

# Surface Modified MgFe Layered Double Hydroxide: An Efficient Photo Catalyst for Degradation of Methyl Orange

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**Abstract:-** Surface modified Mg-Fe layered double hydroxide materials by CTAB are used for photo catalytic degradation of methyl orange. Mg-Fe LDH (material-1) was prepared by co-precipitation method and material-2 was prepared by intercalation of CTAB into material-1. Further, calcination and surface modification of material-2 was done to get material-3. All these materials were characterized by FT-IR. Structure and composition was confirmed by XRD and SEM with EDX. Surface area of prepared material 1,2 and 3 was determined by BET analysis and the values of surface area are 28.54, 18.29 and 4.95m<sup>2</sup>/g and pore size is 10.6, 7.9 and 9.2 nm respectively. The band gap values obtained on the basis of DRS studies for materials-1,2 and 3 are 3.9 , 3.9 & 3.2 eV respectively.

Photo catalytic degradation of methyl orange using material 1, 2 & 3 in the presence of 10 W LED bulb was studied under identical conditions and progress of the reaction was monitored by UV-Vis spectrometer. The catalytic efficiency of material 3, 2 and 1 is 90%, 32%, 2% respectively. Decreasing in particle size after surface modification and enhanced mesoporous nature accounts for the highest catalytic efficiency of material -3 and it is cost effective easy to prepared and eco-friendly.

**Keywords:-** Heterogeneous catalyst, Mesoporous material, Surface modification of LDH, photo catalysis, degradation of methyl orange.

## I. INTRODUCTION

Azo dyes represent one-half of the dyes used in the textile industry. As reported, 20% of dyestuff is discharged directly into the environment by textile factories [1,2]. The decomposition of Azo dyes being difficult results in water pollution and serious environmental issues. New and effective treatment methods are needed for degrading methyl orange in order to reduce the amount of toxic and carcinogenic substances in industrial effluents [3]. This paved

the way for the development of new photo-catalyst with specific semiconductor properties which is able to promote advanced photo-oxidation [4]. LDH photo catalysts represent an appealing alternative to conventional semiconductors. High surface area, unique memory effect, low cost, eco-friendly features, versatility in chemical composition and morphology are some of the unique features which make LDH an effective photo-catalyst for degradation of organic pollutants in waste water [5,6]. Reports are available with bimetallic LDH as catalysts which showed positive results in degrading the methyl orange to a greater percentage but required light source consuming high energy and were not time efficient [7,8,9,10]. Looking into this drawback, we tried to design a photo catalyst which is eco-friendly and is highly effective in degradation of methyl orange in a short span of time under visible light and thus is energy efficient.

Two dimensional Layered Double Hydroxides(LDH) have attracted significant interest of the researchers due to their extra ordinary semiconductor properties. The layered double hydroxides are synthetic clay or hydroxalite like material in which positively charged metal hydroxides layers stack alternately with anion interlayer to form sandwich like structure which give them anion exchange properties [11,12,13]. They are represented by general formula  $[M^{2+} M^{3+} (OH)_2 X^+ (A^{n-})]_{x/n} \cdot yH_2O$ . A large number of LDH are produced by the combination of divalent cations, such as Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and trivalent cations like Al<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup>, La<sup>3+</sup> [14,15,16].

In the present study, we report the synthesis of Mg Fe layered double hydroxide by co-precipitation method which was further intercalated and surface modified by CTAB to improve the properties and efficiency of LDH materials. All the three materials were evaluated for their photo catalytic efficiency to treat methyl orange which is considered as one of the organic pollutants in textile industry.

## II. EXPERIMENTAL SECTION

### A. Materials and reagents

Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Ferric nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Cetyl ammonium bromide (CTAB), Sodium hydroxide (NaOH), Sodium bicarbonate ( $\text{Na}_2\text{CO}_3$ ), Methyl Orange were purchased from CDH. All chemicals used were of analytical grade and used as received without purification. Deionized water was used in all experiments.

### B. Apparatus

Powder X-ray diffraction measurements were performed on Bruker D<sub>8</sub> Advanced X-ray diffractometer under vacuum, using Cu K $\alpha$  radiation ( $\lambda=0.154\text{nm}$ ) with  $2\theta$  angle ranging from  $10^\circ$  to  $70^\circ$ . Interpretations were done using Match software for XRD. Fourier transform infrared (FTIR) spectra were recorded using Bruker FT-IR spectrometer in the range  $4000$  to  $400\text{ cm}^{-1}$ . Scanning electron microscopy (SEM) images were taken using JEOL JSM 5600. EDX (Energy Dispersive X-Ray Analysis) was performed using “Bruker” made X-Flash 6130 EDS attachment and “Esprit” Software. UV-Visible spectral studies were performed using Perkin Elmer Lambda 25 UV-Visible Spectrometer. BET analysis performed by Micro Meritics Instrument Corp. Gemini VII version 3.03. Diffuse Reflectance Spectra (DRS) were recorded by Model-UV-3000.

### C. Synthesis of MgFe Layered double hydroxide (material 1) by co-precipitation method

1M aqueous solution each of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were mixed followed by drop wise addition of 1M NaOH with continuous stirring for 6h to maintain pH-10<sup>[17]</sup>. The resulting brown suspension was centrifuged at 6000 rpm, washed with distilled water several times oven dried at  $60^\circ\text{C}$  for 6 h. to get material 1. this preparation of material 1 is reproducible with the 98% yield.

### D. Preparation of surface modified Mg-Fe LDH by CTAB

1M solution each of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dispersed into 100mL of deionized water. In another beaker, 0.3 mg of CTAB was added to  $\text{Na}_2\text{CO}_3$  (1mmol) and then mixed the contents of beaker by stirring. 1M solution of NaOH was added drop-wise with vigorous stirring at  $60^\circ\text{C}$  for 6 h to maintain pH-10.<sup>[18]</sup> The light brown colored precipitates (material 2) were obtained after centrifugation at 6000rpm for 10 minutes, washed with water several times and then oven dried at  $70^\circ\text{C}$  for 5 h. to get material -2.

Material 2 was further calcinated at  $475^\circ\text{C}$  for 4h in muffle furnace. Then it was suspended in 50ML solution which containing 1g of CTAB,  $\text{Na}_2\text{CO}_3$  (1mmol of 10ML) and NaOH (1M of 10ml), stirred for 4 h at  $60^\circ\text{C}$ , and then refluxed for another 4 h to obtain light brown powder (material-3) with 96% Yield.

