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Spherical Surfaced Magnetic (Fe_3O_4) Nanoparticles as Nano Adsorbent Material for Treatment of Industrial Dye Effluents

Suriyaprabha R. [1], Samreen Heena Khan[1], Bhawana Pathak[2,*] and M. H. Fulekar[2]

[1]School of Nano Sciences, Central University of Gujarat, Gandhinagar, Gujarat, India- 382030

[2]School of Environment and Sustainable Development, Central University of Gujarat, Gandhinagar, Gujarat, India- 382030

(*) Corresponding author: bhawana.pathak@cug.ac.in

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Abstract

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including nano-magnetic fluids, nanocatalysis, biomedical applications, magnetic resonance imaging, and specifically environmental remediation. Nanomaterial like Iron Oxide (Fe_3O_4) is one of the most promising candidates to remove heavy metals and dyestuffs from the industrial effluent. Among these, Fe_3O_4 is the extensively used smart material with magnetic properties that having high surface area. High surface to volume ratio provides more surfaces for chemical reaction for the surface adsorption. Fe_3O_4 nanoparticles have been synthesized using a sonochemical method using ultra frequency in aqueous solution under optimized conditions. The as-synthesized nanoparticle was analyzed using different characterization tools. The Transmission Electron microscope (TEM) images revealed 10-12 nm spherical shape nanoparticles; the crystalline structure was confirmed by X-Ray Diffraction (XRD). The functional groups were identified by Fourier Transform-Infra Red Spectroscopy (FT-IR), revealed the bending and stretching vibrations associated with Iron Oxide (Fe-O) nanoparticles. In the present study, for the efficient adsorption of dyestuff effluents, the samples collected were subjected to adsorption and decolorization at definite time intervals with Fe_3O_4 nanoparticles. The amount of Iron oxide was kept constant for the reaction and the concentrated dyestuff effluents were diluted ten times and observe the absorption in UV –Vis Spectroscopy. It was found that the spherical shaped Fe_3O_4 proved to be the potential material for the adsorption of dyestuff effluents. The result concluded that the effective adsorption and decolorization of contaminants is observed in the maximum time period of 30 minutes with the minimum amount of Fe_3O_4.

Keywords: *Dye effluent, Fe_3O_4, Adsorption, Nanomaterials, TEM.*

1. INRODUCTION

Among the pollutants of an aquatic ecosystem are dyestuff effluents released from many industries such as textile, rubber, paper, plastic, cosmetic etc. Out of all these, the textile industry plays an important role in releasing dyestuff contaminants into the water systems [1]. These effluents from industries cause human health threats and also create problems to the aquatic organisms and enter into the food chain and become the bio-persistence [2]. This is not only because of potential toxicity of dyes but also their resistivity, stability towards the aerobic digestion and oxidizing agents [3]. Since they are being unaffected through conventional wastewater treatment systems, it requires efficient techniques and materials to purify, decolorize, adsorb and degrade the contaminants. Amid of these efficient techniques, adsorption is one of the fascinating methods due to its feasible operation [4]. It is not only the ease of operation and insensitivity to toxic substances and simplicity of design, but the application of adsorption technique is

limited due to its high cost [5]. During last few years, the removal of contaminants from wastewater is done by using efficient low-cost adsorbents such as fly ash, peat moss activated carbon, red mud, biomass etc. [6]. In this era, much attention has been paid to the use of nanomaterials or nano-adsorbents. Application of wastewater treatment using nanoparticles is driven by many factors such as reduction of cost, durability at high temperature, large surface area, high reactivity, high specificity, and ability to penetrate through porous media to remove the contaminants selectively [7]. As the separations of adsorbents after the adsorption is a difficult process, the magnetically driven separations by the use of magnetic nanoparticle has established a great deal of attention because of the ease and simplicity in recovering adsorbent from the liquid phase [8]. Figure 1, depicts the sample collection site from the dye industries.

