Combustion Synthesis of Ferric Oxide as a Photo-catalyst Using Urea as Fuel, for Degradation of Dyes in Aquatic Environment

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Abstract **- This work reports the semiconductor assisted photochemical degradation of reactive azo dye such as congo red (CR) on combustion synthesized ferric oxide as a photo-catalyst. Ferric oxide was characterized by powder XRD, BET surface area, reflectance spectroscopy and powder density. BET surface area was found to be 3.4386 m 2 gm-1and has a particle size equals to 29.33 nm. Energy gap was found to be 2.12 eV by reflectance spectroscopy. 79 % COD removal was observed at pH 6 within 60 min. time duration using UV light (254 nm wavelength) as a source of radiation**

Index Terms **- Combustion synthesis, Ferric oxide, Photo-catalysis, Semiconductors, Optical materials and properties.**

I.INTRODUCTION

A large amount of wastewater containing dyestuff with intensive colour and toxicity are introduced into aquatic system during dye production and textile manufacturing. Some of these dyes are difficult to degrade with standard biological methods [1]. They are resistant to aerobic degradation [2] and under anaerobic conditions they can be reduced to potentially carcinogenic aromatic amines [3]. Therefore, there is a need to investigate new alternative for the adequate treatment of this kind of waste and attempt has been made to degrade the Congo red dye.

Recently, semiconductor – assisted photo-catalysis has been extensively investigated mainly due to its capacity to degrade a large number of recalcitrant chemicals in aqueous system. In this work ferric oxide prepared by combustion method has been used as semiconducting material mainly due to its characteristic include, high photochemical reactivity, relatively low cost of production and environmentally benign material.

Combustion synthesis or the self- propagating high-temperature synthesis (SHS) is a versatile method for the synthesis of variety of solids since it offers advantages with respect to process economics and process simplicity [4]. This method consists of heating an aqueous solution made of inorganic salts, usually nitrates which act as oxidant agent and an organic combustible, which can be also a complexant agent of the metallic ions. Firstly it is necessary to ensure the homogeneity of the system with the complete dissolution of the components. After that, the solution is heated until its ignition, giving rise to a fast exothermic reaction that led to oxide formation [5,6].

II. EXPERIMENTAL PROCEDURE

In this work all chemicals used were of AR grade. In this combustion synthesis method metal nitrates e.g. ferric nitrate acts as oxidizer and Urea is used as fuel. The redox mixture was dissolved in minimum quantity of deionised water taken in a cylindrical pyrex dish of approximately 250 ml capacity. The amount of fuel were taken in such a way that the desired product i.e. Fe2O3formed is 5 gm. Dish containing the solution was introduced into muffle furnace preheated at 623 K. Mixture boils, foams and undergo smouldering (flameless) combustion to produce ferric oxide. The entire process took 15 min. to complete.

The crystallinity and phase identification of the powders were determined by powder XRD using Philips PW-1700 diffractometer with Ni filtered CuKα radiation. A reflectance spectrum was recorded on GBC Cintra 10e, Australia, spectrophotometer. BaSO4 of A.R. grade was used as a reference and diluents. The sample to BaSO4 ratio was 1:10 (w/w). Mixing was done for several minutes with agate and

mortar. The sample pellet was prepared by manually pressing powdered sample in a metal sample holder and ensuring the surface to be perfectly smooth and homogeneous. The spectrum was recorded in the wavelength range 200-900 nm at the data interval of 1 nm. Surface area measurements was done using nitrogen gas adsorption multipoint Brunquer-Emmett-Teller (BET) method using Micromeritics ASAP 2010 model, assuming a cross sectional area of 0.162 nm2for nitrogen molecule. Powder density was measured using pycnometer with xylene as the liquid medium. The diameter of the primary particle was calculated from superficial area using following equation:

$$DBET = 6/SBET.\rho \quad \ldots (1)$$

Where SBET is the superficial area (m2gm-1) measured by BET analyses, ρ is the density of powders (gm cm-3) and DBET is the diameter of the produced particle. SEM micrograph was recorded on JOEL (Japan), JXA-840A electron probe analyser instrument after coating the sample with gold for evaluation of particle morphology.

In this study immersion type photo-reactor manufactured by Heber Scientific, Chennai, India was used. The radiation source was 254 nm wavelength UV lamp with quartz sleeves to accommodate it having air purging and gas outlet provision.

Experiments were carried out to check % colour removal of dye molecules on spectronic 20 spectrophotometer (Milton Roy Company) using these photocatalyst.

In typical experiment a known amount of CR dye was dissolved in 100 cm3deionised water. Dye solution was stirred with photo-catalyst in dark for half an hour. This was then taken in a photo-reactor. Air flow was permitted to enter the photo-reactor. The parameters like pH, catalyst loading, time of exposure and dye concentration were optimized. After each exposure the sample solutions were studied for Chemical oxygen demand (COD) removal. Similar experiment was performed using commercially available Fe2O3 Photocatalyst. The COD test determines the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The organic matter gets oxidized completely by potassium dichromate in presence of sulphuric acid to produce carbon dioxide and water. The excess potassium dichromate remaining after the reaction is titrated with ferrous ammonium sulphate. The dichromate consumed gives the oxygen required for oxidation of the organic matter [7].

