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SYNTHESIS AND CHARACTERIZATION OF NANOSCALE IRON OXIDE PARTICLES FOR DYE
DE-COLORIZATION PROCESS

AL.Kavitha*¹, A.Subhashini*², H. Gurumallesh Prabu*³

*¹ Department of Chemistry, Kings College of Engineering, Punalkulam – 613303, Tamilnadu, India.

*² Research Scholar, Kalasalingam University, Krishnan Kovil, Tamilnadu, India.

*³ Alagappa University, Karaikudi, India

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Abstract

We report preparation and catalytic activity of Iron oxide nano materials. Iron oxide nanoparticles were synthesized by coprecipitation, self-assembled and microwave methods, and resulted size achieved in nanoscale. The synthesized iron oxide nanoparticles were characterized by XRD, FT-IR, SEM and AFM. XRD was used to determine the crystal structure and average particle size. FT-IR was used to confirm the iron oxide nanoparticles. SEM images were obtained to observe the morphology of the iron oxide nanoparticles. Among the three forms of iron oxides synthesized, α -Fe₂O₃ is found to be a better dye decolorizing agent and used for extra studies. The synthesized iron oxide nanoparticles were used for catalytic degradation of synthetic dye Direct Red 7. Chromaticity variation and degradation products formed by catalysis were analyzed using UV-Visible and HPLC techniques.

Keywords: Iron oxide, nanoparticles, catalyst, Direct Red 7, Dye degradation

Corresponding author: alkavitha82@gmail.com

Introduction

Magnetic nanoparticles (NPs) are of great interest for researchers from a broad range of disciplines, including magnetic fluids, data storage, catalysis and bio applications. However, it is technological challenge to control size, shape, stability and dispersibility of NPs in desired solvents. Coating the NPs with a suitable material offers the possibility of attaching them to antibodies, proteins and medical drugs. Therefore studies on surface adsorption, the possibility of functionalizing and (or) conjugating the particle coating with bioactive components are also a crucial issue. One of the important points in the use of magnetic nanoparticles for biomedical applications is the encapsulation of the magnetic materials, in order to make it biocompatible and to have the possibility of producing a bio-ferrofluid [1]. Other application

areas include Biological systems[2], Catalysis[3-5], Surface coatings[6,7] and Effluent treatment[8 -10].

In textile industry, dyeing processes generates large volumes of waste water containing unutilized coloured dyestuffs. The presence of even small amount of dye in water is highly visible and affects the water transparency and the gas solubility of water bodies. Among several types of textile colourants, the reactive dyes represent about 20-30% of the total market share and the most commonly used as chromophore is the azo dye⁰. Reactive dyes cannot be oxidized aerobically and tend to accumulate in sediments, where they are prone to anaerobic degradation to potentially carcinogenic aromatic amines[11]. Reactive dyes contain reactive groups that are capable of forming a covalent bond between a carbon atom of dye molecule and OH-, NH- or SH- groups in fibres (cotton, wool, silk, nylon). The reactive group is often a heterocyclic aromatic ring substituted with a chlorine or fluorine atom. Another common reactive group is vinyl sulphone[12]. Thus, the treatment of the effluent containing these compounds is important for the production of natural waters. Different technological systems such as physical adsorption[13], biodegradation[14,15] chemical methods such as chlorination, ozonation[16], and catalytic degradation[17] for the removal of azo dyes have been developed.

Fenton reaction [18,19] is a catalytic process for the generation of hydroxyl radicals from H₂O₂ and is based on electron transfer between H₂O₂ and iron oxide nanoparticles acting as homogeneous catalyst. These radicals are very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions. The advantage of the Fenton reagent is that no energy input is necessary to achieve H₂O₂. Therefore, this method offers a cost effective source of hydroxyl radicals using easy to handle reagents. The Fenton reagent has been found to be effective in treating various industrial wastewater components including aromatic amines[20], dyes[21], pesticides[22,23] and surfactants[24,25]. Therefore, the Fenton

reagent has been applied to treat a variety of wastes originated from textile and chemical industries.

