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In situ synthesis of ferrites in lignocellulosics

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ABSTRACT

In situ synthesis of iron oxide particles in *O*-(carboxymethyl)ated cellulose fibers and sulfonated wood fibers was performed by careful oxidation of ferrous hydroxide precipitated by alkali from the ferrous ion-exchanged form of the matrix. This "biomimetic" chemistry yielded magnetic fibers containing small ferrite (Fe_3O_4) particles of ~ 10 nm in size. Magnetic hysteresis-loop measurements showed that the material, in the form of a thin parchment-like film, is superparamagnetic, that is, it possesses no remanent magnetization. The process described herein could be practiced with a wide range of natural biopolymers in order to obtain magnetically responsive materials suitable for such biotechnological applications as magnetic separations.

INTRODUCTION

Magnetic bacteria such as *Aquaspirillum magnetotacticum*, which are found in marine sediments, produce chains of intracellular magnetite crystals. These allow the bacteria to probe the earth's magnetic field and to align with the magnetic pole during movement. The quantity, size, morphology, and internal orientation of these particles is believed to be under genetic control[1–3]. Because of the small size and high level of crystal perfection of these biominerals, they are being considered for applications in magnetic toners[4] and for biotechnological magnetic-separation processes[5]. A recent publication by Mann and Hannington[6] described the utilization of phospholipid vesicles as encapsulating sites for synthesis of iron oxide particles (goethite, magnetite, and ferrihydrite) of ~ 20–100 nm dimension, possibly imitating the bacterial biomineralization process. Polysaccharide-gel spheres have been used as a matrix for isolating magnetic particles in an n.m.r. imaging application[7].

Wood tracheids have been converted into magnetic entities, similar in properties to magnetotactic bacteria, by a lumen-loading process[8,9] starting with an aqueous suspension of fibers and commercial magnetic particles. It is also possible to convert natural cellulose fibers possessing appropriate functional groups, or chemically modified cellulose fibers, into superparamagnetic* materials by using *in situ* chemistry

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* Diamagnetism[10] is a weak magnetism in which a magnetization is exhibited opposite to the direction of the applied field. In paramagnetism, the magnetization is proportional to the magnetic field. Superparamagnetism[11,12] is a weak magnetism similar to paramagnetism in the sense of exhibiting a small positive susceptibility but, due to thermal agitation, it presents a random orientation of the spins. These materials display little or no remanence and coercivity phenomena characteristic of ferro(i)magnetic substances.

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inspired by similar developments with synthetic polymers[8,11,13]. Such fibers include *O*-(carboxymethyl)ated cellulose fibers, sulfated cellulose fibers, and sulfonated wood fibers. Other suitable fibers include continuous-filament alginic acid, sodium alginate, cross-linked gels of sulfonic acid-containing polysaccharides, iron-complexing polysaccharides (for example, chitosan), and oxidized particulate carbohydrate polymers (for example, starch).

Using a sodium *O*-(carboxymethyl)cellulose fiber originally developed for water-retention applications[14,15], we have synthesized superparamagnetic particles in the cellulosic matrix and have converted the product into a parchment-like membrane. It appears that this biomimetic approch may have wide applications for converting biopolymers, especially polysaccharides having amino, carboxyl, and sulfonic acid groups, into magnetically responsive particles, fibers, and film materials.

EXPERIMENTAL

Materials. — A sample of sodium *O*-(carboxymethyl)cellulose (Na-CMC) known as CLD-2 (The Buckey Cellulose Corp., U.S.A.), was used in the form of lap pulp. Its carboxyl content was characterized by conductometric titration according to a standard procedure[16,17], and indicated 2.82 ± 0.03 eq/kg of carboxylate groups, corresponding to a degree of substitution of 0.6. For comparison, a sample of chemithermomechanical pulp titrated similarly gave 113 ± 5 meq/kg of carboxylate.

