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Solar light driven degradation of eriochrome black T by photocatalysis

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***Abstract*:** *Nano photocatalysts namely zinc oxide nano particles (nano ZnO), super paramagnetic iron oxide nanoparticles (SPIONs). The were synthesized synthesized catalysts were characterized using various physicochemical techniques like X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), Diffuse reflectance UV-Visible spectroscopy (DRS-UV), Scanning electron microscope (SEM) and Transmission electron microscopy (TEM). The particle size of the synthesized catalysts obtained from the TEM photographs were in the nano meter range. The photocatalytic degradation of one of the pollutant namely mordant black commonly known as eriochrome black T (EBT) was carried out under solar light using TiO_2 and synthesized nano photocatalysts nano ZnO and SPIONs. Among the tested catalysts TiO_2 exhibited high activity with 61% degradation of the pollutant. Reaction time has been optimized for the complete degradation of EBT. In addition, the effect of pH and influence of on the photocatalytic activity of TiO_2 have been studied.*

Keywords: *photodegradation, SPIONs, nano ZnO, eriochrome black T, solar light*

I. Introduction

The world is facing exuberant problem due to water pollution. Organic compounds namely azo dyes are toxic and carcinogenic in nature which causes major health hazards. They pose severe threat to the environment. It is resistant to degradation by many conventional biological treatments or chemical adsorption processes[1]. The photocatalytic degradation of organic pollutants is a promising approach for solving critical environmental issues that confront mankind today.

Photocatalysis converts solar energy into clean hydrogen energy by splitting water and decomposing harmful organic and inorganic pollutants. Photocatalysis under solar light is a facile, economical and eco friendly technique. Of late the semiconductors are mostly used for the photocatalysis due to the property of having a narrow gap between the valence bands and conduction bands.

To act as photocatalyst, the semiconductor needs to absorb the energy equal to more than its band gap. Semiconductors (such as TiO_2, nano ZnO and SPIONs) are important due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band and an empty conduction band [2] and can act as sensitizers for solar light induced redox processes.

Hence in the present study, TiO_2, nano ZnO and SPIONs were used as catalysts for photodegradation harmful azo dye eriochrome black T under solar radiation. Various parameters influencing the photo degradation were also studied for the most active catalyst and the results have been discussed.

II. Experimental

2.1 Materials

Eriochrome black T (Merck), sodium hydroxide (99.9 % Merck), potassium hydroxide (99.99%; Merck), potassium chloride (99.9%; Merck), zinc sulphate heptahydrate(99.9%;Merck),ferroussulphate heptahydrate (99%; Merck), ferric chloride (99.9%; Merck), hydrochloric acid (37%; Merck), hydrogen peroxide (96%; Merck), and titanium dioxide (97%; Merck) was used without purification.

2.2 Synthesis of catalysts

2.2.1. Synthesis of nano ZnO

ZnO was prepared by the incipient method. $ZnSO_4.7H_2O$ was used as the starting material and NaOH as the precipitant in the mole ratio 1:2. The resulting slurry was continuously stirred for 12 h, filtered, and washed with deionized water. The wet powder was dried in the oven at 120 °C for 2 h to 4 h and finally the nano ZnO was obtained.

2.2.2. Synthesis of SPIONs

The synthesis of magnetic nanoparticles has been carried out using a controlled co-precipitation method. The Fe^{2+} and Fe^{3+} used were in the mole ratio 3:2. 25 mL of ferric solution was added drop wise to the 250 mL alkali solution under vigorous mechanical stirring (2000rpm) for 30 min at room temperature. The colloidal solution containing nanoparticles was then separated and used for further characterization.

2.2.3Experimental procedure for photodegradation of Erio chrome black T

In a typical synthesis procedure 100 mL of 1 x 10^{-4} M solution of Erio chrome black T was taken with 0.3 g of the prepared catalyst. The degradation reaction was carried out under solar light with the dye solution containing the catalyst being continuously stirred using a magnetic stirrer. 3 mL of the sample was withdrawn at required time intervals for analysis. . The % degradation was calculated using the formulae(1)

$$\% \text{ degradation} = \frac{Co - C}{Co} \times 100 \quad (1)$$

where Co = initial concentration of dye

C = concentration of dye after photo degradation.