In this study, iron oxide nanoparticles were synthesized by co-precipitation, self-assembled and microwave methods and characterized by XRD, FT-IR and SEM analyses. Dye such as Direct Red 7 (DR7) was taken as model pollutant. The synthesized iron oxide nanoparticles were subjected as catalysis to decolourize the dye.

MATERIAL & METHODS

Synthesis of iron oxide particles

(i) Co-precipitation method: Magnetite particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} ions with ammonia. Ferric chloride and ferrous sulphate (mole ratio 2:1) were dissolved in water at a concentration of 0.3 M Fe ions by passing N_2 gas for 5 minutes. Chemical precipitation was achieved at 25°C under vigorous stirring by adding 30 ml of ammonium hydroxide solution (29.6%). During the reaction process, the pH was maintained at about 10.5. Black precipitate of magnetite thus obtained was heated at 80°C for 30 min and then subjected to washing with deionized water and ethanol several times. Finally, it was dried in a vacuum oven at 70°C for about 3 hours.

(i) Self-assembly method: FeCl_3 (125 mM), urea (125 mM) and tetra-n-butylammonium bromide (62 mM) were added to 100 ml ethylene glycol in a conical flask. The red solution thus obtained was stirred with a magnetic stirrer and heated at 200°C for 1 h. After cooling, the as-synthesized iron oxide precursor was collected as a yellowish green precipitate ($\alpha\text{-Fe}_2\text{O}_3$). The $\alpha\text{-Fe}_2\text{O}_3$ precipitate thus formed was washed with ethanol four times and dried using hot oven at 300°C for 4 hours.

(iii) Microwave method: 250 mM FeCl_3 was initially dissolved in 30 ml of ethylene glycol and 70 ml of water. KOH was added into the solution to maintain the pH 10. In the first process, the solution was stirred with a magnetic stirrer and heated at 200°C for 1 hour 45 min; while in the second process, the solution was refluxed for 45 min in a microwave oven. A brown colour precipitate of $\gamma\text{-Fe}_2\text{O}_3$ settled down was decanted with water and acetone several times and dried in hot oven at 200°C for 2 hours.

Dye Decolourization

The three synthesized iron oxides were used for dye decolourization process and conditions were optimized. Direct Red 7 (DR7) dye was taken as a model pollutant. 0.01% dye stock solution was prepared with water. In each experimental run, 10 ml of dye was taken in a beaker, then H_2O_2 (3 mM), iron oxide (0.01g) were added. To this, required volume of pH 3 solution was added to bring the final volume to 20 ml. Treatment time varied from 15 min to 20 h. Treatment efficiency was measured with UV-Visible spectrophotometer with absorbance (λ_{max}) at 510 nm. The degraded dye solutions were collected and subjected to COD test with Merck Thermoreaktor TR200 setup. For the COD measurement, 0.3 ml of COD solution A (Art.no.1.14538) and 2.3 ml of COD solution B (Art.no.1.14680) were taken in a cell and mixed. Then 3 ml of dye solution to be tested was added to the cell, the lid was closed and the cell content was digested using Thermoreaktor TR200 at 148°C for 2 hours. In another cell, 0.3 ml of COD solution A and 2.3 ml of COD solution B were taken, 3 ml

of distilled water was added to it, the lid was closed and considered as 'blank' and digested. Then the cell was cooled to ambient temperature and the optical absorbance of these solutions were measured at a wavelength of 585 nm against the blank and multiplied with a factor 1636 to get the COD value in ppm.

Results and discussion

XRD pattern of magnetite particles is presented in Figure.1. This pattern matches well with the standard JCPDS 89-5894, 89-5892 patterns for magnetite. Diffraction peaks are observed at 35.65° , 44.89° , 57.44° and 66.19° . The d-space values of these main peaks are 2.5163, 2.0174, 1.6028 and 1.4106 \AA , which are corresponding to h k l planes of 313, 411, 428 and 519 respectively. The average grain size is calculated from the Scherrer formula and found to be 52 nm.

