

# OPTIMIZATION OF *KOLONG* WATER TREATMENT USING ADVANCED OXIDATION PROCESSES (AOPs) METHODS AND HETEROGENOUS CATALYST IMPREGNATION TO REMOVE METALS IN *KOLONG*

## **OPTIMALISASI PEMANFAATAN DANAU BEKAS TAMBANG MENGGUNAKAN METODE ADVANCED OXIDATION PROCESSES (AOPs) DAN IMPREGNASI KATALIS HETEROGEN UNTUK MENGHILANGKAN LOGAM**

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### **ABSTRACT**

*The mining activities in Bangka Belitung Islands in the several past years resulted in forming lakes called kolong. The water in kolong contained high concentration of iron (Fe) and manganese (Mn). An advanced oxidation processes (AOPs) method using heterogeneous solid catalyst and nickel oxide alumina (NiO/Al<sub>2</sub>O<sub>3</sub>) to eliminate Fe and Mn which contain in kolong water has been done. The solid catalyst was prepared using impregnation method and characterized using XRD and FTIR-pyridine method. Based on analysis of metal contaminant using AAS, the concentration of Fe and Mn in water were removed completely after treated with AOPs using Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.*

**Keywords:** AOPs, heterogeneous catalyst, Ni/Al<sub>2</sub>O<sub>3</sub>, metal removal, kolong

### **ABSTRAK**

Aktivitas penambangan di Kepulauan Bangka Belitung dalam beberapa tahun terakhir ini memunculkan banyak danau yang sering disebut dengan istilah kolong. Air permukaan di dalam kolong tersebut terkontaminasi oleh besi (Fe) dan mangan (Mn) dalam jumlah yang sangat tinggi. Metode pengolahan dengan menggunakan *advanced oxidation processes* (AOPs), dikombinasikan dengan katalis padat heterogen dan nikel oksida yang diimpregnasikan ke dalam aluminium oksida (NiO/Al<sub>2</sub>O<sub>3</sub>), berfungsi untuk mengeliminasi besi dan mangan yang terdapat di dalam air kolong tersebut. Katalis padat tersebut dipersiapkan menggunakan metode impregnasi dan dikarakterisasi dengan metode XRD dan FTIR-piridin. Setelah dilakukan proses pengolahan menggunakan AOPs dan katalis serta hasilnya dianalisis menggunakan AAS, kontaminan besi yang ada di dalam air kolong tersebut konsentrasi besi dan mangan tersisihkan secara total.

**Kata kunci:** AOPs, katalis heterogen, Ni/Al<sub>2</sub>O<sub>3</sub>, penyisihan besi, kolong

## **INTRODUCTION**

### **a. Background**

The mining activities in Bangka Belitung Islands in several past years resulted in depression storage called *kolong*. The water in *kolong* contained some high concentrated heavy metals, such as iron (Fe) and manganese (Mn). The nonsignificant mineral used to remove them caused low concentration and the effort to clear water in *kolong* from these metals would be very difficult. Iron and manganese are the most

common metals which are contained in surface water. The previous research mentioned about these metals, whereas their presences are needed in certain amount by living organisms although their very high concentrations can cause poison symptom.<sup>[1]</sup>

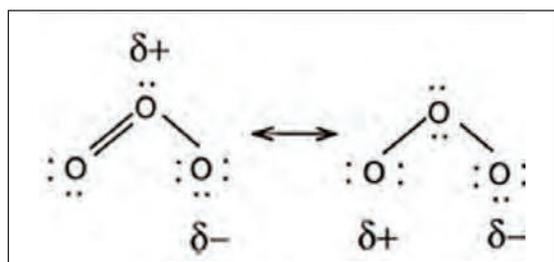
The removal of these metals can be done in physics and chemicals method, which are oxidation, coagulation, flocculation, adsorption, ion exchange, and filtration. However, those regular methods have not removed Fe and Mn which are in organic and colloid form. One of effective

methods to remove metals in organic compound form in the water is by oxidation processes or advanced oxidation processes (AOPs).

