PHOTOCATAYTIC DEGRADATION OF METHYL ORANGE USING NANO FE_2O_3 AND CO DOPED FE_2O_3 OF DIFFERENT COMPOSITIONS

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ABSTRACT

Fe_2O_3 and Co doped Fe_2O_3 were synthesized by sol gel method. Structure and morphology of synthesized Co doped Fe_2O_3 nanocatalyst was investigated using Field emission scanning election microscopy, Electron dispersive X-ray spectroscopy and X-ray diffraction. The photocatalytic activity of Co doped Fe_2O_3 nanocatalyst was investigated for degradation of Methyl orange solution under visible light radiation. The effects of various experimental parameters such as the methyl orange concentration, catalyst dose, pH on the photocatalytic degradation were investigated. Among the different amounts of dopant that like 2, 5, and 10 wt. % Co-doped Fe_2O_3 nanocatalyst. It was observed that 10wt % Co doped Fe_2O_3 shows highest degradation with visible light radiation for methyl orange than pure Fe_2O_3 nanocatalyst. The particle size, morphology and separation of photo induced electron–hole pair are the main factors which influence photocatalytic activity and degradation extent.

Keywords: Methyl Orange, Fe_2O_3 and Co doped Fe_2O_3, photocatalysis

Introduction

Polluted waste water plays significant role in environmental pollution. Industrial effluents contain different chemicals especially synthetic dyes which are carcinogenic in nature1-3. Some dyes decompose aerobically and anaerobically resulting in the formation of carcinogenic compounds. In addition the coloured pollutants decrease light penetration & prevent photosynthesis [1]. This is the adverse consequences of the modern industrialization an environmental pollution. It is extremely necessary to seek efficient and more importantly green technologies to remove these pollutants [2]. Many techniques such as adsorption, electrochemical oxidation, ozonation, membrane filtration and biological treatment have been widely used to remove the dye components from polluted wastewater. These methods generally suffer from disadvantages including complicated processes, need for special operating conditions, high equipment cost, energy intensive time consuming operations, finite versatility and lower adaptability to the extensive range of dye waste waters [3]. The fast moving developments in the field of nanotechnology have stimulated considerable research efforts on the synthesis and manufacturing of novel devices for various high-technological potential applications. Nanocrystalline Iron oxide Hematite (Fe_2O_3) has important applications such as: photocatalytic splitting of water to hydrogen and oxygen, self-cleaning surfaces and degradation of environmental pollutants [5]. Iron oxides nanocrystals have attracted increasing attention for their outstanding new properties such as their biocompatibility, catalytic activity and low toxicity. Due to the stability of modern dyes, conventional biological treatment methods for industrial wastewater are ineffective and insufficient resulting often in an intensively colored discharge from the treatment facilities. Recently, a number of researches have dealt with heterogeneous photocatalytic decomposition of many kinds of azo-dyes [6,7] by UV, visible light and solar irradiation [8]. In addition, hematite has a relatively high band gap value of 3.2 eV. However for many applications it would be desirable to extend the band gap excitations towards the visible region, and also to prolong the lifetime of photogenerated charge carriers. Doping of titanium dioxide with transition metal ions provides a relatively well-studied and convenient way of solving both problems described above. Titanium dioxide doped with transition metal ions can demonstrate extended band gaps and significantly higher photocatalytic efficiencies [9,10]. The dopant

concentration is an important parameter to be considered, as the amount of dopant influences the processes of charge carrier trapping, separation, and recombination [11]. Therefore, the amount of transition metal introduced should be within a so-called optimum concentration, as too low a dopant content does not affect the process of charge carrier generation and too high a content of doping metal results in the formation of extra recombination sites and shortens the lifetime of photo generated electrons and holes. Consequently, defining the optimum concentration of doping metal is a key factor for successful doping. This optimum value may vary significantly and depends on several factors, such as the type of dopent chosen, the coating deposition technique, annealing conditions, *etc.* [12].