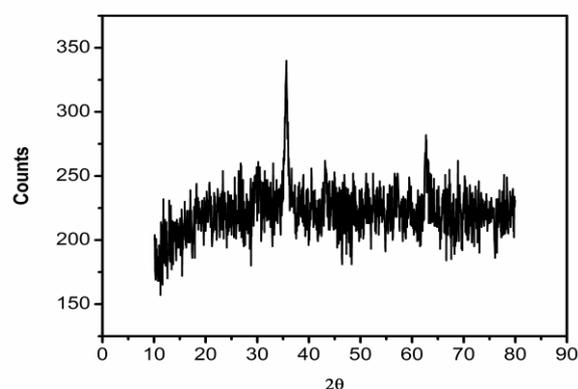


Figure.1. XRD pattern of magnetite particles synthesized by coprecipitation

The X-ray diffraction pattern of $\alpha\text{-iron oxide}$ is shown in Figure.2. Peaks are observed at 24.80° , 33.30° , 35.60° , 39.3° , 43.10° , 54.10° , 56.40° , 62.40° , 64.70° and 72.60° . The d-space values of these main peaks are 3.68, 2.69, 2.51, 2.29, 2.07, 1.69, 1.63, 1.48, 1.45, and 1.35 \AA , which are corresponding to h k l planes of 012, 104, 110, 006, 202, 116, 211, 214, 300 and 119 respectively. This data matches well with the standard pattern for $\alpha\text{-Fe}_2\text{O}_3$ particles [JCPDS 80-2377]. The average grain size is calculated using Scherrer formula and found to be 27 nm.

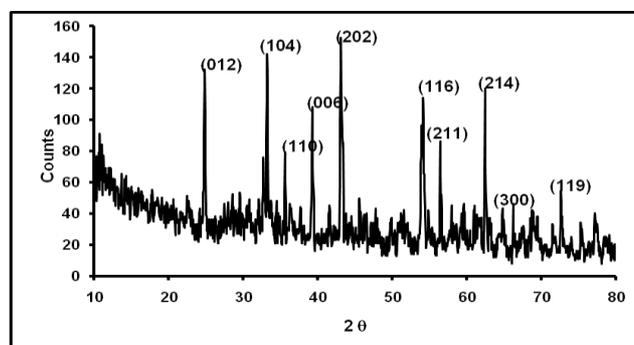


Figure.2. XRD pattern of $\alpha\text{-Fe}_2\text{O}_3$ particles synthesized by self-assembly method.

The microwave method of synthesis yields $\gamma\text{-Fe}_2\text{O}_3$ particles. Figure.3. shows its XRD pattern. This is confirmed with the standard pattern (JCPDS 15-0615). Diffraction peaks of 2θ at 27.6° , 35.30° , 39.57° , 50.70° , 58.31° and 66.19° are observed. The d-space values of these main peaks are 3.750, 2.950, 2.642, 2.089, 1.822 and 1.638 \AA , which are corresponding to h k l planes of 106,

206, 109, 0012, 2112 and 2014 respectively. The average grain size is calculated using Scherrer formula and found to be 28 nm.

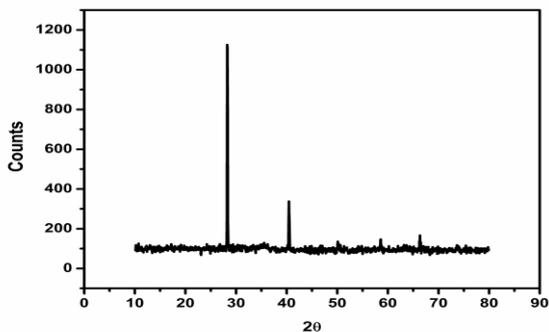


Figure.3. XRD pattern of γ -Fe₂O₃ particles synthesized by microwave method.