The magnetization of the material gets reduced when the size goes below 10 nm, as the surface effect becomes predominant when the surface to volume ratio increases. Hence, the optimum size of particles for the application is considered 10 nm or up to 40 nm and we have synthesized particle of 10-30 nm size [9].

Figure 1. *Sample Collection Site*

So far the work has been done on the commercially available dyes with known concentrations to prove the efficiency of nano-adsorbents which are being synthesized; [13] but the dyestuff effluents released from the industries emerges as a major cause of pollution. To be concerned about the environmental protection, the dyestuff effluents released from the industries needs advance and cost effective adsorption technology. In present work, spherical shaped Fe_3O_4 nanomaterial has been synthesized via the simple sonochemical method and further used as an adsorbent for the treatment of industrial effluents. Aforementioned industrial effluents were directly collected from the dye manufacturing industries located at Vatva, Ahmedabad, Gujarat. The samples were collected prior it reaches to the common effluent treatment plant (CETP) and further adsorption studies have been carried out using the synthesized nanomaterials. The effective adsorption can be obtained by the nanomaterials due to its large surface to volume ratio, shape and size (under 40 nm) [9]. Therefore, the synthesis and characterization of Fe_3O_4 as nano-adsorbent is reported for the efficient adsorption of dyestuff effluents. The sonochemical method is based on acoustic cavitation of sound waves at ultrasonic frequency causes rapid formation and collapse of the bubbles creates a defect in the native structure of material making it highly porous and suitable for the adsorption reaction [10]. Also, it prevents iron oxide from forming aggregates in the solution, which is a major problem associated with the synthesis of Fe_3O_4 nanoparticle. TEM, EDX, SEM, XRD and FT-IR were used for the structural and functional determination of the synthesized material. The amount of the adsorbent was kept constant throughout the adsorption studies to know the efficiency of Fe_3O_4 for dyestuff effluents.

2. MATERIALS AND METHODS

2.1. Synthesis of Fe_3O_4

Fe_3O_4 nanoparticles were synthesized using the sonochemical method. All the materials (Precursor and reducing agent) were of high purity (99%) purchased from Sigma-Aldrich and used as received. $FeCl_3$ and $FeSO_4.7H_2O$ were used as a precursor whereas NaOH was used for the

synthesis of Fe_3O_4 nanoparticles to maintain the pH of (9-11), temperature (32°C) and the sonicating frequency of 40KHZ. The occurrence of black precipitate indicated the formation of magnetic nanoparticles [11]. The initial confirmation of magnetic properties was checked by applying external magnetic field by hand magnets. Further analysis of the as-synthesized material was carried using different characterization tools such as FT-IR, XRD, SEM, and TEM. Figure 2 shows the systematic synthesis methodology of Fe_3O_4.

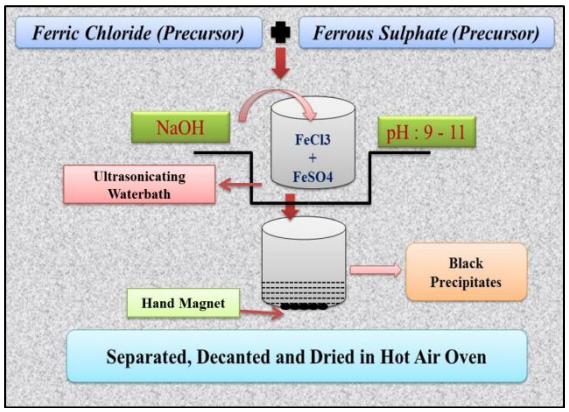

Figure 2. *Synthesis Methodology of Fe_3O_4*

2.2. Characterization

The structural and morphological characters of the as-synthesized Fe_3O_4 nanoparticles were observed through transmission electron microscopy (JEM, 2100 (JEOL). The chemical and elemental composition of the same was carried out separately using EDX (JEOL JSM 5600, EDS Model: INCA Oxford). Fourier Transmission Infrared spectroscopy was performed to determine the functional group of the obtained products (Perkin Elmer – Spectrum 65). The X-Ray diffraction patterns were recorded on Bruker X-Ray Diffractometer using graphite filtered CuK radiation (λ=1.54 Å) at 40 KV with scanning rate of 3/minutes (from 2θ=20-80°). The diffractogram was prepared using the Origin8.5 software.

