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THE EFFECT OF PH VARIATIONS ON THE STRUCTURE OF THE $MnFe_2O_4$/PS NANOCOMPOSITE LAYER AS SELF CLEANING

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ABSTRACT

Manganese is a metal element found in group VII, has an atomic weight of 54.93u, with a boiling point of 20320˚C, while the melting point is 12470˚C, and has a reddish-gray color. Iron (III) oxide (Fe_2O_3) or also known as hematite or maghemite iron ore, iron hematite ($\alpha - Fe_2O_3$) is a simple oxide which has a hexagonal (rhombohedral) structure and has the R3c space group. Manganese was used as reinforcement in this research, while the matrix used was polystyrene. In this study, 5 variations of pH $MnFe_2O_4$/PS, namely 5,6,7,8 and 9 nanocomposites were synthesized using the spin coating method with manganese oxide (MnO_2) and iron ore (Fe_2O_3) precursors. The composite gel is dropped on the glass substrate then the drying process is carried out in an oven. $MnFe_2O_4$/PS nanocomposites were characterized using X-Ray Diffraction (XRD). giving acid and alkaline solutions affects the size of the crystals, when adding a base (25% Na_4OH) the crystal size becomes small while when the acid is added (100% CO_3COOH) the crystal size is larger. : pH 8: pH 9 an increase in crystal size and grain size occurs.

Keywords :*MnFe2O4, pH, nanokomposite, spin coating, self cleaning*

I. INTRODUCTION

Iron ore (Fe_2O_3) has a fairly abundant amount in the world, especially in Indonesia, the availability of iron ore is widely used in technological advances both in the field of electronics, to transportation. While manganese oxide (MnO) is widely used to coat metals in addition to protecting it from rust, it also has hard properties that can be used to strengthen other metals. Manganese is a metallic element found in group VII, has an atomic weight of 54.93u with a boiling point of 20320˚C, while its melting point is 12470˚C, has a reddish-gray color, in various variations manganese can be found in nature with water content that produces a brown color, purple, black and turbidity. Generally, manganese ore is contained in the form of pyrolusite minerals (MnO_2), ($Ba(H_2O)$ $Mn.Mn_4O_{10}$) which are often associated with volcanic activities and rocks that have alkaline properties[1] . The form of iron and manganese ores can be seen in the following Figure 1 and Figure 2.

Fig. 1. Iron ore (Fe_2O_3)

Fig. 2. Manganese oxide (MnO)

Composites are a combination of two or more materials with engineered results to obtain new materials, where each material has different characteristics and properties, both in the form of chemical and physical properties contained in the material, but the final result can still be separated [2]. The matrix is the phase that has the largest volume or fraction in a composite. The matrix usually has a function in transferring stress to the fiber, releasing the bond, the surface of the matrix or fiber protects the fiber, creates a coherent bond, separates the fiber, and remains stable after the manufacturing process. The matrix usually comes from polymer, ceramic, or metal materials contained in the composite structure which has the function of binding/clumping the fibers into one composite structure [3].

Reinforcement is a material or materials used to fill in the composite formation process, the reinforcement used in this study is manganese, while the matrix used is polystyrene so that the combination of matrix and reinforcement produces composite properties. Nanocomposites are solid structures with nanometer-sized dimensions and are arranged repeatedly with different distances and shapes of constituent components, the bonds that occur in nanocomposite materials have an important role in improving and limiting material properties. With the nano size of the particles, there will be interactions between particles, which are larger so as to produce quality materials. This will make the bond between one particle with another particle stronger so that it makes the mechanical properties of the material [4].

On the surface of the composite having self-cleaning which is used to facilitate human work, there are two mechanisms of self-cleaning properties on a surface, namely hydrophobic and hydrophilic mechanisms. Self-cleaning on hydrophilic surfaces requires a photocatalyst mechanism so that its activity requires the activation of UV-A rays or sunlight to degrade dirt. Meanwhile, the glass on the hydrophilic surface has a simpler self-cleaning mechanism, the water droplets will form like perfect spheres on the hydrophobic surface. This is what makes water droplets slide on the surface of the glass so as to bring the dirt that is attached to the surface of the glass [5].

II. METHOD

This research is an experimental study, carried out from August to October 2020 in the Material Physics and Biophysics Laboratory, Physics Department, State University of Padang and in the Laboratory of Chemistry Department, FMIPA State University of Padang.