FT-IR spectrum of magnetite particles is shown in Figure.4. It exhibits characteristic peaks in the lower frequency region (about 600 cm⁻¹) due to the magnetite particles. The bands at 3431 cm⁻¹ and 1629 cm⁻¹ are due to the OH stretching and HOH bending vibration of adsorbed water in the sample [26]. Figure.5 shows the FT-IR spectrum of α -Fe₂O₃ particles synthesized. It exhibits strong peak in the lower frequency region at 676 cm⁻¹. The bands at 3435 cm⁻¹ and 1630 cm⁻¹ are due to the OH stretching and HOH bending vibration of adsorbed water in the sample. The FT-IR spectrum of γ -iron oxide particles is shown in Figure.6. The absorption band appeared at 584 cm⁻¹ is assigned to Fe-O deformation. The bands at 3430 cm⁻¹ and 1630 cm⁻¹ are due to the OH stretching and HOH bending vibration of adsorbed water in the sample. Figures.(7-9) shows the SEM with EDAX image of iron oxide nanoparticles. The particles are found to be spheroid in shape and agglomerate in nature. From the EDAX, the presence of iron and oxygen is confirmed.

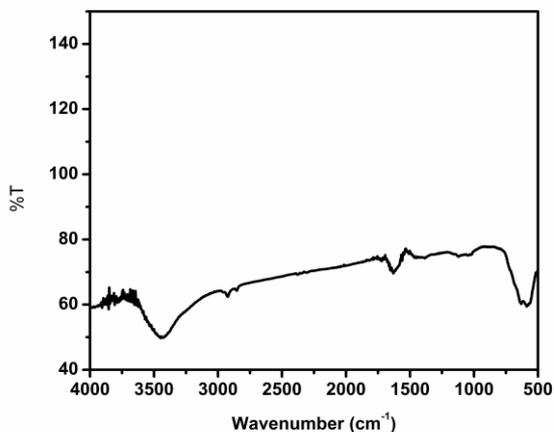


Figure. 4. FT-IR spectrum of magnetite particles synthesized by coprecipitation method.

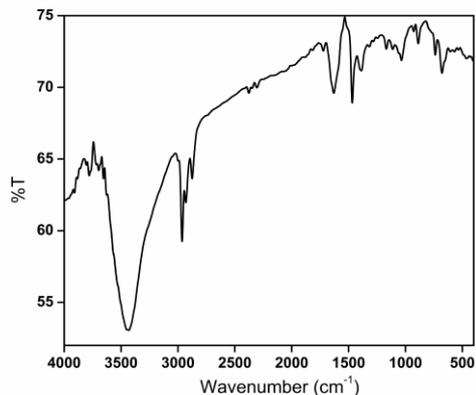


Figure.5. FT-IR spectrum of α -Fe₂O₃ particles synthesized by self assembly method.

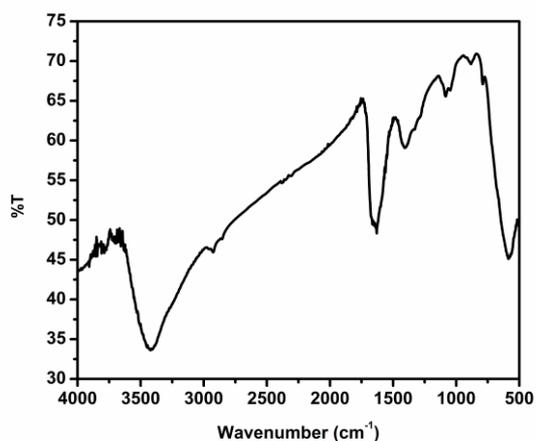


Figure.6. FT-IR spectrum of γ -Fe₂O₃ particles synthesized by microwave method.

