The synthetic activities of TiO2-moringa oleifera seed powder in the treatment of the wastewater of the coal mining industry

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Abstract. To process the coal wastewater, the combination of chemical based technology of Advanced Oxidation Process (AOP) of a strong oxidizer using TiO2 photocatalyst and biological treatment of moringa seed powder (Moringa oleifera) is used in the composite form. AOP can be used as an alternative treatment of coal wastewater which is quite economical and environmentally friendly. The XRD results of TiO2 powder and the synthesis of TiO2 - is moringa seed powder in the form of tetragonal crystals. The degradation results of the quality of the coal wastewater using TiO2 powder reached a decrease of (TSS, Fe, Mn, Zn, Hg, Cu, Co, Cr, Al and Ni) by an average of 70% and the increase of pH value of 7 at 200 minute stirring time. The decrease of the wastewater quality using the synthesis of TiO2- moringa seed powder by using sunlight and without sunlight is detected negative (-) at 200 minute stirring time.

1. Introduction
The release of heavy metals from the wastewater of coal mining industry has become a threat to the ecosystem [1]. One of the damages that occur in coal mining activities is the decrease in water pH due to the interaction between the atmosphere, water and rocks. The decrease in the pH of water is not only due to the interaction between the atmosphere, water and rocks, but also due to the coal itself which can lead to acid mine drainage, because generally coal has a humidity range of between 2 - 40%, sulfur content of 0.2 - 8% and ash content of 5 - 40% which can have an effect on the value of coal as an energy source that can cause pollution in its use. Acid mine drainage has a high acidity and is often characterized by a lower pH value below 5 [9]. In addition, acid mine drainage will erode soil and rocks that causes dissolving of various metals such as iron (Fe), cadmium (Cd), manganese (Mn), zinc (Zn), mercury (Hg), nickel (Ni), cobalt (Co), Cadmium (Cd), lead (Pb) and arsenic, which are heavy metals known for their non-degradable toxicity and are largely non-biodegradable. Therefore, in addition to having a low pH, acid mine drainage also contains high concentrations of metals that can adversely affect both environmental and human health and their presence above specified limits in the body can cause severe damage to the body's vital organs, such as the kidney, the liver and the brain, the reproductive system and the nerves[10].

To overcome this problem, coal wastewater treatment needs to be carried out by combining applied technology, namely chemical-based technology of Advanced Oxidation Process (AOP) using strong oxidizer by using photocatalyst of TiO2 and biology of Moringa oleifera seed powder in composite form. This advanced oxidation process can be used as an economically viable alternative wastewater treatment[22]. Commercially, TiO2 powder is also easy to obtain and to produce in large quantities[20]. In addition, TiO2 is a semiconductor that has a melting point, photoactivity, high thermal and chemical stability, has a non-toxic nature and also one of the best catalysts to be applied in the environment because of its inert biological and chemical
properties and the price is relatively cheap[12]. Based on its properties, TiO$_2$ is the most effective photocatalyst to be used, as one of the semiconductor materials, and has been widely studied mainly in the processing of solar energy sources and the processing of hazardous waste[15], and it is also used for hospital waste treatment[7]. TiO$_2$ photocatalyst is highly efficient in reducing heavy metals of Fe, Cr and Pb in wastewater by 96-98% and TiO$_2$ photocatalyst through the sunlight shows higher result in degrading dye waste compared to commercial TiO$_2$[6]. According to previous studies Moringa seeds contain bioactive compounds of rhamnosylxy-benzyl-isothiocyanate, which is able to adopt and neutralize the particles of sludge and metals contained in the suspension waste with dirt particles floating in water and their effect on the content of bacteria Coli, Moringa oleifera seeds can reduce bacteria Coli by about 28%[14].

