SYNTHETIC STRATEGY FOR TAILORING OF FERRIC OXIDE AS A PHOTO-CATALYST BY DIFFERENT METHODS.

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Abstract

Methods of synthesis plays vital role is producing material with desired properties. In view of the increasing importance being attached to material Synthesis, it was considered appropriate to outline the chemical methods of synthesis of inorganic materials in this work. In the present work, attempt have been made to synthesized ferric oxide (Fe203) by three different methods viz. direct heating of metal salts, precipitation and combustion synthesis and used as semiconducting material mainly due to its characteristics such as catalytic reactivity. 14 samples were selected out of 25 samples prepared. Samples of as synthesized ferric oxide were characterized by powder XRD, BET surface area, scanning electron microscopy (SEM), reflectance spectroscopy and powder density. Solution combustion synthesis is really a versatile, rapid & economic technique by which ferric oxide can be synthesized.Fe2O3 can be used as photo catalyst.96 – 98 % COD removal was observed. Photo degradation can be carried out by solar light induced photo catalysis.

Keywords

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

Introduction

A wide range of semiconductor may be used for photo-catalysis, such as TiO2, ZnO, MgO, WO3, CdS. The ideal photo-catalyst should possess the following properties (i) photoactivity (ii) biological and chemical inertness (iii) stability towards photocorrosion (iv) suitability towards visible or near UV light (v) low cost and (vi) lack of toxicity. The metal and its oxides have desirable structural, magnetic, electrical, chemical and optical properties that are employed in a multitude of applications. Stoichiometric hematite, Fe2O3 is an intrinsic n-type

semiconductor with a band gap of 2.2 eV which is in visible light, insulator at room temp [1,2]. It is possible to produce a less resistive semiconducting oxide material by reducing some of the Fe+3 to Fe+2state. The hematite is then a mixed valence compound with enhanced conductivity at room temperature which is due to a hopping process for electrons between Fe+2 and Fe+3 ion [3]. Chemical methods of synthesis play a crucial role in designing and discovering novel materials. They also provide better and less cumbersome methods of preparing known materials. The tendency now a day is to avoid brute-force methods and instead employ methods involving mild reaction conditions. Soft chemistry routes are indeed becoming popular and will undoubtedly be pursued with greater vigour in the future. In view of the increasing importance being attached to material Synthesis, it was considered appropriate to outline the chemical methods of synthesis of inorganic materials in this work. Methods of synthesis plays vital role is producing material with desired properties. There are many methods of synthesis employed for the synthesis of Fe2O3. In this work we have used simple & important methods of synthesis of Fe2O3 such as precipitation, heating of salts like, nitrates and versatile and novel method like combustion synthesis which utilizes simple instrumentation with economically viable nature. Combustion synthesis or self-propagating high temperature synthesis method proved to be useful in producing materials with different particle size and surface area which play important role in heterogeneous photo-catalysis. The literature on combustion synthesis is vast and most of the materials prepared and their applications have been summarized in many recent publications [4-7]. In the present work, attempt have been made to synthesized ferric oxide (Fe203) by three different methods (e.g. direct heating of metal salts, precipitation and combustion synthesis) and used as semiconducting material mainly due to its characteristics such as catalytic reactivity, low cost of production. Samples of as synthesized ferric oxide were characterized by powder XRD, BET surface area, scanning electron microscopy (SEM), reflectance spectroscopy and powder density.

Material and Method

Synthesis Of Photo-catalyst : In this work photo-catalyst was prepared by three different methods which are explained as follows :

Precipitation method

Ferric Oxide (Fe2O3) was prepared by precipitation method, in which desired quantity of ferric nitrate was dissolved in minimum quantity of double distilled water. To this, equimolar solution of liq. NH3 and water was added slowly and drop wise till foggy

Result and Discussion

The photo-catalyst (Fe2O3) was prepared by precipitation method using known quantity of ferric nitrate and equimolar solution of ammonia and it is used as synthesized for further studies. The photo-catalyst was also prepared by direct heating of known quantity of ferric nitrate (solid) at 4000C temperature for 7 hrs. and materials so obtained is used for further studies. Variety of photo-catalyst samples were prepared by using solution combustion synthesis method are given in Table1. Among the above three methods, solution combustion synthesis method found to be more suitable for tailoring desired photo-catalyst. In order to study the effect of reaction stoichiometry on the physicochemical characteristics of the synthesized materials the F/O ratio was varied from fuel rich to fuel deficient proportions. The variety of samples of photo-catalyst (Fe2O3) thus prepared by above three methods have been tried for % color removal by using Congo red (CR) dye solution as an example. The details of samples with their % color removal of Congo red (CR) dye solution are listed in table 1. On the basis of performance for % color removal studies shown by different sample (Fe2O3) mentioned above, some samples of Fe2O3 selected for further characterization studies are listed in table 2 with their sample code. Above short listed samples of Fe2O3photo-catalyst were characterized by different physicochemical methods which include XRD, SEM, BET surface area, bulk density & diffuse reflectance spectroscopy.