The experiment was carried out in sunlight between 9 am to 3 pm in the months of june, july and august. The digital lux meter LX-101 was used to measure the intensity of the sunlight. During this period, the average intensity of sunlight was 1.2371 x 10^5 lux unit. of 80 KV. The photocatalytic degradation of Erio chrome black T was monitored by using a double beam spectrometer-2203, Systronics

2.4. Characterization

X-ray diffraction study of the catalysts was done by Philips X'Pert model no. PW 3040/60, using Cu Kα radiation (λ = 1.5060 Å). FT-IR study was done by using Nicolet (Avatar 360) instrument using the KBr pellet technique by making 50 scans at 2 cm^{-1} resolution. Diffuse reflectance UV–visible spectra of the catalysts were carried out using DRS spectrophotometer Jasco V 650 model with integrating sphere. $BaSO_4$ was used as a standard. The spectra were recorded at room temperature in the spectral range of 200 nm to 800 nm. The morphology of the catalyst was studied with scanning electron microscopy using a Hitachi S-4200 electron microscope. Transmission electron microscopy measurements were performed on JEM-2100 electron microscope, operated at an accelerating voltage

III. Results and Discussion

3.1. X-ray Diffraction analysis

The XRD pattern of the synthesized nano ZnO showed major reflections between 30° and 40° (2θ values) indicating more crystalline regions in the zinc oxide sample. It is polycrystalline and fits well with the hexagonal (wurtzite) crystal structure with orientation along (002) and (101) reflections. The reason for relatively lower peak intensities is the formation of mixed amorphous and nano crystalline phases. The data is analyzed by using standard diffraction data from Joint Committee for Powder Diffraction Standards (JCPDS) card no.05-0664. Some weak reflections such as (1 0 2), (1 0 3) and (2 0 1) was observed with small intensities (Fig. 1).

The structure and crystallinity of the synthesized SPIONs were analyzed by XRD. The pattern fits well with magnetite Fe3O4 JCPDS file, No. 00-011-0614. The catalyst exhibited a strong peak in the 2 θ range of 33˚ [3]. The sharp peaks represent the crystallinity of SPIONs. The pattern clearly indicates the synthesized particles have a spinal cubic structure of magnetite nanoparticles (Fig. 2).

3.2. FT-IR analysis

A surface hydroxyl group plays an important role in the photodegradation method through their interaction with photogenerated holes. FT-IR transmittance spectra of the samples were recorded in order to obtain the structural information of the catalyst surface (Fig 3 and Fig 4).

The peak at 619 cm^{-1} was related to the stretching vibrations of the Zn-O bonds [4]. The peak at 1120 cm^{-1} and 3455 cm^{-1} indicates the H-O-H bending vibration and the presence of -OH group (Fig. 4). The strong absorption band at 630 cm^{-1} is due to the stretching vibration of iron oxide nano particles in SPIONs (Fig 4).

3.3 Diffuse Reflectance UV-Visible Spectroscopy

Diffuse Reflectance UV-Visible Spectroscopy (DRS-UV) spectrum of SPIONs and ZnO were given in Fig. 5 and Fig. 6 This characterization technique showed the absorption of the synthesized ZnO nanoparticles was in the range of 300 nm to 400 nm and the absorption for synthesized SPIONs was mostly in the visible region. The TiO_2 showed the strong absorption throughout 400 nm to 700 nm.

3.4. SEM analysis

The surface morphology of the ZnO and SPIONs were obtained from SEM and shown in the photograph (Figure 7, Figure 8). The particle size of the synthesized catalysts was found to be in nano range.

3.5. TEM analysis

The morphologies of the ZnO and SPIONs shown by TEM photograph (Fig. 9 and Fig. 10). The particle size of the synthesized catalysts was found to be in nano range with spherical shape. [5, 6]

3.6. Photocatalytic activity of various catalysts

The photocatalytic activity of the synthesized catalysts iron oxide nanoparticles, nano ZnO, and TiO_2 were studied by degrading eriochrome black T. In 100 mL of 10^{-4} M concentrated dye, 0.3 g of the catalyst was added, degradation was carried out as mentioned above and the results were shown in Fig. 11.

Titania have shown the maximum activity exhibiting 65% dye degradation. Under investigation, its activity was noticeably higher than the other synthesized catalysts. Adsorption of the substrate on the photocatalyst has a major role in its photocatalytic degradation [7]. It is highly evident from the present study that lower the particle size of the synthesized catalyst, higher the efficiency. The particle size and the total effective surface area of the semiconductor play a major role in percentage degradation.