Present study involves the synthesis of Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst which was characterized by scanning electron microscopy (SEM), Electron dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The effect of various parameters like pH of dye solution, contact time, dose of catalyst in photocatalytic degradation Methyl Orange (MO) using Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst were studied.

Experimental

Method

From stock solution of MO, different concentrations were prepared in distilled water and pH maintain to 7. The 50 mL MO solution containing Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst taken in the photoreactor. The solution was stirred for 2 hours in the dark to allow to reach the equilibration of the system The dye sensitized Fe_2O_3 and Co doped Fe_2O_3 was subjected to visible light irradiation for the degradation of MO. The catalyst was separated from the solution by centrifugation and the solution was analyzed for determining concentration of dye at λ_{max} 465 nm.

Synthesis of α- Fe_2O_3 *and Co doped* α- Fe_2O_3

Pure and 2, 5 &10 % Co incorporated α-Fe2O3 were prepared by a simple and cost effective solution method. For the synthesis purpose, the preparation strategy of iron oxide from foam-based precursor is used. In a synthesis, iron nitrate and cobalt chloride was dissolved (Fe:Co, 98:2, 95:5 and 90:10; atomic ratio) in deionized water and heated the solution at 70°C to obtain a gel like material [12,13]. The gel was formed after 2 h with continuous stirring of the precursor solution. On the other hand separately, a clear solution containing 4 wt% PVA was made by stirring and warming the solution at 40°C [14]. After that an appropriate amount PVA solution (7 ml) was added slowly to the gel with vigorous stirring. The solution was found to transform into a gel after stirring and warming at 70°C for an hour. The gel was kept at 100°C in an air oven and obtained a foam-like material. In the next, the foam was heat-treated under air atmosphere at 600°C for three hour to remove the organics and the product of cobalt incorporated α- Fe_2O_3 (AFC) was obtained. Similar procedure was also adopted for preparation of undopedα-Fe_2O_3 (AF) without the addition of hydrated cobaltous chloride in the precursor solution. It is important here that the foam formation depends upon the PVA weight percent Co (wt%). In this respect, initially the synthesis was made by adding 2 wt% PVA solution but there was no formation of the foam-like material

Results and discussion

SEM analysis

The SEM image of Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst are shown in Fig. 1 (a, b, c and d). The FESEM image of Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst shows irregular elongated spherical shape with crystal structure having irregular size and shape. It was observed that the particle size increases with increasing doping concentration of Co.

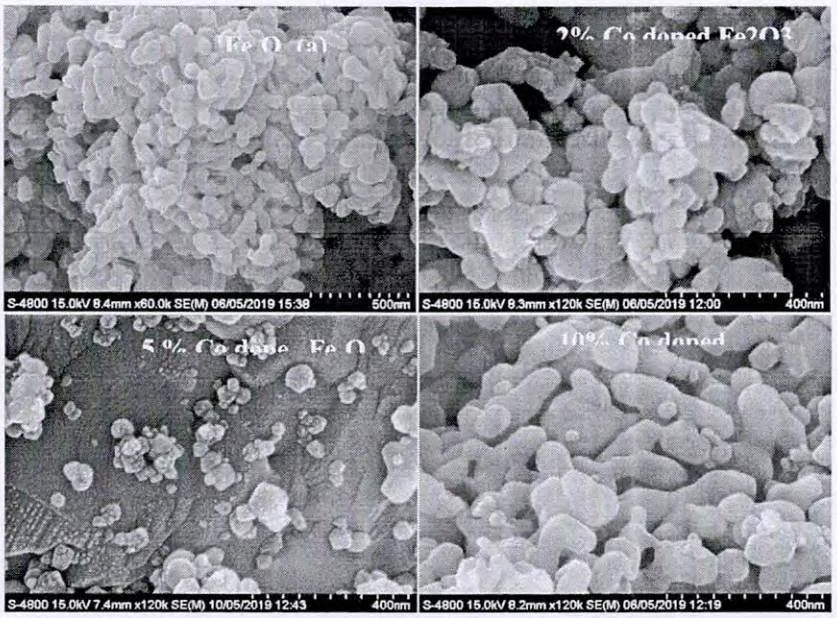

Fig. 1. (a, b, c and d). FESEM image of $Fe_2O_3$and Co doped Fe_2O_3 nanocatalyst