Table 1 : Comparative performance of Fe_2O_3 photo-catalyst prepared by different methods for % color removal.

Sr. No	Photo-catalyst	Method of Synthesis	Oxidant	Fuel	Fuel Composition	% Color removal
1	Fe_2O_3	Precipitation	--	--	--	91.6
2	Fe_2O_3	Direct Heating	--	--	--	88.00
3	Fe_2O_3	Solution Combustion	F. N.	Urea	2(F.N.)+5(U)	78.00
4	Fe_2O_3	Solution Combustion	F. N.	Urea	2(F.N.)+4.5(U)	74.00
5	Fe_2O_3	Solution Combustion	F. N.	Urea	2(F.N.)+4(U)	76.00
6	Fe_2O_3	Solution Combustion	F. N.	Urea	2(F.N.)+5.5(U)	72.00
7	Fe_2O_3	Solution Combustion	F. N.	Urea	2(F.N.)+6(U)	68.00
8	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+3(A.N.)	82.00
9	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+2.5(A.N)	80.00
10	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+2(A.N.)	76.00
11	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+3.5(A.N.)	74.00
12	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+4(A.N.)	70.00
13	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+1.5(A.N.)	75.00
14	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+(A.N.)	73.00
15	Fe_2O_3	Solution Combustion	F. N.	Gly.&A.N.	2(F.N.)+4 (*Gly*)+0.5(A.N.)	61.00
16	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+3(ODH)	81.00
17	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+2.5 (ODH)	91.60
18	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+2 (ODH)	90.80
19	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+1.5 (ODH)	85.40
20	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+ 1 (ODH)	96.00
21	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+0.5 (ODH)	85.40
22	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+3.5 (ODH)	86.80
23	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+4 (ODH)	90.80
24	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+4.5 (ODH)	80.80
25	Fe_2O_3	Solution Combustion	F. N.	O.D.H	2(F.N.)+5 (ODH)	76.40

(F. N. = Ferric nitrate, Gly. = Glycine, A.N. = Ammonium nitrate, U = Urea and ODH = Oxalyldihydrazide)

Table 2 : Short listed samples of Fe_2O_3 photo-catalyst for further studies.

Sr. No.	Photo-catalyst Prepared	Method of Synthesis	Sample Code	Oxidant	Fuel	Fuel Composition(Fuel rich / Fuel deficient)
1	Fe_2O_3	Solution Combustion	A	Ferric Nitrate	ODH	2(F.N.)+2.5(ODH) deficient by 0.5 mole
2	Fe_2O_3	Solution Combustion`	B	Ferric Nitrate	ODH	2(F.N.)+2(ODH) deficient by 1 mole
3	Fe_2O_3	Solution Combustion	C	Ferric Nitrate	ODH	2(F.N.)+1.5(ODH) deficient by 1.5 mole
4	Fe_2O_3	Solution Combustion	D	Ferric Nitrate	ODH	2(F.N.)+1(ODH) deficient by 2 mole
5	Fe_2O_3	Solution Combustion	E	Ferric Nitrate	ODH	2(F.N.)+0.5(ODH) deficient by 2.5 mole
6	Fe_2O_3	Solution Combustion	F	Ferric Nitrate	ODH	2(F.N.)+3(ODH) stoichiometric
7	Fe_2O_3	Solution Combustion	G	Ferric Nitrate	ODH	2(F.N.)+3.5(ODH) rich by 0.5 mole
8	Fe_2O_3	Solution Combustion	H	Ferric Nitrate	ODH	2(F.N.)+4(ODH) rich by 1 mole
9	Fe_2O_3	Solution Combustion	I	Ferric Nitrate	ODH	2(F.N.)+4.5(ODH) rich by 1.5 mole
10	Fe_2O_3	Solution Combustion	J	Ferric Nitrate	ODH	2(F.N.)+5(ODH) rich by 2 mole
11	Fe_2O_3	Solution Combustion	K	Ferric Nitrate	Urea	2(F.N.)+5(U) stoichiometric
12	Fe_2O_3	Solution Combustion	L	Ferric Nitrate	Glycine	2(F.N.)+4(Gly.)+3(A.N.) stoichiometric
13	Fe_2O_3	Precipitation	M	Ferric Nitrate	---	---
14	Fe_2O_3	Direct heating of metal nitrate	N	Ferric Nitrate	---	---