3.7. Time on Stream

The catalytic activity of the TiO_2 was studied for 4 h. The analysis showed 100% degradation in 200 min as shown in Fig. 12. The gradual increase in the percentage of degradation with time is due to the gradual increase in the active site on the catalysts with time.

3.8. Effect of Inhibitors: Sodium Carbonate (Na_2CO_3)

Sodium carbonate is widely used in printing and dyeing industries as it adjusts the pH of the bath which makes the dye adhere to the fabric and the fast fixing of colours. This influences the degradation of the dye in optimum condition. The dye of 1×10^{-4} M concentration was added with 0.3 g of the photocatalyst TiO_2 under sunlight along with different quantities of sodium carbonate in the range of 0-2 gL^{-1} and the results obtained are as shown in the Fig. 13. The decrease in the percentage could be due to the hydroxyl radical inhibiting property of sodium carbonate.

3.9. Effect of electron acceptors: Hydrogen Peroxide (H_2O_2)

The effect of hydrogen peroxide was studied because it is widely used as a bleaching agent. The hydrogen peroxide is added in the concentration of 0-20 $mmolL^{-1}$ to the dye. One strategy to inhibit electron/hole pair recombination is to add other electron acceptors to the reaction. They have several different effects to increase the number of trapped electrons and consequently avoid recombination to generate more radicals and other oxidizing species to increase the oxidation rate of intermediate compounds. H_2O_2 can also become a scavenger of valence band holes and ·OH radicals when present in high concentrations decreasing the dye degradation. Therefore, it shows slight decrease in the degradation of dye. (Fig. 14)

3.10. Effect of pH

The Fig. 15 shows the pH study of the eriochrome black T. The acid solution pH = 4.0 and base solution pH = 10.0 of the dye were prepared by adding HCl and NaOH respectively. The degradation at low pH was due to the adsorption of dye on the surface of the catalyst. In basic solutions, when the pH is 10.0, the adsorption decreased due to the influence of the Na^+ ions present in the dye solution which reduces the adsorption of the dye on the surface of the catalyst. At low pH there might not be adequate concentration of hydroxyl radicals to promote complete degradation of the dye.

3.11. Photo decolourisation of eriochrome black T with TiO_2 with different environments

Photo decolourisation of the dye in the presence and absence of the catalyst were studied. There was no observable colour loss in the absence of the catalyst and sunlight. In dark, there was a slight degradation in the dye solution with the presence of the catalyst which was due to the adsorption of eriochrome black T on the surface of the TiO_2 (Fig.16).In the presence of sunlight, the degradation of eriochrome black T was significantly high when compared to the other two factors