AOPs is a friendly environment technology, that does not need large place for installation, with a rapid, does not have to use chemical compound, and process produces hydroxyl radical (OH<sup>•</sup>), an oxidizer in water from ozone decomposition,<sup>[2]</sup> although ozone has low solubility and stability in water.<sup>[3]</sup>

Many researches of the heavy metals (Fe, Mn, Pb, and Cr) removal using ozone have been done. Rozi described about removing iron and manganese using ozone and filtration which resulted in removing 98.64% of iron and 45.83% of manganese.<sup>[4]</sup> Elfiana mentioned about the degradation of iron concentration using AOPs, ultraviolet (UV), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) removed 92.10% of metals, photochemical process using UV removed up to 64.09%, and aeration was up to 32.49%.<sup>[5]</sup> Among chemical technologies, a novel method that has been growing in recent decades is the advanced AOPs which are potent in oxidization, decolorization, mineralization, and degradation of organic and inorganic pollutants. Due to high oxidation rate of chemical reaction caused by AOPs, chemicals are significantly changed after treatment. AOPs for water treatment was not efficient due to their high operation cost, thus it was suggested to integrate these technologies with chemicals process for cost reduction purpose.

The main object in this research is to develop the AOPs method which is combined with solid catalysts (heterogeneous) in order to make the oxidation reaction more active in degradation of metal concentration in *kolong* water.



**Figure 1.** Reaction Mechanism of Molecular Ozone

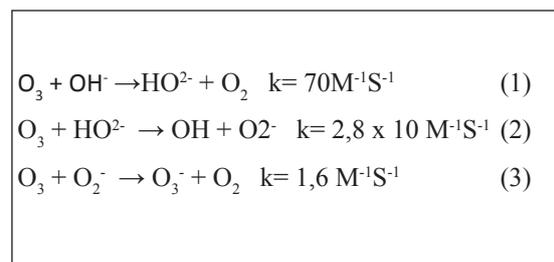
## b. Advanced Oxidation Processes (AOPs) and Catalyst

Ozone (O<sub>3</sub>) is an active and very unstable molecule. According to Figure 1, ozone is capable to react with another compound which has a function as a dipole molecule, an electrophylic or a nucleophylic. Ozone can break a huge complex and a long chain structure into a smaller molecule.<sup>[6]</sup>

According to scheme reactions in Figure 1, ozone is very easy decomposed to form hydroxy free radical (OH<sup>•</sup>), O<sub>3</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup> and O<sup>-</sup>.

An ozone reaction (ozonation) of organic compound could happen through direct reaction with ozone or undirect reaction with free radical OH<sup>•</sup> which is from ozone decomposition in water. An OH<sup>•</sup> is very reactive, but not selective with the contaminants and also can oxidize more effectively compared to ozone. This free radical compound can be produced more by using the combination of ozone with carbon active,<sup>[7]</sup> although the role of carbon active in this reaction is still in discussion whether as a catalyst or as an adsorbent.

Catalytic ozonation can activate ozone, therefore the selectivity of ozone and the rate of reaction can be higher, and it can also have less consumption of ozone. Based on the catalyst phase used, it could be divided into homogeneous and heterogeneous catalytic ozonation.<sup>[8]</sup> Homogeneous catalysts are, Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), and Zn(II), in the same phase with ozone. The mechanism of catalytic homogeneous ozonation with ions transition metal catalyst starts from decomposition of ozone and produces O<sub>2</sub><sup>•-</sup>; then it is transferred into ozone molecule to form free radical molecules, O<sub>3</sub><sup>•-</sup> and OH<sup>•</sup>. The next step



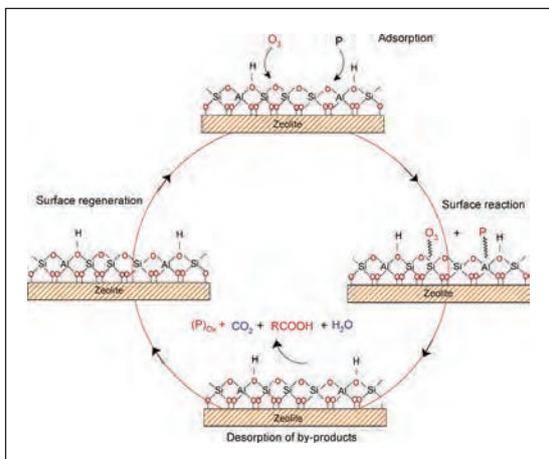
**Figure 2.** Initiation of Decomposition Reaction of Ozone in Water

is the free radical molecules react with metal contaminants.<sup>[9]</sup>

Several researches have done the AOPs combined with heterogeneous catalysts to remove organic compound and metals using  $\text{Al}_2\text{O}_3$ <sup>[10]</sup> and  $\text{TiO}_2$ <sup>[11]</sup>.