Ferrite-containing pulp. — A 3.0-g sample of CLD-2 dry lap-pulp was dispersed in 300 mL of deionized water to yield a gel-like matrix of 10 g/L consistency. To this system was added an aqueous solution of $FeCl_2 \cdot 4H_2O$ of 0.28 g/20 mL. After 5 min of stirring to allow ion exchange, a brownish-yellow coloration developed, and this was followed by stoichiometric precipitation of ferrous hydroxide in the gel by adding 25 mL of 0.112M NaOH. After gentle stirring, a uniform "green rust" coloration developed which was consolidated by heating for 30 min at 65° in a hot bath. Finally, for 2 h oxygen was bubbled into the dispersion at a rate of 6–10 mL of O_2/min, with gentle stirring conditions under N_2.

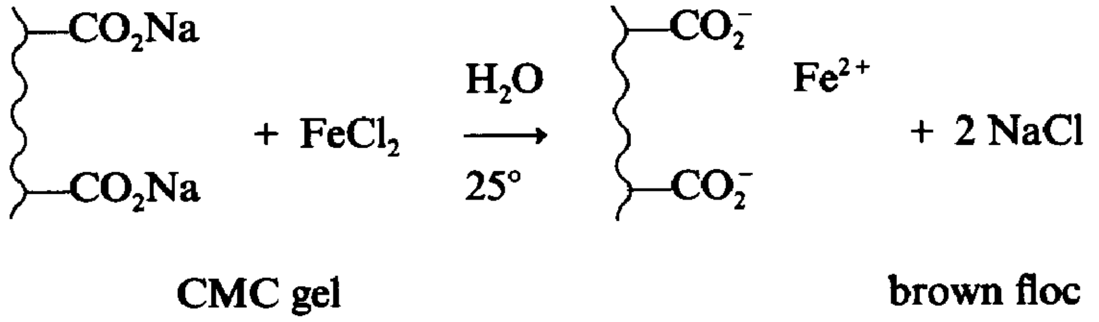
The product was washed by centrifugation to eliminate the excess of NaCl and concentrated to a gel consistency suitable for spreading and drying. After drying on a glass surface, a parchment-like film was obtained exhibiting good toughness and paper-like hand.

In a second experiment, 3 g of highly sulfonated pulp[18] was dispersed in 300 mL of deionized water (10 g/L) and then mixed with $FeCl_2 \cdot 4H_2O$ in excess. After dispersion during 30 min for ion exchange, precipitation of $Fe(OH)_2$ occurred in the fibers using 8.1 mL of 0.1M NaOH. The suspension was gently mixed and heated at 65°. The ferrous hydroxide was oxidized to magnetic particles of iron oxide by bubbling O_2(10 mL/min) under N_2 during 2 h. After multiple washing steps and filtration, the magnetic fibers were dried at room temperature.

RESULTS AND DISCUSSION

The following schematic outlines the steps involved in the afore-described synthesis of sodium *O*-(carboxymethyl)cellulose fibers having magnetic properties:

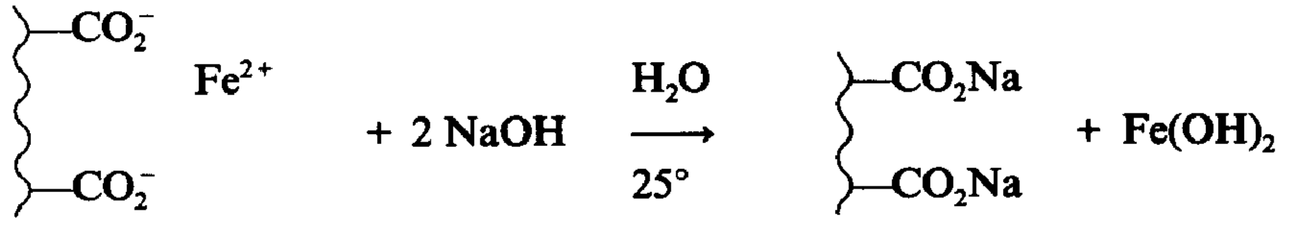
Ion exchange



$$\begin{matrix}-CO_2Na\\ \\ -CO_2Na\end{matrix} + FeCl_2 \xrightarrow[25^\circ]{H_2O} \begin{matrix}-CO_2^-\\ \quad Fe^{2+}\\ -CO_2^-\end{matrix} + 2\,NaCl \qquad (1)$$

