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Optimization of $FeSO_4$ Molarity for Synthesis of Prussian Blue Pigment from Iron Sand from Sunur Beach Estuary, Pariaman

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Abstract. The objective of this research was to see how the molarity of Iron(II) sulfate ($FeSO_4$) solution affected the coloring of the Prussian blue pigment produced, to find the best synthesis conditions. The coprecipitation methods were used to synthesize Prussian blue from $FeSO_4$ and $K_3[Fe(CN)_6]$ solutions. The molarity of iron(II) sulfate ($FeSO_4$) was varied to 0.005 M, 0.0025 M, and 0.00125 M in this research, with the resulting products referred to as K1, K2, and K3. The UV-Visible spectrophotometer was used to analyze the produced pigment. The molarity of Iron(II) sulfate ($FeSO_4$) impacts the final Prussian blue pigment, as observed in the experiment with variations in the molarity of $FeSO_4$. The optimum color of Prussian blue, with a peak near-standard UV-Visible spectra at 686 nm, was produced at 11.85 mM $FeSO_4$ molarity, which was very much by the standard absorbance wavelength Prussian blue pigment.

Introduction

One of the wealth of natural resources in the province of West Sumatra that can be used as research development material is iron sand. Several areas in West Sumatra that have relatively large amounts of iron sand include Pasaman, Pariaman, Solok, Pesisir Selatan, and Sijunjung. Iron sand in Pariaman district has a relatively high percentage of iron and susceptibility/sensitivity to magnets ($1307.34 \times 10^{-8} m^3/kg$) (Aini, 2020). Blackish/dark gray color, can be attracted by magnets, often found in various beaches and mountains are characteristics that iron sand has. Iron sand is found in many river estuaries in West Sumatra, such as the Batang Sukam Sijunjung river in West Sumatra, the estuary of the Sunur Pariaman coastal river, and the river estuary in Pasaman. Iron sand has a relatively high susceptibility (susceptibility/sensitivity) to magnetism because it is dominated by black magnetite minerals. In a previous study, Fe_3O_4 iron sand in Purwokerto was used as a dye. Further development of this research is needed, including by synthesizing blue pigment based on iron sand so that all basic colors can be made available. Prussian blue has been used in various areas because it is stable when exposed to light. This material can be used in the coating industry, namely as a mixture in baking varnish, ink dyes, and detergent additives (Saputra et al., 2016). Further development of this research is needed, including by synthesizing blue pigment based on iron sand so that all basic colors can be made available. Prussian blue has been used in various areas because it is stable when exposed to light. This material can be used in the coating industry, namely as a mixture in baking varnish, ink dyes, and detergent additives (Saputra et al., 2016). Further development of this research is needed, including by synthesizing blue pigment based on iron sand so that all basic colors can be made available. Prussian blue has been used in various areas because it is stable when exposed to light. This material can be used in the coating industry, namely as a mixture in baking varnish, ink dyes, and detergent additives (Fandi., 2014).

Synthesis of dyes generally uses several methods, such as; coprecipitation and hydrothermal methods. Generally, Prussian blue is synthesized using the coprecipitation method. This method has a number of advantages such as; The preparation process is simple, requires low energy, and the pure phase product is readily available (Wahyuni et al., 2014). The main technology for the preparation of Prussian blue by coprecipitation method is the control of $K_3[Fe(CN)_6]$ concentration conditions. In this research,

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coprecipitation technique is used because the mechanism uses low temperature and it is easy to control the particle diameter so that the time required is shorter. Coprecipitation is a secondary deposition process, namely; the process of a single ion/molecule which is normally soluble, is deposited during the deposition of the required substance. Reference (Legodi and Waal, 2007) in his research has synthesized Prussian blue pigment from sijunjung iron sand. However, Sunur Pariaman iron sand has a different chemical composition from Sijunjung iron sand. Because of this, to be used as the basic material for the synthesis of Prussian Blue pigment, Sunur Pariaman iron sand requires different reaction conditions. Reference (Wahyuni and Aini, 2021) in his research also found the UV-Vis absorbance peak of Prussian Blue around 560 nm, where the peak is still relatively far from the Prussian Blue standard, which is 680-740 nm (Rajendran et al., 2016).

