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Synthesis of Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles pigment from lathe waste by sonication – calcination method

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Abstract. Polyethylene glycol (PEG) coated maghemite nanoparticles were synthesized using precursor variation through sonication-calcination method. The precursor was manufactured from lathe waste digested using (a) HCl: HNO₃, (b) H₂SO₄: HNO₃, and (c) H₂SO₄: HCl solvents. Samples were characterized using XRD, FTIR, color reader, and SEM-EDX. The X-ray diffraction pattern shows that Rietveld Refinement confirmed only one single-phase assigned to magnetite (Fe₃O₄) after sonication, one single-phase assigned to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) after calcination, and widened peaks indicating nano-sized particles. Fourier transform infrared (FTIR) spectroscopy measurements confirmed the bonding of PEG to the magnetite and maghemite nanoparticles. Color reader measurement denoted the highest brightness level was achieved using precursor A. SEM-EDX data shows that the distribution of $\gamma\text{-Fe}_2\text{O}_3$ particles was not uniform. There were impurities detected, one of which was silica.

1. Introduction

Iron oxide pigments are commonly found in various forms of iron oxide minerals, such as magnetite (Fe₃O₄) for black pigments, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) for brown, and hematite ($\alpha\text{-Fe}_2\text{O}_3$) for red [1]. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is the second most stable polymorph of iron oxides [2], it is nontoxic [3], biocompatible, and highly paramagnetic [4]. Due to these properties, maghemite have been widely used as pigments.

In general, $\gamma\text{-Fe}_2\text{O}_3$ has displayed some drawbacks along the way hindering its applications as pigments, including the tendency to aggregate and the difficulties to yield nanoparticles. In order to solve these inconveniences, one possible solution is by coating the polymorph with biodegradable and biocompatible polymers, one of which is the polyethylene glycol (PEG) [5]. PEG is a biologically safe and degradable polymer which is highly soluble in aqueous solution, thus preventing self-aggregation and undesired adsorption of plasma proteins onto their surfaces [6], hydrophilic and biologically inert [7].

A number of methods have been reported for the synthesis of maghemite, such as hydrothermal [8], thermal decomposition of magnetite [9], co-precipitation, and the ultrasonic method [10]. Sonochemical method might affect crystal size alteration, lattice parameters, and morphology of the particles due to the shock wave during sonication enabling the separation of agglomerates and there is perfect dispersion with the inclusion of surfactant as a stabilizer [11].

Many factors are known to affect the structure of iron oxides, including the precursor employed [12]. Precursors greatly affect the change in structure, size, and shape of the maghemite nanoparticles [13]. Synthesis of maghemite using Fe(NO₃)₃ precursor were reported to produce a mixture of hematite and



maghemite phase [14], while the use of a mixture of Fe^{+3} and Fe^{+2} has produced tetragonal maghemite structures [3].

In this study, we investigated the effect of precursors to the structure, crystallite size, color parameter, and morphology of the products. Precursors were manufactured of lathe wastes digested using several solvent mixtures to produce black magnetite using sonication method. After calcination for 3 hours, black magnetite will transform to maghemite nanoparticles. The products were characterized using X-Ray Diffraction (XRD), FT-IR, color reader, and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS).

2. Experimental

2.1. Materials

All reagents used in synthesis were of analytical grade and required no further purification. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), chloride acid (HCl), ammonium hydroxide (NH_4OH), and sodium hydroxide (NaOH), polyethylene glycol (PEG) 400 were purchased from Merck, Germany. The iron lathe waste used in synthesis was obtained from Malang, Indonesia.

2.2. Methods

2.2.1. Ferric Precursor. Powdered lathe waste was digested with 300 mL of 15% HNO_3 to yield ferric ions. The mixture was stirred and heated at 90°C for further drying. The resulting muddy solid was then used as the starting material for the synthesis. Ferric ions produced were qualitatively assessed using NaOH solution. Preliminary investigations showed that the product was soluble in water and the yielding of reddish-brown sediments resulted from when NaOH solution was added.

Secondly, 20 g of powdered lathe waste were digested using 200 mL of 38% HCl and then heated on a hot plate at 90°C until completely dissolved. Further heating resulted in a cream green homogeneous substance which was cooled to room temperature and allowed in an open air for a month. During this time, the product gradually turned into brownish yellow sediment. The product was soluble in water and an inclusion of NaOH generated reddish-brown sediments. The chemical behaviour was characterized by the formation of $\text{Fe}(\text{OH})_3$ which indicates the presence of ferric ions. The method used in precursors preparation is demonstrated on Table 1.