SEM

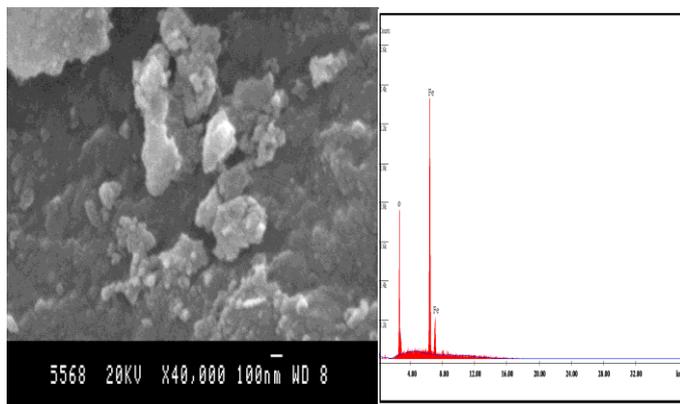


Figure.7(a). SEM image of magnetite particles synthesized by coprecipitation method, (b) EDAX of magnetite particles synthesized by coprecipitation method.

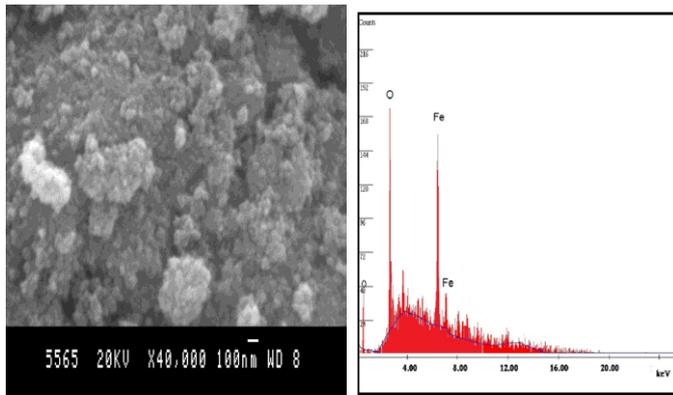


Figure.8(a). SEM image of α -Fe₂O₃ particles synthesized by self assembly method, (b) EDAX of α -Fe₂O₃ particles synthesized by self assembly method.

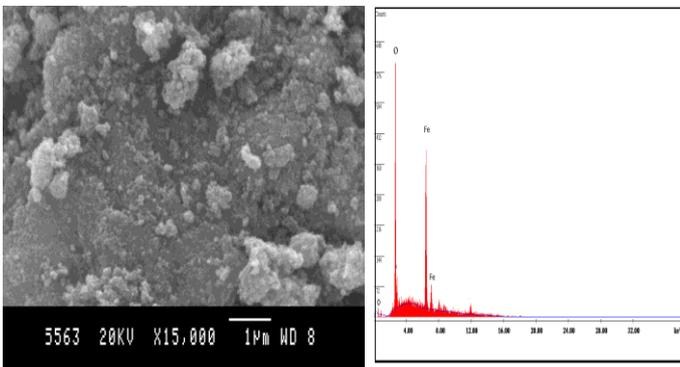


Figure.9(a) SEM image of γ -Fe₂O₃ particles synthesized by microwave method, (b) EDAX of γ -Fe₂O₃ particles synthesized by microwave method.

Decolourization of DR7 dye using iron oxide nanoparticles

Experiments were carried out to find out the efficiency of iron oxide as catalyst (Fenton-like) for dye decolourization. The dye solution was subjected to decolourization with iron oxide particles and the resultant solution was analyzed using UV-Visible analysis (Figure.10). Colour removal is evidenced from the absence of absorbance peaks in the visible region. The UV-Vis spectrum of original untreated dye solution is given as inset. The catalytic oxidation and the colour removal efficiency of different iron oxides synthesized are given in Figure.11.