### E. Procedure for photo catalytic activity for degradation of methyl orange.

In order to evaluate photo catalytic activity, 0.4 mg of catalyst was added to the aqueous solution of methyl orange (100 ML of 50mg/L). Solution was stirred in dark for 30 minutes to establish the adsorption desorption equilibrium. Then, the reaction mixture was irradiated with visible light using 9W LED Philips lamp Fig-1 and the progress of the reaction was monitored by observing change in concentration of methyl orange after fixed interval of time by UV spectrometer<sup>[19]</sup>. The blank experiment was also carried out by the same procedure without adding any catalyst.

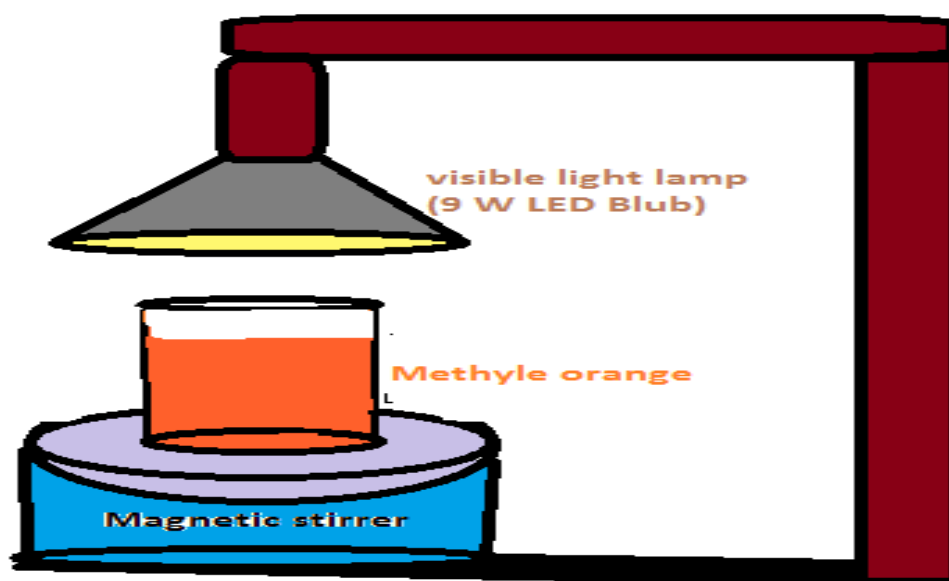


Fig. 1: Experimental set-up for photo catalytic studies

### III. RESULTS AND DISCUSSION

#### A. Structural characterisation

##### ➤ XRD Analysis

The PXRD pattern of material 1, 2 & 3 are shown in fig-2 respectively matched with (JCPDS card no.70-2150)<sup>[20]</sup>. The presence of more intense and sharp peaks at  $2\theta = 10.84^\circ$  &  $22.5^\circ$  corresponding to (003) and (006) planes show basal spacing of material-1. The reflection of planes (009) (015) (018) and (110) at  $2\theta = 34^\circ, 39^\circ, 41^\circ$  indicate well crystallized hydroxylated like structure with hexagonal lattice<sup>[21]</sup>. The basal interlayer spacing corresponding to (003) plane was calculated for all the three materials and results are listed in table-1. The lattice parameters “a” and “c” were calculated using  $d_{003}$  and  $d_{110}$  reflection respectively shown

in table -1. The parameter “a” shows the distance of cation-cation in the layers and parameter “c” shows thickness of the layers.<sup>[22,23]</sup> The basal spacing of material-1 was found to be 8.1Å. However, intercalation of CTAB into LDH resulted in increased basal spacing (8.61 Å) which was confirmed by high crystallinity of material-2 shown in (fig-2b). In material-3 the basal reflection peak slightly shifted to higher angle from  $2\theta = 10.84^\circ$  to  $2\theta = 11.07^\circ$  in fig-2c and basal space decreased to 8.02Å and sharp peaks at  $2\theta = 22^\circ$  observed in material-3. No change was observed in “a” and “c” parameter of material-3 which confirms the adsorption of CTAB molecules on the surface of LDH. The presence of peaks at  $2\theta = 27^\circ, 31^\circ$  &  $45^\circ$  (fig-2 b & c) corresponds to that of CTAB which is seen to be absent in Fig-2a.

S. NO.	Samples	Particle size (nm)	Basal spacing in Å	Lattice parameter (a=b) in Å	Lattice parameter (c) in Å
1	Material-1	25.7	8.13	3.08	24.39
2	Material -2	53.06	8.61	3.04	25.83
3	Material-3	46.26	8.02	3.08	24.09

Table 1: Structural parameters of LDH materials calculated using Scherrer Equation.