X-ray diffraction analysis

Fig.1 (a, b, c and d). The FESEM image of Fe_2O_3 and Co doped Fe_2O_3

The XRD patterns of the samples show well-defined peaks, indicating that the samples are crystalline. The pattern exhibits the characteristic XRD pattern of hematite (α-Fe_2O_3) in accordance with data from the ASTM (American Society of Testing Materials) cards. The Scans were performed over 2θ = 20-80° for each sample. Fig. 2 indicate different peaks at 24.10°, 33.26°, 36.30°, 42.23°, 51.37°, 42.23°, 54.00° and 63.54° corresponded to planes (012), (104), (110), (112), (024), (116) and (118). The diffraction peaks of the samples were found to be in a good agreement with those reported for hematite in the literature (JCPDS Card no. 89-0529).

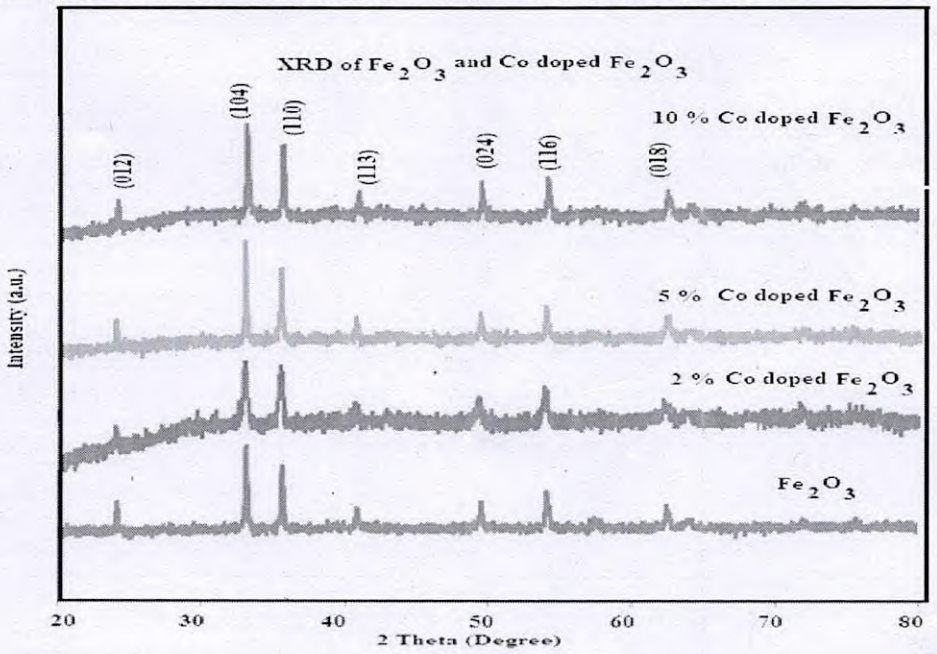

Fig. 2 XRD of Fe_2O_3 and Co doped Fe_2O_3

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Effect of pH

The influence of pH on photocatalytic degradation of MO was performed. Degradation of MO is lower in basic media that is increase in pH, the percentage degradation decreases and higher degradation is observed to neutral medium. The pH 5 is suitable for degradation of MO in presence of Fe_2O_3 nanocatalyst.