Table 1. Detail of Precursors Preparation.

Precursor	Lathe waste (g)	Solvent (mL)				Cation
		30 % H_2SO_4	25 % HCl	38 % HCl	15% HNO_3	
A	50	250	-	-	-	Fe^{2+}
B	30	-	150	-	-	Fe^{2+}
C	20	-	-	200	-	Fe^{3+}
D	30	-	-	-	300	Fe^{3+}

2.2.2. Ferrous Precursor

Cons. H_2SO_4 250 ml was added to 50 g lathe waste, then heated to dry on a hotplate. The mixture was heated and stirred to form blue/green solution. Further heating generated greyish white sediments used as the starting material for the synthesis. Preliminary investigations demonstrated that the product was soluble in water and that the addition of NaOH resulted in blue green sediments. This chemical behavior is the characteristic of the presence of $\text{Fe}(\text{OH})_2$ in solution, indicating that the greater part of iron comprising the muddy green substance is indeed the Fe^{2+} ions. The identical method of precursor preparation was performed by dissolving 30 g of lathe waste in HCl , as shown in Table 1.

3. Results and discussion

The raw material used was the waste of lathe home industry, black powder in appearance that was easily drawn by magnet. Table 2 shows that the highest composition of elements comprising the waste is iron, rendering lathe waste a potential raw material to be used as a precursor in the synthesis of maghemite nanoparticles.

Table 2. Composition of lathe waste.

Component	Content (%)
Si	0.69
Ca	0.41
Sc	0.030
Cr	0.0090
Mn	0.22
Fe	98.21
La	0.010
Ir	0.33

3.1. X-Ray Diffraction

A black precipitate was obtained through sonication under conditions described in section 2.2.3. All resulting samples exhibited high magnetic properties, implying that they highly attracted and attached to magnet. Characterization of the materials was performed by X-ray diffraction. Figure 1 shows the diffraction pattern of all sample variations. All peaks were indexed to the corresponding standard magnetite (reference code ICSD 82237) and analysed based on the emergence of peaks characteristic to magnetite, in which the highest peak was observed at $2\theta(^{\circ}) = 35.46^{\circ}$. Although all samples experienced a slight peak shift, no traces of impurities were detected.

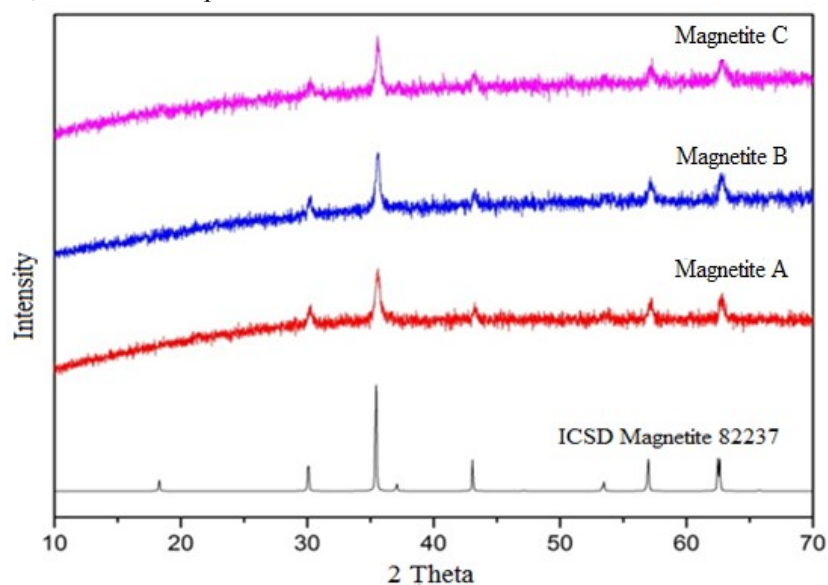


Figure 1. X-ray diffraction pattern of materials after sonication using different synthesis precursors. Magnetite A) from HNO_3 : HCl solvent; B) from HNO_3 : H_2SO_4 solvent; C) HCl : H_2SO_4 solvent.