(F. N. = Ferric nitrate, Gly. = Glycine, A. N. = Ammonium nitrate, U = Urea and ODH = Oxalydihydrazide)

Above short listed samples of Fe_2O_3photo-catalyst were characterized by different physicochemical methods which include XRD, SEM, BET surface area, bulk density & diffuse reflectance spectroscopy.

Table 3 : The Values of powder density, surface area particle size& Energy gap of various samples of Fe_2O_3 photo-catalyst.

Sr. No.	Samples of Fe_2O_3	Powder density (gm/cm^3)	BET Surface area (m^2gm^{-1})	Particle Size in Nano meter	Particle Size (D) from XRD	Energy gap Eg (eV) from reflectance spectra
1	A	3.4800	50.6375	34.048	47.90	2.91
2	B	1.5746	81.5504	46.72	7.012	3.09
3	C	2.2684	17.4574	151.5	14.04	2.81
4	D	2.7438	32.8966	66.74	21.43	2.91
5	E	2.7949	48.0182	44.70	21.42	2.79
6	F	1.9575	34.3568	89.21	29.33	2.75
7	G	3.1900	11.9425	157.49	47.90	2.75
8	H	3.4800	18.3472	93.09	47.90	2.12
9	I	0.1566	6.5107	588.48A^0	47.90	2.12
10	J	6.3995	7.4740	125.44	47.90	2.12
11	K	4.8763	3.4386	357.90	29.33	2.12
12	L	3.8471	9.4320	165.30	21.42	2.25
13	M	0.05133	29.7468	392.95A^0	47.96	2.79
14	N	-----	-----	----	47.96	2.75

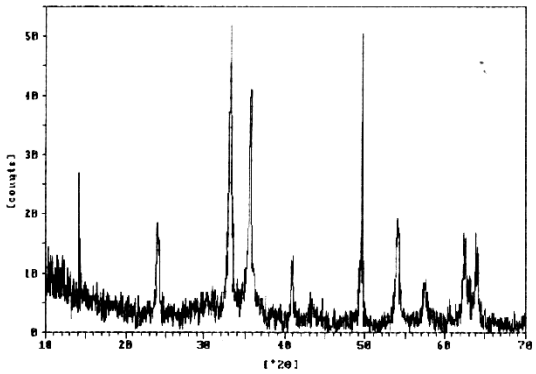


Fig. 1 : XRD pattern Sample 'A'

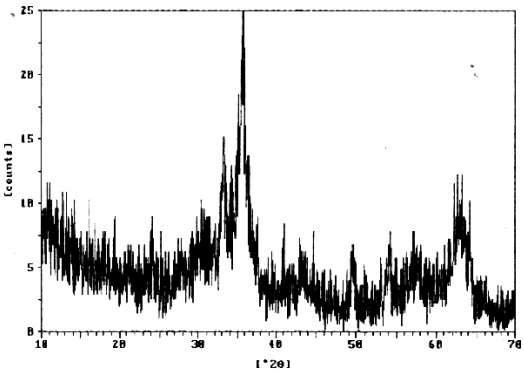


Fig. 2 : XRD pattern Sample 'B'

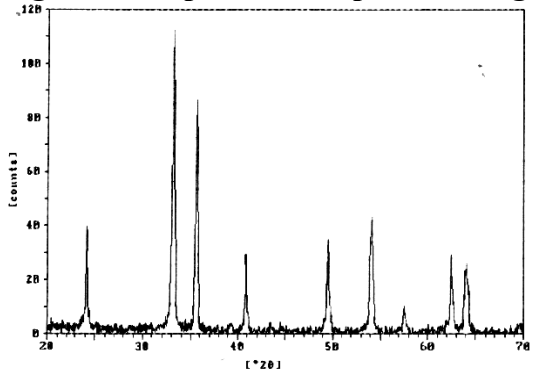


Fig. 3 : XRD pattern Sample 'C'