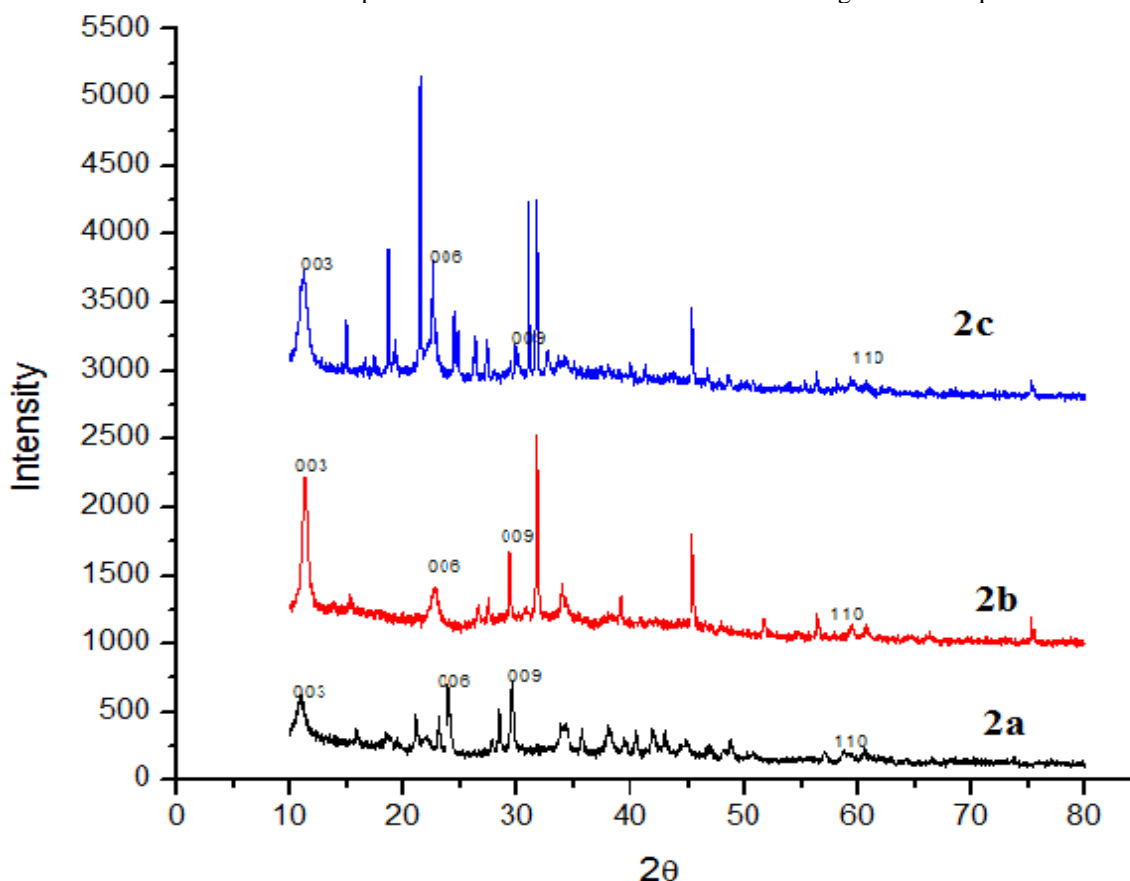


Fig. 2: PXRD patterns of (a) material -1(b) material-2(c) material-3

##### ➤ FT-IR Analysis

The FT-IR peak assignment of material 1, 2 & 3 are summarised in table -2<sup>[23,24,25,-36]</sup> The peak observed at 2917 and 2849  $\text{cm}^{-1}$  confirms intercalation of CTAB in material-

2. The presence of sharp and intense peaks at 2917, 2849  $\text{cm}^{-1}$  shows all  $-\text{CH}_2$  of alkyl chain in trans configuration which confirms attachment of CTAB on the surface of LDH material.

Material	Wave number (cm <sup>-1</sup> )	Assignment of IR peaks	Ref
Material-1	3696	O-H stretching of free hydroxyl group	[24]
	3400-3200	O-H stretching of interlayer hydroxyl group	[24]
	1632	Bending vibration mode of water molecules	[23]
	1439	Vibration of nitrate ions in interlayer of LDH material.	[23]
	879	Metal-oxygen stretching and bending vibration modes.	[28,30,31]
Material-2	3331	Electrostatic interaction between nitrogen of CTAB and hydroxyl group.	[29]
	2917 & 2849	Asymmetric & symmetric stretching of (-CH <sub>2</sub> ) of alkyl chain .	[25,26]
	1418 & 1479	Symmetric mode of vibration of the methylene moiety (N <sup>+</sup> --- CH <sub>3</sub> )	[27]
	1351	Vibration of carbonate ions in interlayer of LDH .	[25]
Material-3	3500-3400	Stretching and vibration mode	[26]
	3017	Anti-symmetric vibration mode	[29]
	2917 & 2849	Sharp & peaks show all -CH <sub>2</sub> of alkyl chain in trans configuration.	[27]
	1467	Anti-symmetric vibration mode	[29]
	1347	Lateral interaction of CH <sub>2</sub> between adjacent alkyl chain	[32,33,34,35, 36]
	910	Anti-symmetric vibration mode between C of alkyl chain and N of ammonium moiety	[29]

Table 2: Assignment of IR peaks for material-1,2 & 3.

➤ UV-Vis Diffuse Reflectance Spectroscopy (DRS)

The UV-Vis DRS spectra of material-1, 2 & 3 were recorded by UV-Vis spectrometer shown in fig-3. Using the absorption spectrum data, the band gap of prepared materials is calculated by Tauc equation<sup>[37,1]</sup>.

$$\alpha \quad hv = A \quad ( \quad hv \quad - E_g ) \quad n/2 \quad (1)$$

$\alpha$  = absorption co-efficient = light frequency

A = proportionality constant  $E_g$  = band gap energy  $n = 1/2$  responds direct transition.

$n = 2$  responds indirect transition

Optical transition for all the materials is indirectly allowed. A plot of  $(\alpha hv)^2$  against  $h\nu$  photon energy was plotted for all the three materials and the energy of the band gap was estimated from the intercept of the tangent<sup>[38]</sup>. The band gap ( $E_g$ ) of material -1, 2 & 3 were found to be 3.9, 3.9, and 3.2 eV as shown in fig-4. The results show that band gap energy of material -3 is less than that of materials-2, 1 which makes material-3 a better photo-catalyst.

