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Properties of Magnetic Paper Prepared via *in situ* Synthesis Method

(Sifat Kertas Bermagnet Disediakan Melalui Teknik Sintesis *in situ*)

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ABSTRACT

Magnetic paper were prepared via the in situ *synthesis method with ferrites in the presence of polyethylenimine (PEI). In this work, the thermomechanical pulp (TMP) fibers were used due to low percentage of collapse lumen and the large lumen size for optimum loading degree. Four cycles of the reaction were performed on the TMP fibers with pH values of 4-10. It was found that variation of pH value played an important role in the loading degree of pulp during synthesis process. The magnetic, morphological and structural properties of the magnetic paper obtained were reported. At the optimum pH of 6.0, saturation magnetization was found to be 3.08 emu/g, remainance magnetization was 0.11 emu/g and coercive force was 12.64 Oe. The optimum loading degree was found to be 23.25%.*

Keywords: Fibers; magnetic filler; paper; thermomechanical pulp

ABSTRAK

Kertas bermagnet telah disediakan melalui kaedah sintesis in situ *ferit dengan kehadiran polietilenemina (PEI). Dalam kajian ini, gentian pulpa termomekanikal (TMP) digunakan kerana peratus kerebahan lumen gentiannya adalah rendah dan ia mempunyai saiz lumen yang besar bagi darjah pemasukan yang optimum. Empat kitaran tindak balas telah dijalankan ke atas gentian TMP menggunakan nilai-nilai pH 4-10. Didapati variasi nilai pH larutan memainkan peranan penting pada darjah pemasukan pulpa semasa sintesis. Sifat magnet, morfologi dan struktur kertas bermagnet yang diperolehi dilaporkan. Pada pH optimum 6.0, pemagnetan tepu ialah 3.08 emu/g, pemagnetan baki ialah 0.11 emu/g dan daya paksa ialah 12.64 Oe. Darjah pemasukan yang optimum didapati sebanyak 23.25%.*

Kata kunci: Kertas; pengisi magnetik; gentian pulpa termomekanikal

INTRODUCTION

Magnetic paper is generally made of cellulose pulp and magnetic particles, derived mainly from wood, rags, and certain grasses, processed into flexible sheets or rolls by deposit from an aqueous suspension. It is use chiefly for information storage, security paper applications, paper handling, reprographic applications such as magnetographic printing substrate as well as for speciality uses such as electromagnetic shielding and magnetic separation of antibodies based on selective adsorption (Rioux et al. 1992).

Magnetic paper handsheets with pigment loading have been made using the established "lumen loading" technology. These sheets have bulk magnetic properties comparable with the computer floppy-disk products. In order to minimize the particle size of pigments and thereby explore a new level of optical and magnetic properties, *in situ* synthesis of pigment particles is possibly a suitable approach. This can be achieved by loading the lumens of cellulosic fibers with magnetic particles or by generating magnetic particles *in situ* in a paper forming fiber which contains ionic groups effective for ion exchange with ferrous ions (Ricard & Marchessault 1990).

Magnetite (Fe_3O_4) is the most widely used magnetic pigments in the production of magnetic recording and information storage media. An example of the application for ferrites is the encoding of information on subway tickets in the form of a thin magnetic strip coated on the cardboard stock (Rioux et al. 1992).

Common cationic polyelectrolyte such as polyethyleneimine (PEI) is reported to be an excellent retention aid to improve the filler retention and has been used for many years in paper making as a wet end additive to improve drainage, fines and filler retention and wet strength paper (Zakaria 2005).

The objective of this work was to gain insight into the effect on the variation of the pH value in the solution during synthesis process towards the lumen loading capacities of magnetite filler in termomechanical pulp (TMP).

METHODS

The Radiata pine softwood TMP pulp was supplied by Graduate School of Agriculture, Kyoto University. The pulp was classified at the Forest Research Institute of Malaysia (FRIM). Better properties are possible by using

long fibers pulp (2.3-3.4 mm). Polyethyleneimine (PEI) (Aldrich Chemical Co.) with mass-average molecular weight Mw = 750000 was used without further purification. Ferrous chloride ($FeCl_2 \cdot 4H_2O$) and ferric chloride ($FeCl_3$) powders (both from Aldrich Chemical Co.), were used without further purification.