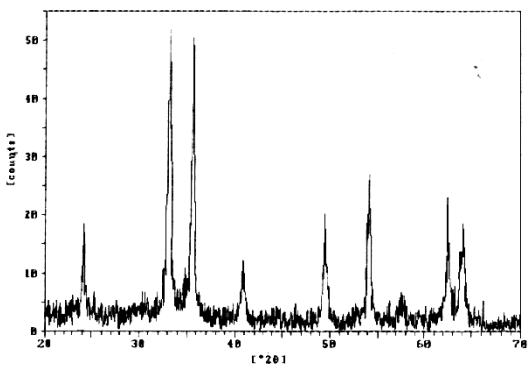
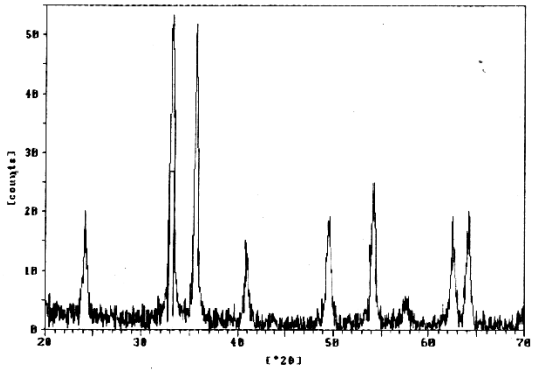


Fig. 4 : XRD pattern Sample 'D'



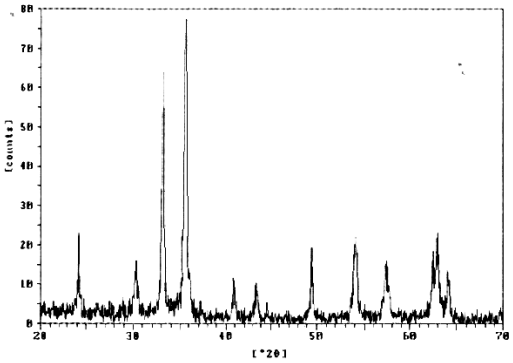


Fig. 5 : XRD pattern Sample 'E' **Fig. 6 : XRD pattern Sample 'F'**

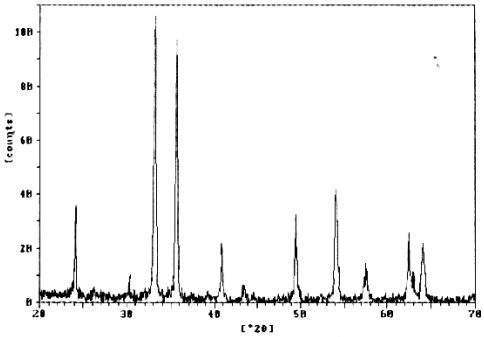


Fig. 7 : XRD pattern Sample 'G'

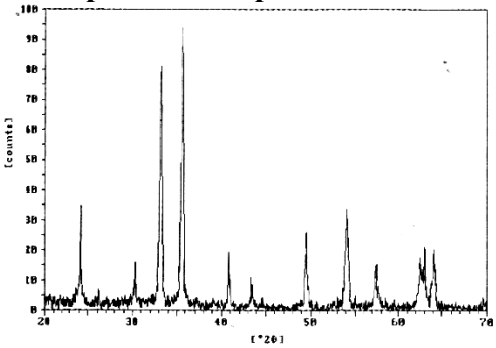


Fig. 8 : XRD pattern Sample 'H'

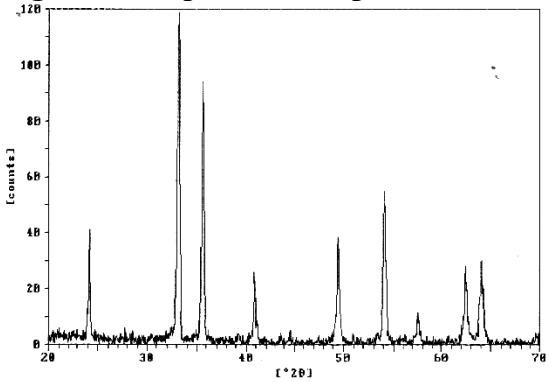


Fig. 9 : XRD pattern Sample 'I'