This research uses tools, namely; High Energy milling (HEM), X-Ray Diffraction (XRD) Ultrasonic Cleaner, Spin Coating, UV-vis Spectrophotometry, Digital Scales, Oven, Magnetic stirrer, Cup, Beaker, Spatula, Glass substrate, Thermometer, Dropper, Erlenmeyer, Injection, Aluminum foil, Measuring cup.

This study uses materials, namely; Iron ore (Fe_2O_3), Manganese oxide (MnO), pH litmus paper, Polystyrene (PS), Ethylene glycol, Methyl orange (MO), Tetrahyrofuran (THF), Polyethylene glycol, NH_4OH (25% ammonium hydroxide), CH_3COOH (acetic acid 100%).

Process of Sample Preparation and Coating Engineering , The Process Of Making Iron Nanoparticles,preparing iron ore (Fe_2O_3) obtained from the warehouse of substances and materials in the Chemistry laboratory of Padang State University will be used to obtain nanohematite (Fe_2O_3). The iron ore (Fe_2O_3) obtained is still in the form of granules.The iron ore (Fe_2O_3) which is still in grain size is then ground again to obtain hematite size in nanometer scale using a HEM (Haig Energy Milling) tool for 5 hours.

The Process Of Making manganese Nanoparticles , prepare manganese (Mn) obtained from the warehouse of substances and materials in the Padang State University Chemistry laboratory to be used to obtain nanoparticles. The manganese obtained is still in the form of granules. Manganese (Mn) which is still in the grain size is then mashed again to get the nanoparticle size using the HEM (Haig Energy Milling) tool for 20 hours [11].

The Process of Making MnO-Fe_2O4/Ps Nanocomposite layer, prepare 50 ml of Tetrahydrofuran (THF), 0.1 grams of PEG 400 0.5 grams of Polystyrene, 0.4 grams of iron ore (Fe_2O_3), 0.4 grams of Manganese oxide (MnO), Acetic Acid (CH_3COOOH) and Ammonium Hydroxide (NH_4OH). pour 50 ml of Tetrahydrofuran (THF), 0.1 grams of PEG 400, 0.5 grams of Polystyrene into 250 ml Elenmeyer, then heated using a magnetic stirrer at a speed of 250 rpm at a temperature of 60˚C, at the 15 minute then enter Manganese oxide (MnO) 0.4 grams into Elenmeyer. In the 25 minute, add 0.4 grams of iron ore (Fe_2O_3) into Elenmeyer. Add 0.1 ml of NH_4OH to get a basic solution with a pH of 8 and 0.2 ml to get a pH of 9. Meanwhile, to get an acid solution by adding 0.1 ml of CH3COOOH with a pH of 5 and 0.2 ml for a pH of 6, the solution was stirred using a magnetic stirrer for 60 minutes, the aim was that all components were evenly mixed and formed a $MnFe_2O_4$/PS nanocomposite gel.[12]

Substrate Preparation, the substrate used in this study is glass preparations with a thickness of 1.2 mm, the glass preparations were cut to the size of 1 cm x 1 cm, 0.5 cm x 0.5 cm, 2 cm x 2.5 cm, the glass was washed with ethylene glycol using an ultrasonic cleaner for 2 hours, the slides were dried for 1 hour, the $MnFe_2O_4$/PS nanocomposite coating process using spin coating. Gluing the glass preparations on the spin coating round, ropping the precursor solution using a dropper onto the substrate, spin the substrate at 1000 rpm in 60 seconds, then the sample was removed and dried using an oven at 60˚C for 2 hours.

Analysis Phase, MnFe2O4/PS layer was varied with 5 variations of pH, from pH 5 to pH 9 by using spin counting to make a thin layer. results of diffraction pattern analysis using HighScore Plus Software. Based on the FWHM value to calculate the crystal size using the Scherrer equation

$$t = \frac{0{,}9 \times \lambda}{\mathrm{B} \times \cos\theta} \quad (1)$$

Information:
t = crystal size (nm)
λ = the X-ray wavelength is worth 1,54 Å
θ = diffraction angle
B = maximum half-peak width FWHM (rad)

III. RESULTS AND DISCUSSION

The results of characterization using XRD test of a thin layer of $MnFe_2O_4$/PS nanocomposite with several variations of pH 5, pH 6, pH 7, pH 8, pH 9 were used. The XRD pattern can be seen in Figure 3.