This study aims to determine the optimum conditions for the amount of $FeSO_4$ molarity reacted to obtain Prussian Blue pigment which has the same color as the standard Prussia Blue. The amount of molarity of the reactants generally affects the product of the reaction. Because of this, in this study, the amount of reactant molarity was varied, in this case, $FeSO_4$ to determine the effect of $FeSO_4$ molarity on the Prussian Blue color, and to determine the optimum conditions for the synthesis reaction of Prussian Blue dye. Based on the description above, the authors studied the synthesis of Prussian Blue dye using iron sand with the coprecipitation method.

Experimental

Materials and Methods

The tools used in this research are: NP305 respirator mask, 50 mL burette, mortar & pestle, 200 mesh sieve, analytical balance, beaker, measuring flask, dropper, stir bar, spatula, magnetic stirrer, whatman No. 1 filter paper, mask, gloves and UV-Vis spectrophotometer (Legodi and Waal, 2007). The materials used in this study were Iron Sand at the estuary of Sunur Pariaman Beach, $K_3[Fe(CN)_6]$, 96% H_2SO_4, and aquadest.

Procedures

Synthesis of $FeSO_4$

The iron sand is pulled with a magnet, crushed, and sieved through a 200 mesh sieve. An amount of 40.03 grams of iron sand was reacted with 201 mL of 96% sulfuric acid while stirring at a speed of about 540 rpm at a temperature of 163 °C for 46 hours, the container was opened, a cloudy green-blue mud was obtained, filtered, diluted, to obtain $FeSO_4$ solution (Legodi and Waal, 2007).

Prussian blue pigment synthesis

Prussian blue is synthesized with various molarity $FeSO_4$ that is; 106.65 mM 10 mL, 35.55 mM 30 mL, and 11.85 mM 90 mL, each sample was dripped with 1.3 mL of $K_3[Fe(CN)_6]$ 0.1215 M. The synthesis process was carried out by dripping a solution of $K_3[Fe(CN)_6]$ using a burette into each variation of the molarity of the $FeSO_4$ solution. During the reaction process, the solution was stirred at a speed of about 540 rpm at room temperature. The pigment suspension obtained was decanted and dried. The resulting blue precipitate was centrifuged, rinsed with distilled water, and dried in a desiccator to produce an insoluble Prussian blue dye as $Fe_4[Fe(CN)_6]_3$ (Wahyuni et al., 2014).

UV-Vis Spectrophotometer

UV-Vis spectrophotometer is used to determine absorbance at certain wavelengths. UV-Vis spectrophotometer analysis in this study aims to determine the wavelength interval of UV-Vis absorbed by Prussian Blue pigment (Wahyuni et al., 2014).

Result and Discussion

Synthesis of $FeSO_4$ from Iron Sand

Iron oxide Fe_3O_4 is reacted with 96% sulfuric acid to obtain a solution of Fe(II) ions (Legodi and Waal, 2007), which is then reacted with potassium ferricyanide to produce a precipitate of Prussian blue pigment. Synthesis of the Prussian Blue Pigment starts from the synthesis of its precursors namely; Fe(II) and Fe(III) [6] ions, which are produced from the reaction between strong acid (in this case sulfuric acid is used) (Legodi and Waal, 2007) and Fe_3O_4 powder. Fe_3O_4 was obtained from the iron sand of Sunur Pariaman beach after being pulled by a magnet tens of times so that visually the coarse Fe_3O_4 powder was black and physically attracted to a magnet. To obtain a relatively high percentage of Fe(II) ions, the iron sand powder was ground to pass a 200 mesh sieve, so that the Fe_3O_4 and sulfuric acid particles collided effectively (according to the collision theory based on the surface area of the contact area).

$$4Fe_3O_{4\,(s)} + O_{2\,(g)} \rightarrow 6Fe_2O_{3\,(s)} \quad (1)$$

The $FeSO_4$ synthesis reaction can be explained by the following chemical equation.

$$1{,}5Fe_3O_{4\,(s)} + 4{,}5H_2SO_{4\,(l)} \rightarrow 4{,}5FeSO_{4\,(aq)} + 4{,}5H_2O_{\,(l)} + 0{,}75O_{2\,(g)} \quad (2)$$

Fe_3O_4 powder is reacted with sulfuric acid to produce bluish-green $FeSO_4$ (ferrous sulfate) and if certain reaction

conditions are changed, it will produce ferric sulfate (Legodi and Waal, 2007).