After calcination, magnetite underwent phase transformation to maghemite. Figure 2 shows that maghemite of high crystallinity was successfully synthesized using calcination method. The diffraction

pattern of all sample variations is in line with the standard pattern of maghemite (ICSD 79196). Based on refinement data by Le Bail refinement method, the reflection of maghemite was revealed to be the cubic structure of P 43 3 2 space group as the predominant phase with cell parameters of ($a = 8,347 \text{ \AA}$), and Z value = 4 [1]. The unit cell parameters obtained are shown in table 3. Refinement result shows that the unit cell parameters of maghemite B (using the HNO_3 : H_2SO_4 solvent) possessed a lower value of R_p , R_{wp} compared to the others, indicating a high similarity degree of maghemite B to the standard. The crystallite size of all maghemite yields was calculated based on the XRD line broadening using Scherer's equation. The calculation results denoted the average crystallite size of the products was around 36.4 nm.

Table 3. Refinement Result using Le Bail Method

Parameter	Standard*	Maghemite A	Maghemite B	Maghemite C
A	8.347	8.373	8.327	8.376
B	8.347	8.373	8.327	8.376
C	8.347	8.373	8.327	8.376
Cell Volume	581.64	587.036	577.55	587.67
R_p		3.92	3.36	3.99
R_{wp}		5.62	4.77	5.15
GOF(χ^2)		0.1254E+01	0.1331E+01	0.8302E+00

*Standard was based on Cornell and Schwertmann [1]

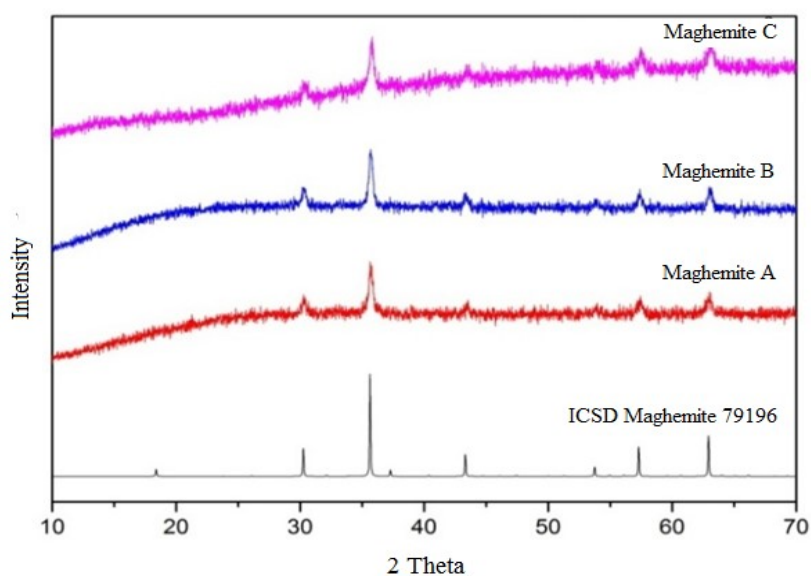


Figure 2. X-ray diffraction pattern of materials after calcination using different synthesis precursors. Maghemite A) from HNO_3 : HCl solvent; B) from HNO_3 : H_2SO_4 solvent; C) HCl : H_2SO_4 solvent.