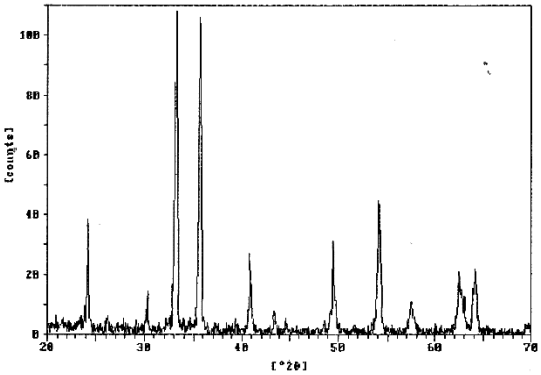


Fig. 10 : XRD pattern Sample 'J'

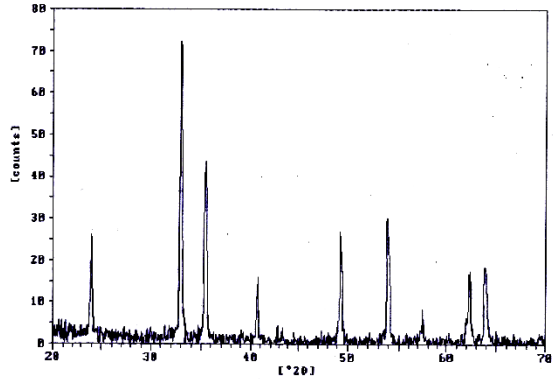


Fig. 11 : XRD pattern Sample 'K'

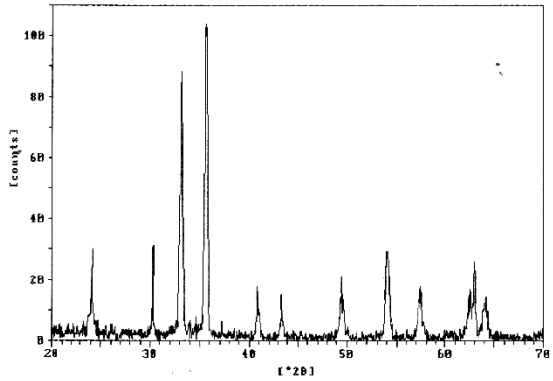


Fig. 12 : XRD pattern Sample 'L'

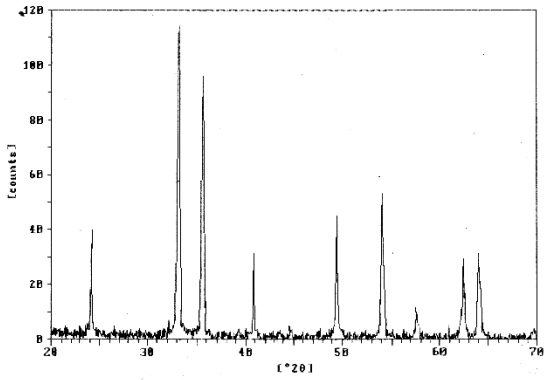


Fig. 13 : XRD pattern Sample 'M'

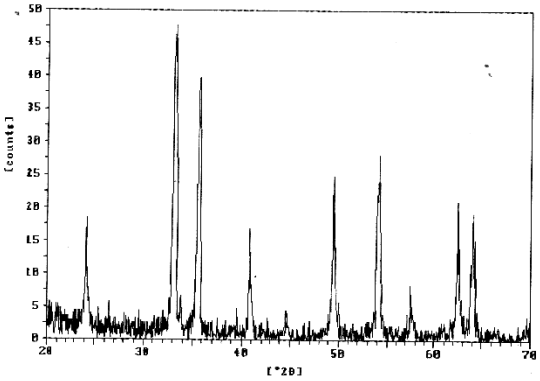


Fig. 14 : XRD pattern Sample 'N'

Some of the XRD pattern shows line broadening indicating that nanosized, high surface area Fe_2O_3 photo-catalyst has been formed e.g. Sample 'B'. The particle size have been evaluated from XRD studies and discussed in following section.

