

Photocatalytic studies over $Ce_{1-x}Fe_xO_2$ for the degradation of azo dye

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Photocatalytic degradation of textile diazo dye Naphthol Blue Black with $Ce_{1-x}Fe_xO_2$ ($x = 0, 0.1, 0.2, 0.3$ and 1.0) has been carried out in presence of sunlight. The effects of variation of different parameters like pH, amount of catalyst, presence of oxygen, etc., on the rate of degradation of dye have been studied. Solid state properties such as surface area, magnetic susceptibility, ESR and electrical resistivity have been correlated with the photocatalytic activities.

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Semiconductor assisted photocatalysis as a method for destroying pollutants has been the subject of recent investigations¹. Photocatalytic degradation of several organic contaminants using semiconductors like TiO_2 , ZnS , ZnO , Fe_2O_3 etc have been widely studied^{2,3}. Waste water from paints, dyes, textile and chemical industries contain harmful dyes which are toxic to micro organisms, aquatic life and human beings. Therefore, it is essential to remove or destroy these toxic dyes or chemicals by physicochemical processes such as semiconductor photocatalysis. Pandurangan *et al.*⁴ have reported the degradation of basic yellow Auramine O on ZnO and showed that addition of H_2O_2 and Fenton's reagent enhanced the rate of dye degradation. Zhang⁵ has reported the pseudo first order kinetics of photocatalyzed N-demethylation and degradation of Methylene blue in titania dispersions. Galindo *et al.*⁶ have studied the photocatalytic degradation of an indigoid dye. Kartal *et al.*⁷ investigated the photocatalytic destruction of phenol by TiO_2 powders. The degradation of textile diazo dye Naphthol Blue Black (NBB) with TiO_2 photocatalysis has been studied by Vinodgopal *et al.*⁸ and others⁹.

Cerium dioxide has various catalytic applications, especially in the treatment of exhaust gas from automobiles. Its catalytic applications relies primarily on the high efficiency of the reduction/oxidation cycles by shifting between Ce^{4+} under oxidizing conditions and Ce^{3+} under reducing conditions respectively¹⁰. The capabilities of the redox couple are strongly enhanced if other elements are introduced into the CeO_2 lattice by forming solid solutions¹¹. In the present investigation, photodegradation of textile

diazo dye, NBB, over $Ce_{1-x}Fe_xO_2$ solid solution using solar radiation has been studied along with magnetic, electronic, ESR and surface properties. Attempts have been made to correlate these results with the photocatalytic activity.

Materials and Methods

$Ce_{1-x}Fe_xO_2$ ($x = 0, 0.1, 0.2, 0.3$ and 1.0) has been prepared by co-precipitation technique. The required metal nitrates of AR grade were taken in stoichiometric proportion and dissolved in distilled water to obtain a clear homogeneous solution. To this, a solution of 10% AR grade sodium hydroxide was added with constant stirring until the precipitation was complete. The precipitate thus obtained was digested on a water bath for 3 h. The precipitated hydroxide mixture was subjected to oxidation by dropwise addition of 30% H_2O_2 with continuous stirring. The precipitate was then washed with water, filtered and dried at $100^\circ C$. The precipitate was homogenized well in a mortar and then heated in a furnace at $400^\circ C$ for 4 h. The decomposed sample was then sintered in a furnace at $800^\circ C$ for 10-12 h to form a solid solution except in the case of Fe_2O_3 sample.

The compounds prepared by co-precipitation method were characterized by recording X-ray diffractograms. Surface areas were measured using B.E.T. nitrogen adsorption method (SMARTSORB 91). FTIR analysis was made on a Shimadzu (model 8101A). Thermal analysis was done on a NETZSCH- Geratebau GmbH thermal analyzer to find out the decomposition temperature and thermal stability. Magnetic susceptibility in air were determined by Guoy method at room temperature in a field of the

order of 8000 gauss using $\{\text{Hg}[\text{Co}(\text{SCN})_4]\}$ as a standard material. Electrical resistivity (ρ) of the prepared samples were measured by two probe method by recording cooling cycles from 250°C to room temperature. Band gap energies of the samples were measured using diffuse reflectance spectroscopy (Shimadzu UV-2450).