2. Research Method

One hundred fifty (150) ml of Moringa seed powder solution is added with 300 gram of sol Tetanium Tetra Isopropoxide (TTIP) which is then stirred with stirrer slowly for 24 hours at room temperature to form a nanoparticle suspension. The suspension is sonicated for 30 minutes. Then, it is evaporated to free water and calcined at a temperature of 500°C for 2 hours. The wastewater of the coal industry of 2 L is added to the photocatalytic synthesis of TiO$_2$-powder of moringa seed. The activity test is carried out without sunlight and with sunlight for 50 minutes, 100 minutes, 150 minutes, 200 minutes, 250 minutes and is added with 1.0 mL H$_2$O$_2$ 30%. Then it is put into the reactor, stirred at a speed of 60 rpm. The results of the observation were analyzed using AAS (Atomic Absorption Spectrophotometry) to measure the quality of residual wastewater degradation and X-Ray Diffraexion (XRD) for the analysis of the concentration test of the synthesis of TiO$_2$-Moringa oleifera seed powder.

3. Research Results and Discussion

3.1. Analysis Results of XRD Synthesis of TiO$_2$- Moringa oleifera Seed Powder

The XRD results of TiO$_2$ powder and the synthesis of TiO$_2$- Moringa oleifera Seed Powder in the anatase phase are shown in Figures 1a and 1b.

![Figure 1a. XRD TiO$_2$](image1)

![Figure 1b. XRD Synthesis TiO$_2$-Moringga oleifera](image2)

The results of the study showed that the powder of TiO$_2$ and the synthesis of TiO$_2$-Moringa oleifera seed powder had a tetragonal crystalline form with the space group of 141/amd and the lattice parameter data as shown in Table 1.
Table 1. Lattice parameters of TiO$_2$ and Synthesis of TiO$_2$-Moringa oleifera Seed Powder

| Sample                     | a (Å)  | b (Å)  | c (Å)  | Alpha (°) | Beta (°) | Gamma (°) |
|----------------------------|--------|--------|--------|-----------|----------|-----------|
| TiO$_2$                    | 3.7760 | 3.7760 | 9.4860 | 90        | 90       | 90        |
| Synthesis of TiO$_2$-Moringa oleifera Seed Powder | 3.7760 | 3.7760 | 9.4860 | 90        | 90       | 90        |

3.2. The Effects of the Quality of Coal Wastewater using TiO$_2$ Crystals

The ability of TiO$_2$ as a photocatalyst is to provide H$^+$ with a large oxidation radical. It can provide a continuous hydroxyl radical in accordance with the source of the light. The nature of TiO$_2$ as a strong oxidizer makes it capable of oxidizing heavy metal compounds contained in coal wastewater. The results of the measurement of the quality of the coal wastewater using TiO$_2$ with the stirring variables showing a rise in pH up to 7 in 250 minute stirring time and decreasing the quality of wastewater (TSS, Fe, Mn, Zn, Hg, Cu, Co, Cr, Al and Ni) reaching the average of 70% in stirring time of 200 minutes (Table 2). This is because TiO$_2$ is a strong oxidant that is chemically and biologically inert, producing OH ions and can oxidize and mineralize almost all chemicals that are environmentally friendly [15,23] and can also damage microbial cells by attacking cell walls, cytoplasmic membranes and intracellular structures[18].

Table 2. The Effect of the Quality of Coal Wastewater on TiO$_2$ Crystals

| Parameters | Quality of Wastewater | Maximum Concentration * | Unit | Stirring Time (Minutes) |
|------------|-----------------------|-------------------------|------|------------------------|
|            |                       |                         |      | 50         | 100       | 150       | 200       | 250       |
| TSS        | 70                    | 200 mg/L                |      | 60         | 45        | 27        | 12        | 2         |
| pH         | 2.68                  | 6 - 9 mg/L              |      | 3.5        | 5         | 6.3       | 6.8       | 7         |
| Fe         | 15                    | 7 mg/L                  |      | 14.8       | 11.5      | 8.2       | 5.6       | 1.9       |
| Mn         | 10                    | 4 mg/L                  |      | 9.32       | 7.35      | 5.29      | 2.47      | 0.88      |
| Zn         | 5                     | 5 mg/L                  |      | 4.39       | 3.67      | 2.56      | 0.98      | <0.01     |
| Hg         | 0.0045                | 0.002 mg/L              |      | 0.0040     | 0.003     | 0.0021    | 0.001     | <0.001    |
| Cu         | 2.5                   | 2 mg/L                  |      | 2.5        | 2.13      | 2.01      | 1.99      | 1.72      |
| Co         | 0.5                   | 0.4 mg/L                |      | 0.49       | 0.35      | 0.31      | 0.29      | 0.25      |
| Cr         | 0.7                   | 0.5 mg/L                |      | 0.69       | 0.62      | 0.62      | 0.51      | 0.45      |
| Al         | 2.4                   | 0.5 mg/L                |      | 1.73       | 1.23      | 0.89      | 0.13      | <0.001    |
| Ni         | 0.25                  | 0.2 mg/L                |      | 0.24       | 0.19      | 0.001     | <0.001    | <0.001    |