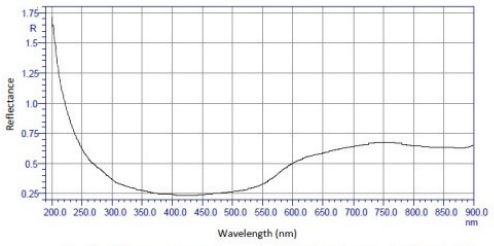


Fig. 15 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'A')

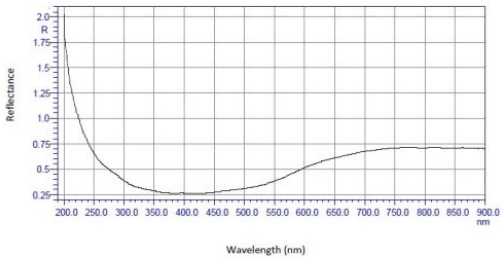


Fig. 16 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'B')

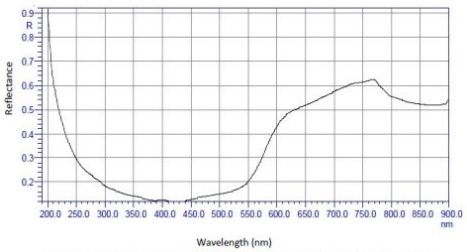


Fig. 19 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'E')

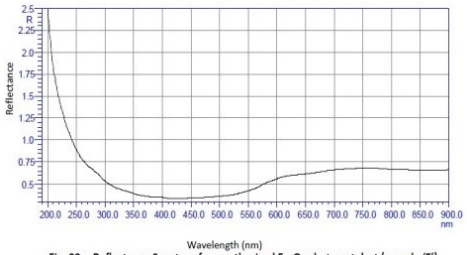


Fig. 20 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'F')

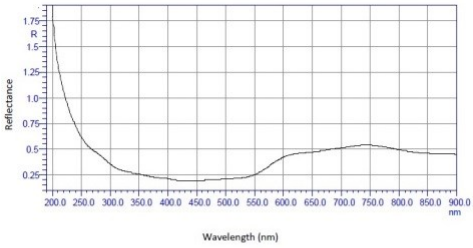


Fig. 17 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'C')

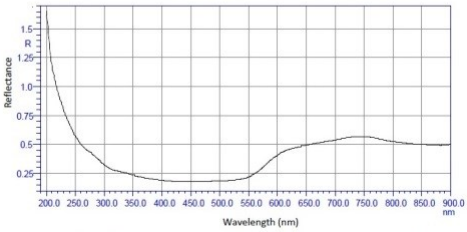


Fig. 18 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'D')

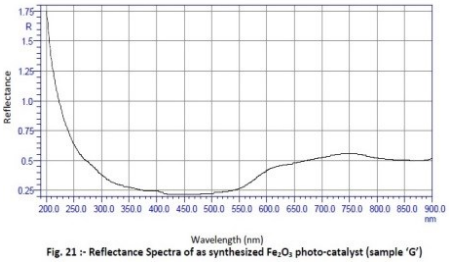


Fig. 21 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'G')

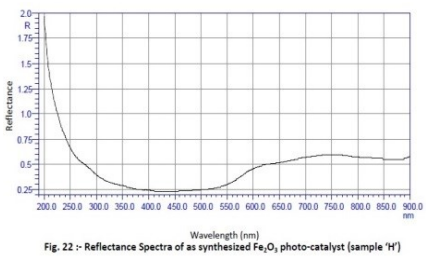


Fig. 22 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'H')

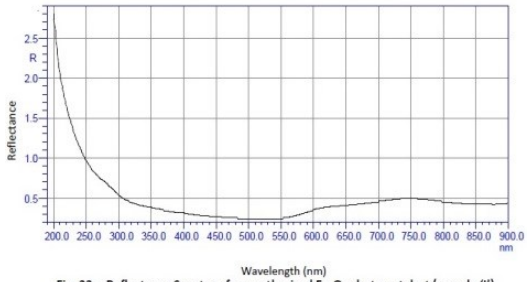


Fig. 23 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'I')

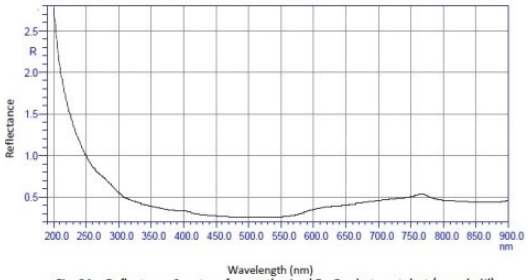


Fig. 24 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'J')