Ikhlaq et al. studied the catalytic ozonation for the removal of organic contaminants in water on ZSM-5 zeolites.<sup>[10]</sup> They used HZSM-5 as the catalyst and ozone to remove ibuprofen, volatile organic compounds (VOCs), humic acid, and acetic acid which are dissolved in water. The ibuprofen and VOCs were removed in significant number compared with using only ozone, and also HZSM-5 absorbed the VOCs effectively. Figure 3 shows the mechanism reaction of catalytic ozonation on HZSM-5 as heterogeneous catalyst.<sup>[10]</sup>

Based on those theories, the combination between ozonisation and heterogeneous catalyst can improve the effectiveness of ozone to reduce metal contaminants in *kolong* water. This research focused on studying heterogeneous catalyst combined with AOPs to remove Fe and Mn contaminants in water using nickel and alumina as the catalyst. The alumina has the ability to absorb the VOCs contaminants, meanwhile nickel has the active side to raise the oxidation number of Fe and Mn which could be dispersed into solid form and filtered respectively.



**Figure 3.** Proposed Mechanism of Catalytic Ozonation on ZSM-5 Zeolites

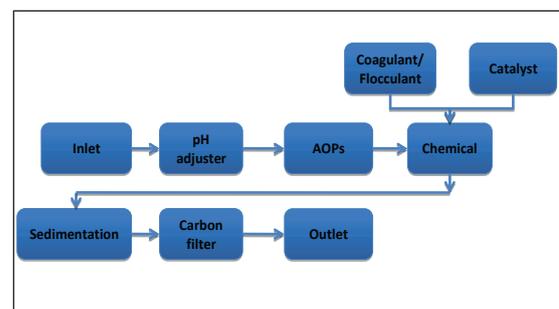
## MATERIALS AND METHOD

### a. Preparation of Catalyst

The catalyst used for the experiment is commercial gamma alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) which is modified with metal promoter, nickel (Ni) as the active sites, through impregnation method. Nickel was impregnated to  $\gamma\text{-Al}_2\text{O}_3$  by adding  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with 98% purity pro analyst from Merck in aqueous solution. To obtain  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ , nickel loading was 5% weight of nickel oxide (NiO). After impregnation, the catalyst was dried at  $120^\circ\text{C}$  for twelve hours, then calcified at  $500^\circ\text{C}$  for five hours. The modified catalyst was characterized using x-ray diffraction (XRD) and fourier transform infra red (FTIR) from Shimadzu, based on pyridine method. XRD was employed to determine the structure and framework Si/Al ratio of catalysts. Meanwhile, FTIR-pyridine provided the acidity and Brönsted-Lewis acid sites.

### b. Advanced Oxidation Process (AOPs) Using Heterogeneous Catalyst ( $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ )

The raw water was included into AOPs reactor with the catalyst already inside the reactor, where catalyst concentration was 1% from adding volume, and the ozone was given in certain doses, i.e. 16 ppm, 24 ppm, and 32 ppm. The process took one hour and then the processed water was flown through filtration divided into two types, i.e. silica sand and activated carbon filtration. The flow diagram of the AOPs is shown in Figure 4. The product outlet was analyzed using atomic absorption spectrophotometry (AAS).



**Figure 4.** Flow Diagram Process Reaction

## RESULT AND DISCUSSION

### a. X-ray Diffraction Analyst of Catalyst

Characterization x-ray diffraction of the modified catalyst was done to find out whether the impregnation of nickel and molybdenum into  $\gamma\text{-Al}_2\text{O}_3$  was successful. The analysis of x-ray diffraction were measured in the range of 2 theta = 20–80°C. Figure 5 shows the crystalline phases of the catalysts before and after impregnation with nickel. The intensity spectra of Ni/ $\text{Al}_2\text{O}_3$  catalyst (Figure 5) is higher than the  $\gamma\text{-Al}_2\text{O}_3$  (before impregnation) at 2 theta = 37° and lower intensity spectra at 2 theta = 46°. It means there was interaction or exchange between the  $\gamma\text{-Al}_2\text{O}_3$  with nickel which was successfully impregnated into  $\gamma\text{-Al}_2\text{O}_3$ .