The suspensions were produced by the following process. TMP pulp with 8.6% moisture content was soaked for 24 hours. Then, TMP pulp (15 g dry weight) was disintegrated in 1.5 L of distilled water for 30 minutes. The pulp suspension was then poured into a 3 round neck flask with a mechanical laboratory stirrer at the rotor speed of 1000 rpm and nitrogen gas kept passing through the suspension all the time to degas the solution. The suspension was then heated to 100°C. A stoichiometric ratio 1:2 ferrous chloride ($FeCl_2 \cdot 4H_2O$) and ferric chloride ($FeCl_3$) were added into the suspension immediately after weighing since Fe^{2+} and Fe^{3+} salts are oxidatively unstable. The suspension was then stirred for around 5 minutes to allow Fe^{2+} and Fe^{3+} salts to homogenously dissolved into the pulp suspension. Sodium hydroxide (NaOH) was then added into the suspension which immediately turned the suspension into black colour, indicating the formation of magnetite. After 15 minutes, PEI (2%, w/w polymer on pulp) was added into the mixture as a steric stabilizer for magnetite nanoparticles and cationic polyelectrolyte for paper formation. Here, the pH solution was controlled to get the best result. The conditions of the *in situ* synthesis of magnetic fibre are shown in Table 1. The suspension was stirred under a nitrogen atmosphere approximately for 1 h for the nucleation and growth of magnetite particles in the lumen of the fibers. At the same time, vigorous stirring condition forcing the magnetic particles formed in the suspension to enter the fibers. When the diameter of the particles is smaller than the dimension of the pits that distributed along the fiber wall, the deposition of particle will be much easier. The excess particles in the suspension and on the external surface of the fibers were removed by washing. The pulp was used to produce magnetic paper according to the standard methods of the Technical Association of the Pulp and Paper Industry (TMP T205 om 81).

The *in situ* synthesized pulp samples were analyzed by using Leo 1450 VP model Scanning Electron Microscope (SEM). The papers were cross cut to observe the deposition of particles in the lumen of the fiber and to measure the fiber dimension.

The magnetic papers produced via the *in situ* synthesis method were then characterized by XRD using Siemens diffractometer D5000 with Cu K_α radiation ($\lambda = 1.5418$ Å) in the 2θ range of 25-70°. XRD is essential for identification and purity determination of the sample.

The magnetic loading degree of the paper was estimated on a Pyris 1 Thermogravimetric analyzer by heating the sample (6-8 mg) from 30ºC to 900ºC with nitrogen purging at heating rate of 20ºC min^{-1}. The zero setting of the sample was started once the sample temperature reached 100ºC to ignore the moisture content of the sample. The control sample (untreated) was also tested in order to make the correction of the ash content and to determine the loading degree of the treated samples. The loading degree of paper is given as:

Loading degree of paper = % Weight of treated paper – % weight of empty paper.

Hysteresis loops were measured using a computerized vibrating sample magnetometer (VSM) for weighed (10-15 mg) pulp samples with their surface parallel to the horizontally applied DC magnetic field. The sample vibrates vertically and the dipole field of the sample induces an AC signal in a pair of detection coils, which is proportional to the magnetization of the sample.

Zeta potential of Fe_3O_4, PEI and TMP fibres were determined using a Nano ZS Zetasizer from Malvern. The instrument determines the electrophoretic mobility of the particles automatically and converts it to the zeta (ζ) potential using Smoluchowski's equation. Zeta potentials were determined for pH range from 4.0 to 12.0 adjusted using the NaOH and HCl solutions. The pH measurements were performed using a Mettler–Toledo Model MP220 pH meter combined with a Mettler–Toledo Model InLab 413 pH electrode.