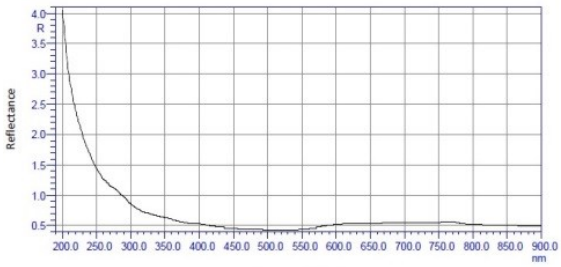


Fig. 25 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'K')

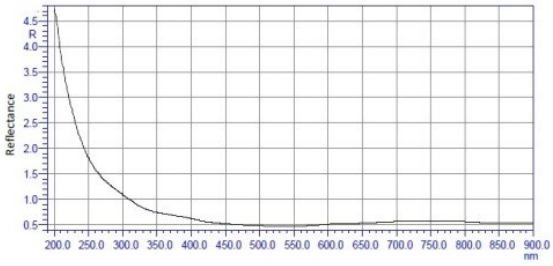


Fig. 26 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'L')

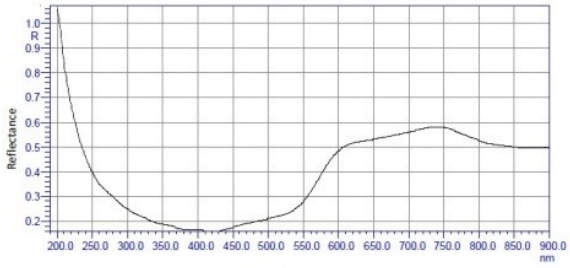


Fig. 27 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'M')

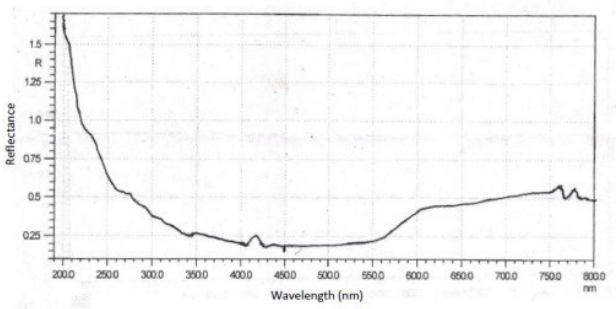
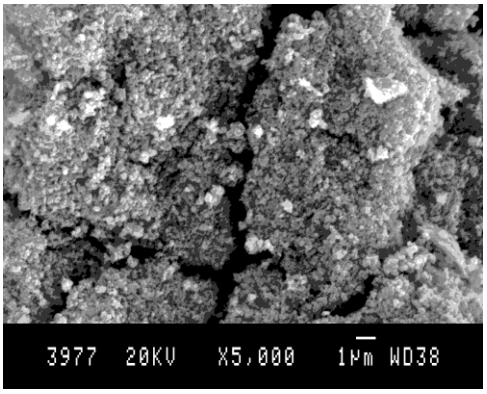
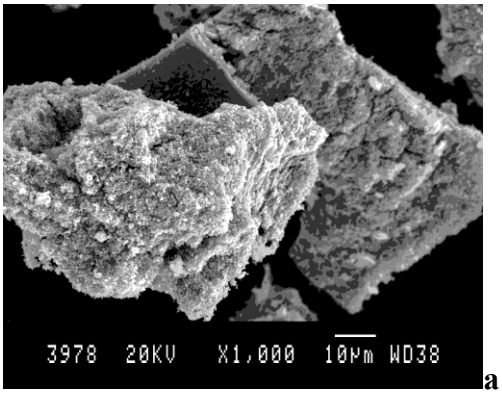


Fig. 28 :- Reflectance Spectra of as synthesized Fe_2O_3 photo-catalyst (sample 'N')





a

Fig. 29a &29b SEM micrographs of as synthesized Fe_2O_3 Photo-catalyst (Sample 'D')

Conclusion

Solution combustion synthesis is really a versatile, rapid & economic technique by which ferric oxide can be synthesized.BET surface area was found to be 32m2 gm-1 & bulk density was found to be 2.7438 gm cm-3Crystalline size from BET surface area and density was found to be 66.74 for sample D. Band gap from reflectance spectroscopy was found to be 2.91 eV.Fe2O3 can be used as photo catalyst.96 – 98 % COD removal was observed.Photo degradation can be carried out by solar light induced photo catalysis. Photo-catalyst synthesized is economic & environmentally benign material Photo catalyst material can be use for versatile & valuable treatment option for purification of diluted colored waste water effluents discharged.

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