Source: Government Regulation No. 82 of Year 2001 (PP No. 82 Tahun 2001) * Minisstral Decree on the Environment No. 51 of Year 2004 (Kepmen-LH No. 51 Tahun 2004)

3.3. The Effects of Using Synthesis of TiO$_2$-Moringa oleifera Powder With Sunlight and Without Sunlight on the Quality of Coal Wastewater

The test of the effects of long illumination shows that the longer the time spent in illumination using sunlight, the more heavy metal concentration (TSS) will decrease and the higher the value of pH will be. TiO$_2$ photocatalyst material has a very strong oxidizing power when activated by sunlight. The results of the study are shown in Table 3.
Table 3. Effects of Using Synthesis of TiO$_2$-Moringa oleifera Seed Powder Without Sunlight on the Quality of Coal Wastewater

| Parameter | Quality of the Wastewater (mg/L) | Stirring time (Minutes) | Without Sunlight Illumination | With Sunlight Illumination |
|-----------|---------------------------------|-------------------------|-------------------------------|---------------------------|
| TSS       | 0.0045                          | 27                      | 7                             | 7                         |
| pH        | 2.68                            | 5.5                     | 21                            | 21                        |
| Fe        | 15                              | 13.46                   | 10.21                         | 6.47                      |
| Mn        | 10                              | 8.32                    | 6.21                          | 3.15                      |
| Zn        | 5                               | 4.12                    | 3.07                          | 1.01                      |
| Hg        | 0.0021                          | 0.0013                  | <0.001                        | <0.001                    |
| Cu        | 2.5                             | 2.01                    | 1.001                         | <0.001                    |
| Co        | 0.5                             | 0.32                    | 0.101                         | <0.001                    |
| Cr        | 0.7                             | 0.69                    | 0.037                         | <0.001                    |
| Al        | 2.4                             | 2.09                    | 1.27                          | 0.001                     |
| Ni        | 0.25                            | 0.199                   | 0.0009                        | <0.001                    |

Source: Government Regulation No. 82 of Year 2001 (PP No. 82 Tahun 2001)  
* Ministrial Decree on the Environment No. 51 of Year 2004 (Kepmen-LH No. 51 Tahun 2004)

The results of the observations with naked eyes showed that the wastewater that was originally yellow looked more clear with the addition of illuminating time, so that the results of the wastewater quality of 200 minutes stirring time showed a negative result, but the results of the analysis without the use of sunlight with 250 minutes stirring time just produced negative water quality. The wastewater treatment conducted through AOP (TiO$_2$) by sunlight[11-16,4-18] could substantially reduce waste treatment costs and was more favorable from an environmental perspective[17]. The effect of adding 30% H$_2$O$_2$ is enlarging the concentration of coal wastewater quality and more °OH is produced through reduction reactions. Excessive H$_2$O$_2$ can have a negative effect on degrading heavy metals in coal wastewater rather than °OH which can partially reshape H$_2$O$_2$. HO$_2^-$ can prevent the transfer of photon energy, this is because HO$_2^-$ is a gas molecule that is not dissolved

4. Conclusions

The degradation of coal wastewater quality using TiO$_2$ shows that the quality of wastewater at 200 minutes of stirring time reaching an average of 70%. The synthesis of TiO$_2$- Moringa oleifera seed powder with and without illumination of sunlight can be applied as a coal wastewater treatment with a stirring time of 200 minutes resulting in a decrease in the quality of coal wastewater which is detected negative.

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