Synthesis of Prussian Blue Pigment with Variation of Molarity $FeSO_4$

Prussian Blue Pigment is synthesized from an aqueous solution of Potassium ferricyanide and Iron(II) sulfate by the following reaction.

$$4{,}5FeSO_{4\,(aq)} + 3K_3[Fe(CN)_6]_{\,(aq)} \rightarrow Fe_4[Fe(CN)_6]_{3\,(s)} + 4{,}5K_2SO_{4\,(aq)} \quad (3)$$

Finding the optimum conditions for pigment synthesis can also be done by varying the molarity of the reactants, according to the stoichiometry of the reaction. The molarity of the reactants usually affects the reactant products in several aspects, such as particle size, reaction rate, amount of reaction products, and absorbance wavelength when exposed to an electromagnetic wave beam. In this study, the optimum conditions for reactant molarity were tested for the synthesis of Prussian Blue. A total of 3 variations of $FeSO_4$ molarity, hereinafter referred to as K1, K2 and K3, were reacted with $K_3[Fe(CN)_6]$ as a control variable, each sample was dripped with 1.3 mL of 0.1215 M $K_3[Fe(CN)_6]$.

Prussian blue is a dark blue dye that can be produced from the oxidation of ferrocyanide salts (Wahyuni and Aini, 2021). Prussian blue can also be produced from the reduction of the ferricyanide salt to give the ferrocyanide salt, followed by the oxidation of the ferrocyanide salt. This 2nd reaction is used in this study. Theoretically, Prussian Blue pigment derived from $Fe^{2+}{}_{(aq)}$ ions, will react in 2 simple steps, the first step is the oxidation of Fe^{2+} to Fe^{3+} and the reduction of $[Fe(CN)_6]^{3-}$, which can be explained by the following net ionic reaction equation (Rajendran et al., 2016).

$$Fe^{2+}{}_{(aq)} + [Fe(CN)_6]^{3-}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + [Fe(CN)_6]^{4-}{}_{(aq)} \quad (4)$$

The product of this reaction, will be the reactant for the next reaction, producing Prussian blue pigment [6].

$$4Fe^{3+}{}_{(aq)} + 3[Fe(CN)_6]^{4-}{}_{(aq)} \rightarrow Fe_4[Fe(CN)_6]_{3\,(s)} \quad (5)$$

It can be seen from the reaction above, if in this study using $Fe^{2+}{}_{(aq)}$, then there will be at least 2 times the visible color changes of these 2 reactions. When the $K_3[Fe(CN)_6]$ solution was dropped, it was observed that the color changed from a dark bluish-green to a Prussian blue pigment. The dark bluish-green color is also affected by the excess of $[Fe(CN)_6]^{4-}{}_{(aq)}$, which comes from the first step reaction because it is a light turquoise color. The $FeSO_4$ solution obtained is not 100% pure, because it also mixes with $Fe^{3+}{}_{(aq)}$ in the form of $Fe_2(SO_4)_3$ (Legodi and Waal, 2007). This is indicated by the color of the solution yellowish green. However, this compound will not react with $[Fe(CN)_6]^{3-}$, according to the following reaction (Rajendran et al., 2016).

$$Fe^{3+}{}_{(aq)} + [Fe(CN)_6]^{3-}{}_{(aq)} \rightarrow \text{no reaction} \quad (6)$$

The top layer of the M3 sample was tested qualitatively for the presence of ferrous sulfate which was proven to be non-existent, indicated by the absence of pigment color when added $K_3[Fe(CN)_6]$ solution (Rajendran et al., 2016). From the results of the qualitative test, obtained a dark blue color typical of Prussian blue. From these results, the research was continued with a small-scale quantitative pigment synthesis, to get a prediction of the equivalence point of the mole ratio between $FeSO_4$ and $K_3[Fe(CN)_6]$, as well as to calculate the percentage of iron sand that reacts with sulfuric acid and calculate the stoichiometric reaction. After the visually visible equivalence point was obtained and a characteristic Prussian blue color was produced and the precipitate, followed by synthesis according to the stoichiometry, to obtain a relatively large amount of solid yield for a UV-Vis Spectrophotometric characterization test. The number of moles of reactants in the synthesis of pigments usually affects the quality of the yield of the pigment (Saputra et al., 2016). Therefore, the variation of the molarity $FeSO_4$ to test the quality of each amount of molarity $FeSO_4$ which will produce 3 quality differences that can produce authentic data between the molarity variables $FeSO_4$ to the resulting Prussian Blue. It can be seen from the UV-Vis characterization, where the test will inform the absorbance wavelength of the molarity variation (Wahyuni et al., 2014).