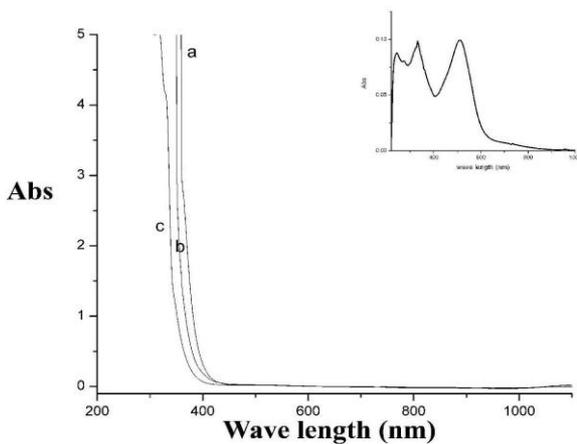


Figure.10. UV-Visible spectra of Direct Red 7 dye decolourized with iron oxide particles synthesized by (a) coprecipitation method, (b) self assembly method and (c) microwave method. Inset: UV Visible spectrum of Direct Red 7 dye solution (untreated).

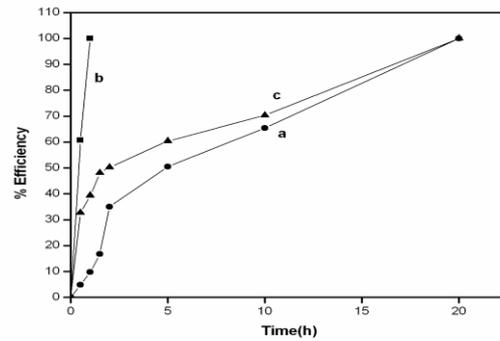


Figure.11. Decolourization percentage obtained with iron oxide particles synthesized by (a) coprecipitation method, (b) self assembly method and (c) microwave method.

The difference in reactivity and in turn the efficiency obtained may be due to the difference in the physical nature of Fe₂O₃ (magnetite form obtained in coprecipitation method, α -Fe₂O₃ form obtained in self assembly method and γ -Fe₂O₃ form obtained in microwave method). Under the specified experimental conditions, α -Fe₂O₃ particles decolourized the dye completely within 3 hours, whereas it took about 20 hours in the case of other two forms such as magnetite and γ -Fe₂O₃.

COD analysis

It is important to measure the reduction of pollution strength by COD analysis of the treated dye solution after the oxidative decolourization. The COD of untreated and treated solutions were measured. It is found that 65%, 75% and 50% COD reductions were noticed for dye solutions treated with iron oxide particles synthesized by coprecipitation, self-assembly and microwave methods respectively. Thus, among the three forms of iron oxides synthesized, α -Fe₂O₃ is found to be a better dye decolourizing agent and used for further studies.

HPLC analysis

HPLC analysis was performed for DR7 dye to understand the nature of degradation product. The result (Figure.12a) shows the retention time of 3.163 min for undegraded DR7 dye. The dye degraded with iron oxide nanoparticles shows the retention time of 2.772, 2.738 and 2.757 min (Figure.12 b, c, d). The degraded dye solution shows the lower retention time than undegraded dye solution. It may be concluded that dye with iron oxide nanoparticle has the highest polarity.

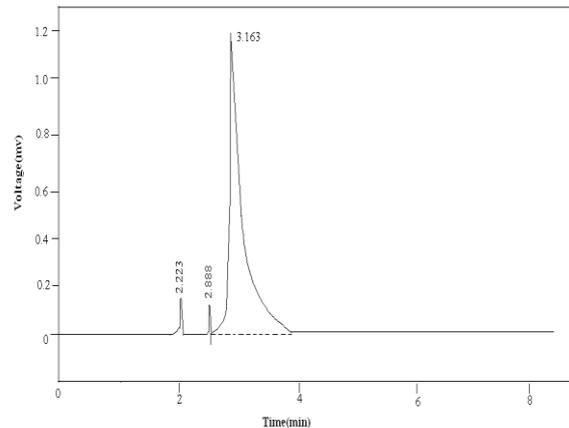


Figure.12a. HPLC chromatogram of Direct Red 7 dye (original)