CMC gel brown floc

In situ precipitation



$$\begin{matrix}-CO_2^-\\ \quad Fe^{2+}\\ -CO_2^-\end{matrix} + 2\,NaOH \xrightarrow[25^\circ]{H_2O} \begin{matrix}-CO_2Na\\ \\ -CO_2Na\end{matrix} + Fe(OH)_2 \qquad (2)$$

emerald-green floc

Oxidation

$$3\,Fe(OH)_2 + 0.5\,O_2 \xrightarrow[\text{Stir at } 65^\circ \text{ for } 2\,h]{H_2O} Fe_3O_4 + 3\,H_2O \qquad (3)$$

Under the stated experimental conditions, the dry-product film displayed a specific magnetization at saturation of 2.0 ± 0.1 e.m.u./g, which is ~ 67% of what would be calculated for 100% yield based on the original added $FeCl_2 \cdot 4H_2O$. If time of oxidation or oxygen bubbling are varied, secondary reactions tend to diminish the main oxidation product, which was clearly identified by X-ray diffraction, electron diffraction, and photoacoustic i.r. spectroscopy as Fe_3O_4 (magnetite).

Analysis of the magnetic films/paper using a classical vibrating-sample magnetometer instrument (EG&G Princeton Applied Research) provided quantitative evidence concerning the magnetic properties. Fig. 1 shows the specific magnetization as a function of the applied field. This typical S-shaped curve or hysteresis loop passes directly through the origin, indicating that these materials are superparamagnetic[10–12], that is, they do not display the remanence and coercivity phenomena characteristic of commercial ferrites used in information-storage applications. This factor is attributed to the small size of the *in situ*-synthesized particles, which is also responsible for the

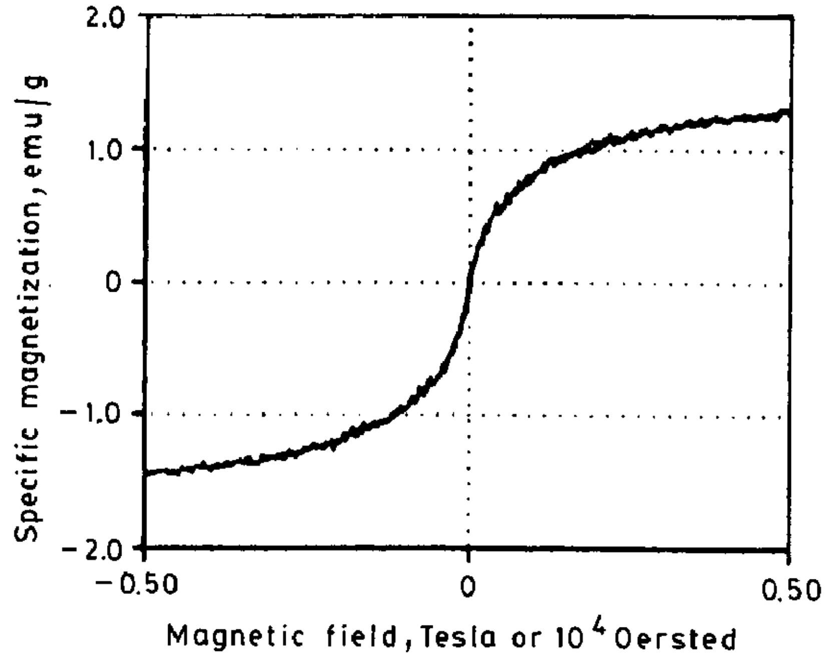


Fig. 1. Hysteresis loop of a superparamagnetic film composite.

