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Structural and Magnetic Characteristics Evaluation of Iron Oxide Extracted from Printer Toner Wastes

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Abstract. The need to recycle and develop valuable materials from wastes, and use them in various applications have become increasingly important in recent decades. Printer toner waste is one of the most polluting electronic wastes due to the toxic nature of the material content inside it. Despite the toxicity of the material in the toner powder, it contains iron oxide that can be extracted and recycled to make a beneficial material. Therefore, this study aims to investigate a facile and effective method to extract iron oxide from printer toner waste powder. Magnetic separation and oxidation processes were used as a method for extraction and phase conversion. The structural transformation was investigated using X-ray diffraction (XRD), microstructural observation using scanning electron microscope whereas static magnetic characteristics were investigated using vibrating sample magnetometer. The results from XRD spectra showed that printer toner wastes that have been subjected to magnetic separation process and chemical treatment, even without any heat treatment process, have produced a single phase magnetite. Through the process of heat treatment on the sample, phase transformation from magnetite to hematite occurred, in which a single phase of hematite is obtained at a temperature of 1400 °C. The saturation magnetization of the sample also showed a reduction where the sample before undergoing the heat treatment process had a saturation magnetization value of 18.81 emu/g but after the heat treatment, the saturation magnetization value decreased to 0.42 emu/g. These results are in line with the phase transformation shown where magnetite has high ferrimagnetic characteristics, whereas hematite is basically antiferromagnetic at room temperature. However, the saturation magnetization that has been obtained in hematite shows a little difference to that of commercially sold hematite. This proves that iron oxide extracted from the printer toner waste has high potential as an alternative to commercial iron oxide available in producing high-performance magnetic materials.

Introduction

Today, one of the fastest growing wastes due to the development of industrialization and internet of things (IoT) is electronic wastes (e-waste) which is also known as electrical and electronic equipment wastes (WEEE). With an increase in total waste by 5% or 40 million metric tons per year, it is the waste that contributes the most to environmental problems [1]. Although WEEE contains high toxicity, there are many precious metals that can be extracted and recycled from the WEEE during the disposal process such as gold [2], zinc [3], copper [3] and so on [4]. Waste toner powder from printer cartridges is also part of the WEEE and has been disposed of globally where millions of them end up in landfills around the world. Disposal of toxic chemicals mainly from toner powder into the soil resulting in major changes to the environment. Typically, for each discarded cartridge, there is about 8% of the remaining toner powder left [5]. In fact, the remaining toner powder has a very

fine particle size and flammable which can also increase the risk of dust explosions. As printing technology still adopts toner as the main material, actions should be taken to recycle toner powder waste into materials that are useful to preserve the environment. Apart from carbon black as a coloring pigment, resin as a plasticizer and fumed silica to keep the powdered toner particles loose and flowing freely inside the cartridge, toner powder also contains iron (II, III) oxide as known as magnetite as a charge control agent for electrophotography printing. Since ancient times, iron oxide, either it is magnetite (Fe_3O_4), hematite (Fe_2O_3) or wustite (FeO), is the most widely used raw material in developing various technological applications [6]. Hence the process of recycling and extraction of magnetite from printer toner waste is very important in reducing the cost of production of magnetic-based applications based on the magnetic characteristics found in magnetite. Furthermore, magnetite, through the process of oxidation, has high potential to be transformed into hematite, which is basically utilized as a raw material in hard magnet and soft magnet fabrications [7].

Therefore, this study aims to initiate a simple and low cost extraction method of magnetite from printer toner powder wastes by using magnetic separation, followed by heat treatment process for phase transformation to hematite. The resultant powder from the extraction process will be tested in terms of its structural and phase transformation, microstructure and magnetic properties to comprehend the potential of iron oxide extracted from printer toner waste powder to be used as a raw material in development of magnetic products as an alternative to the commercially available high purity iron oxide for further research.

