The green synthesis of iron oxide micro/nano structures for photocatalytic applications

Rajita Ramanarayanan 1,2, Sindhu Swaminathan3

1 Department of Physics, Government Victoria College, Palakkad, Kerala, India
2 Department of Physics, S.A.R.B.T.M Government College, Koyilandy, Kerala, India
3 Department of Nanoscience and Technology, University of Calicut, Kerala, India

rajitaarun2006@gmail.com

Abstract. Iron oxide nanoparticles are continuously drawing researcher’s attention because of their unique electronic and physicochemical properties in the field of catalysis, drug delivery and energy harvesting applications. The green synthesis of iron oxide magnetic micro/nano one dimensional structures (Fe2O3) using Black tea as a reducing agent was conducted in this report. The cotton was used as a template to obtain needle like structures as characterized using scanning electron microscopy (SEM). Finally the synthesized iron oxide structures showed good photocatalytic activity under solar illumination in the degradation of Methylene Blue dye.

1. INTRODUCTION
Among the metal nanoparticles, the magnetic nanoparticles have assumed great significance in the last decade due to their biomedical applications apart from their catalytic and sensory applications. In magnetic nanoparticles iron is a great interest because it is cheap, easily available and shows more magnetic properties than other metallic elements. [1]. The magnetic nanoparticles like iron oxide (Fe3O4, Fe2O3) structures have been extensively studied due to their exceptional properties in nanoregime. These materials have high specific area and exhibit superparamagnetic properties to be used in targeted drug delivery and chemotherapy applications [2, 3]. Among various synthesis procedures green synthesis of iron oxide nanoparticles is being widely accepted in scientific community since the last decade due to its cost effective and environment friendly approach [4]. The use of black tea extract as reducing agent for the synthesis of iron oxide particles has been previously reported [5]. This work reports the use of black tea extract as reducing agent for the synthesis of iron oxide nano/micro structures with cotton as bio-template. The obtained iron oxide needle like structures was used in the photocatalytic degradation of methylene blue dye to be used for water purification purposes.

2. MATERIALS AND METHODS
2.1 Materials
Ferric nitrate [Fe3 (NO3)3.9 H2O] purchased from Merck Chemicals, black tea and surgical cotton was collected from local market. The extract of the tea was prepared (Figure 1) by taking 8.00 g of tea...
using weight machine in 80 ml of distilled water. The solution was heated at 60°C in the magnetic stirrer (IKA Basic) to get the tea extract. After the cooling, the solution was by using whattsman grade one filter paper to remove the tea grains. The filtered black tea extract was used as the reducing agent.

**Figure 1.** Preparation of extract (a) tea powder (b) Heating (c) Filtering the extract

2.2 Synthesis of iron oxide micro/nano needles
The iron oxide nano/microstructures (Figure 2) were prepared by taking 100 mm of 100 ml Ferric nitrate solution as a precursor. The cotton was soaked in black tea extract for 10 minutes so that extract was absorbed in the cotton. The surgical cotton (8cm x 6cm) was added to the precursor solution and stirred well for 10 minutes. The colour of the cotton changes to brown and it was first air dried and then dried at 60°C in oven. The dried template was placed inside furnace at 450°C for 2 hours to remove the template. On cooling we get a reddish brown powder of iron oxide.

**Figure 2.** Synthesis (a) precursor solution (b) template in precursor (c) iron oxide template

2.3 Photocatalysis
5 mg of the iron oxide nanopowder was mixed with 50ml of 20 ppm Methylene Blue (MB) dye stirred for two minutes and placed in solar illumination (870-880 Watt/m²) for 6 hours. After six hours the supernatant solution was taken using a pipette and UV absorbance spectrum was taken and compared with the original dye solution.

2.4 Measurements
The UV-vis absorption measurements were recorded using spectrophotometer (Shimadzu) in the range of 200-900 nm. The solar illumination measured through Solar power meter SP 1300. Fourier transform infrared spectra (FTIR) of the extract were measured using Perkin Elmer spectrometer in the
range 4000-450 cm\(^{-1}\). X-ray diffraction data was recorded by using Cu-K\(\alpha\) radiation (1.5406\(\text{Å}\)) and morphology observed through field emission electron microscope (FE-SEM).