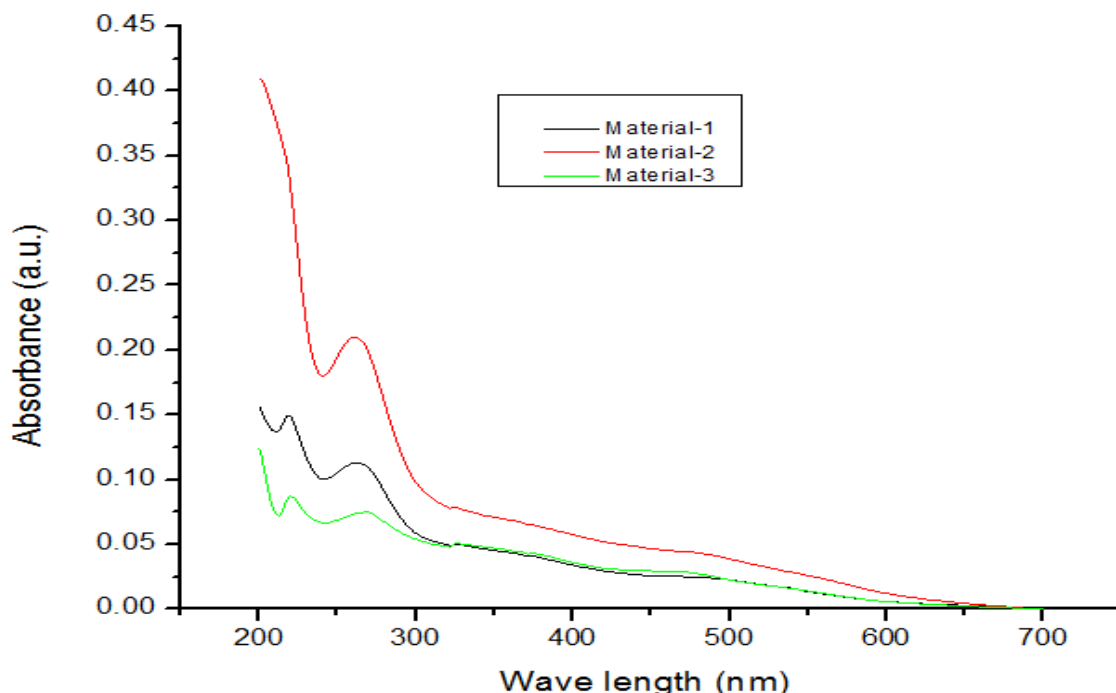


Fig. 3: UV-vis adsorption spectra of materials -1,2 and 3.

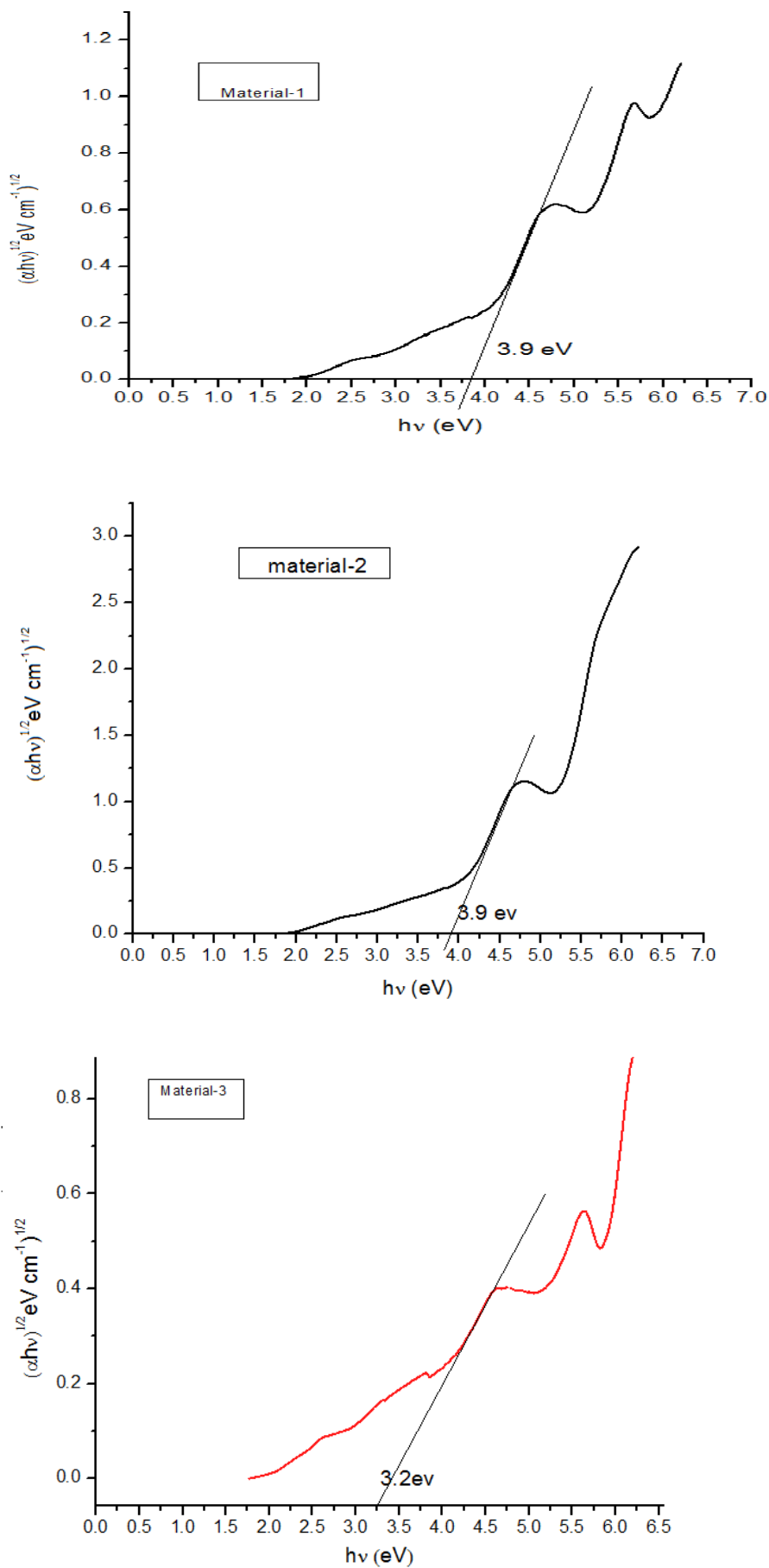


Fig. 4: Band gap energy of (a)Material-1 (b) Material-2 (c) Material- 3.

*B. Morphological analysis*

➤ *SEM & EDX analysis*

The morphological features of LDH material 1, 2 & 3 are shown in Fig-5 respectively. Mg-Fe LDH possesses fluffy agglomerated numerous clusters as depicted<sup>[39]</sup> in Fig-5a. After intercalating CTAB in Mg-Fe LDH, a change in morphology (fig -5b) is observed which is due to

interactions taking place between CTAB & LDH. (Fig-5c) shows excess CTAB draped over the surface of material.

In order to find the composition of all the three materials, EDX analysis was performed and the results are summarised in table -3 and the spectral data is shown fig-6 for material 1,2 & 3 respectively.