Results and Discussion

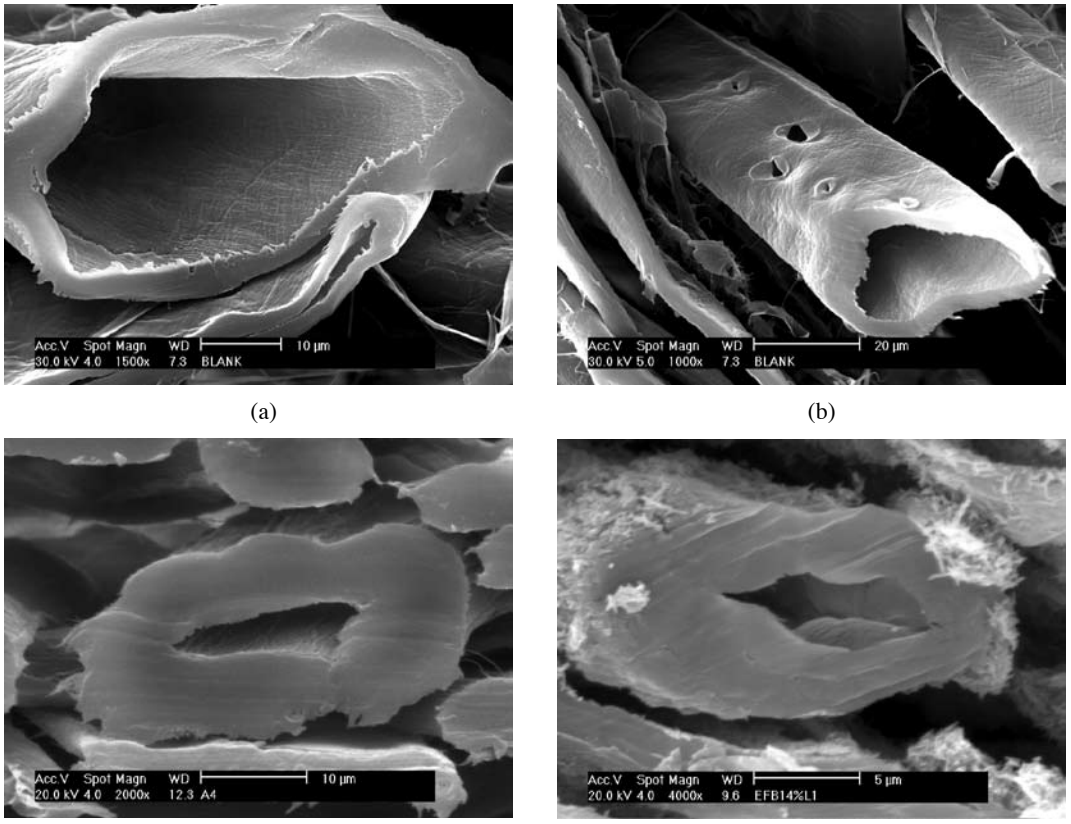
The development of a fibre structure after treatment may be determined by, e.g. the degree of the fibre wall splitting, fibre wall thickness and collapsability. These parameters may be quantified based on cross-sectional analysis. Several microscopy techniques have been utilised for pulp fibre assessment, including light microscopy, confocal laser scanning microscopy and scanning electron microscopy (SEM) (Chinga-Carrasco et al. 2009; Wanrosli et al. 2007).

TABLE 1. The parameter of the *in situ* synthesis of magnetic fiber

Samples	Stirring Speed (rpm)	Temperature (°C)	pH	PEI (%)
IS4	1000	100	4.0	2
IS6	1000	100	6.0	2
IS8	1000	100	8.0	2
IS10	1000	100	10.0	2

The magnetic particles deposition can be introduced into the TMP fibers through the lumens (Figure 1a) and pits (Figure 1b). The TMP pulp was selected because it has a bigger lumen and high percentage fiber collapse. Figure 1(c) showed that TMP has much thinner fiber walls and large lumen compare to mixed tropical fiber walls (Figure 1d) (Ainun 2006) and empty fruit bunch fiber walls (Humaizah 2006). The fiber dimension values of different fiber are presented in Table 2. According to Pulkkinen et al. (2006), fibers with thin wall collapse more readily therefore conformable in a sheet structure. This is contradictory to fibers which is has thick cell wall to gain a sheet of higher bulk (Wanrosli et al. 2007). Bigger lumen eases the magnetic particles penetrate through inside the lumen. Fiber flexing during high turbulence agitation (impregnation stage) was less pronounced for mechanical than for chemical pulp fibers thereby influencing the mechanism which encourages filling of the lumen via the pit apertures (Ricard & Marchessault 1990).

The deposition of particles in the lumen have been studied by scanning electron microscopy (Figure 2). As can be seen in Figure 2, the particles were successfully embedded into the lumen. These particles appeared as small regular ferrite particles. The size of magnetite particles in the *in situ* synthesis sample was smaller than the lumen fibers. A large tendency of particles to form chain or agglomerations was observed to be cause by their magnetic adjustment. Almost all the magnetic particles were attached inside the fiber at lower pH (IS4-IS6) but began to detach (IS8-IS10) as the pH was increased, leaving the external surfaces with some of the fillers.