Visually, the smaller the molarity $FeSO_4$ added, it will produce a brighter Prussian Blue, and close to the standard Prussian Blue. More pigment mass was also produced from the addition of $K_3[Fe(CN)_6]$, which indicated that the predicted equivalence point visually was relatively slightly off, where $FeSO_4$ which was thought to have been used up had reacted with $K_3[Fe(CN)_6]$, the $FeSO_4$ had not been exhausted. reacted, as seen in the taking of the top layer of the sample liquid, the $FeSO_4$ was still reacting to form pigments (Moosvi et al., 2016). Prussian blue is synthesized by varying the molarity $FeSO_4$ that is; 106.65 mM 10 mL, 35.55 mM 30 mL, and 11.85 mM 90 mL. The synthesis process was carried out by dripping a solution of $K_3[Fe(CN)_6]$ using a burette into each variation of the molarity of the $FeSO_4$ solution.

UV-Vis Characterization of Prussian blue Pigment

out by dissolving a sample of Prussian blue pigment

using a solvent that could dissolve relatively large amounts of the pigment. Prussian Blue Pigment dissolves well-using ethanol as solvent (Busquets, 2019).

Figure 1. Characterized samples of $FeSO_4$ molarity variation

The results of the $FeSO_4$ molarity variation test showed that in all samples the addition of $K_3[Fe(CN)_6]$ was less than the equivalence point.

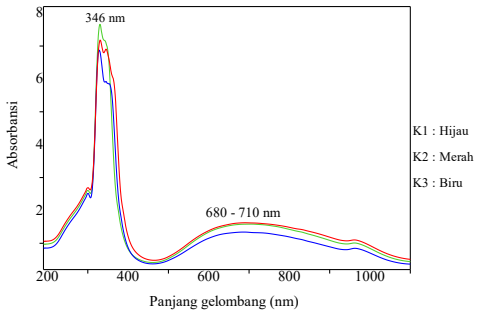

Figure 2. Molarity variation of $FeSO_4$; samples K1, K2, and K3 on UV-Vis test

The equivalence point of the reaction is indicated by a color change; it begins with the distinctive color Prussian blue, then gradually looks blue-green at a glance. From the reaction equivalence point, the $FeSO_4$ molarity of each sample can be calculated. Because the equivalent mole ratio of $FeSO_4$ and $K_3[Fe(CN)_6]$ reagent; 3:2, then the $FeSO_4$ molarity of each sample K1, K2 and K3 are obtained respectively as follows; 106.65 mM, 35.55 mM, and 11.85 mM.

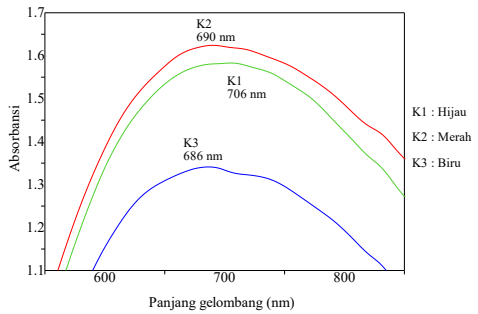

Figure 3. Samples K1, K2, and K3 on UV-Vis test when the graph is enlarged

The peak of 680-740 was higher because more $K_3[Fe(CN)_6]$ solutions reacted with 0.018 mM $FeSO_4$ to form Prussian blue [4]. In this study, the excess $FeSO_4$ solution and K_2SO_4 salt were cleaned of pigment by rinsing using distilled water which was previously centrifuged.

Figure 4. Samples K1, K2, and K3 after washing and drying with a desiccator

All standard graphs of Prussian blue and $K_3[Fe(CN)_6]$ show absorbance at about 346 nm, so it can be assumed that it is not an impurity of Prussian blue pigment [4]. In all samples, the peak absorbance wavelength is quite close to the standard Prussian blue wavelength; i.e. at 680-740 nm (Wahyuni et al., 2014). From the results of visual observations, it was found that the pigment suspension was visible, the K3 sample looked brighter, followed by the K2 and then K1 samples. In the UV-Vis test, it appears that the three samples are identical at first glance. However, when the graph is enlarged, it can be seen that the dilution of $FeSO_4$ reduces the absorbance wavelength.

Table 1. Wavelength Shift in $FeSO_4$ Molarity Variation Samples.