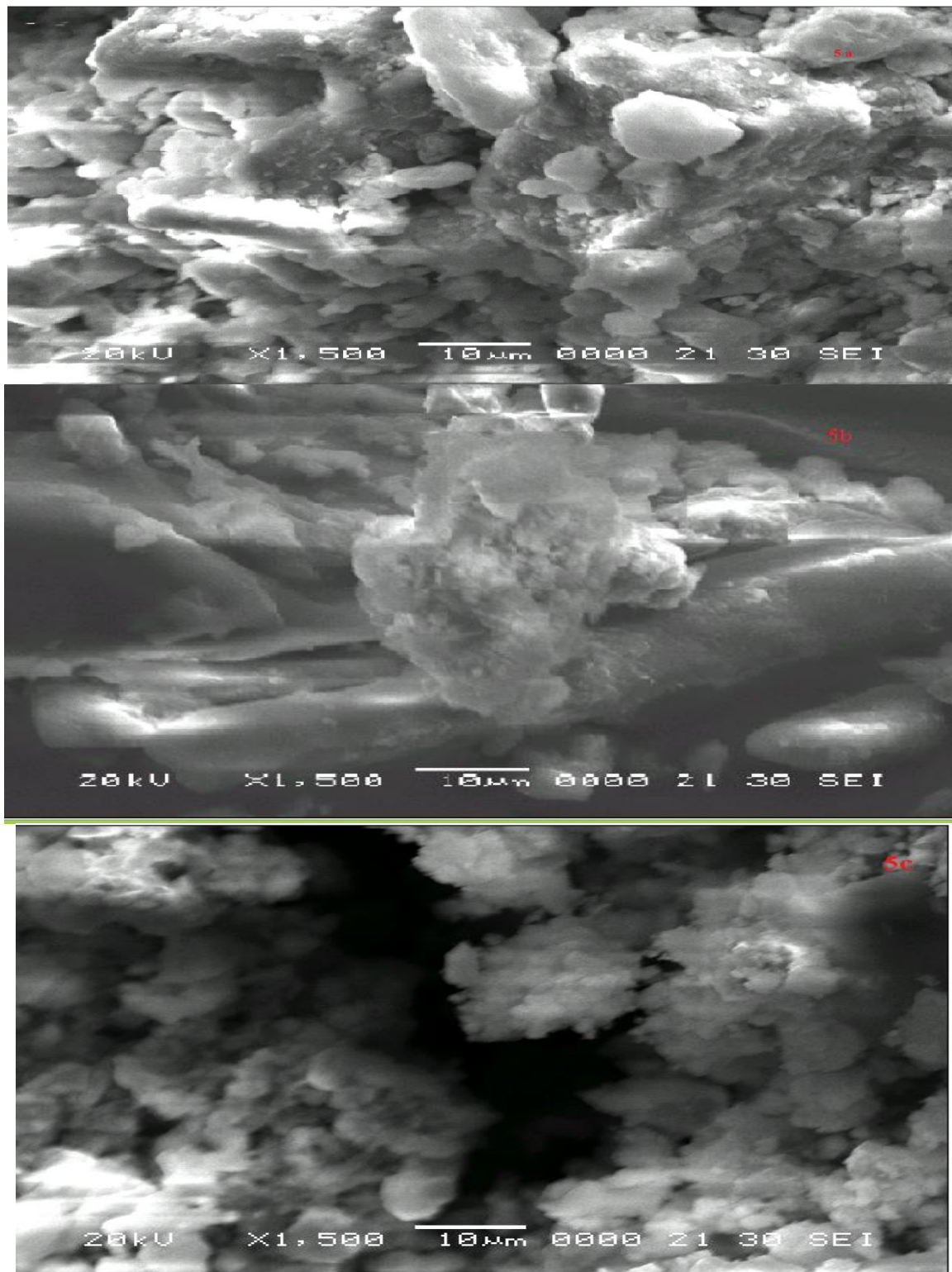


Fig. 5: SEM IMAGES OF (a) material -1 (b) matrial -2 (c) material -3

ELEMENTAL % BY WEIGHT					
Samples	Mg	Fe	C	O	Br
Material-1	9.04	3.84	—	58.38	—
Material-2	13.90	14.10	14.78	47.37	5.32
Material-3	14.06	14.21	12.34	52.49	9.24