IV. Figures

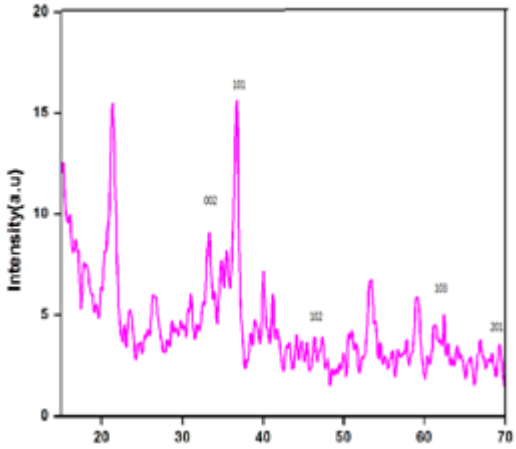

Fig.1. XRD of nano ZnO

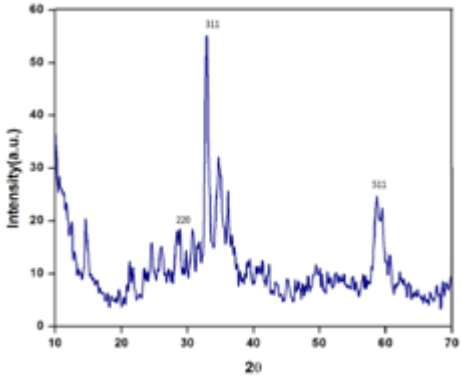

Fig.2. XRD of SPIONs

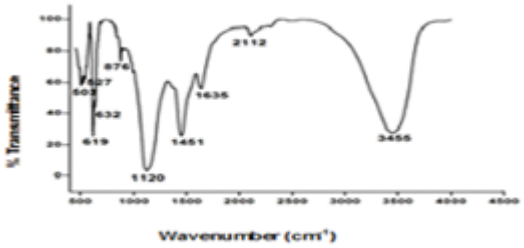

Fig. 3. FT-IR of nano ZnO

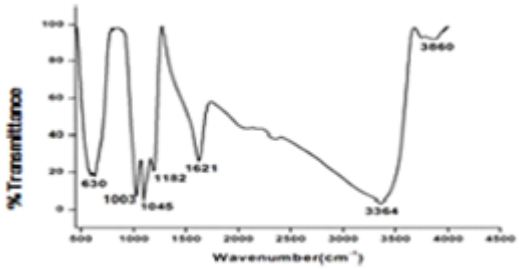

Fig. 4. FT-IR of nano ZnO

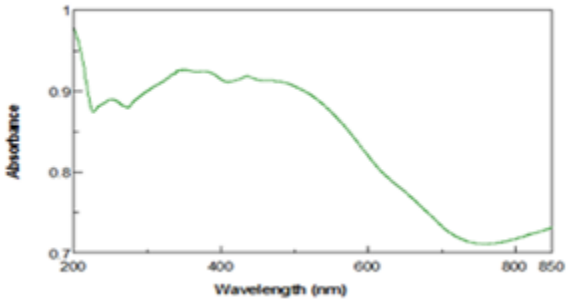

Fig. 5. DRS-UV of SPIONs

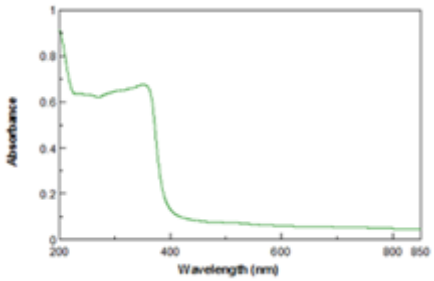

Fig. 6. DRS-UV of nano ZnO

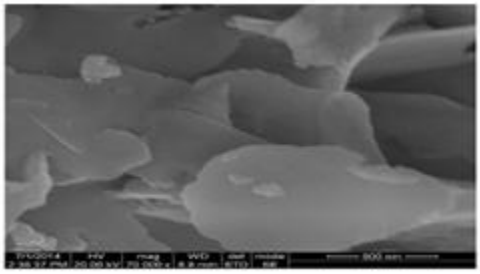

Fig. 7 SEM of nano ZnO

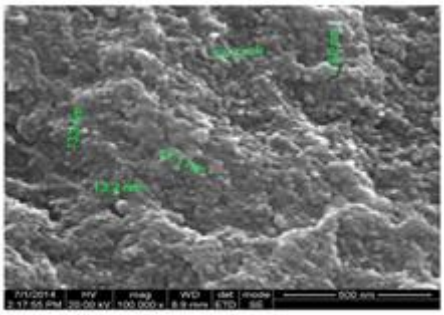

Fig 8. SEM OF SPIONs

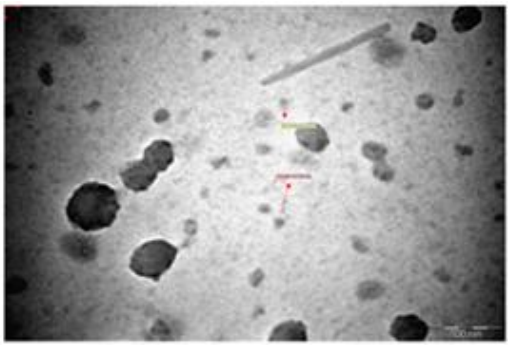

