Article

The Analysis of Total Dissolved Iron from Mud Sedimentation Ponds Wastewater in PT Bukit Asam (Persero) Tbk Tanjung Enim Using Individual Control Diagram

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Abstract

The tests have been carried out on the iron content of wastewater in the inlet and outlet of the mud sedimentation ponds PT Bukit Asam (Persero) Tbk Tanjung Enim, South Sumatra Province. Referring to Governor's Decree No. 18 of 2005 concerning Coal Mining, the maximum iron metal concentration is 7.0000 mg/L and if it passes these standards then it is indicated to pollute the environment. The measurement of iron concentration was carried out by Atomic Absorption Spectrophotometer (AAS) method in accordance with SNI 06-6989.4: 2004. Analysis of iron concentration using calibration curve methods and individual control diagrams. The results of data analysis showed that the iron content of the inlet and outlet MSP (Mud Sedimentation Ponds) wastewater was still fulfill the standard set with an average concentartion of 1.4488 mg/L inlet and outlet 0.4061 mg/L. Based on the results of the study the concentration of iron meets the established quality standards.

Keywords: Iron content, Atomic Absorption Spectrophotometer (AAS), calibration curves, individual control diagrams.

Abstrak (Indonesian)

Telah dilakukan pengujian terhadap kadar besi pada air limbah Kolam Pengendap Lumpur (KPL) inlet dan outlet di PT Bukit Asam (Persero) Tbk Tanjung Enim Provinsi Sumatera Selatan. Mengacu pada SK Gubernur No. 18 Tahun 2005 Tentang Pertambangan Batubara kandungan logam besi maksimal sebesar 7,0000 mg/L dan jika tidak sesuai dengan standar pemerintah dapat mencemari lingkungan. Pengukuran kadar besi dilakukan dengan metoda Spektrofotometri Serapan Atom (SSA) sesuai dengan SNI 06-6989.4: 2004. Pengukuran kadar besi yang terkandung menggunakan metode kurva kalibrasi dan diagram kontrol individual. Hasil analisis data menunjukkan bahwa kadar besi pada air limbah Kolam Pengendap Lumpur (KPL) inlet dan outlet masih sesuai dengan standar yang ditetapkan dengan nilai rata-rata inlet 1,4488 mg/L se dan outlet 0,4061 mg/L. Berdasarkan hasil penelitian konsentrasi besi memenuhi standar baku mutu yang telah ditetapkan.

Kata Kunci: Kadar besi, Spektrofotometer Serapan Atom (SSA), kurva kalibrasi, diagram kontrol individual.

INTRODUCTION

Minerals and chemical elements in coal play an important role in coal utilization. Organic and inorganic materials are the main composition of coal but more than half of it come from organic substances which were remain from decomposed plants [1]. Basically, local coal has main mineral content such as humotelinite, huminte, inernite, liptinite and pyrite [2]. Materials that construct the coal will effect the produced calor [3]. Therefore, coal is used as an energy

source. However, the coal mining process can also damage the environment.

In general, imperfect mechanical, physical, chemical and biological mining is characterized by instability and limited cohesion, with low amounts of nutrients and organic matter and high amounts of heavy metals [4]. In some cases Coal Mining Waste (CMW) contains 18%-32% aluminum oxide (Al_2O_3), 48%-52% silica dioxide (SiO_2), 2%-8% iron oxide (Fe_2O_3), and about 2% s metal compounds the other [5]. In some cases, water pollution often occurs both surface and ground water pollution can also occur due to coal mining [6]. The presence of sulfide minerals in coal waste under oxidized conditions can produce sulfate (SO_4^{2-}) and contaminate ground and surface water [7]. These sulfide compounds can cause acid mine drainage. Acid mine water arising from mining activities has a very negative effect on the environment [8].

The effect of eco-toxicology from acid mine drainage and sediment results in geochemical parameters such as acidity, dissolved metals, deposition of metal hydrycides and sediments from the mine area is very difficult to separate [9]. Acid mine water can dissolve heavy metals and Fe (II) is the most abundant in acid mine drainage. Fe (II) in acid mine water reacts with oxygen to obtain iron oxide deposits which are usually called "yellow substances" and can be left at the mouth of a water source [10]. The chemical properties of waters from iron are redox, complex formation and metabolism by microorganisms. Low oxidation iron, Fe (II) is commonly found in groundwater compared to Fe (III) because ground water is not related to oxygen from the atmosphere [11]. Iron compounds are generally difficult to dissolve and are quite a lot found in the soil but sometimes iron is also found as siderite (FeCO3) which is easily soluble in water [12]. If the iron contamination is consumed by humans it can interfere with health. Excess iron can cause tissue damage as a result of its free radical form [13].