Photocatalytic degradation of the diazo dye, Naphthol Blue Black, was studied using prepared samples in the presence of sunlight during 11.00 am to 4.00 pm. Aqueous solution of Naphthol Blue Black dye (100 ml of 10^{-5} M) was aerated with oxygen and kept in sunlight for 4 h with 0.2 g of the catalyst powder. The photodegradation rate was determined by measuring the absorbance of the dye solution after every hour using UV-visible spectrophotometer (SPECTRO119).

Results and Discussion

The samples prepared by co-precipitation method have been characterized by recording the X-ray diffractograms. The d_{hkl} and 2 θ values obtained have been compared with the values reported in the literature (ICDD-PDF files) and found to be monophasic. XRD pattern of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) sintered at 800°C shows that pure CeO_2 has a cubic fluorite structure while pure Fe_2O_3 is in the hexagonal phase and $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$, $\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_2$ and $\text{Ce}_{0.7}\text{Fe}_{0.3}\text{O}_2$ are in cubic phase. It was observed that the crystal lattice parameter decreases with increasing Fe content. This may be due to insertion of Fe into the CeO_2 crystal lattice. Since the radius of Fe^{3+} ion is smaller than that of the Ce^{3+} ion, the CeO_2 crystal lattice parameter decreases. On increasing x of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ from 0.4 to 0.9, the XRD diffraction peaks due to CeO_2 became weak and Fe_2O_3 phases were observed. Only up to $x = 0.3$ for Fe in the CeO_2 lattice solid solution is formed. At higher values of x , monophasic solution could not be formed.

Surface areas obtained by using B.E.T. nitrogen adsorption method were in the range of 3.86-26.41

m^2/g (Table 1). FTIR studies were carried out to ascertain the metal-oxygen bonding nature of the solid solution in the range 1000-400 cm^{-1} . Bands at 546 and 450 cm^{-1} are observed in the samples as x increased, which may be assigned to the Fe-O stretching vibrational modes. These two bands are sharp and of strong intensity in Fe_2O_3 .

The magnetic susceptibility (χ_g) of the samples was determined by Guoy method at room temperature employing a field of 8,000 gauss. The gram susceptibility values obtained at room temperature for $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ compositions are presented in Table 1. All the samples are paramagnetic in nature and the gram susceptibility value increased as the x increased. Pure Fe_2O_3 is ferrimagnetic.

Electrical resistivities (ρ) of the samples were measured by two probe method during cooling cycles from 250°C to room temperature. Plots of log resistivity versus $1000/T$ for $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ samples show that resistivity decreased with rise in temperature indicating semiconductor behaviour of these compounds. Solid solutions show higher value of ρ than CeO_2 which is an n-type semiconductor. This may be due to oxygen vacancies created by lower valent ions.

The prepared samples were tested for photocatalytic degradation of NBB using sunlight. The NBB dye showed absorption in the visible region at 618 nm in aqueous solution. The progress of the photocatalytic degradation was monitored by measuring the absorbance of the reaction mixture at this wavelength. The optimum amount of catalyst required for solar induced photocatalytic degradation of NBB was found to be 200 mg for 100 ml of the solution. The rate of dye degradation increased with increase in amount of photocatalyst which may be attributed to the increase in the exposed surface area of the semiconductor. But after a certain limit (200 mg), if the amount of photocatalyst is increased further, there will be a saturation point. According to Kartal *et al.*⁷ the amount of photocatalyst affects both the number of active sites on photocatalyst as well as

Table 1—Surface area, the magnetic susceptibility values and band gap energy of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ samples

Sample	Surface area (m^2/g)	Magnetic susceptibility (χ_g cgs unit)	μ_{eff} (B. M.)	Band gap (eV)
CeO_2	7.36	2.98×10^{-6}	1.06	3.64
$\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_2$	8.92	8.98×10^{-6}	1.80	--
$\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_2$	5.62	11.21×10^{-6}	1.95	2.68
$\text{Ce}_{0.7}\text{Fe}_{0.3}\text{O}_2$	3.86	14.37×10^{-6}	2.14	--
Fe_2O_3	26.41	Ferrimagnetic	--	2.17

the penetration of light through the suspension. As the amount of photocatalyst increase, the number of active sites increases although the penetration of light into the suspension decreases due to a shielding effect. It has also been suggested by Sakthivel *et al.*¹² that increasing the loading of photocatalyst increases the rate of deactivation of active sites by collision.

