Synthesis of iron sand into yellow nano-pigment using sol-gel method

A Yulianto*, M Fitriawan, Sulhadi, Khumaedi and I Sumpono

Physics Department, Faculty of Mathematics and Natural Sciences Universitas Negeri Semarang

*Corresponding author: yulianto566@mail.unnes.ac.id

Abstract. The organic pigment was synthesized from iron sand, and alum used sol-gel method. Iron sand was soluted on chloride acid to made FeClx. The chelating agent was used oxalic acid to form metal organic as iron oxalic (FeC2O4). Adjustment of pH about 2 has done by NH4OH titration with precursor volume ratio variation. The gel was formed with PEG addition on 150°C heating temperature for 8 hours. The gel was washed with distilled water to eliminate salts residue. The gel was heated on temperature 200°C for 5 hours then yellow pigment is formed. XRD characterization showed that the yellow pigment has a structure of Jarosite. The color of pigment was analyzed using CIE Lab and identified that the yellow color composition is dominant on 1:1 volume ratio of precursor NH4OH. The color and magnetic properties of the pigment were changed by heating treatment.

1. Introduction

The pigment existed since pre-history era. Many pictures were found in the wall of caves using pigment of hematite, brown iron ore, and other minerals. Sciences give the human competence to synthesize various pigment using ion of chromosphere metal, as blue cobalt, yellow chrome cadmium and several kinds of iron oxide, in the interval color of yellow, red and black [1]. The pigment can be classified into two main groups based on the element of its compound; those are organic and an organic pigment. Organic pigment or dyes can be extracted from flowers, vegetables, and other plants [2].

The mineral of jarosite is hydroxide-sulfide and minerals with the compound of $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$ where M is monovalent ion such as H3O+, Na+, K+, Rb+, Ag+, Tl+, or divalent ions like Cu2+, Pb2+, and Hg2+. The Jarosite can be applied as a pigment, even was used in the culture of ancient Egypt [3]. Iron sand is the material that distributed in many regions in Indonesia, especially around volcanoes area. This mineral contains ion of Fe (Fe3+ and Fe2+) naturally. The dominant material in iron sand is a compound of iron oxides like magnetite (Fe3O4) and hematite (Fe2O3). There are other minerals in iron sand such as silicon oxide, titanium oxide, and others but a little amount [4]. Based on the materials contain, in fact potentially iron sand can be processed into some functional products. The iron sand was synthesized into composite magnet [5], the plastic composite of ferrite magnet [6], core inductor [7], multiferroic [4], and magnetic pigment using precipitation methods.

In this study, iron sand was synthesized into pigment using the sol-gel method. This method is usually to be used to process material become to ceramics and glasses [8]. By this methods, the solution of the precursor is transformed into gel using the process of hydrolysis and condensation [9].
2. Materials and Methods

The synthesis process was started by preparation of precursor solution; those are iron chloride ($\text{FeCl}_2$, $\text{FeCl}_3$) and alum ($\text{KA}_2\text{(SO}_4)_2\cdot12\text{H}_2\text{O}$). To provide an iron chloride solution, 0.1 moles of magnetite ($\text{Fe}_3\text{O}_4$) of iron sand was dissolved into 100 ml of chloride acid, heated on the temperature of $90^\circ \text{C}$ and stirred continuously along 2 hours. The formation process of Ferro-chloride and ferrichloride solution is indicated as equation (1).

$$\text{Fe}_3\text{O}_4 + \text{HCl} \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + \text{H}_2\text{O} \quad (1)$$

The solution of alum was made using alum ($\text{KA}_2\text{(SO}_4)_2\cdot12\text{H}_2\text{O}$). It is dissolved in the water, heated at the temperature of $90^\circ \text{C}$ along 30 minutes. The second step, two precursors was mixed and then was added a chelating agent that was 6 gram of oxalate acid ($\text{C}_2\text{H}_2\text{O}_4$) to get an oxalate metal by heating at $90^\circ \text{C}$ and stirring along 2 hours. The homogenate solution then adjusted its acidity at about pH of 2 using ammonium hydroxide. The next, at a mixed solution, was added a gelatin agent that was polyethylene glycol (PEG) with a volume ratio of PEG is 1:1. The gel was formed after heating at a temperature of $150^\circ \text{C}$ and stirring along 8 hours. The volume of $\text{NH}_4\text{OH}$ solution was varied with a ratio of 1:1, 1:2, and 1:3. The third step, the gel was washed out using aqua bides and dried using the oven at the temperature of $200^\circ \text{C}$ along 5 hours. The result was a chunk of pigment colored of yellow.