Conventional handling of some of the problems above that results in water pollution in the form of the addition of alkaline compounds (lime) to neutralize acidity and precipitate hydroxide tablets [14] . Therefore, it is very necessary to test the parameters of the wastewater that is accommodated in the MPA (Mud Sedimentation Ponds) and through various processes, especially to reduce the content of ferrous metals (Fe) in wastewater before being discharged into the mining area. This test is needed to meet the quality standards set by the government and as a form of concern for the parties concerned about the environment around mining. This study uses AAS [15] to analyze Fe metal uptake so that data are obtained to analyze the linearity of the analysis results and control charts.

MATERIALS AND METHODS
Materials

The materials used in this study were wastewater samples from 34 inlet sludge ponds and 34 outlet sludge ponds, 65% Nitric Acid (HNO_3), 1000 mg/L iron standard solution, distilled water, and Acetylene gas.

Methods
Analysis Procedure (Reference Method SNI 06-6989.4: 2004)
Test Sample Preparation

100 mL of the sample that has been shaken until homogeneous was placed into Erlenmeyer then added 5 mL of Nitric Acid (HNO_3) 65%. The solution was heated with an electric heater until the sample solution becomes 10-20 mL. Strain the hot solution and dilute with distilled water in a 100 mL volumetric flask.

Solution Preparation
Iron Metal Stock Solution

A iron standard solution (Fe) of 100 mg/L was prepared by diluting 10 mL of initial iron solution (Fe) concentrating 1000 mg/L into 100 mL of volumetric flask and continued by adding distilled water and homogenized it.

Iron Standard Solutions

The iron standard solution was made with a series of different concentrations, namely 0 mg/L, 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L from a standard solution of 100 mg/L ferrous metal.

Determination of the Calibration Curve

The standard solutions that have been prepared were measured for their absorbance with Atomic Absorption Spectrophotometer at a wavelength of 248.3 nm. Calibration curves were made from the measurement data of the absorption. Determination of the straight line equation using equation model (2), then it is transferred to equation (3), (4) and (5) to determine the linearity value of the curve and range.

$$y = bx + a \qquad (1)$$

$$r = \frac{\sum i\{(x-\bar{x})(y-\bar{y})\}}{\{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2\}^{1/2}} \qquad (2)$$

$$b = \frac{\sum i\{(x-\bar{x})(y-\bar{y})\}}{\sum (x-\bar{x})} \qquad (3)$$

$$a = \bar{y} - bx \qquad (4)$$

Whereas :
y = absorbance
b = slope
x = concentration
a = intercept
r = correlation coefficient

Determination of Standard Deviation, Interval Confidence Slope and Intercept Regression Lines and Detection Limit Value (LoD)

Determine the standard deviation, the confidence interval between the slope and the intercept of the regression line and the detection limit value (LoD) are measured by the equation:

$$yi = bxi + a \qquad (5)$$

$$Sx/y = \left\{ \frac{\sum (yi - \bar{y})^2}{n-2} \right\}^{1/2} \qquad (6)$$

$$Sb = \frac{Sx/y}{\{\sum (x - \bar{x})^2\}^{1/2}} \qquad (7)$$

$$Sa = Sx/y \left\{ \frac{\sum x}{n \sum (x - \bar{x})^2} \right\}^{1/2} \qquad (8)$$

$$b = b \pm 2.13 \times Sb \qquad (9)$$
$$a = a \pm 2.13 \times Sa \qquad (10)$$
$$LoD = a + 3Sx/y \qquad (11)$$

Whereas:
y_i = Absorbance
$S_{y/x}$ = Standard Deviation
S_b = Standard Slope Deviation
S_a = Intercept Standard Deviation
b = Slope
a = Intercept

Data Analysis
Iron Levels Calculation
Calculate the levels of ferrous metals (Fe) and evaluate the test results using the formula:
$$Fe \left(\frac{mg}{L} \right) = C \times f_p \qquad (12)$$

Whereas:
C = Levels obtained from measurement results
fp = Dilution factor

Sample Individual Control Diagram Plotting
The individual value diagram is used to monitor each value observed in a process based on a normal distribution. The diagram elements are determined by the equation:

$$CL = \bar{x} \qquad (13)$$
$$UCL = \bar{x} + 3S_d \qquad (14)$$
$$LCL = \bar{x} - 3S_d \qquad (15)$$

Whereas:
CL = Center Line
UCL = Upper Center Line
LCL = Lower Center Line

RESULTS AND DISCUSSION
Sample Preparation from Inlet and Outlet MSP (Mud Sedimentation Ponds)

The analyzed sample consists of 68 samples taken from several different locations. The samples were divided into two parts which were 34 inlet samples and 34 outlet samples Mud Sedimentation Ponds. The MSP wastewater treatments were the same in every location that distinguishes only processing locations. Coal mining wastewater caused by excavation and washing activities is channeled to the MSP based on the mining location.