Oxygen is an electron scavenger and traps the photogenerated electrons from the conduction band forming O_2^- ions, thus preventing the electron-hole recombination¹³. In the absence of oxygen, electron-hole recombination occurs thus decreasing the rate of degradation. Similar results were observed by Zhang⁵ and others⁶ who have reported that dissolved O_2 in the reaction plays an important role by trapping the conduction band electrons forming super oxide ions (O_2^-). This delays the electron-hole recombination ($O_2 + e^- \rightarrow O_2^-$) while at the same time H_2O_2 is formed from O_2 .

Dye degradation was studied at different pH conditions, pH which is one of the important factors for the degradation because of the amphoteric nature of most of the semiconductors^{13,14}. It has been observed that degradation of dye is faster in alkaline pH. In alkaline medium, there is a greater probability of the formation of hydroxyl radical (OH^\cdot), which can act as an oxidant, thus increasing the rate of photodegradation of the dye¹⁵.

The removal efficiency is minimum at acidic pH range. At alkaline pH, the negative surface of the semiconductor with OH^- ions acts as an efficient trap for the photo-generated holes and produce hydroxyl radicals. At higher pH, the hydroxyl radical and O_2^- radical can easily diffuse from the negative surface of the semiconductor into the bulk of the reaction solution. Hence, hydroxyl radical is responsible for the dye degradation.

In the absence of O_2 and catalyst the dye is unable to degrade on irradiation with sunlight. Under solar irradiation, along with oxygen and catalyst the dye is degraded completely within a time of 240 minutes. Absorption spectra obtained after completion of the NBB dye degradation indicate that the degradation products are colourless. Thus, the photocatalytic degradation provides an efficient way to mineralize this textile diazo dye.

The photocatalytic degradation of Naphthol Blue Black over different compositions of $Ce_{1-x}Fe_xO_2$ ($x = 0, 0.1, 0.2, 0.3$ and 1.0) at neutral pH is shown in

Fig. 1. It was observed that concentration of the dye solution decreased with irradiation time. CeO_2 had negligible activity for the degradation of NBB dye. Cerium-iron solid solutions showed higher photocatalytic activity. As x increases, the photocatalytic activity increases and it is maximum for $Ce_{0.8}Fe_{0.2}O_2$. As the iron content increased in CeO_2 , activity increased. However, in the case of $Ce_{0.7}Fe_{0.3}O_2$, in spite of higher Fe lower activity than that of $Ce_{0.8}Fe_{0.2}O_2$ was observed, but higher than for $Ce_{0.9}Fe_{0.1}O_2$. This may be because $Ce_{0.7}Fe_{0.3}O_2$ has lower surface area and also higher particle size than $Ce_{0.8}Fe_{0.2}O_2$ which may have resulted in lower activity. Fe_2O_3 showed higher activity because of high surface area and low particle size. Table 1 shows band gap energy of the representative samples. Lower the band gap energy, faster is the promotion of electrons using visible light. Also very low band gap may result in recombination of electron-hole pairs. Certain electron scavengers like O_2 can be used to inhibit recombination. The dye is degraded faster at pH 10 as shown in Fig. 2. When the system is illuminated by light of adequate wavelength, some electrons are promoted to the conduction band. Since the conduction band shifts toward higher potential, the energy of the electrons on the conduction band is enough to reduce oxygen dissolved in aqueous media. Thus, the photoexcited electrons and holes on the solid solution can be separated effectively and have a longer lifetime. Therefore, the increase in the photocatalytic oxidation-reduction potential of the