Table 3: EDX ANALYSIS OF SAMPLES

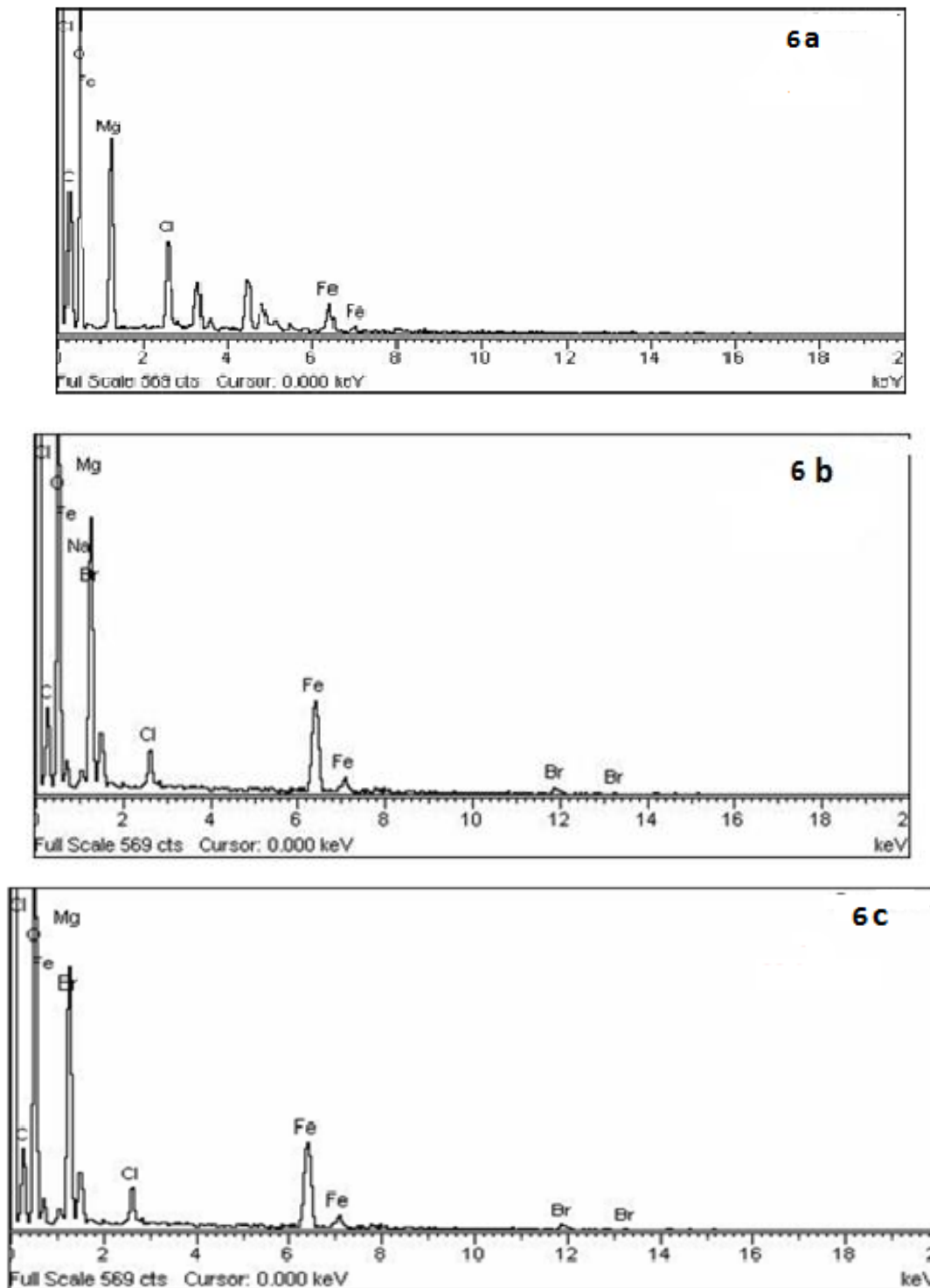


Fig. 6: EDX SPECTRUM OF (a) material-1 (b) material-2 (c) material-3

Samples	BET surface area (m <sup>2</sup> /g)	BJH pore size (nm)	BJH pore volume (cm <sup>3</sup> /g Å)
Material -1	28.54	10.63	0.0794
Material -2	18.29	7.98	0.0498
Material-3	4.95	9.27	0.0135

Table 4: BET and BJH analysis results of material-2 and 3

N<sub>2</sub> Adsorption- desorption measurements were performed in order to study the surface area and porosity of material 1,2 and 3 as shown in fig-(7). According to the IUPAC classification (2-50nm),<sup>[40,41.]</sup>the nitrogen adsorption desorption isotherm of material-2 belongs to a typical type (ii) with a very narrow hysteresis loop(H<sub>3</sub>) that is typical for pore with narrow mouth like mesopores. N<sub>2</sub> adsorption –

desorption curve for Material-3 shows type (iv) with hysteresis loop(H<sub>3</sub>) that is typical aggregates of plate like particles forming slit like mesopores. Surface area, pore size and pore volume of materials shown in table-4. Results show that surface area, pore size and pore volume of materials decreases after intercalation and surface modification.

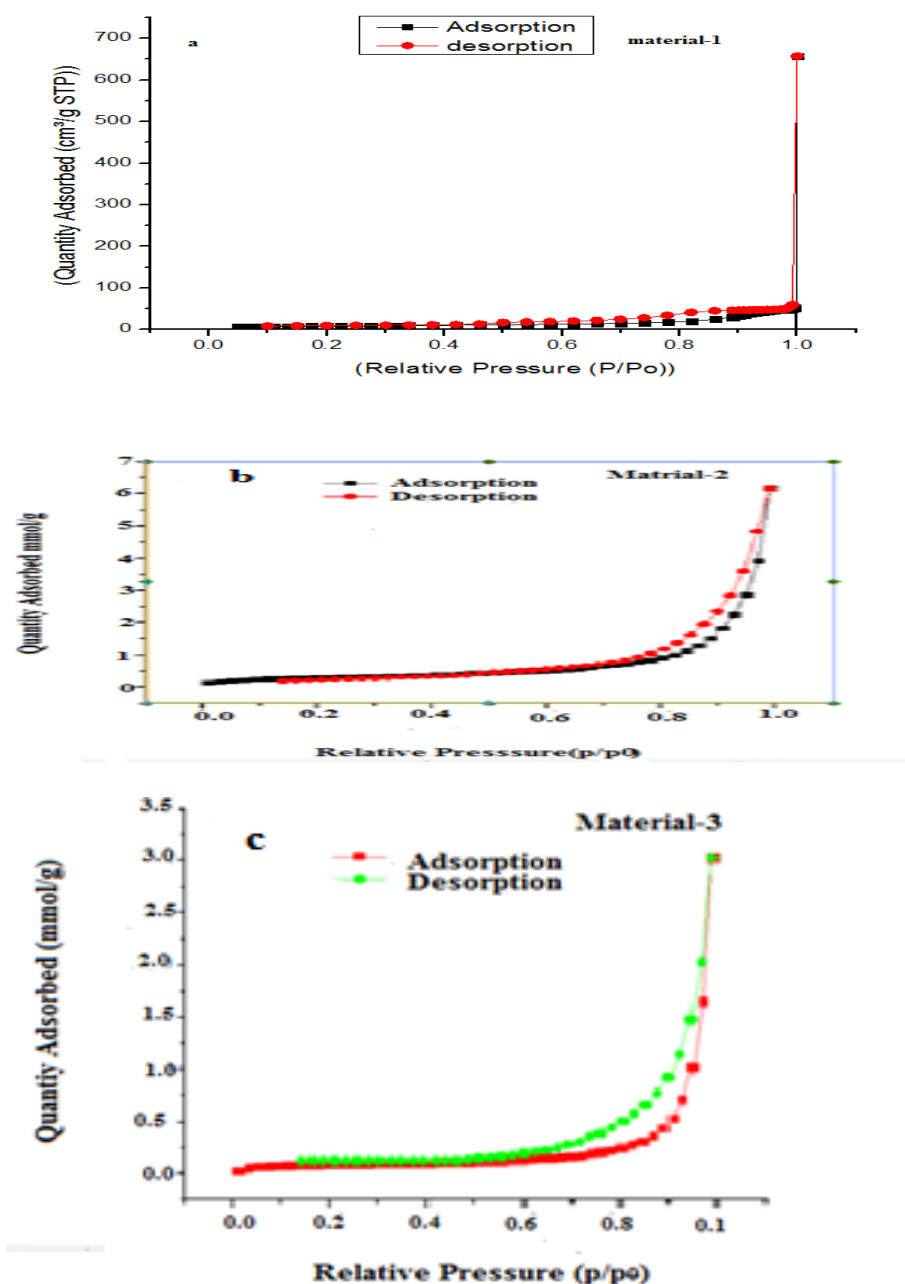


Fig. 7: Nitrogen adsorption-desorption isotherm and Barret- JoynerHalenda (BJH) pore size distribution for (a)material-1 (b) material-2 (c) material-3.