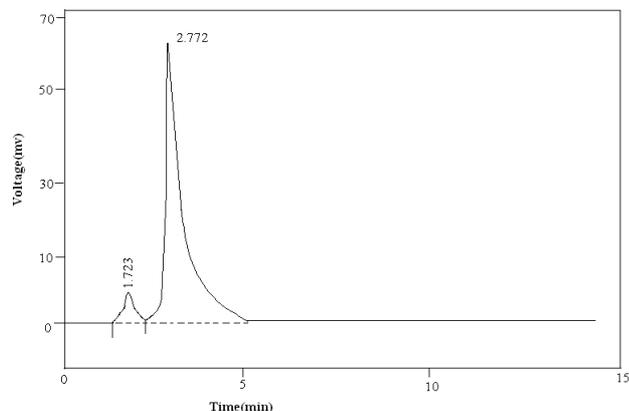


Figure.12b. HPLC chromatogram of Direct Red 7 dye degraded with iron oxide nanoparticles prepared by Co-precipitation method.

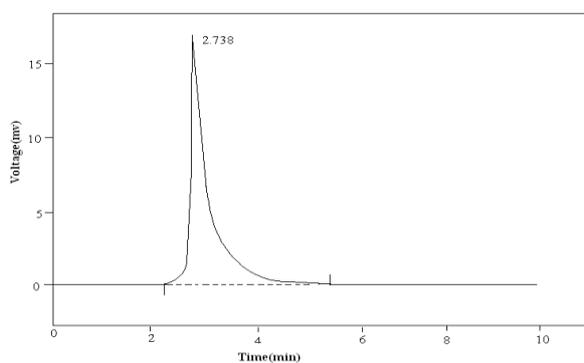


Figure.12c. HPLC chromatogram of Direct Red 7 dye degraded with iron oxide nanoparticles prepared by self assembly method.

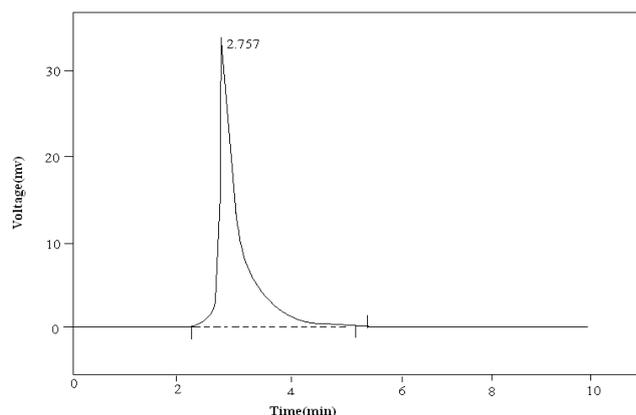


Figure.12d HPLC chromatogram of Direct Red 7 dye degraded with iron oxide nanoparticles prepared by microwave method.

Conclusions

In the present work, different forms of iron oxide nanoparticles have been synthesized and characterized. XRD results show the crystal structures and average particle size of nanoparticles synthesized. SEM images reflect good morphology of the iron oxide nanoparticles. The synthesized iron oxide nanoparticles may be used as a Fenton based catalyst for the dye decolorization. The dye was completely decolorized in 3 hours with self assembly synthesized iron oxide nanoparticles. The co-precipitation and microwave synthesized iron oxide nanoparticles took about 20

hours for the same dye decolorization. This difference in % decolorization may be due to the formation of α - Fe_2O_3 by self assembly method, magnetite particles by co-precipitation and gamma iron oxide by microwave method. Thus, among the three forms of iron oxides synthesized, α - Fe_2O_3 is found to be a better dye decolorizing agent and used for further studies. This is also evidenced from the HPLC analysis of degraded products formed by catalysis.

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