### b. Acidity Properties of Modified Catalyst

Acid catalyst is needed in advanced oxidation process with ozone. In this case, impregnation of this catalyst must have acidity in certain level. The acidity properties of  $\gamma\text{-Al}_2\text{O}_3$  and the modified catalyst were analyzed by using FTIR-pyridine absorption method. The method was counting the pyridine absorption in the surface of catalyst. The amount of absorbed pyridine was observed by gravimetric method. The result of this experiment was acid amount with an assumption that the size of pyridine molecule was large enough which can be absorbed at the surface of catalysts.<sup>[11]</sup> Figure 6 shows the acid amount of the catalysts and the increasing

acidity amount of  $\gamma\text{-Al}_2\text{O}_3$  after impregnated with nickel metal. Increasing the acidity amount was probably due to an increase in the hands of the free electron pairs which were interacted among nickel with  $\gamma\text{-Al}_2\text{O}_3$ . It increased the absorbed pyridine's vapor on the surface of the catalyst of Ni/ $\gamma\text{-Al}_2\text{O}_3$ .

### c. The FTIR Analysis of Catalysts (Brönsted and Lewis Acid Site)

To observe Brönsted and Lewis acid sites of unmodified and modified catalysts qualitatively were using FTIR. The acid sites were observed at wave numbers of 4000–400  $\text{cm}^{-1}$ , while the Lewis acid site was shown at 1450  $\text{cm}^{-1}$ . The pyridine ions were attached with Lewis acid on catalysts. The infrared spectra of modified catalysts were recorded for the analysis of Brönsted and Lewis acid sites with wave numbers between 1700–1400  $\text{cm}^{-1}$ . FTIR spectra can identify the type of acidity owned by its wave numbers. In general, there are two types of acid sites, i.e. Brönsted and Lewis sites. Brönsted site tends to donate electrons or  $\text{H}^+$  ions, while the Lewis site tends to capture or receive electrons or  $\text{H}^+$ . Figure 7 shows  $\gamma\text{-Al}_2\text{O}_3$  only has one Brönsted site and it means from the number of acid sites after impregnation with nickel arise new absorption peaks around 1440  $\text{cm}^{-1}$  which states Lewis type. It means the increasing acidity of  $\gamma\text{-Al}_2\text{O}_3$  and this is consistent with the results obtained from the analysis of acidity by gravimetry, as shown in Figure 6.

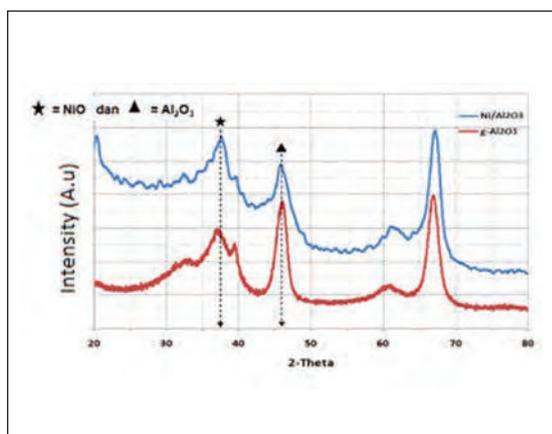


Figure 5. XRD Patterns of  $\gamma\text{-Al}_2\text{O}_3$  and Ni/ $\gamma\text{-Al}_2\text{O}_3$  Catalyst

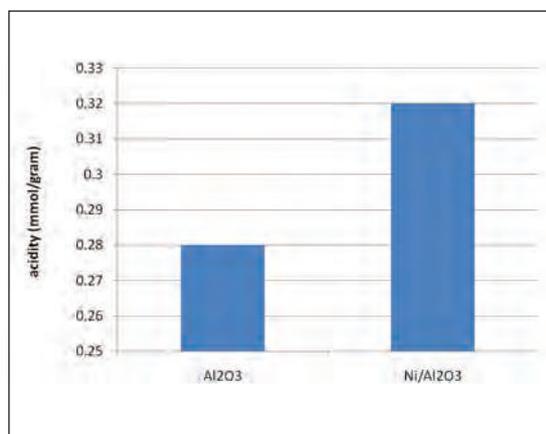
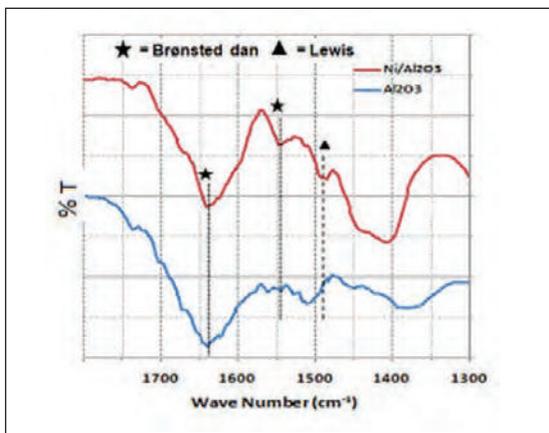