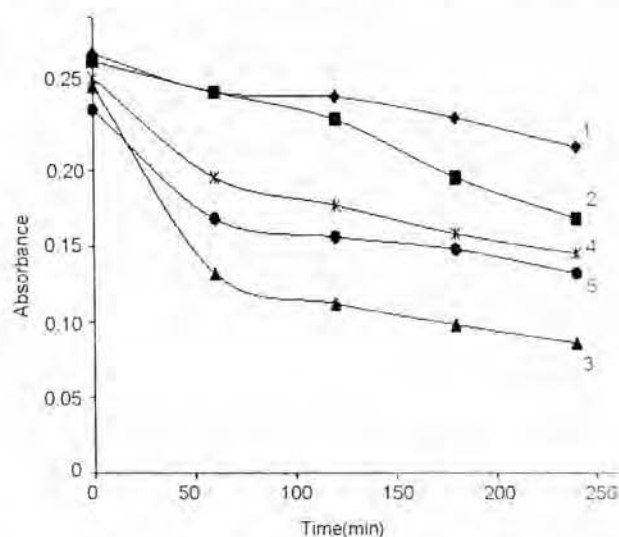


Fig. 1—Degradation of NBB dye over $Ce_{1-x}Fe_xO_2$ at neutral pH. [1, CeO_2 ; 2, $x = 0.1$; 3 $x = 0.2$; 4, $x = 0.3$; 5, Fe_2O_3].

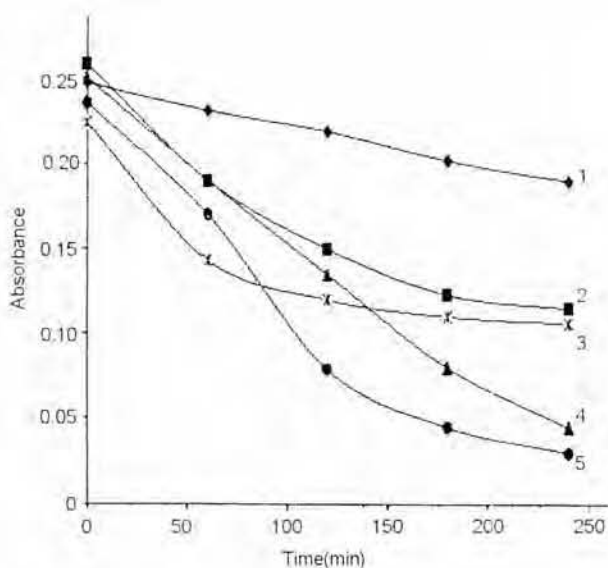


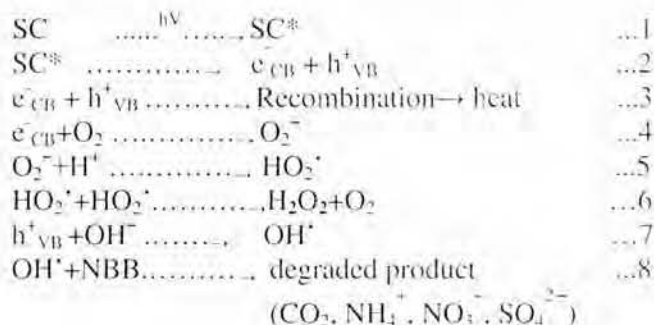
Fig. 2—Degradation of NBB dye over $Ce_{1-x}Fe_xO_2$ at pH 10. [1, CeO_2 ; 2, $x=0.1$; 3 $x=0.2$; 4, $x=0.3$; 5, Fe_2O_3].

semiconductor is inferred to be the origin of the enhanced photoactivity of $Ce_{1-x}Fe_xO_2$ system.

The degradation products were analyzed by high performance liquid chromatography (HPLC) using Novapak C18 column. The chromatograms obtained at different irradiation time indicate that degraded products are different from the original dye molecule. The formation of CO_2 , SO_4^{2-} , NO_3^- and NH_4^+ was identified. This observation was similar to that reported earlier¹⁵.

Many investigators have suggested various mechanisms for the degradation of dye pollutants^{9,13}. Scheme 1 shows one of the possible reaction mechanism which is in concurrence to that observed by Galindo *et al.*⁶

On exposure to solar radiation, the semiconductor (SC) will be excited to give SC^* . This excited state will provide an electron (e^-) in the conduction band leaving a hole in the valence band. This electron is then trapped by molecular O_2 forming O_2^- ions. The



Scheme 1

valence band hole generates hydroxyl radical (OH^*) from hydroxyl ions, which can easily attack the adsorbed dye, thus leading finally to their complete mineralization.

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