3. RESULTS AND DISCUSSION

3.1. Transmission Electron Microscopy (TEM)

The TEM image of the as-synthesized Fe_3O_4 nanoparticle confirms the morphology and size of the particle. The micrograph confirms the morphology of the nanoparticle is spherical whereas the minimum particle size was found to be around 10 nm and maximum average particle size of the material was 20 nm. The Selected Area Diffraction Pattern (SAED) of the same revealed that synthesized nanoparticle is partially crystalline. The d-spacing was also calculated which was found to be around 4.5 nm, also supported by XRD data. As mentioned in the previous literature [9], for adsorption and decolorization studies, the most suitable size of Fe_3O_4 nanoparticle was 10-30 nm [12]. Figure 3.a depicts the TEM micrograph of spherical Fe_3O_4 (inset-particle size histogram), b & c depicting the d-spacing value; whereas d is the SAED pattern of the as-synthesized nanoparticle. Even after choosing a sonochemical method, the micrographic image shows the slight aggregation because the metal oxide nanoparticle tends to react more with each other as the capping agent was also not provided in the reaction [13, 14].

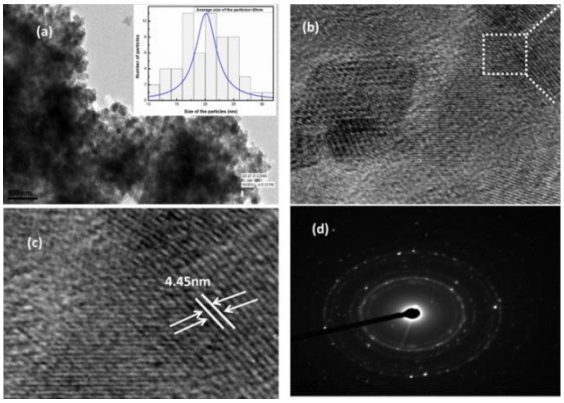

Figure 3. *(a) TEM Micrograph of Fe_3O_4; (b& c) D-Spacing; (d) SAED Pattern*

Figure 4 depicts the EDX spectra of the synthesized material showing the peaks of Fe and O in good elemental composition with no additional peak of any impurity.

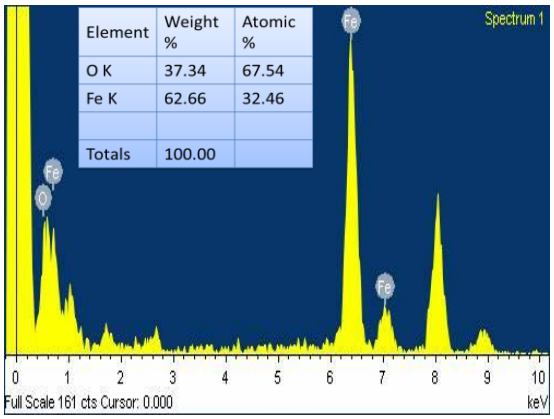

Figure 4. *EDX of Fe_3O_4 (Inset- Elemental Composition).*

3.2. X-Ray Diffraction (XRD)

The XRD pattern (Figure 5) indicates the crystalline nature of the material. The XRD results were compared with the standard JCPDS data and it is confirming the crystal structure and lattice planes associated with the crystalline structure of Iron Oxide. The broadening of peak demonstrates the smaller size of the particles [15]. The peak between the 2θ values of 30-40 at 35.06 having the d-spacing value of 4.54 nm confirms the presence of Fe.