Effect of catalyst on initial Dye Concentration

The effect of catalyst on initial dye concentration of MO was investigated by changing the doping amount Co in Fe_2O_3 as 2%, 5% and 10% using 2 g/L of Fe_2O_3 and Co doped Fe_2O_3 nanocatalyst at pH 5. The results showed that dye concentration decreases from 20 mg/L to 6.6 mg/L, 6.23 mg/L, 5.26 mg/L, 5.52 mg/L with increasing in doping concentrations from Fe_2O_3, 2 % Co doped Fe_2O_3, 5% Co doped Fe_2O_3, 10% Co doped Fe_2O_3 (Fig. 3). This was due to the reason as doping concentration increased the concentration of unabsorbed dye in the solution decreases which lead to more penetration of light through the solution on to the surface of Fe_2O_3 and Co doped Fe_2O_3 thereby increase the concentration of ·OH radicals on the surface and hence increases the percentage degradation [15].

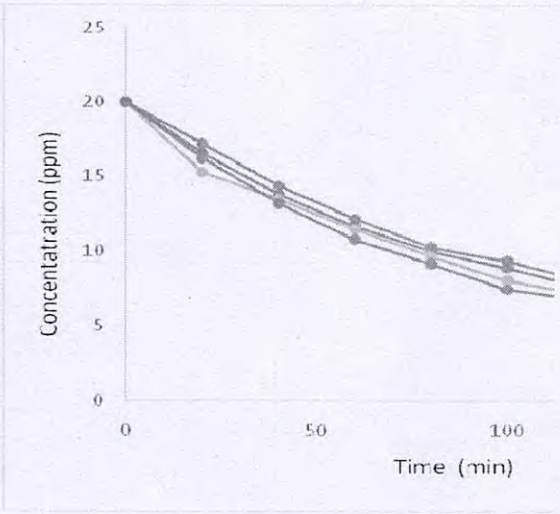

Fig. 3. Effect of catalyst on initial dye concentration

Effect of Dose

To avoid the excessive use of catalyst, the optimum dose was determined using concentrations of Fe_2O_3. It was found that rate of degradation initially increases with the increase in catalyst dose, but beyond a certain level it remained almost constant. From Fig. 4 it is observed that after 1g/L of catalyst dose percent degradation remains almost constant so in present case 1g/L was found to be the optimum catalyst concentration [16]. The increase in catalyst concentration has a positive influence on the number of photons absorbed and number of dye molecules adsorbed. This in turns enhances the rate of dye degradation. Above a certain catalyst concentration the numbers of substrate molecules are not sufficient to fill the surface active sites of Fe_2O_3. Hence, further addition of catalyst does not lead to the enhancement of degradation rate. The surplus addition of the catalyst makes the solution more turbid and light penetration is hindered from the sample observed that the increase in photocatalyst loading leads to availability of more number of catalytic sites for adsorption further increase in the dosage results in saturation and very high dosage results in increased turbidity of the suspension hindering the light penetration due to shielding effect thus reducing the efficiency of the process decreases. [17].

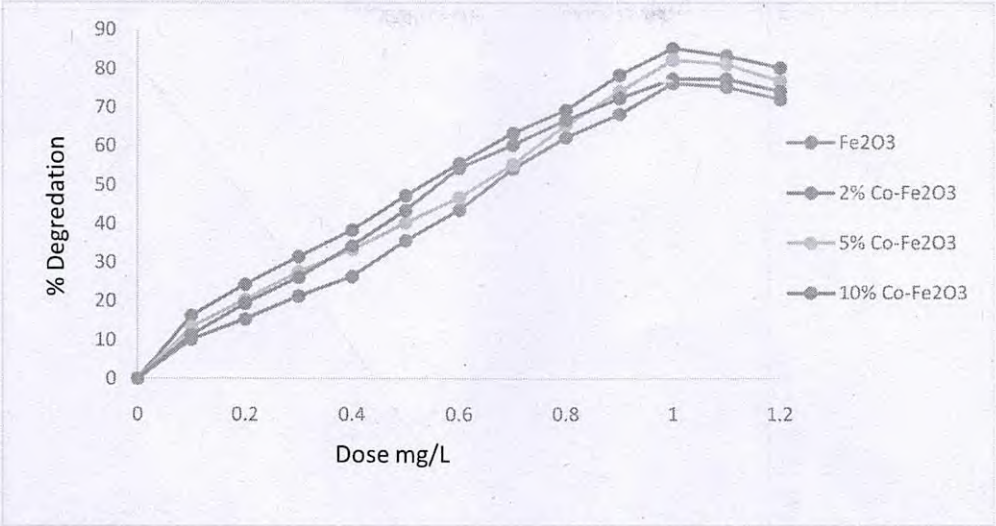

Fig. 4 Effect of dose on percentage degradation of MO (pH=5, MO conc.= 40 mg/L and reaction time 120 min.)