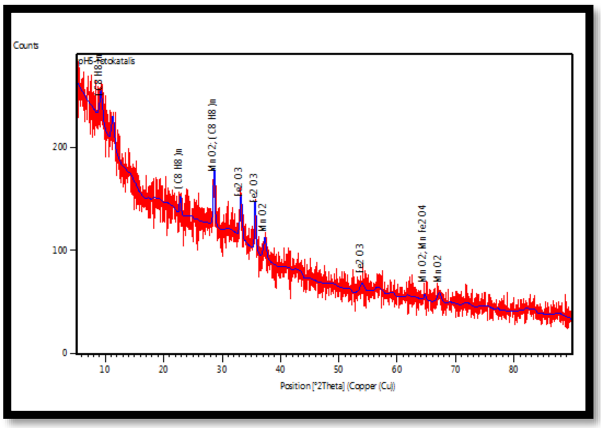

Fig. 3. The Diffraction Pattern of $MnFe_2O_4$/PS nanocomposite with a pH value of 5

Figure 3. shows the diffraction pattern of a thin layer of $MnFe_2O_4$/PS nanocomposite. In this process, it can be seen that the deposition results formed have three peaks, namely with an angle of 9.243^o, 23,791^o, 65.781^o with an FWHM of 0.6140^o, 3070^o, 0.3070^o. With the help of HighScore Plus software, it is possible to identify the peak Miller index associated with the emerging phases, namely (422), (200), (331),. The average lattice parameters on ICDD codes are 00-058-1348, 01-074-2403, and 01-081-2261. Based on the results, the diffractogram pattern can be used to determine the average crystal size using the Scherrer equation obtained from the peak value of FWHM. The crystal size calculated by the Scherrer equation is 0.40385 nm .

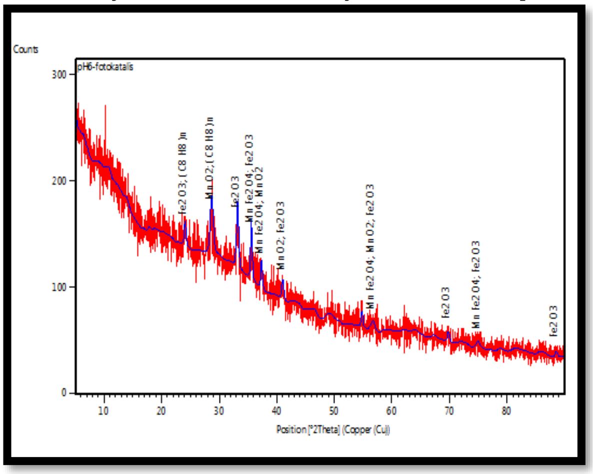

Fig. 4. The Diffraction Pattern of $MnFe_2O_4$/PS nanocomposite with a pH value of 6.

Figure 4. shows the diffraction pattern of a thin layer of $MnFe_2O_4$/PS nanocomposite. In this process, it can be seen that the deposition results formed have six peaks, namely with an angle of 25.00^o, 28.458^o, 35.331^o, 36.956^o, 56.775^o, 74.734^o with FWHM, 0.4093 ^{o}, 0.6140^o ,0.3070^o, 0.3070^o ,0.8187^o, 0.8187 ^{o}. With the help of HighScore Plus software, it can be identified the peak miller index associated with the emerging phases, namely (311), (222), (511), (622), (022), (132), the average lattice parameter in the ICDD code 00-001-0799, 00-058-1348, 01-071-4919, and 01-073-3825 . Based on the results, the diffractogram pattern can be used to determine the average crystal size using the Scherrer equation obtained from the peak value of FWHM. Ucrystal calculated by the Scherrer equation is 0.9241 nm.

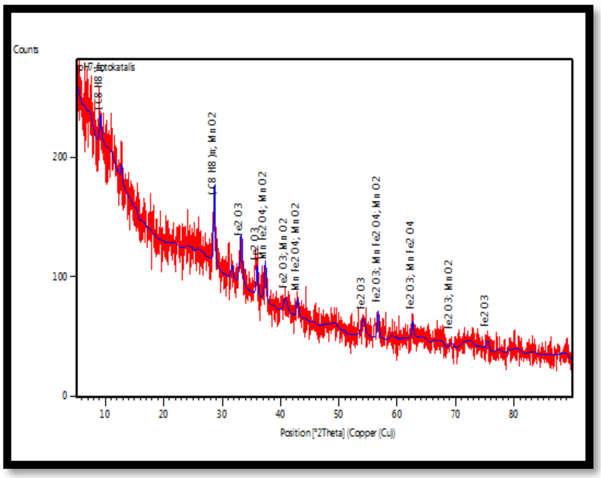

Fig. 5. The Diffraction Pattern of $MnFe_2O_4$/PS nanocomposite with a pH value of 7