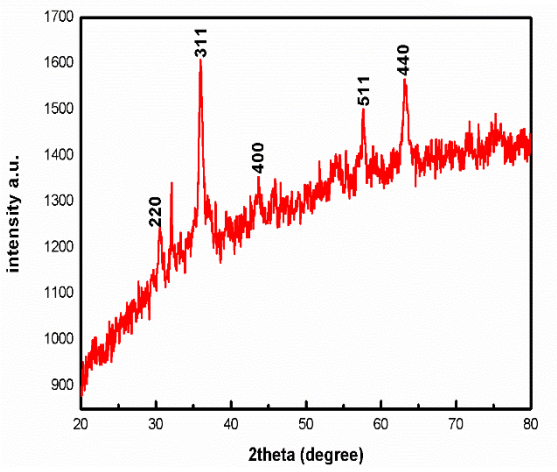

Figure 5. *XRD diffractogram of Fe_3O_4*

The position of peaks observed at 2θ value is 30.78 (2 2 0), 35.9 (3 1 1), 43.65 (4 0 0), 57.53 (51 1), 63.0 (4 0 0) was in good agreement with standard JCPDS value of Fe_3O_4 [11]. It was confirmed that the crystalline structure of obtained magnetic nanoparticles agreed with the oxide structure of the material. The crystalline size measurements were determined from Full-Width Half Maximum (FWHM) value of the strongest peak (35.69, 3 1 1) by using Scherer's formula, and it was found to be 7 nm. The XRD data was well supported by TEM results where the size of nanoparticles was 10-30 nm.

3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum of as-synthesized nanomaterial is depicted in Figure 6. The IR spectra basically aim to determine the functional groups associated with the structure [16]. The FT-IR spectrum at the wave number of 600 cm-1 shows the characteristic stretch and bending because of the presence of Fe-O [17]. The metal-oxygen bonding shows the iron oxide formation in the FT-IR.

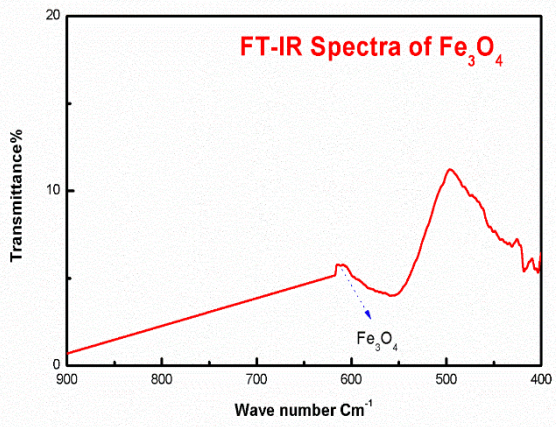

Figure 6. *FT-IR spectra of Fe_3O_4*

3.4. UV-Vis Spectroscopy

The absorption intensity of Fe_3O_4 was measured between 200-800 nm. The synthesized Fe_3O_4 shows the maximum absorption peak at 363 nm. The UV-Vis spectrum of the same is shown in Figure 7.

3.5. Adsorption and Decolorization Studies

The decolorization and adsorption of dyestuff effluents were performed using synthesized Fe_3O_4 nanoparticles. The minimum amount of the nanoparticles was