Effect of doping percentage

Fig. 5 shows that the effect of different doping ratios on the photocatalytic degradation of MO. The values of catalyst dose 1 g/L, pH 5 and the concentration of MO were 20 mg/L, respectively. As shown in Fig. 5, during the contact time, the MO degradation efficiency (%) was increased slightly with the increase of doping ratio from 2 to 10 %. Photocatalytic activity of doping concentration increases with decreasing the band gap energy [18]. In addition, rapid transfer of the electrons from the Fe_2O_3 to the Co may improve the photocatalytic activity and increase the efficiency of photodegradation [19].

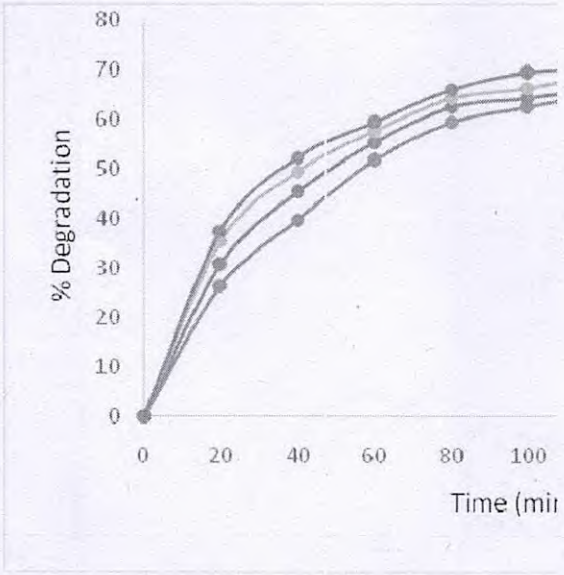

Fig. 5. Effect of doping percentage on percentage degradation of MO (Catalyst dose= 1.0 g/L, pH=5 MO conc. = 20 mg/L and reaction time 200 min)

Effect of initial dye concentration

The effect of initial dye concentration on photocatalytic degradation of MO was studied by varying the dye concentration from 10 to 40 mg/L (Fig. 6) at fixed catalyst concentration 5% Co doped Fe_2O_3. It can be observed that, as the dye concentration increases percent degradation decreases. As the concentration of dye increases the color of solution becomes

more intense due to more dye molecules which alters the light to reach the catalyst surface to produce active species responsible for degradation and thereby decreases the degradation efficiency of catalyst and secondly, less number of active site of catalyst is available due increase in adsorption which also lowers the catalyst efficiency.

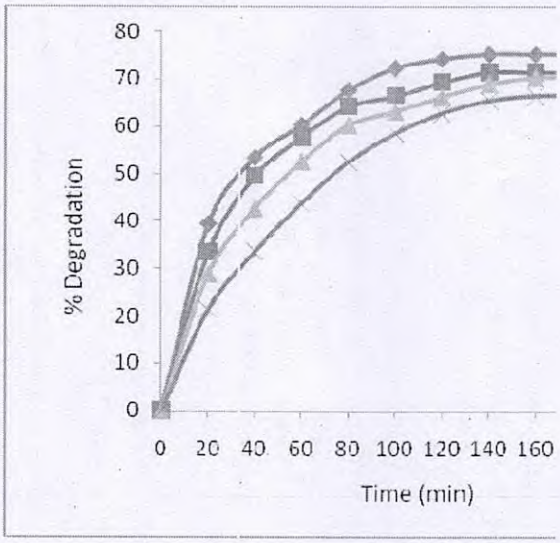

Fig.6. The effect of initial dye concentration on photocatalytic degradation of MO.