(a) (b)

(c) (d)

FIGURE 1. Scanning electron micrographs of TMP lumens fiber (a), TMP pits fiber (b), mixed tropical lumens fiber (c) (Ainun 2006) and efb lumens fiber (d) (Humaizah 2002)

TABLE 2. Fiber dimension of TMP, mixed tropical and EFB

Particulars	TMP	Mixed tropical	EFB
Fiber diameter (D), µm	31.7	17.24	16.84
Lumen width (L), µm	20.83	9.33	6.90
Cell wall thickness (T), µm	1.89	2.87	2.66
Rigidity index[a] ($(T/D)^3 \times 10^4$)	2.12	46.14	39.41

[a] Rigidity index is inverse of collapsibility of fibers (Akamatsu et al. 1987; Wanrosli et al. 2007)

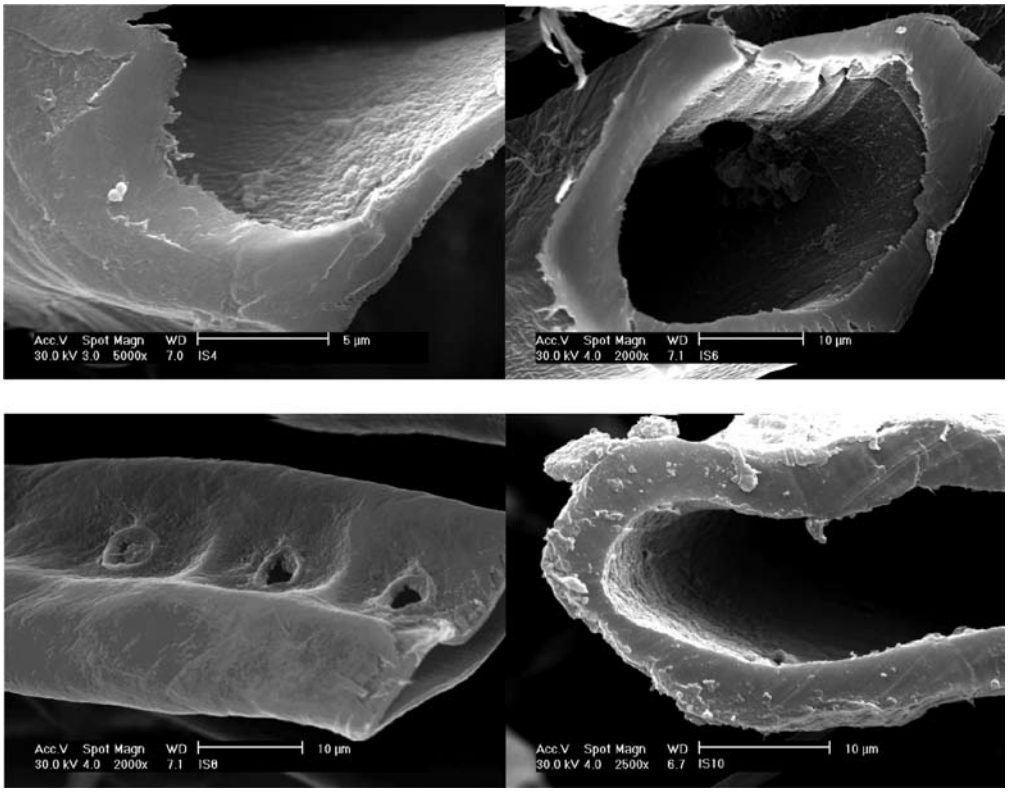


FIGURE 2. Scanning micrograph of magnetic fibers, (acidic condition, IS4 & IS6: alkaline condition, IS8 & IS10)

The XRD patterns for particles separated from the pulp sludge (Figure 3b) by filtration was obtained. The crystallite size calculation from the 311 reflection (d_{311}) gives values ranging from 60-80 nm. XRD analysis also shows that the Fe_3O_4 phase was present in all the paper samples examined (Figure 3a). The mean crystallite size of Fe_3O_4 was determined by using the Scherrer's equation:

$$D_{hkl} = 0.9\,\lambda / \beta \cos\theta, \qquad (1)$$

where D_{hkl} is the mean crystallite size, β is the broadening of full width at half maximum intensity (FWHM) of diffraction peaks (311) in radian, θ is the Bragg angle and λ is the X-ray wavelength.

The magnetization of saturation extrapolated to zero temperature, M_o, increased proportionally due to acidic condition to alkaline condition (Figure 4a), The coercivite force decreased for pH ≥ 6 (Figure 4b). The TGA result showed the same trend (Figure 5). The loading degree increased from pH 4 (21.01%) to pH 6 (23.25%), then it decreased with increasing pH.