Figure 6. Acidity Analysis of Catalysts Using Gravimetric-Pyridine Method

**d. The Advanced Oxidation Process (AOPs) Heterogeneous Catalyst of Water Contained Fe and Mn**

The Fe contained in raw *kolong* water was 0.4512 mg/L. After fifteen minutes of processing with only AOPs, it decreased into 0.2842 mg/L. Meanwhile, after fifteen minutes processing with AOPs and catalyst, it decreased into 0.0864 mg/L. Figure 8 shows how the reduction of ferrum or iron (Fe) after being treated with AOPs. The reduction of Fe contained processed only with AOPs was 90.31 % after two hours process. However, when the AOPs used catalyst, the reduction rate of iron reached 90.65% after ninety minutes. It means, using catalyst can proceed reaction rate of iron reduction earlier than only using AOPs. Therefore, the main function of the catalyst which is to reach equilibrium reaction was success, it helped to contact ozone with the Fe contaminant better than with AOPs. It also means that the optimum process for iron reduction using AOPs with catalyst is ninety minutes.

Figure 9 shows how manganese (Mn) reduced after being treated with AOPs uncatalysed and catalysed. It is almost similar to iron removal process. The equilibrium of AOPs using catalyst to remove manganese was achieved after two hours, while with only using AOPs, the process needed more optimum time to reach the equilibrium reaction. It also means the Ni// $\gamma$ - $Al_2O_3$  is more selective to remove iron (Fe) and needed more time to remove manganese (Mn).



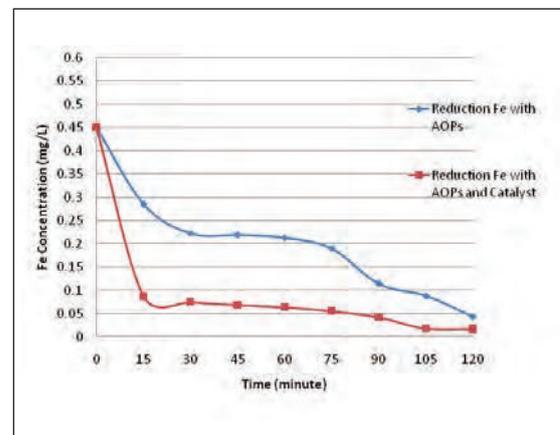
**Figure 7.** FTIR Spectra of  $\gamma$ - $Al_2O_3$  and Ni/ $\gamma$ - $Al_2O_3$

**CONCLUSION**

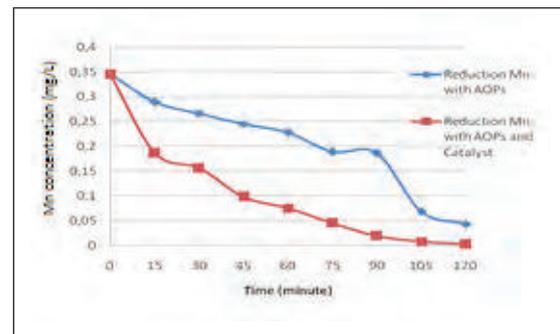
The impregnation of nickel into  $Al_2O_3$  was successful based on XRD and the FTIR data that showed the acidity of the catalyst was increased after nickel impregnation and the acidity influenced the ability of the catalysts for oxidation reaction. The removal of Fe and Mn using AOPs was successful based on the AAS analysis. The AOPs using catalyst could help the process become more effective and could reach optimum time process faster than AOPs.

**ACKNOWLEDGMENT**

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**Figure 8.** Ferro Removal Process



**Figure 9.** Manganese Removal Process

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