Recycle performance of Co doped Fe_2O_3 nanocatalyst

To find out the stability and efficiency of Co doped Fe_2O_3 nanocatalyst as well as cost effectiveness of the process, the reusability of Zn doped Fe_2O_3 nanocatalyst was investigated for the % degradation of MO. To study its reusability, the powdered nanocatalyst was centrifuged after completion of each photocatalytic experiment. The recovered sample was reused for 3 times under same experimental conditions. Fig. 7 shows % degradation of MO by Co doped Fe_2O_3 nanocatalyst after 1st run achieved up to 85.6% (100 min). After 4th run it decreases down to 81.55%. The catalytic activity was found to decrease marginally after 4th run. This decrease may be attributed to loss of reused catalyst during sampling each time and irreversible changes of the surface of the photo catalyst by pollutants. Fig. 7 shows that Co doped Fe_2O_3 have excellent stability and do not undergo photocorrosion.

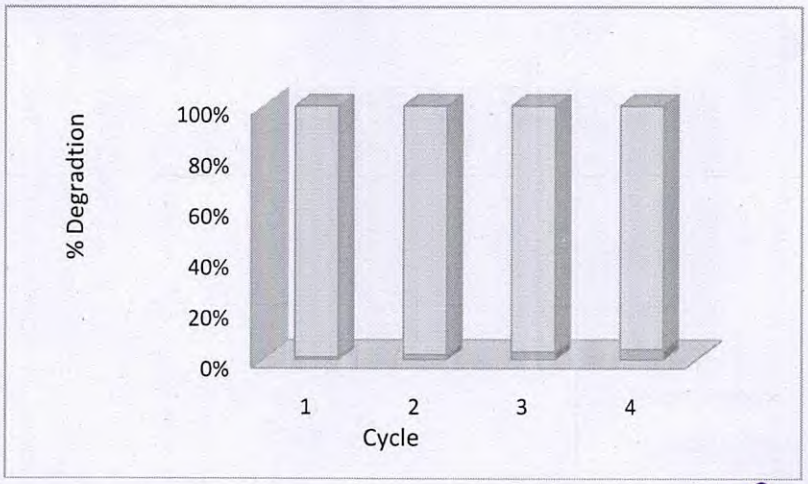

Fig. 7. Reusability study of Zn doped Fe_2O_3 nanocatalyst.

Efficiency study of catalyst by effluent treatment

For estimating the extent up to which the organic moieties degraded in the effluent after treatment, total organic carbon (TOC) analysis of the sample is the most appropriate method. As TOC is the measure of the level of organic molecules or contaminants in purified water [20]. To estimate the degradation level of organic contaminants TOC analysis of the sample before and after degradation was conducted along with other parameters like electrical conductivity, colour by absorbance at λ_{max}, associated with water quality by treatment with catalyst. For this purpose 4 % Zn doped CuO was used as it was found most efficient among all compositions of doped and undoped materials. 5 g/L of catalyst effluent was used for the treatment. The result is summarized in the Table.

Sample Parameters	Before treatment	After treatment
pH	7.9	7.6
Electrical conductivity	15.96 X 10-3 mhos	12.64 X 10-3 mhos
TOC	325.6 ppm	44.78ppm
Absorbance	0.96	0.41

The degradation results are near about the pollutants discharged by each plant are limited by a Central Pollution Control Board New Delhi [21].

Conclusions

The photocatalytic degradation of MO in the presence of Fe_2O_3 and Co doped Fe_2O_3 were show promising results towards degradation of MO. The percentage degradation of dye increased with an increase doping percentage of Co and decrease with increase in initial concentration of dye. The pH 5 found to be suitable for photocatalytic degradation of MO. A comparative study shows that 5% Co doped Fe_2O_3 nanophotocatalyst degradation of MO. The reusability study shows the stability of the Co doped Fe_2O_3 nanocatalyst.

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