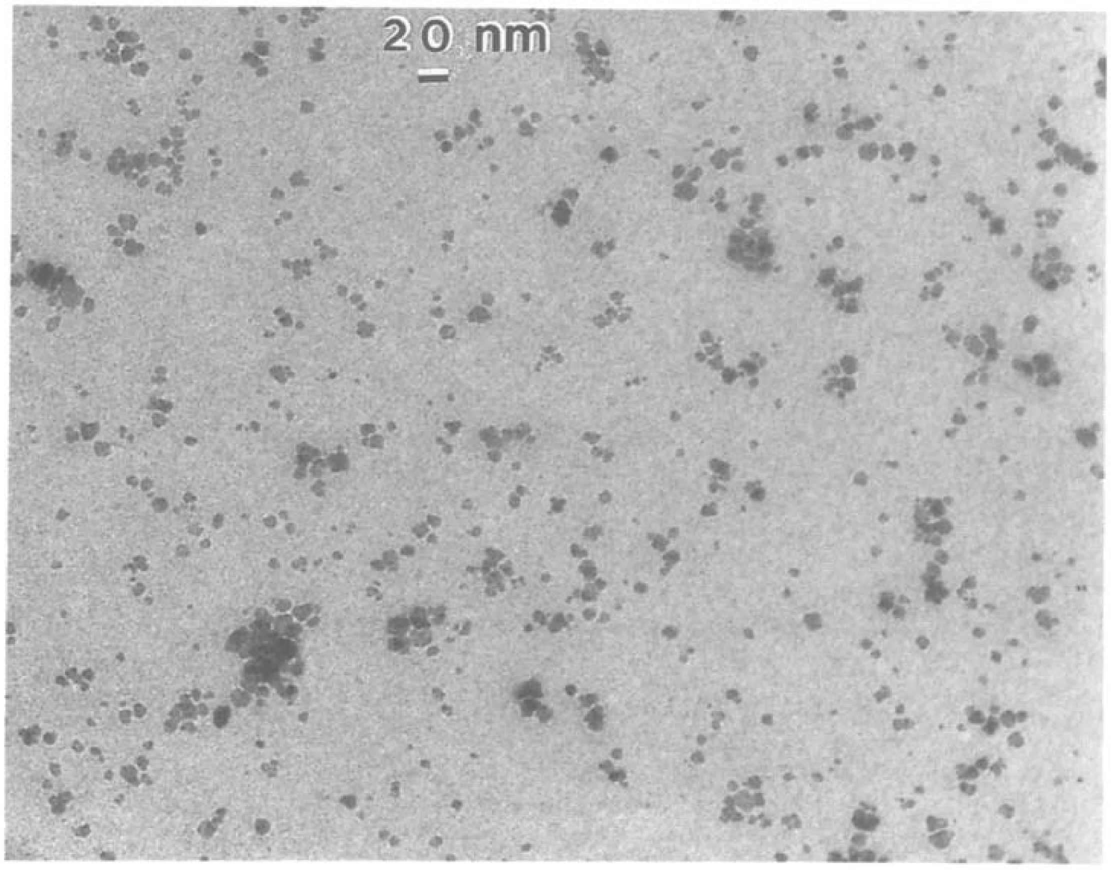


Fig. 2. Transmission electron micrograph of ferrite particles (~ 10 nm) in a superaramagnetic Na–CMC matrix.

relatively light-brown color as compared to commercial synthetic magnetite particles, which are 10–100 times larger.

Transmission electron microscopy on ultrasound-dispersed samples of the wet gel provided a picture of tiny thin crystals, well-dispersed (Fig. 2). An average size of ~ 10 nm was estimated for the particles, which appeared plate-like. The appearance of these crystals is similar to what has been reported previously in such a matrix-controlled synthesis[11]. Larger crystals and higher loadings could be expected by performing repeated cycles of reaction on the fiber suspension. A detailed mechanistic process for crystal formation and growth has been proposed by Sugimoto and Matijević for such matrix reactions as this one[19].

Fig. 3 shows the appearance of the original CLD-2 fibers as received and after gelification and drying. As CLD-2 fibers had been midly cross-linked, they swell to a limit of ~ 25 times their weight in water, even though the level of carboxymethylation would normally result in dissolution. Furthermore, the lap-pulp sheet was laid down from the methanol suspension so that the original dry fibers appear unswollen. After swelling and drying onto a solid substrate, the fibers collapsed and bonded into a porous, parchment-like film. The magnetite particles were dispersed in this matrix, which on exposure to X-ray diffraction analysis provides a powder pattern typical of Fe_3O_4.