Fig. 9 TEM of nano ZnO

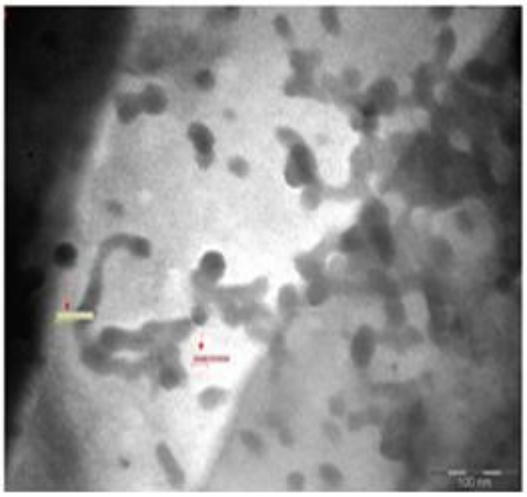

Fig. 10 TEM of SPIONs

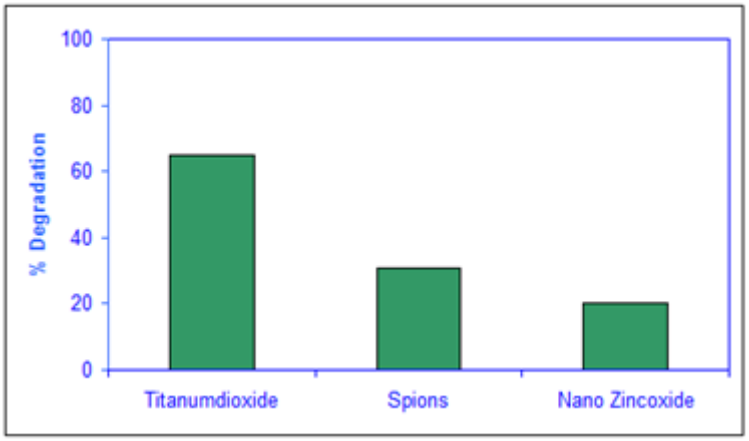

Fig.11. Comparison of photo degradation of eriochrome black T with different photocatalyst [Dye] = 1 x 10^{-4} M, under solar light

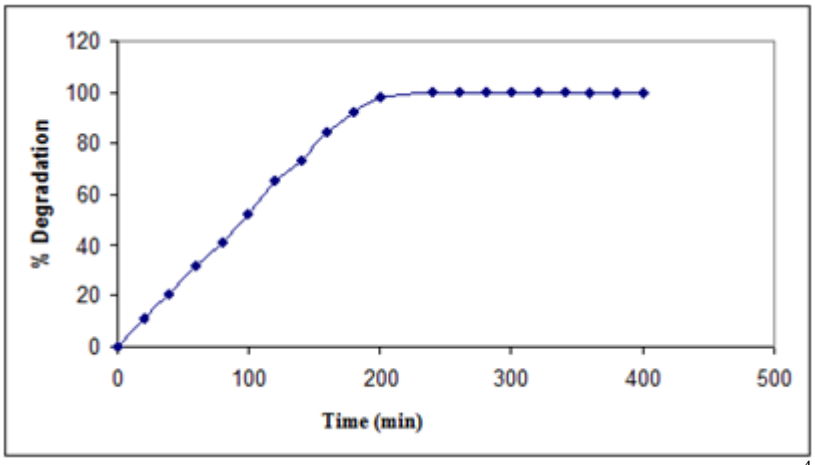

Fig. 12. Effect of % degradation of eriochrome black T in presence of TiO_2[Dye] = 1 x 10^{-4} M, Time = 4 h, under solar light

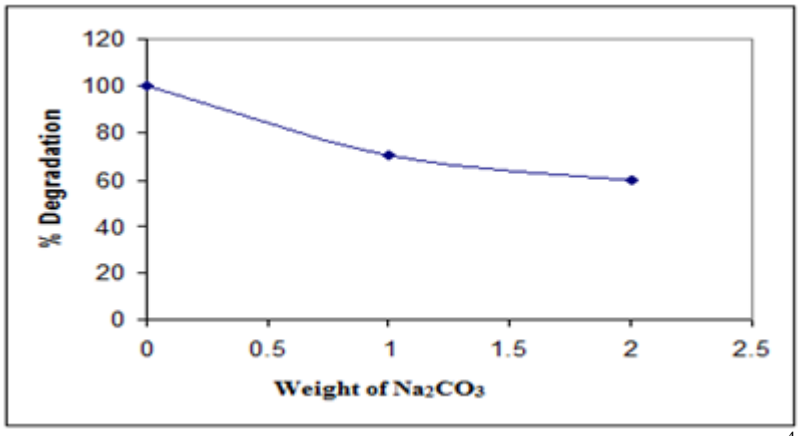

Fig.13. Effect of Sodium Carbonate on the degradation of eriochrome black T[Dye] = 1×10^{-4} M, TiO_2 = 1.5 gL^{-1} at neutral pH.