The MSP consists of six reservoirs. Tubs one and two are used to precipitate solid particles through a process of sedimentation. Tubs three and four are used for the neutralization process using lime (CaO) and NaOH to raise the pH of wastewater. Tubs five and six were the place for phytoremediation process. The sample of the Inlet section is the sample taken before the wastewater passes through the six reservoirs while the outlet sample is the sample taken after the wastewater undergoes several processing processes through the six tanks.

The initial step of the iron metal (Fe) concentration of wastewater were analyzed using Atomic Absorbtion Spectrophotometer from the preparation sample. The sample to be analyzed can not be used directly to get the total metal concentration, but must went through the stages of adding acid and heating. The addition of nitric acid serves to reduce the metal iron Fe (III) to Fe (II). Furthermore, the addition of nitric acid aims to dissolve the analyte and remove the matrix substances contained in the sample with the help of an electric heater. In addition, the heating process also aims to concentrate the sample by evaporation so that it can be read by AAS and get the metal which was totally dissolved [16].

Determination of Linearity of Calibration Curves for Iron Metal Standard Solutions

The curve linearity determined through a calibration curve. The calibration curve was made by measuring the absorbance of standard metal iron solutions at six concentrations, namely 0.0 mg/L, 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L. The

absorbance data of the iron standard solution were shown in Figure 1. The concentration range in making the calibration curve was adjusted so that the concentration of the iron metals in the sample studied was within that range. The standard solution used for making the calibration curve was made from a standard solution of 100 mg/L ferrous metal diluted with distilled water according to the desired concentration. The measurement results of absorbance of standard metal lead solutions are plotted against the concentration to obtain a calibration curve in the form of a linear line as shown in Figure 1. The calibration curve is made with the aim of knowing the linearity between the concentration of the standard solution and the absorbance produced. Linearity indicates how good a calibration curve that connects absorbance and concentration. Linearity is the ability of an analytical method to provide test results proportional to the concentration of analytes in a sample.
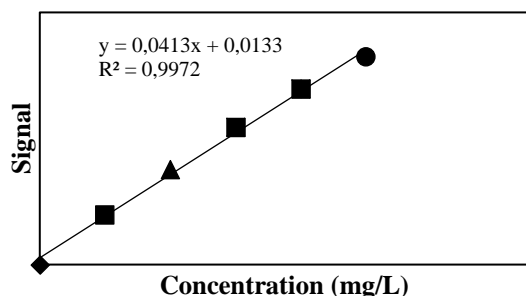
Figure 1. Calibration curve of iron standart solution

Slope and intercept values were obtained at 0.0413 and 0.0133, so the regression line equation of the calibration curve was $y = 0.0413x + 0.0133$ with a correlation coefficient (r) of 0.9972. The value of the relation coefficient close to 1 shows the ideal linear relationship between concentration and absorbance in accordance with Lambert-Beer's law which states the absorbance (A) is directly proportional to concentration (c) through the equation:

$$A = abc \qquad (16)$$

Whereas:
A = Absorbance
a = Molar absorptivity
b = Path lenght
c = Molar concentration

According to SNI (2009) the value of the correlation coefficient must be greater or equal to 0.995.

Determination of Standard Deviation, Intermediate Confidence of Slope and Intercept of Regression Lines and Detection Limit Value (LoD)

The slope standard deviation was 0.0114 and 0.0254 was intercepted. One-way t test results for four degrees of freedom with a 95% confidence interval obtained slope value = 0.0413 ± 0.0242 and intercept = 0.0133 ± 0.0541. The LoD value is 0.2896. Determination of the detection limit is used to determine the lowest concentration of analyte in a sample that can be detected.

Graph of Differences in Iron Concentration in Inlet and Outlet MSP

Based on Figure 2, it was found that the highest levels of iron metals were found in sample 27 from inlet MSP which was located in MSP PIT 1 Timur Baru. The iron concentration was 3.6682 mg/L. In the same location, the highest concentration was also obtained with a value of 2.77237 mg/L from the outlet MSP. According to these results, after going through six storage tanks with a predetermined process Fe concetation was decreased.
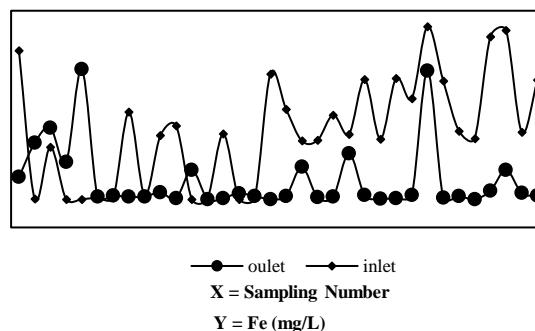

Figure 2. The difference concentration of Fe (mg/L) in inlet and outlet.