Materials and Method

The discarded cartridges were dismantled to recover the toner residue in it. The toner residue was dissolved in ethanol in a ratio of 1:10 and stirred vigorously in a beaker affixed with a magnet around the beaker. Through the process of magnetic separation, the powders having magnetic properties will be attracted to the magnet, while the rest will be left in the solution. The process was repeated several times to ensure that all magnetic powders have been separated from non-magnetic particles. After that, the powder obtained from the magnetic separation was mixed with butyl acetate in a ratio of 1: 3. The stirring process was taking for 30 minutes to remove the foreign matter. The solution containing iron oxide was re-centrifuged several times, filtered and washed with deionized water. It was then dried in an oven overnight. Later on, the dried powder was calcined at a temperature of 500 °C for 2 h and milled for 30 minutes. The powders were then annealed at 1400 °C for 5 h at a heating rate of 4 °C/minute to complete the oxidation process.

All the pre-calcination and post-calcination samples were analyzed for structural characterizations using Rigaku Miniflex X-Ray Diffractometer using Cu-Kα radiation at 0.02° scan steps. Microstructure analyses were carried out using Hitachi/TM3030 PLUS Benchtop Scanning Electron Microscope and JEOL JSM 6700 Scanning Electron Microscope whereas Lakeshore 7404 Vibrating Sample Magnetometer was used to measure the static magnetic characteristics of the samples at room temperature with a maximum magnetic field of 12 kG.

Results and Discussion

Fig. 1 shows the XRD multi-plot of treated printer toner powder before and after heat treatment process. After the magnetic separation process, samples that were chemically treated using butyl acetate and ethanol showed the presence of a single phase of magnetite (Fe_3O_4) (Ref. code: 98-010-9587) with cubic crystal structure. This shows that the process of magnetic separation and purification using butyl acetate and ethanol is very effective in removing other non-magnetic elements contained in the printer toner such as carbon black, resin and other additives. To increase the purity of the resultant magnetite, the samples were calcined at a temperature of 500 °C. The XRD spectra of the samples after calcination showed that most of the magnetite had undergone a phase transformation to hematite (Ref. code: 98-006-0281) with hexagonal crystal structure. Whereas after the annealing process at 1400 °C, a single phase of hematite was obtained. This shows that the heat treatment process has caused the oxidation process to magnetite through the formation of hematite (Fe_2O_3), in

addition to the oxygen loss process that only occurs at high temperatures [8]. In fact, hematite is more desired than magnetite in producing high-performance magnetic materials such as nickel zinc ferrites and barium hexaferrites because magnetite has lesser iron content as compared to that of hematite which has higher iron content, resulting in non-stoichiometric samples being produced when it is reacted with other raw materials. Besides that, magnetite is easily oxidized and the ratio of Fe to O is not fixed, therefore hematite is generally used as raw material for magnetic ferrites fabrication [9]. Apart from the increase in the volume fraction of hematite after heat treatment, crystallization also increases where it is shown through an increase in its peak intensity. In addition, the crystallite size also increases with temperature, indicated by the reduction in the peak width broadening of the FWHM in the XRD spectra. Detailed data on phase and structural changes are shown in Table 1.