C. Photo catalytic activity

The photo catalytic degradation of methyl orange was performed by the prepared material 1, 2 & 3 in order to evaluate the photo catalytic efficiency of these materials. The progress of the reaction was monitored by UV-Visible spectra. As observed, the material -1 did not show degradation property and material-2 can degrade only 32% methyl orange in 120 minutes fig-8a under visible light irradiation whereas under identical condition, the material-3 degrades up to 90% methyl orange in 65 minutes fig-8b. The higher degradation efficiency of material 3 can be attributed to the presence of CTAB at the surface which enhances the

surface area for adsorption [38]. In material-2, CTAB is intercalated in between LDH, hence less amount of methyl orange gets adsorbed on CTAB which results in slow & less degradation of dye. As clearly seen from (fig -8a & 8b), the intensity of absorption peak at 465 nm decreased with time after visible light irradiation which finally disappeared indicating cleavage of azo group (N=N) of methyl orange [42,43]. The de-colorization and photo catalytic degradation % of materials-2 & 3 at specific time interval have been calculated by following formula [29] and the results are shown graphically in fig-9 respectively.

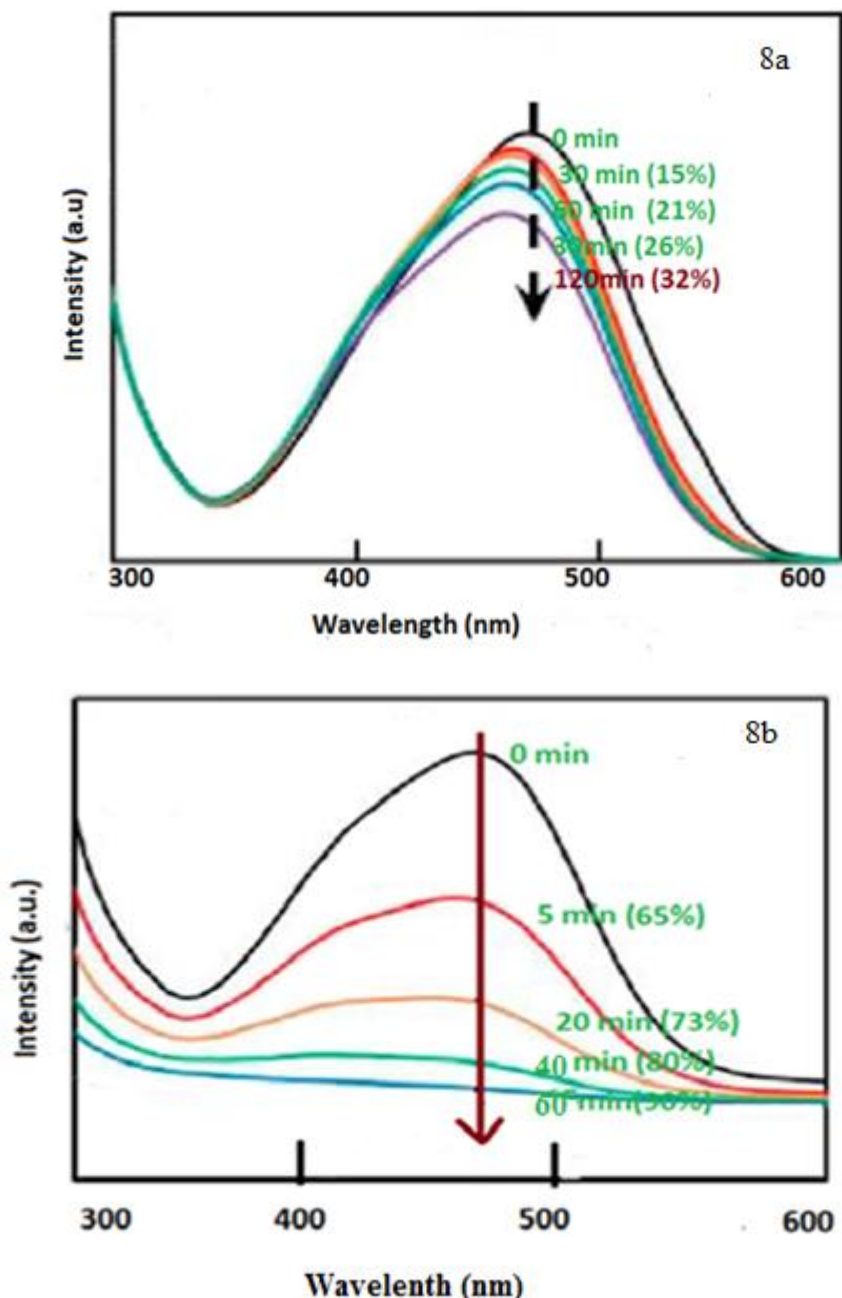


Fig. 8: UV spectra showing photo-catalytic degradation of methyl orange using (a) CTAB intercalated (b) surface modified layered double hydroxide material.

$$\text{Degradation \% of MO} = \frac{C_n - C_t}{C_n} * 100 \quad (2)$$

Where  $C_n$  is initial concentration of methyl orange and  $C_t$  is concentration after degradation test. [44]