The conductometric titriation curve of the highly sulfonated pulp is shown in Fig. 4. This curve shows 810 meq/kg of sulfonate groups available for the *in situ* synthesis of magnetic particles, as schematically illustrated:

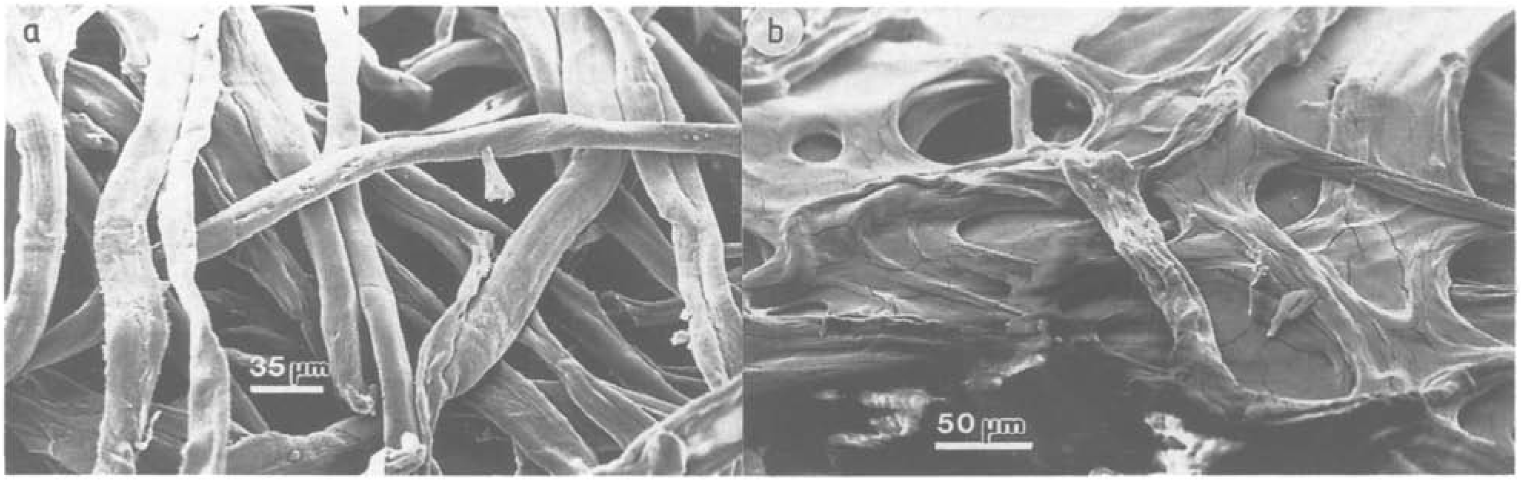


Fig. 3. Scanning electron micrographs of(*a*) Na-CMC CLD-2 fibers "as received (The Buckey Cellulose Corp., U.S.A.) and (*b*) an Na–CMC film, air-dried after a gelification.