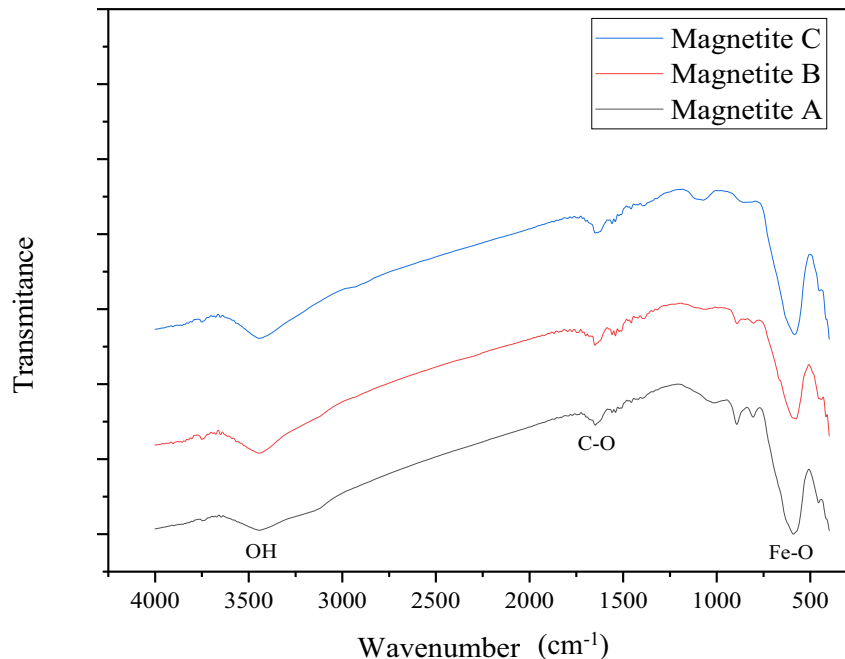


Figure 3. FT-IR spectra of materials after sonication using different synthesis precursors. Magnetite A) from $\text{HNO}_3\text{:HCl}$ solvent; B) from $\text{HNO}_3\text{:H}_2\text{SO}_4$ solvent; C) $\text{HCl:H}_2\text{SO}_4$ solvent

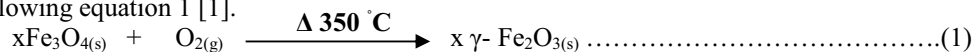
3.2. FT-IR Spectra

In order to confirm the structure of the samples, FT-IR analysis was carried out under ambient conditions in a range between 250 and 4250 cm^{-1} . As depicted on Figure 3, a strong absorption band was observed at 576.4 cm^{-1} assigned to the vibration of Fe-O bond in Fe_3O_4 . Additionally, a peak appeared at 3445.44 cm^{-1} is generally attributed to the presence of hydroxyl group. The FT-IR spectrum of PEG is characterized by a number of absorption bands at $1649\text{-}1069\text{ cm}^{-1}$. The most intense absorption band in this region, located at 1069 cm^{-1} , is attributed to the vibration of C-O bond and at $1649 - 1541\text{ cm}^{-1}$ assigned to the vibration of carboxyl salt of sodium acetate, similar to that of reference [7].

Figure 4 shows the result of FT-IR analysis, revealing the presence of impurities in $\gamma\text{-Fe}_2\text{O}_3$ indicated from the PEG. The presence of IR absorptions at $1647\text{-}1030\text{ cm}^{-1}$ indicates that the PEG in magnetite has not been lost during calcination. As an aside, there was a vibration of C-O bond attributed to the vibration of carboxyl salt of sodium acetate in maghemite. The strong absorption band at $638 - 455\text{ cm}^{-1}$ is assigned as the vibration of Fe-O bond in $\gamma\text{-Fe}_2\text{O}_3$ and a peak at about 3445.44 cm^{-1} is attributed to that of hydroxyl group, especially in maghemite A which exhibited a fairly high absorption intensity.

3.3. Colour Reader

The formation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phase was occurred during the calcination stage on a furnace at 350°C for 3 hours. The resulting products after calcination are an assortment of brownish pigment powders presumed to be maghemite target compound, as shown in Figure 5. Phase transformation from magnetite to maghemite also caused discoloration from black to brown to dark brown. The reaction occurs during the phase transformation of magnetite (Fe_3O_4) to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is shown in the following equation 1 [1].