The average yield of iron metals in the MSP inlet section is 1.4488 mg/L while the average yield of iron metals in the MSP outlet is 0.4061 mg/L. The decreasing analysis results of the iron concentration after processing in the MSP. Referring to Governor's Decree No. 18 of 2005 concerning Coal Mining iron metal content a maximum of 7,0000 mg/L then PT Bukit Asam has met these requirements so that mining waste water can be discharged to the environment around the mine activities.

Determination of Inlet and Outlet MSP Control Diagrams

The individual control diagram used was a Shewhart control chart of variable type that can be measured and expressed in numbers.
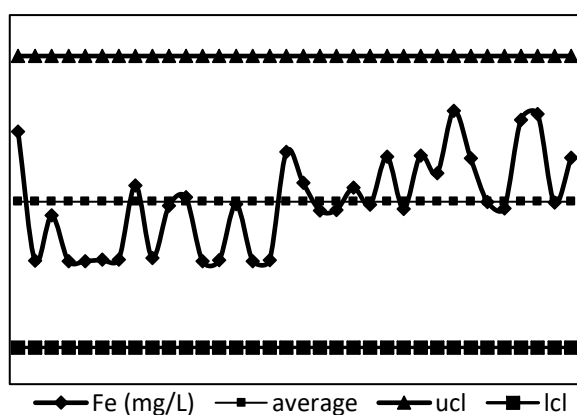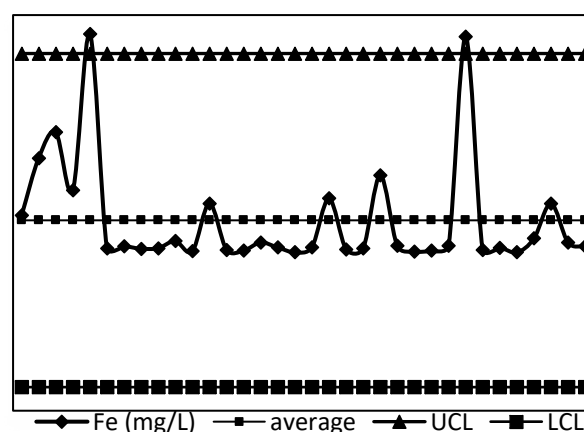
Figure 3. Inlet MSP individual control diagram

Based on Figure 3 individual control diagrams in the inlet MPA wastewater analysis sample show that all data analysis results are located between the Lower Center Line and Upper Center Line boundaries. The diagram shows that the results of the sample analysis are non-final. Then it can be concluded that the analysis of MSP inlet wastewater samples is within reasonable limits. The PT Bukit Asam inlet KPL wastewater analysis process states that the uncontrolled process is statistically rejected.

Figure 4, is an individual control diagram on the MSP outlet wastewater analysis sample. The analysis shows that there are two samples that are above the UCL boundary, namely sample 5 and 27. Sample 5 is at the MPA location. Tupak River (701) where the comparison of the results of inlet and outlet analysis is 0.0000 mg/L and 2.7576 mg/L. The results of the analysis of sample 5 proved to be abnormal because the outlet concentration was greater than the inlet which should have been of the opposite value after passing the management stage at six tanks in the MSP.

Sample 27 is located in the location of KPL.Timb.Pit 1 Timur Timur where theiron concentration difference of inlet and outlet analysis results was 0,9445 mg/L. Through the treatment in six management tanks in the MSP, the results of the outlet analysis should have a smaller value. Therefore samples 5 and 27 are considered abnormal and the PT Bukit Asam MSP wastewater analysis process states that the process is not statistically controlled. Nevertheless, iron concentrations in MSP outlets still meet government standards.

Figure 4. Outlet MSP individual control diagram

CONCLUSION

Based on the objective of practical work, namely analyzing and comparing the concentration of iron metals (Fe) in the inlet and outlet wastewater of MSP (Mud Sedimentation Ponds) at PT Bukit Asam (Persero) Tbk, it can be concluded that the results of the analysis of waste water fulfills the Governor's Decree No. 18 of 2005 which is the maximum iron metal concentration is 7.0000 mg/L.

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