Figure 5. shows the diffraction pattern of a thin layer of $MnFe_2O_4$/PS nanocomposite. These data can show the crystals formed on the glass substrate during the process of growing a thin layer of MnFe2O4/PS nanocomposite. In this process, it can be seen that the deposition results formed have seven peaks, namely with an angle of 9.243^o, 28.458^o, 36.956^o, 42.935^o, 56.775^o, 62.339^o with FWHM 0.4093^o, 0.3070^o, 0.3070^o, 0.4093^o, 0.3070^o 0.3070^o. With the help of HighScore Plus software, it is possible to identify the peak Miller index associated with the emerging phases, namely (132), (222), (400), (511), (440), (200), (132). The average lattice parameters on ICDD codes are 01-076-8393 , 00-058-1348 , 00-002-1392 and 00-001-0799. Based on the results, the diffractogram pattern can be used to determine the average crystal size using the Scherrer equation obtained from the peak value of FWHM. Ucrystal calculated by the Scherrer equation is 1.06909 nm.

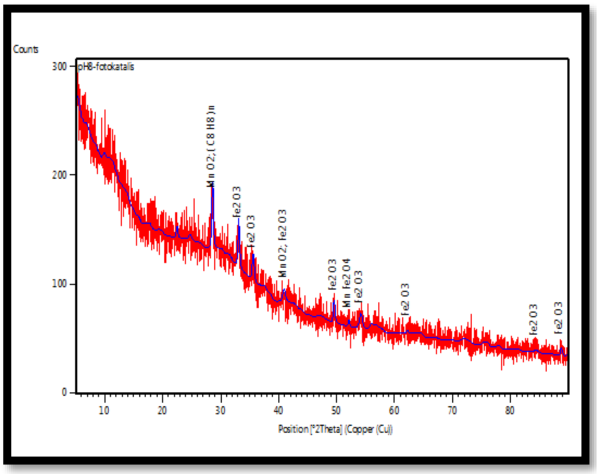

Fig. 6. The Diffraction Pattern of MnO-Fe_2O_4/PS nanocomposite with a pH value of 8

Figure 6. shows the diffraction pattern of a thin layer of $MnFe_2O_4$/PS nanocomposite. In this process, it can be seen that the deposition results formed have two peaks, namely with an angle of 28.458^o, 52.455^o with an FWHM of 0.3070^o, 0.3070^o. With the help of HighScore Plus software, it can be identified the peak miller index associated with the emerging phase, namely (422), (224) the average lattice parameters on ICDD codes 00-002-1392 and 00-001-0799. Based on the results, the diffractogram pattern can be used to determine the average crystal size using the Scherrer equation obtained from the peak value of FWHM. Ucrystal calculated by the Scherrer equation is 1.36652 nm.

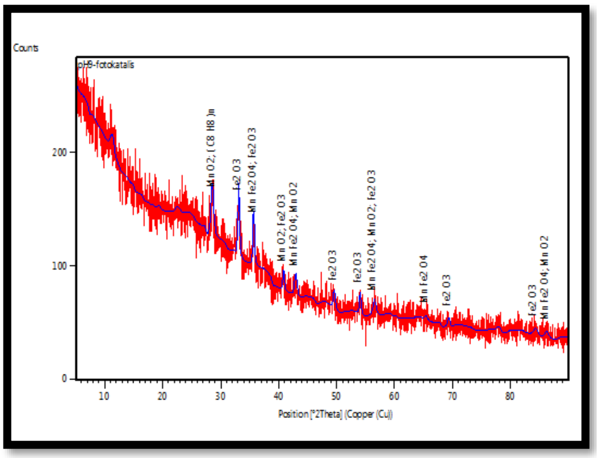

Fig. 7. The Diffraction Pattern of $MnFe_2O_4$/PS nanocomposite with a pH value of 9

There were six peaks of deposition, namely with angles of 28.5549^o, 36.956^o, 42.935^o, 56,775^o, 66.591^o, 86,426^o. with FWHM 0.6140^o, 0.3070^o, 0.3070^o, 0.3070^o, 0.5117^o, 0.4093^o . With the help of HighScore Plus software, it is possible to identify the peak Miller index related to the emerging phases, namely (222), (400), (511), (442), (642), (132). The average lattice parameters on ICDD code 01-081-2261, 01-089-0596, 01-071-4919 and 00-058-1348 Based on the results, the diffractogram pattern can be used to determine the average crystal size using the Scherrer equation obtained from FWHM value. Ucrystal calculated by the Scherrer equation is 3.77176 nm.