3. RESULTS AND DISCUSSION

3.1 FTIR Measurements

FTIR of the tea extract (Figure 3) corresponds to the functional groups associated with reduction of the metal salt solution. Peak at 3418 corresponds to OH groups (OH stretching) then a small peak at 2926 corresponds to carboxyl group (COO\(^{-}\)). A sharp peak at 1644 corresponds to H-O-H bending. Peaks at 1450, 1390, 1231 corresponds to aromatic C=C and phenolic C-O vibrations. This group corresponds to Gallic acid which is a good reducing agent in agreement with literature reports [6].

Figure 3 FTIR spectrum of black tea extract

3.2 XRD Measurements

XRD analysis (Figure 4) shows the peaks for iron oxide consistent with that of the JCPDS reference file for Iron Oxide (JCPDS card number 39-1346). The dominant diffraction peaks at 33.33, 35.37, 54, 57, 62.67 theta correspond to (2 2 0), (3 1 1), (4 2 2), (5 1 1) and (4 0 0) crystal planes, respectively of \(\gamma\)-Fe\(_2\)O\(_3\).
3.3 SEM Analysis

The size and the morphology of the synthesised product by SEM analysis shows needle shaped one dimensional structures as shown in Figure 5. SEM image shows the synthesized Nano needles have breadth in nanometer and length in micrometer range.

3.4 Photocatalytic study

The dye degradation of MB dye upon addition of the synthesized sample under solar illumination after 6 hours has been plotted in Figure 6. It is seen that the dye degraded to 90.3 % after solar illumination observed from the decrease of the absorbance peak of MB dye at 663.5 nm. The use of very small amount of photocatalyst (5mg) to 50ml of 20ppm MB dye shows good activity of the iron oxide synthesized in this work as a photocatalytic agent coherent with the reported literature of iron oxide nanoparticles [7]. The increased performance could be due to enhanced formation of hydroxyl ion responsible for dye degradation due to increased surface area of needle type one dimensional nano/micro structures.
4. CONCLUSION

In this study Iron oxide nano/micro one dimensional structures was synthesised by green synthesis by using black tea extract and cotton template. The synthesized sample was characterized using X ray diffraction and scanning electron microscopy (SEM) which shows Fe₂O₃ needle type structures. The Black tea extract was studied using Fourier Transform Infrared spectroscopy (FTIR). FTIR of tea extract gives information about functional groups corresponding to Gallic acid in the Black tea extract which is good reducing agent. The obtained iron oxide powder was used for the photocatalytic degradation of methylene blue dye under solar illumination. It was observed that 90.3% degradation was seen after 6 hours of exposure showing good potential for waste water treatment.

ACKNOWLEDGEMENTS

The authors acknowledge Sophisticated Test and Instrumentation Centre (STIC) Cochin University of Science and Technology for SEM analysis. The authors also acknowledge, Department of Physics, University of Calicut for XRD analysis.

References

[1]. Abolfazal A, Mohammed S and Soodabeh D 2012 Nanoscale Research letters 7 144.
[2]. S F Hasany, I Ahamed, Rajan J and A Rehman 2012 Nanoscience and Nanotechnology 2(6) 148
[3]. Alina M P, Simona L I, Carmen S C, Mariana C C, Milhai S and Daniela P 2013 Journal of Nanomaterials 2013 1
[4]. Ranjana J, Ranjana D and Nandini S 2016 International Journal of Innovations in Engineering and Technology 7 663
[5]. Sevil C and Nursah K 2018 Materials Focus 7 316
[6]. Carmen C, Rafael G and M Carmen L 2003 J. Agric. Food Chem. 51 4427
[7]. Shahana B, Aarti K and Raja S 2018 Materials Research Bulletin 97 121