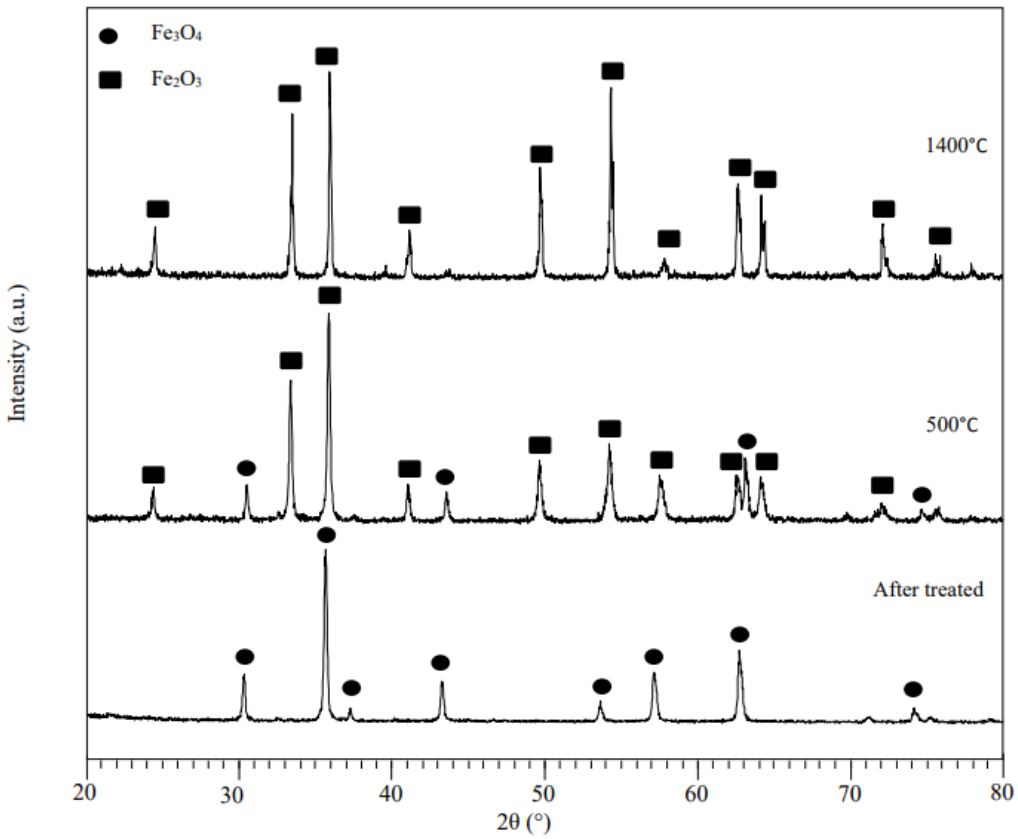

Fig. 1. XRD multi-plot for treated waste toner powder before and after heat treatment at 500 °C and 1400 °C

Table 1. Structural parameter based on XRD data for all samples

Sample	Most intense phase	Position [°]	FWHM [°]	*d*-spacing [Å]	*hkl*	Space group	Crystal Structure
Before heat treatment	Magnetite	35.5844	0.177	2.5209	113	*Fd-3m*	Cubic
After calcination: 500 °C	Hematite	35.778	0.177	2.5077	104	*R-3c*	Hexagonal
After annealing: 1400 °C	Hematite	35.8606	0.0984	2.5021	104	*R-3c*	Hexagonal

Fig. 2 and 3 depicted the morphological structures of the treated powder sample before heat treatment and after heat treatment. Before calcination, the particles show almost regular shaped particles (Fig. 2), however when subjected to calcination at 500 °C, the particles show a flake-like

shape (Fig. 3 (a)). The same observation is obtained for the powder after annealing at 1400 °C (Fig. 3 (b)). It has been expected that no changes in particle size will occur even after heat treatment because the analyzed sample is in powdered form, which does not allow grain growth to occur, as the grain growth only occurs in compacted bulk particles through atomic diffusion process.