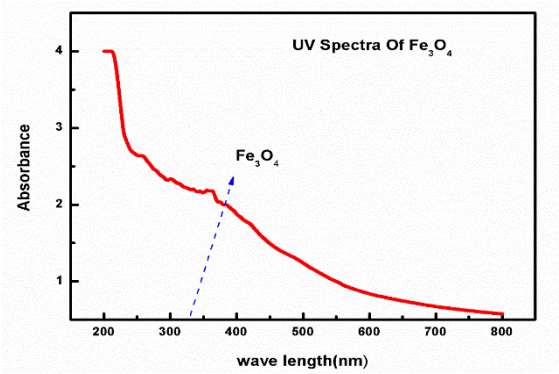

Figure 7. *Absorption Spectra of Fe_3O_4.*

taken for the adsorption is 10 mg which was added to the dyestuff effluent. Since the collected dyestuff effluent was highly concentrated, it was diluted up to 10 times for the experiment and the condition was optimized. The experiment was performed in the laboratory under constant mechanical shaking. To observe the absorption pattern, the sample was monitored using UV-Vis spectroscopy before and after adsorption by separating the magnetite nanoparticles by applying external magnetic field. Figure 8 depicts the comparative UV-Vis absorption spectra of the dyestuff effluents at different time intervals. It was found that maximum adsorption and decolorization of the dyestuff effluent is achieved in 30 minutes. After prolonged time period, the efficiency of the nanoparticles tends to reduce as it reaches the adsorption maximum in 30 minutes.

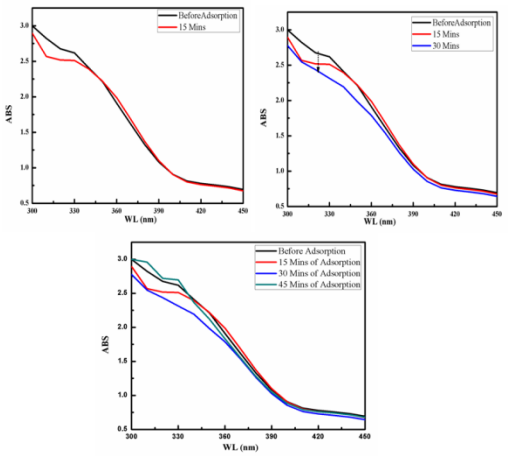

Figure 8. *Comparative UV-Vis Absorption spectra of dyestuff effluents at different interval of time.*

Thus, it was confirmed from the results that Fe_3O_4 proved to be the potential candidate for the adsorption of dyestuff effluents due to its highly active adsorbing surfaces [18]. The Adsorption and decolorization efficiency of the material can be increased by increasing the amount of the nanoparticles taken for the studies [19-24].

Figure 9 depicts the effective decolorization of dyestuff effluents by the addition of iron oxide nanoparticles

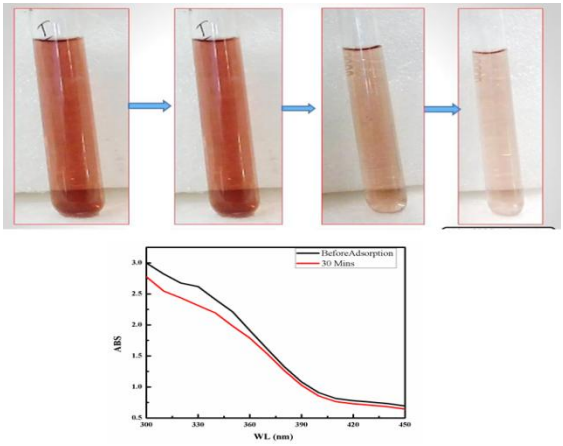

Figure 9. *Decolorization and Adsorption of the dyestuff effluent from initial to final at 30 minutes.*

4. CONCLUSION

In the present work, the synthesis of Iron oxide nanoparticles using sonochemical method and decolorization as well as adsorption study of contaminants from industrial dyestuff effluent. The as-synthesized nanoparticles were characterized using different characterization tools. The result confirms the formation of spherical surfaces magnetic nanoparticles. The maximum decolorization and adsorption of contaminants were achieved at the maximum time period of 30 minutes with a minimum concentration of nanoparticles. It is concluded that the large surfaced spherical shaped magnetic nanomaterial shows excellent adsorption efficiency of industrial dyestuff effluents. The efficiency of the adsorbent can be increased with

increasing the amount of the nanoparticles and the duration of the experiment.

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