$FeSO_4$ molarity variation sample	Wavelength (shift)
K1	706 nm
K2	690 nm
K3	686 nm

The absorbance wavelengths are K1, K2, and K3, respectively; 706 nm, 690 nm, and 686 nm. The optimum condition for the most dilute sample is the K3 sample at an absorbance of 686 nm because it is closer to the Prussian blue standard, which is 680 nm, the color is brighter, the particle size of the suspension looks finer, and the agglomeration is smaller. The effect of the amount of Molarity $FeSO_4$ on the Prussian blue color can be seen from the wavelength of the absorbance peak obtained from the UV-Vis characterization, namely; the higher the Molarity of $FeSO_4$, the wavelength of the absorbance peak tends to shift to a larger wavelength and the amount of $FeSO_4$ that reacts with $K_3[Fe(CN)_6]$ reagent is increasing.

The tendency to shift the wavelength is related to the

particle size of the resulting pigment. If a more dilute solution of the reactants is used, agglomeration is reduced, which results in brighter color because the number of electromagnetic waves reflected by the pigment suspension particles is relatively large. Qualitatively, it appears that the absorbance wavelength tends to increase with the increase in $FeSO_4$ molarity. The amount of impurity from the resulting pigment is estimated to be small; it can be seen from the amount of noise that appears slightly in the three variations. The noise that appears is probably due to the presence of suspended particles in the sample because the Prussian blue pigment is relatively difficult to dissolve in almost all solvents. However, the Prussian blue pigment tends to be relatively soluble in ethanol (Busquets et al., 2019).

Conclusion

Prussian blue with a brighter color and peak UV-Vis spectra close to the standard obtained by the addition of $FeSO_4$ molarity at the equivalence point. The increase in the Molarity of $FeSO_4$ shifts to the right/increases the absorbance wavelength of the Prussian blue pigment in the UV-Vis test. The results of this study showed the absorbance at 680-710 nm, which was in close agreement with the absorbance of the Prussian blue standard. Molarity of iron(II) sulfate ($FeSO_4$) affects the resulting Prussian blue color, the brightest/optimum color with peak UV-Vis spectra is close to the standard obtained at 11.85 mM $FeSO_4$ molarity.

References

Aini, S. (2020). The Characterization of West Sumatera Iron Sand as a Raw Material to Synthesize Magnetic Nanoparticles. *Redwhite Press*, *5*, 144-147.

Saputra, F.M.A., Yulianto, A., and Aji M.P. (2016). Sintesis Pigmen Magnetik Copper Ferrite ($CuFe_2O_4$) Berbahan Dasar Pasir Besi Menggunakan Metode Kopresipitasi. *Unnes Physics Journal*, *5*(2),14-20.

Legodi, M.A. and Waal, D.D. (2007). The preparation of magnetite, goethite, hematite, and maghemite of pigment quality from mill scale iron waste. *Elsevier*, *74*(1), 161-168.

Rajendran, S., Rathish, R. J., Prabha, S. S., and Anandan, A. (2016). Green Electrochemistry – A Versatile Tool in Green Synthesis. *Portugaliae Electrochimica Acta*, *34*(5), 321-342.

Wahyuni, M. and Aini, S. (2021). Sintesis Zat Warna Prussian blue ($Fe_4[Fe(CN)_6]_3$) Berbahan Pasir Besi Alam. *Chemistry Journal of Universitas Negeri Padang*, *1*(1), 73-76.

Wahyuni, L. T., Mufti, N., and Yudyanto. (2014). Sintesis dan Karakterisasi Nanopartikel Pigmen (Biru) Prussian blue Ferric Ferrocyanida ($Fe_4[Fe(CN)_6]_3$) Berbahan Pasir Besi Alam. *Perpustakaan Digital Universitas Negeri Malang*, 1-6.

Busquets, M. A., Novella-Xicoy, A., Guzmán, V., and Estelrich, J. (2019). Facile Synthesis of Novel Prussian blue – Lipid Nanocomplexes. *Molecules*, *24*(22), 1-11.

Moosvi, S. K., Majid, K., and Ara, T. (2016). Studying the electrical, thermal, and photocatalytic activity of nanocomposite of polypyrrole with the photoadduct of $K_3[Fe(CN)_6]$ and diethylenetriamine. *Department of Chemistry, National Institute of Technology Srinagar*, *19*(5), 1-8.