Green Synthesis of Monodispersed Iron Oxide Nanoparticles for Leather Finishing

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Abstract

Leather industry is facing a challenge of replacing pigments based on lead, chromium(VI), cadmium etc due to its toxicity. α-Fe_2O_3 nanoparticles (Hematite) are found to be a good replacement for these toxic pigments owing to their high biocompatibility, good chemical stability and less toxicity. This work reports the green synthesis of biocompatible α-Fe_2O_3 nanoparticle based colorants on starch template for leather finishing applications. Particle size of α-Fe_2O_3 nanoparticles synthesized found to be 48±5nm. α-Fe_2O_3 nanoparticles exhibited good compatibility to the finish medium and also provided excellent covering of surface, improved levelness, no overloading of grain, excellent physical properties and ageing resistance.

1. Introduction

Pigment provides protection against rain, dirt, wear, UV radiation etc, in addition to covering the natural blemishes in the skin. It has been recognized that the cutting value of leather increases on account of pigments as they end up producing even shades. Leather finishing industry is facing challenges of replacing pigments containing metal ions such as nickel, chromium, lead and cobalt etc (Pérez Estébanez 2006). There is also a growing need to develop eco-benign processes for synthesis of pigments without toxic chemicals. Introduction of nanoparticles to the leather finishing sounds interesting and would play an important part in leather manufacture (Niesert 2004). Nanotechnology offers tremendous opportunity. Even though, there are pigment-free finishes for leather, a reasonable amount of pigment is being used in leather finishing (Liang 2006). Biological methods of nano pigment synthesis using microorganisms, fungi, plants or plant extracts and polysaccharides have been suggested as possible ecofriendly alternatives to chemical and physical methods (Glisenti 1998). The high surface energy of these particles makes them extremely reactive, and most systems undergo aggregation without protection or passivation of their surfaces. Through our concerted efforts methodologies to synthesize α-Fe_2O_3 nanoparticles by calcination method on polysaccharide template such as starch has been standardized (Sreeram 2008; Nidhin 2008). The nanoparticles of α-Fe_2O_3 synthesized on starch templates are chemically stable, biocompatible and biodegradable (Nidhin 2008). The preparation of nanoparticles has been evaluated from a green chemistry perspective and the choice of the solvent medium used for the synthesis has been water, alongside an environmentally benign stabilizing agent starch.

2. Materials and Methods

All chemicals were procured from Sigma-Aldrich and used without any further purification. The source of iron for this study was confined to ferrous sulfate ($FeSO_4.7H_2O$) and starch was chosen as the polysaccharide template for evaluation. MilliQ water with a conductivity of 18Ω was used throughout. High temperature calcination reactions in 98% alumina crucibles were employed to synthesis iron oxide nanoparticles preferably α-Fe_2O_3. For the preparation of molar solutions, the molecular mass of the polysaccharide starch was determined through intrinsic viscosity measurements.

2.1 Synthesis of α-Fe_2O_3 nanoparticles

A stock solution of 0.2 mM starch was prepared. To 50 mL of the stock solution, requisite weight of ferrous sulfate was added under vigorous stirring to obtain a Polysaccharide:Fe mole ratio of 1:500, 1:1000, 1:1500, and 1:2000. Stirring was continued for 30 min to ensure complete complexation of the metal ion with the polysaccharide. The complex thus obtained was subjected to a two stage heat treatment, wherein a slow heating up to 100^{o}C, ensured the removal of free water and the formation of a film of the complex, which was treated at high temperature. The product cooled to ambient conditions in the furnace itself was taken for characterization without any further processing.

2.2 Characterization of the Synthesized Nanoparticles

Powder XRD studies were carried out on a Rigaku, Miniflex (II) Desktop X-ray diffractrometer and the diffraction patterns were recorded using CuKα (λ=1.5406Å), 30kV, 15mA with a scan speed of 4^{o}C/min; step size of 0.05^o. Morphology of products was analysed by scanning electron microscopy (FEI Quanta 200 FEG High resolution Scanning Electron Microscope). Reflectance measurements of the synthesized samples were recorded with Perkin-Elmer Lambda 35 spectrophotometer.

3. Results and Discussion

Unified green chemistry approach to the overall process of nanoparticle synthesis is extremely important. Only limited numbers of green chemistry approaches are reported. Most of the synthetic methods reported to date heavily on organic solvents (Wang 2007). This is mainly due to the hydrophobicity of the capping agents used. The polysaccharide template synthesis especially starch as a template for the synthesis of α-Fe_2O_3 nanoparticles was interesting. The extensive number of hydroxyl groups present in starch can, in the present case, facilitate the complexation of iron ions to the molecular matrix (Sreeram 2008).