The preparation of paper involves a study of colloidal materials and retention aid. All the properties above can be related to the interactions charge between materials through zeta potential analysis. Zeta potential is a function of surface coverage by charged species at a given pH, and it is theoretically determined by the activity of the species in solution.

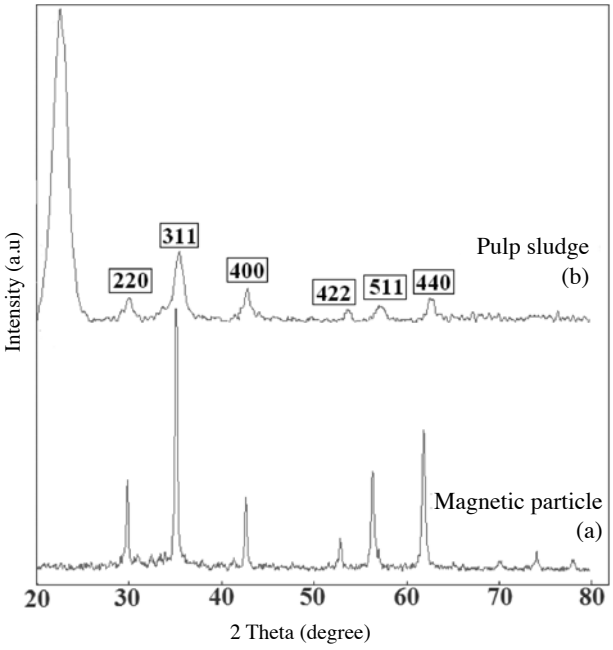


FIGURE 3. X-Ray diffractograms of magnetic particle Fe_3O_4 (a) from pulp sludge (b) for IS6

Figure 6 shows the zeta potential measurement results of Fe_3O_4 suspensions at different solution pHs. The isoelectric point of Fe_3O_4 in water was found at pH 5.8 from the zeta potential curve. The zeta potential of

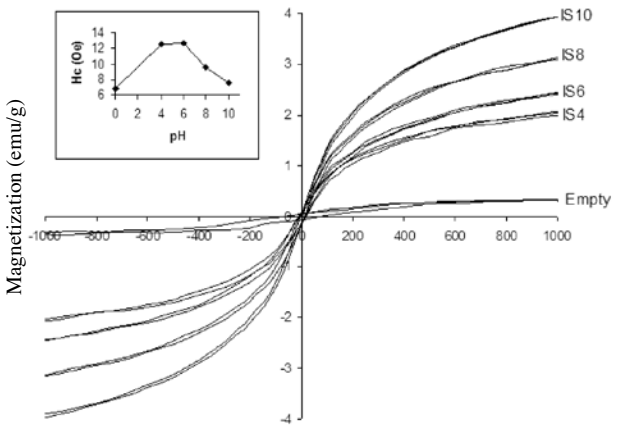


FIGURE 4. Hysteresis loops of the *in situ* synthesis magnetic papers. The inset figures represent the effects of pH on coercive force, Hc

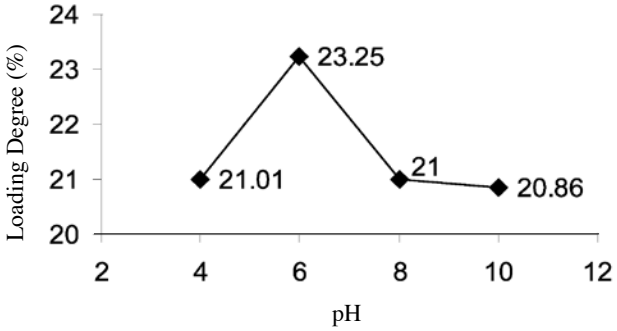


FIGURE 5. Effect of pH on the degree of loading of the magnetic paper

the PEI and pulp suspension has a positive and negative value in the whole pH range examined in this study, respectively.