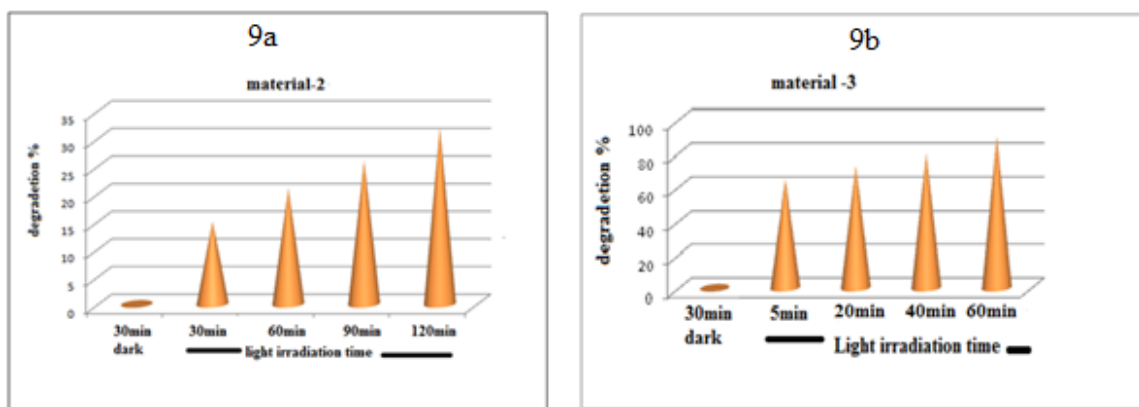
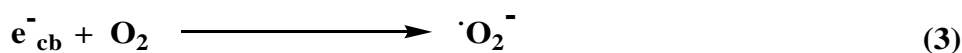
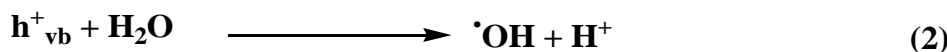


Fig. 9: Graphical representation of Degradation % of methyl orange with time for (a) Material-2 (b) Material-3

The photo catalytic activity of material-2 and 3 are strongly influenced by its particle size and specific surface area. From the XRD results, the particle size of material 3 decreased from 53 nm to 46nm after surface modification of material-2 by CTAB which led to the enhancement of the photo catalytic performance and BET results confirmed the mesoporous nature of material-3. The mesopores are responsible for better diffusion of the dye molecules on the catalyst surface and its further transportation resulting in increase in the photo catalytic performance.

#### D. Mechanism

According to the experimental data, a plausible mechanism for photo catalytic degradation of methyl orange is proposed and discussed below.<sup>[45,46]</sup> On irradiation of visible light at 465 nm, the catalyst absorb the light which results in ejection of  $e^-$  from valence band to conduction band, thereby generating a hole in the valence band. The electron of the conduction band and the hole of valence band then generate oxidizing radicals  $\cdot O_2^-$  &  $\cdot OH$  respectively shown in scheme-1. Photon generated electrons ( $e^-$ ) and hydroxyl radicals ( $\cdot OH$ ) are believed to degrade methyl orange.<sup>[47]</sup>



#### ➤ Scheme-1 Mechanism for formation of hydroxyl and peroxy free radical

In our case, it is the hydrated electron which is responsible for the degradation of azo dye. The hydrated electron behaves as a nucleophile and attacks the azo connected benzene ring as it has low electron density. This forms radical anion which is highly unstable and gets protonated. It then leads to the breaking of  $N=N$  and finally form p-amino N, N dimethylaniline and 4- aminobenzene sulfonic acid as an intermediate. Their formation can be justified by the presence of absorption peaks at 284 nm & 243 nm respectively (fig. 8b). These intermediates further decomposed into carbon dioxide and water indicated by

disappearance of peaks and confirm the photo-degradation of methyl orange.

#### E. Recycling of catalyst

Recovery test of material-3 is shown in fig-10, multiple runs for the degradation of methyl orange upon material-3 were performed. After five runs of photo-catalytic reaction, the photo-catalytic efficiency decreases by 8% and the catalytic ability of material completely recovered after washing with distilled water. There is no loss in catalytic activity. It indicates that surface modified material-3 possess high efficiency and stability and can be used upto five runs.

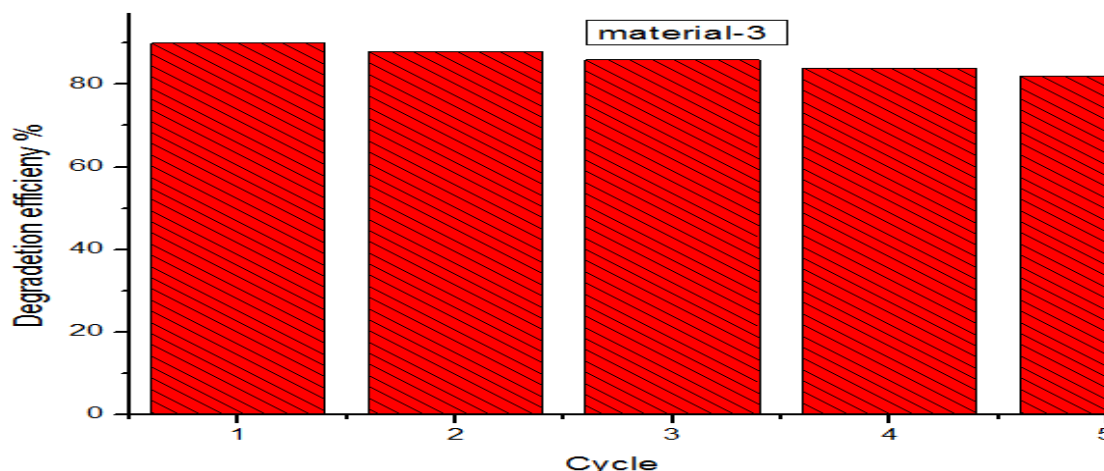


Fig. 10: Catalytic efficiency of material-3

#### IV. CONCLUSION

In this piece of work we used a convenient and viable method to develop an efficient heterogeneous catalyst by functionalisation of LDH by CTAB. Interaction between CTAB and MgFe LDH was confirmed by FT-IR and XRD. SEM images and BET studies confirmed the mesoporous nature of the material. The surface modified material (material-3) efficiently promoted the photo catalytic activity towards the degradation of methyl orange (up to 90%). Mesoporosity of the materials allowed to rapid diffusion and supplies the efficient transport pathway for photo generated free radicals, which is supportive for the photo catalytic activity. UV-Visible diffuse reflectance spectroscopy (DRS) confirmed that the band gap of material-3 which is lower than material 2. Presence of CTAB on the surface, markedly improves the adsorption capacity and hence photo catalytic oxidation of dye molecule. Photo catalytic efficiency of material -3 has increased 3 fold in comparison to CTAB intercalated LDH (material-2) under identical conditions. It can be concluded that material-3 possesses outstanding capabilities and hence played a key role in the removal of dye molecules in aqueous medium.

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