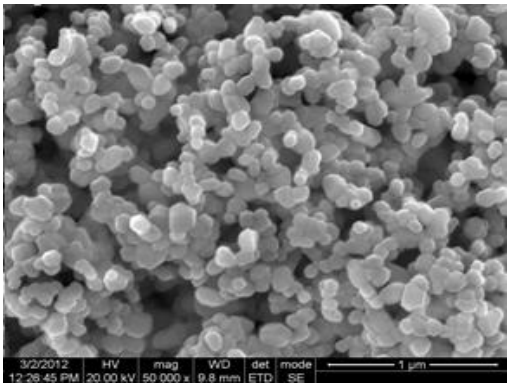

Figure 1: FESEM images of the synthesized α-Fe_2O_3 nanoparticles

The morphology of the synthesized α-Fe_2O_3 nanoparticles was measured using FESEM. The FESEM image (Figure 1) clearly showed the synthesized α-Fe_2O_3 nanoparticles to be spherical with particle size of around 48±5nm. The nanoparticles synthesized on starch template showed good uniformity and monodispersity. The starch template through its hydroxyl groups provide spacial separation of iron centre, nucleation and growth and prevent the aggregation of the nanoparticles. The particles produced are stable and comparable in size and polydispersity to those produced using typical methods. The combination of solvent (water) and renewable reactant (starch) presents a wide range of possibilities for the further development of green nanoparticle synthesis.
The crystallinity and phase identification of the synthesized α-Fe_2O_3 nanoparticles were carried out using XRD. Figure 1 shows the XRD pattern of the synthesized α-Fe_2O_3 nanoparticle on starch template. The XRD peaks clearly show good crystallinity and matched well with that of standard hematite (JCPDS 33066). No or very few impurity peaks were observed. The diffraction peaks would be indexed to rhombohedra structure of α-Fe_2O_3 (Space group: *R-3c*), which are in good agreement with literature results (JCPDS 33-0664). The crystallite size was found to be 31±3nm using the Debye–Scherrer formula (Sreeram 2011). Differences in crystal size obtained by Debye-Scherer approximation and FESEM analysis could be attributed to the fact that the Scherer formula only provides the lower limit on mean crystalline size.

Each color in the CIELAB color space has a unique location defined by its Cartesian co-ordinates with respect to the axes L, a and b where L is the degree of lightness and covered a range from white (100) to black (0) along a gray scale, a is the degree of redness and greenness and b is the degree of yellowness and blueness (Giable 2008). L, a, b, Parameters of α-Fe_2O_3 nanoparticles on starch template was found to be 38.24, 20.74 and 24.33, respectively. This shows that the α-Fe_2O_3 nanoparticles are reddish brown in color.

Figure 2 show the leather finished using the synthesized α-Fe_2O_3 nanoparticle pigment. The pigment exhibited a good compatibility to the medium. Excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water were observed. Due to the high surface to volume ratio of α-Fe_2O_3 nanoparticles, only small quantities of the α-Fe_2O_3 nanoparticles were required compared to the conventional pigments. The resulting leather showed better covering and uniform color throughout leathers. The wet and dry fastness of the finished leather showed a grey scale

rating of 4/5. The film adhesion test results showed that the film formed was strong. The leathers passed the perspiration resistance test as well.

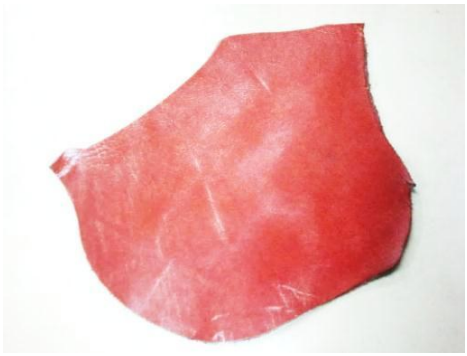

Figure 2. Photograph of leather finished with α-Fe_2O_3 nanoparticles

3. Conclusion

Nano colorants of α-Fe_2O_3 nanoparticles are the new class of materials that receive great attention both in academy and in industry. They have been utilized as replacement for traditional to toxic chemicals such as chromium, lead and cadmium. Green method of synthesis has been used to prepare the new class of α-Fe_2O_3 nanocolorants. Nano pigments of α-Fe_2O_3 were synthesized with a size of 48±5nm. α-Fe_2O_3 nanoparticles exhibited a good compatibility to the medium,excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water were observed.

4. Acknowledgement

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5. References

Giable, G., Sandhya, K.L., Vishnu, V.S., Ananthakumar, S., Reddy, M. L. P., 2008, J Solid State Chem,181,487p.
Glisenti, A., Favero, G., Granozzi, G., 1998, J. Chem Soc, Faraday Transactions *94* (1), 173-182p.
Liang, X., Wang, X., Zhuang, J., Chen, Y. T., Wang, D. S., Li, Y. D., 2006, Adv. Funct. Mater. 16 (14), 1805-1813p.
Niesert,A., Sievers,R., Siggel,A., Langer,K., Jansen,M., 2004, Solid State Sci. 6, 1149p.
Nidhin, M., Indumathy R., Sreeram K. J., Nair, B. U., Bull. Mater. Sci., 31, (1) 2008, 93–96p.
Pérez Estébanez, M., Pastrana-Fabregas , R., Isasi-Marin, J., Saez-Pche, R., 2006, J. Mater. Res. 21, 1427p.
Sreeram, K. J., Nidhin, M., Nair, B.U., 2011, *Journal of Experimental Nanoscience*, 1-13p.
Sreeram, K. J., Kumeresan, S., Radhika, R., Sundar, V. J., Muralidharan, C., Nair, B. U., Ramasami, T., 2008, Dyes Pigm, 76, 243p
Sreeram, K. J., Nidhin, M., Nair, B. U., 2008, Bull. Mat. Sci. 31 (7), 937-942p.
Sreeram K J, Srinivasan R, Meena Devi J, Nair B U, Ramasami T, 2007, Dyes Pigm, 75, 687-692p.
Wang, S.-B.; Min, Y.-L.; Yu, S.-H., 2007, J. Phys. Chem. C, *111* (9), 3551-3554p