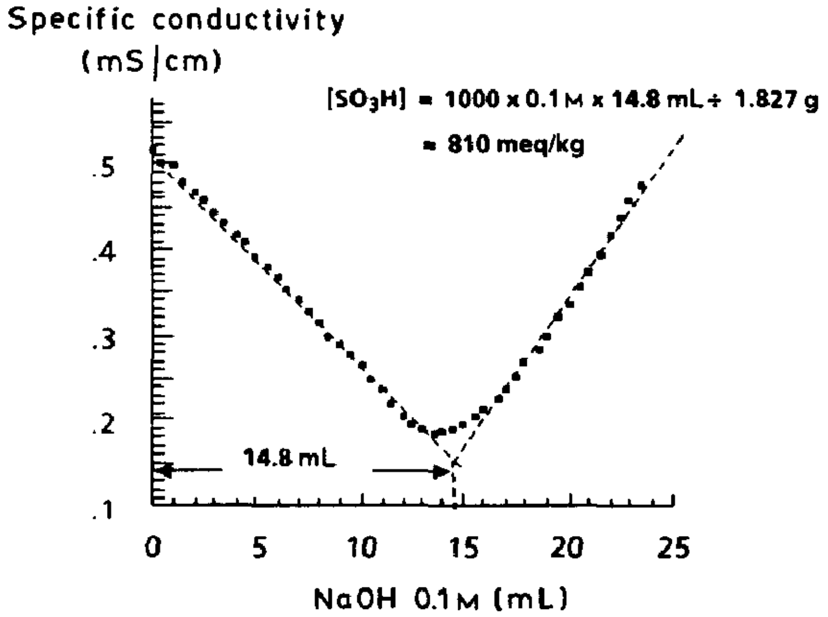
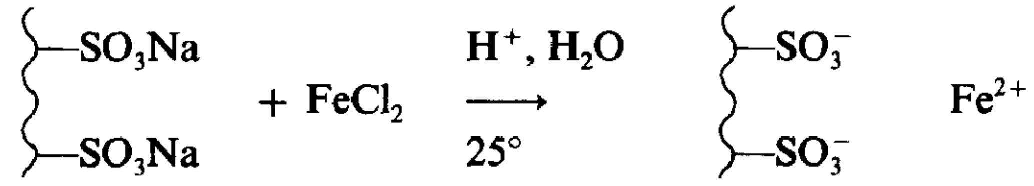


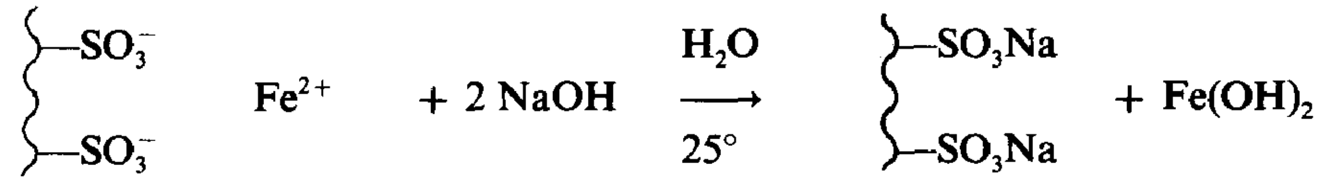
Fig. 4. The specific conductivity (mS/cm) of a sulfonated pulp suspension as a function of the titration volume of 0.1M NaOH.

Ion exchange



$$\begin{matrix}\text{—SO}_3\text{Na}\\ \\ \text{—SO}_3\text{Na}\end{matrix} + FeCl_2 \xrightarrow[25^\circ]{H^+,\ H_2O} \begin{matrix}\text{—SO}_3^-\\ \\ \text{—SO}_3^-\end{matrix}\ Fe^{2+} \qquad (4)$$

In situ precipitation



$$\begin{matrix}\text{—SO}_3^-\\ \\ \text{—SO}_3^-\end{matrix}\ Fe^{2+} + 2\ NaOH \xrightarrow[25^\circ]{H_2O} \begin{matrix}\text{—SO}_3\text{Na}\\ \\ \text{—SO}_3\text{Na}\end{matrix} + Fe(OH)_2 \qquad (5)$$

Oxidation

$$3\ Fe(OH)_2 + 0.5\ O_2 \xrightarrow[\substack{\text{Stir at}\\ 65^\circ \text{ for } 2\,\text{h}}]{H_2O} Fe_3O_4 + 3\ H_2O \quad \textit{incomplete oxidation} \qquad (6)$$

$$2\ Fe(OH)_2 + 0.5\ O_2 \xrightarrow[\substack{\text{Stir at}\\ 65^\circ \text{ for } 2\,\text{h}}]{H_2O} \gamma - Fe_2O_3 + 3\ H_2O \quad \textit{slow oxidation} \qquad (7)$$

Ferrites were formed in the sulfonated pulp because of the presence of >20 times the number of sulfonate groups as compared to a chemithermomechanical pulp. Because the synthesis has not been optimized, quantitative ferrite composition is not given. Nevertheless, the ultra-fine grained superparamagnetic ferrite synthesized using this process appeared to be more uniform in size than ferrimagnetic biogenic magnetites (30–100 nm)[20].