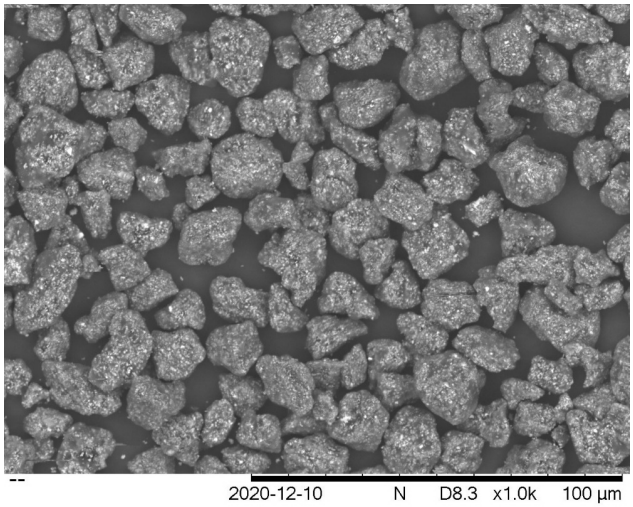

Fig. 2. A SEM micrograph of the printer toner waste powder after chemically treated with butyl acetate and ethanol

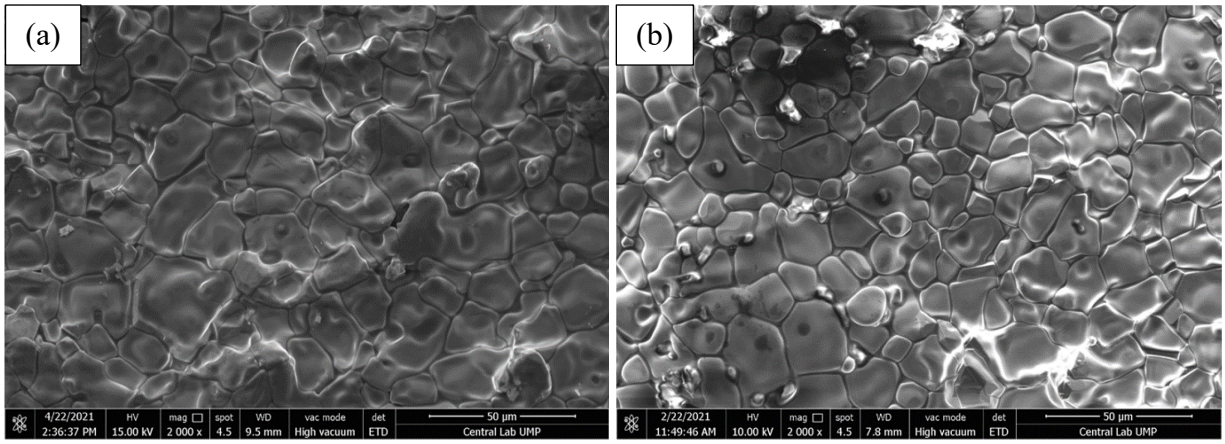

Fig. 3. SEM micrographs for powdered samples: (a) after calcination at 500 °C and (b) after annealing at 1400 °C

In order to investigate the effectiveness of the method used to extract iron oxide from printer toner wastes, the magnetic characteristics of the resultant samples before heat treatment and after heat treatment are necessary. Typically, the basic magnetic features of the samples have been determined using the hysteresis loops for evaluation of intrinsic properties. Fig. 4 shows the magnetization of the samples as a function of the applied magnetic field at room temperature for all samples. Data on the magnetic *M-H* parameters are tabulated in Table 2. Prior to the heating process, the saturation magnetization, M_s of the sample showed a value of 18.81 emu/g, which contributed by the magnetite phase of the samples. In fact, magnetite exhibits strong ferrimagnetic properties, in which the magnetization of the sample is attributed to the negative superexchange interaction of Fe-O between magnetic moments per unit volume. Ferrimagnetic characteristics in magnetite is originated by the alignment of the magnetic moment of the unpaired $3d^5$ electrons in Fe^{3+} ions when subjected to the magnetic field. The magnetite structures contain magnetic moments where each of the moment has independent moment vector with different magnitudes and directions. Therefore, owing to the vectors of moment with opposite directions that are canceled by one another, the total magnetization of magnetite is weakened. The remanent magnetization, M_r value of 1.28 emu/g in the sample indicates the value of magnetization retained in the sample when the magnetic field is removed.