The chunk of pigment then was crushed become to colored yellow powder. The powder was characterized its physical appearance, crystal structure using XRD method, and color coordinates using the CIE Lab system.

3. Results and Discussion

The result of synthesis iron sand into pigment using sol-gel method is a powder colored yellow. Photo picture of chunk pigment after drying gel is provided at Figure 1. At this synthesis of jarosite, iron sand was taken as a source of $\text{Fe}^{3+}$ ion, while alum as source ion of $\text{SO}_4^{2-}$ and $\text{OH}^-$.

![Figure 1. Synthesized pigment](image)

XRD method was used to get information about the structure of pigment. The result shows that synthesized pigment has the crystal structure of jarosite. It is suitable with similar material that was dried at a temperature of $200^\circ \text{C}$ [10]. Matching the synthesized pigment with Crystallography Open Database (COD) data no. 96-901-2097 is showed at Figure 2.
Figure 2. XRD pattern of synthesized pigment (top) and database (bottom)

Using quantitative analysis of XRD pattern was identified that the formed jarosite mineral has a structure of rhombohedra with space-group (R -3 m), length of lattice a=7.13Å and c=17.61Å. The crystal of Jarosite has a size about 35.1Å. Crystal model of jarosite can be demonstrated using software of Vesta, such as showed at Figure 3.

Figure 3. Crystal model of jarosite pigment

Based on the model some ions are detected, like SO\textsuperscript{4}\textsuperscript{2-} is formed by an atom sulfur S connected with two atoms of oxygen O. Ion OH\textsuperscript{-} is detected too formed by bonding of oxygen atom O and hydrogen H.

The Qualitative analysis above is used as basic of quantitative analysis that is Rietveld refinement method. The result shows that synthesized jarosite pigment in the sample is about 85.03% from whole mass, the rest is aluminum about 14.97%. The sample has Rietveld’s parameter or Goodness of Fit (GoF) $\chi^2 = 1.45$ that satisfies criteria of $\chi^2 \approx 1$ [11]. The matching pattern between the sample and model is shown at Figure 4.
Figure 4. Matching of XRD pattern between the synthesized sample and calculated model

Contain the compound in pigment take effect to color when it is analyzed using the CIE Lab system. The color coordinates show that synthesize pigment has a yellow color. The optimal yellow color was obtained by ratio precursor and NH$_4$OH about 1:1. This result is suitable with Basciano’s condition that at pH 2 optimum colors can be obtained using ratio 1:1 [12]. When the ratio is taken 1:2 or 1:3 the formed pigment in more alkaline condition will be reduced. Reduced Fe$^{3+}$ ion will take effect to the color of the pigment. The color tends to dark, suitable with analysis of CIE Lab, such as shown at Figure 5.

Figure 5. Color coordinates of jarosite pigment.

4. Conclusion
The yellow pigment was successfully synthesized from iron sand using sol-gel method. Pigment has a crystal structure of jarosite and size of 35.1-88.8 nm. Optimal condition of pigment formation is in the ratio precursors and NH$_4$OH about 1:1 and pH about 2. More NH$_4$OH make pigment tend to dark.

References
[1] Herbst W and K. Hunger 2004 Ind. Org. Pigments (Weinheim: WILEY-VCH Verlag GmbH & Co. KgaA)
[2] Rahman T P, Sukarto A, Rochman N T and Manaf A 2013 J. Fisika 3 1
[3] Berry M 1999 J. Am. Indian Cult. Cent. Mus. Bull 24 1-9
[4] Arifani M B, Malik A and Darminto 2012 Jurnal Sains POMITS 11
[5] Wicaksono R, Yulianto A and Sulhadi 2013 Prosiding Seminar Nasional 2nd Lontar Physics Forum (Semarang: IKIP PGRI Semarang Indonesia) p LPF13471
[6] Maulana L Z, Yulianto A and Sulhadi 2013 Prosiding Seminar Nasional Fisika Universitas Negeri Jakarta 2 44
[7] Yulianto A and Aji M P 2010 Prosiding Pertemuan Ilmiah XXIV HFI Jateng & DIY 2 128
[8] Loembe L, Fu Z, Wang W and Wang H 2015 Int. J. Res. Eng. Technol. 4 6
[9] Danks A E, Hall S R and Schnepf Z 2016 Material Horizon 3 91
[10] Mireles I, Reyes I A, Flores V H, Patiño F, Flores M U, Reyes M, Acosta M, Cruzb R and Gutiérrez E J 2016 J. Braz Chem. Soc. 27 1014
[11] Toby B H R 2006 Powder Diffr. 21 67
[12] Basciano L C and Peterson R C 2007 Am. Mineral. 92 1464