53 cm\(^{-1}\), the carbonyl group at 1694.15 cm\(^{-1}\), and the vibrational strain of the C-O group at wave number of 1258.26 cm\(^{-1}\). Meanwhile, the isolated oxalic acid from corn stalk contained hydroxyl group vibrations at 3411.84 cm\(^{-1}\), carbonyl group vibration at 1627.81 cm\(^{-1}\), and strong vibration of C-O group at 1124.42 cm\(^{-1}\). Based on the similarity of vibrations wave of hydroxyl and carbonyl groups between standard oxalic acid and the isolated oxalic acid from corn stalk powder, it can be concluded that the resulting compound is oxalic acid.

The analysis of the melting point test for isolated oxalic acid has been done using the Melting Point Apparatus. The melting point of oxalic acid was observed at 100.3\(^{0}\)C. The melting point of oxalic acid standard is between 106 and 107 \(^{0}\)C. The difference in melting point is probably due to the results of crystallization which are not yet pure or there are still many impurities, this is supported by the results of the FTIR analysis as shown in Figure 2.
3.2. **Photocatalytic Reduction of Cr(VI) with the isolated Oxalic Acid**

The amount of oxalic acid as the oxidant in the photocatalytic reduction of Cr(VI) affects the efficiency of reduction. In this study, the dose of oxidant was varied to reduce Cr(VI) at the initial concentration of 300 mg/L.

A shown in Figure 3, the oxidant dose did not affect the efficiency of Cr(VI) reduction significantly at a low mass of 10-30 mg. The optimum dose of oxalic acid to reduce 300 mg/L Cr(VI) was 30 mg with the percentage of Cr(VI) reduction was up to 45.97%. Increasing the mass of the oxidant has decreased the efficiency of Cr(VI) reduction. Oxalic acid as much as 0.04 g only reduced Cr(VI) up to 19.95%. This is because the more dose of oxalic acid added, the solution becomes more turbid, so the intensity of the light used for illuminating the Fe decreases. It causes a decrease in reduced Cr(VI) ion [7]. The process of photocatalytic reduction of Cr(VI) ions using Fe(III) as a catalyst can be assumed to
follow the scheme as shown in Figure 4. At first, oxalate forms a Fe(III)-oxalate complex compound. Irradiation of this compound results in Fe (II) and carbonyl radicals. Both compounds reduce Cr(VI) to Cr (III). The secondary photochemical process of carbonyl radical produces hydroxyl radicals, oxygen radicals, and peroxide radicals. These radicals are strong oxidants that contribute to the reduction of Cr(VI) [8].

Possible reactions of Cr(VI) reduction is [2]:

$$2\text{HCrO}_4^- + 3\text{C}_2\text{O}_4^{2-} + 14\text{H}^+ \xrightarrow{h\nu, \text{Fe(II,III)}} 2\text{Cr}^{3+} + 6\text{CO}_2 + 8\text{H}_2\text{O}$$

(2)

4. Conclusion
Oxalic acid could be isolated from the corn stalk with the yield production was about 30%. The isolated oxalic acid has similar IR spectra as the oxalic acid standards with the functional groups available were hydroxyl and carbonyl groups. The lower melting point of isolated oxalic acid than the standard could be due to the presence of impurities. The isolated oxalic acid could be used as an oxidant for the photocatalytic reduction of Cr(VI). By using 30 mg the isolated oxalic acid, Cr(VI) at a concentration of 300 mg/L could be reduced for up to 45.9%.

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