After the sample was calcined at 500 °C, the phase transformation from single phase magnetite (before heat treatment) to the mixtures of hematite-magnetite resulted in a decrease in the M_s and M_r values to 3.49 and 0.51 emu/g, respectively where as compared to that of magnetite which has high ferromagnetic properties, hematite exhibits antiferromagnetic properties or weakly ferromagnetic over Morin temperature (above 260 K) due to the totally antiparallel alignment of the magnetic moment in hematite [10]. This causes the net magnetic moment in hematite to be very small. A similar trend can be seen in sample after annealing at 1400 °C, where the M_s and M_r of the sample decreases to 0.42 and 0.11 emu/g, respectively, which is contributed by the existence of single phase hematite. However, this value, when compared with the M_s of commercial hematite, has shown a very small difference as reported by Ahmadzadeh et al. [11]. This shows that the method of extracting magnetite from printer toner wastes and converting to hematite that has been done has produced a product that can match the hematite sold in the market. However, before the conclusion can be made, it is necessary for further investigations to determine the level of purity, structural deformation and magnetic effectiveness of the samples that have been extracted.

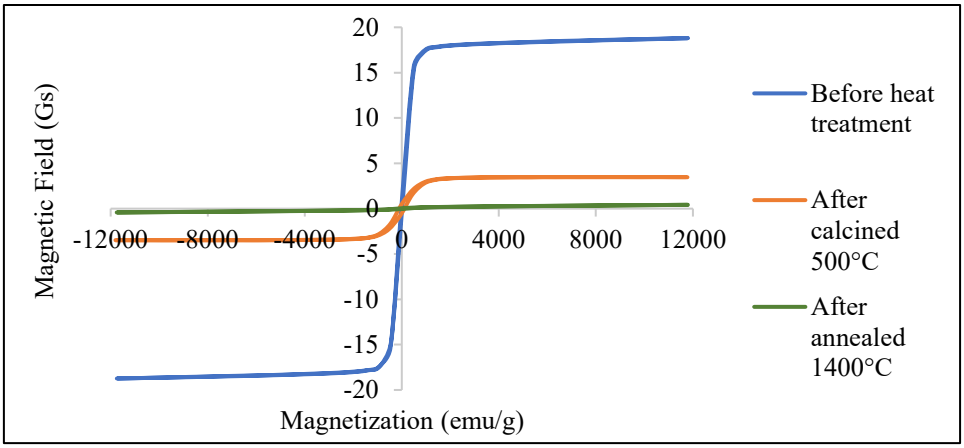

Fig. 4. Magnetization as a function of magnetic field for all samples

Table 2. Magnetic parameters of all samples before and after heat treatment

Sample	Saturation magnetization, M_s [emu/g]	Remanent magnetization, M_r [emu/g]	Coercivity, H_c [Gs]
Before heat treatment	18.81	1.28	430.90
After calcination: 500 °C	3.49	0.51	104.64
After annealing: 1400 °C	0.42	0.11	295.50

Conclusion

In this work, magnetite has been successfully extracted from printer toner waste via magnetic separation method and followed by oxidized to hematite via oxidation method at high temperature. It is evidenced by XRD spectra which shows that single phase magnetite has been achieved after magnetic separation process, while single phase hematite has been obtained after annealing process at 1400 °C. The results show that the method used is very effective in extracting iron oxide from printer toner waste. Evaluation of the magnetic properties of all samples showed properties parallel to the resulting phase, where the resultant magnetite phase after magnetic separation showed the highest saturated magnetization as compared to that of the resultant hematite phase after oxidation process at high temperature. However, the results of this study will be able to be elucidated in-depth

through analysis of X-ray Fluorescence (XRF) for composition identification, Fourier Transform Infra-Red (FTIR) for chemical bonding analysis and Differential Scanning Calorimetry-Thermal Gravimetric Analysis (DSC-TGA) for temperature degradation measurement which is proposed for further investigations.

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