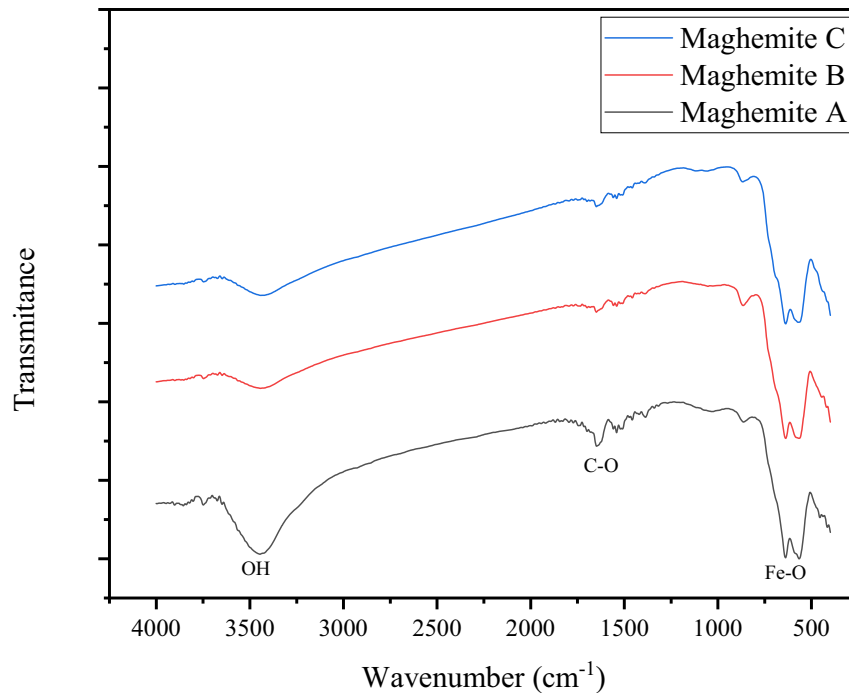


Figure 4. FT-IR spectra of materials after sonication using different synthesis precursors. Magnetite A) from $\text{HNO}_3\text{:HCl}$ solvent; B) from $\text{HNO}_3\text{:H}_2\text{SO}_4$ solvent; C) $\text{HCl:H}_2\text{SO}_4$ solvent

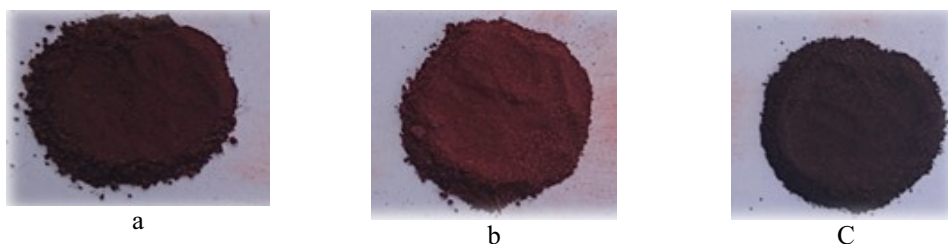


Figure 5. Synthesis of maghemite pigment using different synthesis precursors, A) from $\text{HNO}_3\text{:HCl}$ solvent; B) from $\text{HNO}_3\text{:H}_2\text{SO}_4$ solvent; C) $\text{HCl:H}_2\text{SO}_4$ solvent

Table 4 shows the difference in the brightness (L^*) level of the synthesized pigments. Variant A exhibited the highest brightness level compared to variant B and C. The standard value of L^* in maghemite ranges between 25 and 37, which means that the L^* value of variant A, B and C syntheses have all met that of standard maghemite.

Based on data (Table 4), the level of blue-yellow color (b^*) decreased sequentially from variant A, B and C. The decrease in the value of b^* near point 0 indicates that the color is getting closer to that of blue, unlike variant A whose b^* value inclined to that of yellow. The level of green-red color (a^*) in variant B and C after calcination tends to fall closer to point 0 which means that it was bordering on green, while in variant A there was an increase in the value of a^* which renders it closer to red. The L^*

value of the three synthesized compounds shows its compatibility to the standard, of which the L* value is in the range of 25-37. Thus, the synthesis product of all variations evidently meet the range of L* value of the standard maghemite. The H° (color pattern) of the maghemite compounds after calcination tends to be below the standard value which ranges from 61-72. The result indicates that the color tone of the compounds underwent a decrease.

Table 4. Colour reader identification

Sample	L	a*	b*	C*	H° (Tan ⁻¹)
Standard Maghemite	25-37			15-24	61-72
	32			20	68
Magnetite A	32.6	20.1	18.7	27.45	42.92
(Maghemite A)	35.0	25.2	21.6	33.19	40.59
Magnetite B	30.1	17.7	11.7	21.21	33.46
Maghemite B	25.4	12.2	7.0	14.065	29.81
Magnetite C	25.3	12.5	6.2	13.95	26.38
Maghemite C	25.5	10.7	6.3	12.41	30.45

The determination of the preeminent maghemite product can be specifically established through the chroma (C*) value. The C* value exhibited by three synthesis products have not yet met the standard range which spans around 15-24. Based on the comparison of the results to the standard maghemite pigment, variant B exclusively showed the closest characteristics to the standard maghemite.