The effect of compositional variations on the structure of $MnFe_2O_4$/PS nanocomposite can be seen from the diffraction pattern generated from each composition variation. Based on the diffraction pattern formed in each composition variation, it shows that there are differences in the diffraction peaks, intensity and peak width of the resulting diffraction angles. The difference in intensity and peak width of the diffraction angles is due to the difference in the value of the crystal size produced in each variation of the $MnFe_2O_4$/PS composition.

Based on the Scherrer equation, the size of the crystal formed according to the crystal plane is determined from the FWMH value. The lower the FWMH value of the resulting XRD peaks, the larger the crystallite size obtained. On the other hand, the larger the FWMH value of the XRD peaks obtained, the smaller the value of the resulting crystallite size. The decrease in crystal size correlates with a decrease in the thickness of the layer. The FWHM value shows the peak width of the diffraction pattern, the greater the FWHM value obtained with increasing milling time, the size of the sample will change, so that it can affect changes in the morphology of the upper part of the material on the comparison of the grain size scale of the sample [6]. The effect of the pH of the $MnFe_2O_3$/PS nanocomposite on the crystal size, the relationship between the two can be seen in Figure 8.

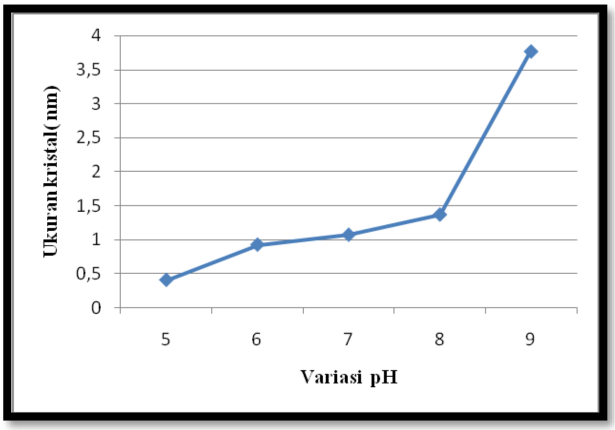

Fig. 8. Graph of pH Variation on Crystal Size of $MnFe_2O_4$/PS Nanocomposite.

The graph shows the effect of variations in pH of the $MnFe_2O_4$ /PS nanocomposite. The greater the pH used, the greater the value of the crystal size, and vice versa. The crystal size of -Fe2O3 at pH 7 and 9 was relatively the same, while at pH 11 the crystals of Fe_2O_3 had a smaller size. If observed at pH 9, it should have a particle size smaller than pH 7. The largest crystal size value is found when the NH4OH solution (base) is added, namely at pH 8 and pH 9 [7]. If the more NH_4OH concentration or the greater the pH value used, the larger the crystal size[8].

The XRD test results also show the presence of a $MnFe_2O_4$ phase with a cubic crystal system and a PS phase with an Orthorhombic crystal system. The intensity of X-Ray diffraction shows the perfection of the crystal and the density of the arrangement of atoms in the crystal. The sharper or sharper and the reflection of the intensity of a material, the tighter the arrangement and the better the crystallinity [9]. The peak intensity of the orientation of the crystal planes in each composition variation, namely, the variation of pH 5 which is more dominant (110) in the PS phase, the variation of pH 6 which is more dominant (012) in the PS phase, variation 7 which is more dominant (110) in the phase PS, the variation of pH 8 was more dominant (110) in the PS phase, and the variation of pH 9 crystal planes was more dominant (024) in the Fe_2O_3 phase. This can be interpreted that the arrangement of the orientation of the crystal planes at each pH variation indicates that polystyrene (C8H8)n has a dominant amount in solution so that it is higher than other substances .

IV. CONCLUSION

From the results of the research that has been carried out, it is found that the $MnFe_2O_4$/PS nanocomposite structure has been prepared by the sol-gel spin coating method. In the XRD test results it can be explained that the $MnFe_2O_4$/PS nanocomposite blended with $MnFe_2O_4$ composite in the PS matrix due to the interaction of $MnFe_2O_4$ with polymer molecules giving an acid and base solution affects the crystal size, when NH_4OH base is added (ammonium hydroxide 25%) the crystal size becomes small while at added CH_3COOH acid (100% acetic acid) larger crystal size.

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