III. RESULTS AND DISCUSSION

Preparation of catalyst

The Fe2O3 photocatalyst was prepared by stoichiometric oxidiser to fuel ratio by using Urea as fuels. Stoichiometric molar ratio of oxidiser to fuel ratio (O/F) found to be suitable for effective degradation of congo red dye (on the basis of % colour removal). This proportion forms crystalline, nanosized high surface area with desired band gap value catalyst. Further studies were carried out using this photocatalyst.

Characterization of catalyst

XRD pattern of as synthesized Fe2O3 is shown in fig.1 which shows that α-Fe2O3is the dominant form. BET surface area was found to be 3.4386 m2g-1and bulk density was found to be 4.8763 gm cm-3. Particle size was calculated from these values of BET surface area and bulk density (using equation 1) was found to be 170 nm. Band gap (Eg) was evaluated from reflectance spectra in fig 2 which has 2.12 eV value. This value indicates that Fe2O3 synthesized is semiconducting in nature.

Fine sized particles have different physical and chemical properties from bulk materials. When used as a catalyst, their catalytic activity expected to be enhanced not only because of their increased surface area, but also because of change of surface properties such as surface defects. Small size of cluster vastly reduces electron-hole recombination rate and undesired light scattering. By adjusting size alone, the conduction and valence band energy levels can be shifted allowing new type of catalytic behaviour.

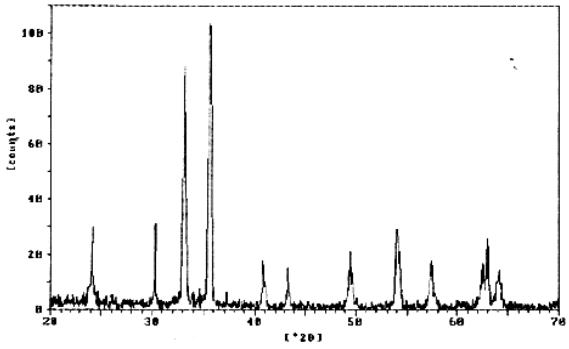

Fig. 1: XRD pattern of as synthesized Fe2O3, Photo-catalyst

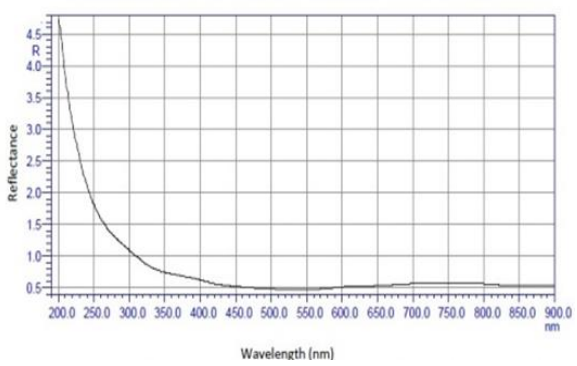

Fig 2: Reflectance Spectra of as synthesized Fe2O3, photo-catalyst

Photo-degradation studies

In the present study immersion type photo-reactor (model HPSLVJ 16254) was procured from HEBER scientific Chennai. Photo-degradation process assisted by a semiconductor depends on various parameters like nature and concentration of the organic substrate, concentration and type of semiconductor, light source and intensity, pH, temperature etc. Several earlier studies reported that photo-catalytic degradation of dyes follows first order kinetics [8].

The chemical oxygen demand (COD) test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO2 and water. The COD of dye molecule before and after the treatment was estimated.

Effect of irradiation time

Effect of irradiation time on COD removal was studied by varying the duration of time of exposure. It is observed that at 60 min and above the COD was found to be negligible. Therefore, irradiation time was kept 60 min. This can be attributed to high surface area of the photocatalyst for effective adsorption and subsequent degradation of dye molecules.

Effect of pH

The pH of the dye solution in the present study was adjusted using varying concentrations of HNO3 and NaOH. The maximum COD removal was observed at pH 6.

Effect of catalyst loading

Experiments were carried out by taking different amounts of Fe2O3 and keeping dye concentration at 50 mg l-1.it was found that the increase in degradation efficiency of CR with an increase in the catalyst amount may be due to an increase in active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation.

Effect of initial dye concentration

The effect of initial dye concentration on the degradation efficiency was studied by varying the concentration from 50 mg l-1to 200 mg l-1 keeping catalyst loading 2 gm l-1as constant. The degradation efficiency of CR was found to decrease with an increase in the initial dye concentration. Therefore, the concentration of dye is selected as 50 mg l-1 . At still higher concentration of dye, the path length was further reduced and photo-degradation was found to be negligible [9].

IV.CONCLUSION

It is observed that the Solution combustion synthesis method is found to be suitable for the preparation of active Fe2O3 photo-catalyst of desired characteristics. 79% COD removal was observed by using this photo-catalyst at pH 6 of Congo red dye.

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