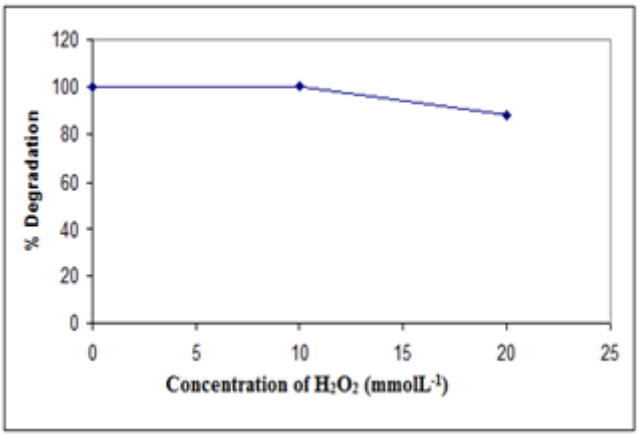

Fig.14. Effect of H_2O_2 on the photodegradation of eriochrome black T, [Dye] = 1×10^{-4} M, TiO_2 = 1.5 gL^{-1} at neutral pH.

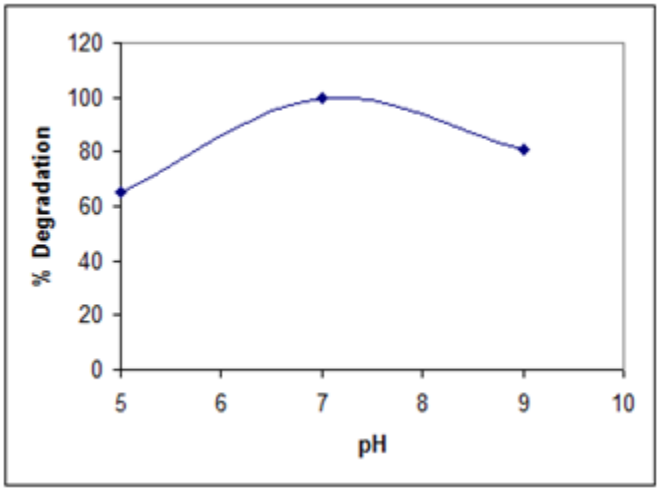

Fig.15. Effect of pH on the degradation of eriochrome black T,[Dye] = 1×10^{-4} M, TiO_2 = 1.5 gL^{-1}, Time = 4 h, under sun light

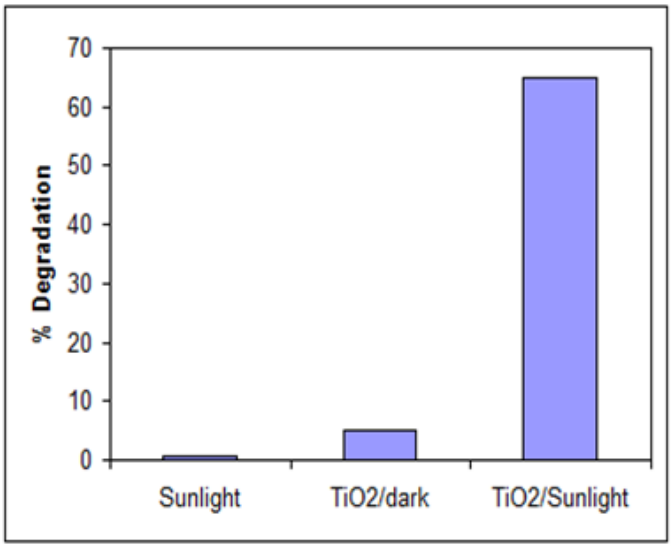

Fig. 16. Comparison of photodegradation of eriochrome black T with various environment,[Dye] = 1x 10^{-4} M;time = 6 h; neutral pH.

V. Conclusion

Nano ZnO and SPIONS were successfully synthesized. The synthesized catalysts were characterized by XRD, FT-IR, DRS-UV, SEM and TEM techniques. They confirmed the authenticity and nano particle size of the synthesized catalysts. The photocatalytic activity of these synthesized catalysts and TiO_2 were tested for eriochrome black T degradation under solar light irradiation. Among the catalyst tested TiO_2 was found to be most active. The optimum reaction condition for 100 % degradation of eriochrome black T was found to be, 1 x10^{-4}M dye concentration; 0.3 g of catalyst, neutral pH and the duration of degradation is 4 h.

Acknowledgements

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