3.4. SEM-EDX Characterization

The morphology and composition of maghemite products were investigated with SEM-EDX. Figure 6 shows the SEM images of variant B maghemite nanoparticles at assorted magnifications. The images distinctly confirm that the sample exhibited varying shapes and experienced agglomeration. The data on Table 5 denote that the highest compositions of the resulting maghemite are Fe (iron) and O (oxygen), with traces of impurities such as Si (silica). This result indicates that the presence of Si in the final product originated from the raw material. Si (silica) remained present even after calcination at high temperature of 350°C as the element has a melting point of 1414 °C.

Table 5. Composition of maghemite B

Sample	Element (%)			Total
	Fe	O	Si	
Maghemit	76.37 %	23.20 %	0.43 %	100 %

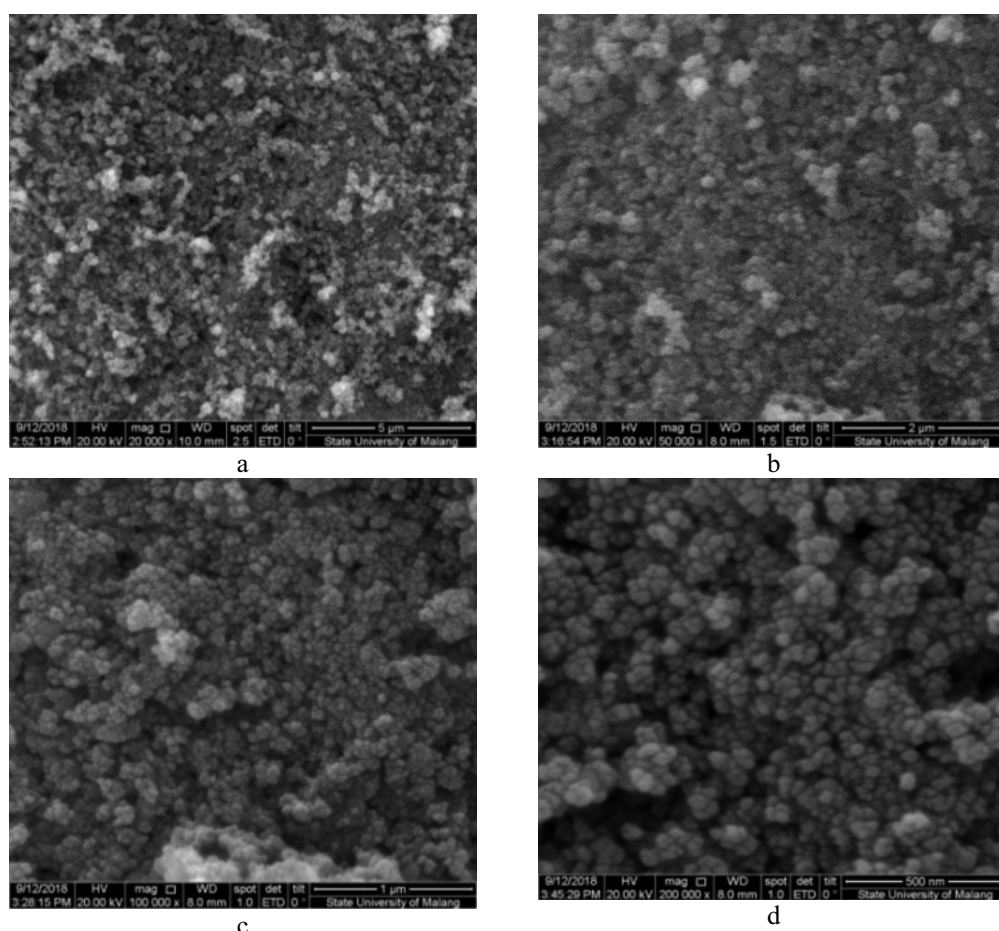


Figure 6. SEM images of maghemite B after (a) 20,000x magnification, (b) 50,000x magnification, (c) 100,000x magnification and (d) 200,000x magnification.

4. Conclusion

The preeminent precursor variant was obtained in variation B, in which the product exhibited the highest degree of crystallinity and cell parameters similar to those of standard. FTIR analysis on magnetite and maghemite product of all variations showed the presence of PEG absorption. Colour purity (C^*) of product resulted from synthesis B after calcination was the closest to that of standard maghemite. In the other hand, the highest brightness level was achieved using precursor A. SEM-EDX analysis of maghemite pigments showed that the morphology of the particles was not uniformly distributed and there were impurities detected, including silica.

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