CONCLUSIONS

Sodium *O*-(carboxymethyl)cellulose fibers derived from chemically modified wood pulp have been given magnetic properties. The *in situ* synthesis of Fe_3O_4 in the fiber matrix takes place at neutral pH and under mildly oxidative conditions which do not damage the cellulosic substrate. The crystalline magnetic particles are ~ 10 nm in size and well entrapped in the cellulosic matrix. A thin parchment-like film displays a magnetic hysteresis behavior typical of a superparamagnetic material.

The reaction may be performed with a wide range of natural biopolymers, either in their native state or suitably chemically modified both as to composition and/or physical state. Accordingly, this process could be used with such substrates as continuous-filament alginic acid, cross-linked gels of sulfate-containing polysaccharides, oxidized particulate carbohydrate polymers (such as starch), and iron-complexing polysaccharides (such as chitosan) for transformation into a magnetic state.

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REFERENCES

1 R. Blakemore, *Science*, 190 (1975) 377–379.
2 R. B. Frankel, *Ann. Rev. Biophys. Bioeng.*, 13 (1984) 85–103.
3 T. Matsunaga and S. Kamiya, *Appl. Microbiol. Biotechnol.*, 26 (1987) 328–332.
4 H. Kishi, T. Yano, N. Yamamoto, M. Sakuranaga, and K. K. Cana, Jpn. Pat. 62,294,089 (1987); *Chem. Abstr.*, 108 (1988) 196038J.
5 B. B. Schwartz and N. Blakemore, U.S. Pat. 4,667,067 (1987); *Chem. Abstr.*, 107 (1987) 112210C.
6 S. Mann and J. P. Hannington, *J. Colloid Interface Sci.*, 122 (1988) 326–335.
7 J. H. Braybrook and L. D. Hall, *Carbohyd. Res.* 190 (1989) c14–c18.
8 S. Ricard and R. H. Marchessault, *Mater. Res. Soc. Symp. Proc.*, 197 (1990) 319–324.
9 H. V. Green, T. J. Fox, and A. M. Scallan, *Pulp Pap. Can.* 83 (1982) 39–43.
10 R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Addison–Wesley, Reading, MA, 1964.
11 R. F. Ziolo, U.S. Pat. 4,474,866 (1984); *Chem. Abstr.*, 102 (1985) 15114P.
12 C. J. Goss, *Phys. Chem. Minerals*, 16 (1988) 164–171.
13 C. A. Sobon, H. K. Bowen, A. Broad, and P. D. Calvert, *J. Mater. Sci. Lett.*, 6 (1987) 901–904; P. D. Calvert and S. Mann, *J. Mater. Sci.*, 23 (1988) 3801–3815.
14 W. L. Dean and G. N. Ferguson, Ger. Offen. 1,912,740; *Chem. Abstr.*, 72 (1970) 14015g.
15 R. H. Marchessault, M. Dubé, J. St-Pierre, and J. F. Rèvol, *Fiber–Water Interactions in Paper-Making*, Vol. 2, Techn. Div. Brit. Pap. Board Ind. Federation, Oxford, 1977, pp. 795–813.
16 S. Katz, R. P. Beaton and A. M. Scallan, Svensk Papperstidn. 87 (1984) R48–R53.
17 A. M. Scallan, S. Katz, and D. S. Argyropoulos, in C. Schuerch (Ed.), *Cellulose and Wood- Chemistry and Technology*, 1457–1471, Wiley, New York, 1989, pp. 1457–1471.
18 B. Fleming, personal communication.
19 T. Sugimoto and E. Matijević, *J. Colloid Interface Sci.*, 74 (1980) 227–243.
20 N. Peterson and T. von Dobeneck, *Nature*, 320 (1986) 611–615.