Dispersion of Fe_3O_4–water suspension was enhanced with appropriate choice of solution pH. Active adsorption of TMP onto Fe_3O_4 takes place only at pH levels below the isoelectric point. According to Illés & Tombácz (2006), Fe_3O_4 particles are hydrated in aqueous systems, and Fe–OH groups cover completely their surface. Hydrous in aqueous systems have amphoteric character. The Fe–OH sites on surface can react with H^+ or OH^- ions from dissolved acids or bases, and positive ($Fe–OH_2^+$) or negative($Fe–O^-$) charges develop on the surface in protolytic reactions depending on the pH of electrolyte solution:

$$Fe–OH + H^+ \Leftrightarrow Fe–OH_2^+ \quad (2)$$

$$Fe–OH \Leftrightarrow Fe–O^- + H^+$$

or

$$Fe–OH + OH^- \Leftrightarrow Fe–O^- + H_2O. \quad (3)$$

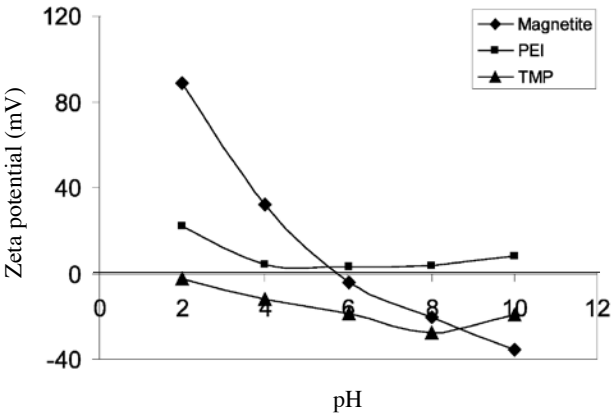


FIGURE 6. Zeta potential of magnetite, PEI and TMP fibre as a function of pH

In the absence of specific adsorbing materials, amphoteric Fe_3O_4 has a characteristic pH, the pH of the point of zero charge (PZC), where the net surface charge is zero, i.e., the positive and the negative sites are in equal amount. At pHs lower than the PZC, the pure Fe_3O_4 surface is positively charged, while it has negative charges above it.

Commercial PEI is a hyperbranched polymer containing three different types of amino groups: primary amino groups in the side-chain, secondary amino groups in the main chain and side-chain, and tertiary amino groups in the main chain. The mole ratio of primary to secondary to tertiary amino groups is 1:2:1. PEI is practically a neutral polymer in basic solution because the amino group is a weak electrolyte. Only in acidic solution can PEI behave as a cationic polyelectrolyte (Wang et al. 2005). The most prominent feature of the protonated PEI is its extremely high cationic charge density. However, PEI achieves its cationicity through protonation of the amine groups in acidic solutions

$$[–CH_2–CH_2–NH–]_n + H_3O^+ \rightarrow [–CH_2–CH_2–NH_2^+–]_n + H_2O \quad (3)$$

It is known that significant amounts of acid are necessary for PEI protonation . Therefore, PEI can act as a good retention aid in acidic condition (Zhitomirsky 2004).

It is thought that adsorption behavior is greatly dependent upon the isoelectric point, because remarkable adsorption is observed only at pH levels below the isoelectric point. The large amount of adsorption at pH levels below the isoelectric point is due to the electrostatic attraction force between magnetite and TMP pulp because the surface of magnetite has a negative charge in the pH range and TMP pulp has a positive charge in the pH range. At a pH level above the isoelectric point, adsorption is hindered by electrostatic repulsion forces resulting from the fact that both the surfaces of magnetite and TMP pulp

are charged negatively while PEI became a neutral polymer. This explains why a higher loading degree can be achieved at a pH level above the isoelectric point. However, small amounts of adsorption are observed at pH 6, probably due to the adsorption to positive sites located discretely on the surface of inorganic particles.

CONCLUSION

Magnetite surface has a positive charge in solutions up to pH 5.8 and a negative charge above this pH. Adsorption of magnetite TMP fibres onto magnetite is remarkably affected by the surface charge of magnetite, as evidenced by active adsorption only taking place at solution pHs lower than the isoelectric point. The preparation of paper involves a study of colloidal materials and retention aid. *In situ* synthesis method has been used in the preparation of the magnetic papers. From the morphology observation, the size and distribution of the magnetic particles in the lumen of fibers was even and homogenous. The XRD diffraction patterns also show that magnetite (Fe_3O_4) nanoparticles were precipitated onto the fibers. Adsorption capacity of ferrite particles increased with an increase of pH value. The optimum pH value for loading degree was determined to be 6.0 (23.25%). The saturation magnetization is found to be 3.08 emu/g, remainence magnetization is 0.11 emu/g and coercive force is 12.64 Oe The ferrite adsorption capacity of TMP fiber was favored at low pH; being attributed to the presence of excess positive charge on its surface by PEI. Simple chemical modifications of the fiber using polyethyleneimine (PEI) and pH treatment were required to enhance the adsorption capacity, thereby preserving the economic aspects of the treatment.

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