

# CHAPTER 2

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## MATERIALS AND METHODS

This chapter covers the details of all chemicals and experimental techniques that have been used in the study. The procedures of sample preparation and details of characterization techniques are described herein. The procedures of various reactions employed in this investigation are described in details.

### 2.1 Materials

The chemicals and solvents used in the present study with the suppliers are listed below:

Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NaOH, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH, HCl, absolute ethanol were purchased from Merck, Mumbai; nitromethane was purchased from G.S. Chemicals Testing Lab & Allied Industries, New Delhi; silica gel, iodine and solvents were purchased from RANKEM, New Delhi. Methyl Orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S), bromothymol blue (C<sub>27</sub>H<sub>28</sub>Br<sub>2</sub>O<sub>5</sub>S), eriochrome black T (C<sub>20</sub>H<sub>12</sub>N<sub>3</sub>NaO<sub>7</sub>S), methylene blue (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S·2H<sub>2</sub>O), rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>) and methyl red (C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>) were purchased from RANKEM, New Delhi. Congo Red (C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>) was purchased from HIMEDIA, Mumbai. All the chemicals were used without further purification and dye solutions were prepared using deionized water.

### 2.2 Synthetic procedures

#### 2.2.1 Synthesis of NiMgAl LDHs with variable composition

Five different LDHs were prepared by varying molar ratio of divalent cations, Ni<sup>2+</sup>/Mg<sup>2+</sup> in NiMgAl LDHs by keeping molar ratio of (Ni<sup>2+</sup> + Mg<sup>2+</sup>)/Al = 3. LDHs were prepared by co-precipitation of a aqueous solution of metal nitrates- Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with another aqueous solution of NaOH and Na<sub>2</sub>CO<sub>3</sub> at a constant pH of (10±0.2). After the formation of the precipitate, the gels were aged at 80 °C for 24h. The solid product was then centrifuged, washed several times with distilled water until pH of the filtrate was 7 and then dried in the oven at 80 °C for 15h. For convenience, the as-

prepared LDHs were renamed as LDH1, LDH2, LDH3 and LDH4 according to the Ni:Mg:Al molar ratio as shown in box below:

LDHs	Ni:Mg:Al molar ratio
LDH1	0:3:1
LDH2	1:2:1
LDH3	1.5:1.5:1
LDH4	2:1:1

### 2.2.2 Synthesis of CuMgAl LDHs

A co-precipitation method was used to synthesize CuMgAl LDHs with (Cu+Mg):Al ratio of 3:1. Here, we have changed the Cu:Mg concentrations and accordingly denoted as CuMgAl1, CuMgAl2, CuMgAl3, and CuMgAl4 as shown in the box below. The synthesis was carried out by adding two solutions of one containing a mixed salt solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and another containing aqueous solution of NaOH and  $\text{Na}_2\text{CO}_3$  under continuous stirring. During the addition, pH of the solution was kept constant at 10 using 1M NaOH and stirred for 1h at room temperature. After that, the mixture was aged in the mother liquor at 80°C for 24h. The resulting products were filtered, washed thoroughly with deionized water until pH of the filtrate was 7 and dried at 80°C in the oven for 15h.

LDHs	Cu:Mg molar ratio
CuMgAl1	0:3
CuMgAl2	1:2
CuMgAl3	1:1
CuMgAl4	2:1

### 2.2.3 Synthesis of NiAl LDHs using sonochemical method

NiAl LDH with molar ratio of Ni/Al = 3 was synthesized using co-precipitation method followed by ultrasound irradiation under controlled pH. The synthesis was carried out by the addition of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  into distilled water under vigorous stirring at 25 °C. The pH of the mixture was adjusted to 10 using  $\text{NH}_4\text{OH}$  solution. The resultant solution was then immediately subjected to ultrasonic irradiation for 1h at 65 °C [1]. The apple green colored solid product was then centrifuged, washed several times with distilled water until pH of the filtrate was 7. The obtained product was dried at 60 °C overnight and named as NiAl-S<sub>1</sub> LDH. The ultrasonic irradiation time was also varied for 0.5 and 2h and accordingly, the products were named as NiAl-S<sub>0.5</sub> and NiAl-S<sub>2</sub> LDH. For comparison, NiAl LDH was also synthesized under normal reflux condition and named as NiAl-R LDH. For convenience, the renaming of the samples is shown in the box below:

LDHs	Ultrasonic irradiation time
NiAl-R	Normal reflux
NiAl-S <sub>0.5</sub>	0.5h
NiAl-S <sub>1</sub>	1h
NiAl-S <sub>2</sub>	2h

### 2.2.4 Synthesis of ZnFe LDH

ZnFe LDH was synthesized by using co-precipitation method with Zn/Fe molar ratio of 3. An aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added dropwise into a two necked round bottom flask containing an another aqueous solution of NaOH and  $\text{Na}_2\text{CO}_3$  under vigorous stirring at room temperature and constant pH of  $10 \pm 2$ . The pH of the mixture was adjusted by using 1 M NaOH. The resulting solution was then allowed to stir for 6h at room temperature. The obtained precipitate was filtered, washed several times with deionized water until pH of the filtrate was 7 and dried in oven overnight at 80 °C.

### 2.2.5 Synthesis of $M^{2+}$ MgAl ( $M^{2+} = Ni^{2+}$ or $Co^{2+}$ ) LDHs and their derived mixed oxides

LDHs were prepared by co-precipitation of an aqueous solution of metal nitrates –  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Mg(NO_3)_2 \cdot 6H_2O$  and  $Al(NO_3)_3 \cdot 9H_2O$  with an aqueous solution of NaOH and  $Na_2CO_3$  at a constant pH of  $(10 \pm 0.2)$  with a  $M^{2+}/M^{3+}$  ratio of 3 : 1. After the formation of the precipitate, the gels were aged at 80 °C for 24h. The solid product was then centrifuged, washed several times with distilled water until pH of the filtrate was 7 and then dried in the oven at 80 °C for 12h. In MgAl LDH,  $Mg^{2+}$  was partially substituted with  $M^{2+}$  ( $M^{2+} = Ni^{2+}$  or  $Co^{2+}$ ) keeping the metal ratio ( $M^{2+}Mg/Al^{3+}$ ) = 3 and  $Mg^{2+}/M^{2+} = 1$ .

The precursor LDH samples were calcined at 450 °C for 6h in flowing air and at the heating rate of 2 °C  $min^{-1}$  to obtain mixed oxides, accordingly renamed as MgAl (O), NiMgAl (O) and CoMgAl (O), respectively.

### 2.2.6 Synthesis of NiMgAl LDHs derived mixed oxides

The precursor NiMgAl LDHs with variable compositions were synthesized according to the procedure described in 2.2.1 section. The precursors were subjected to thermal treatment at 450 °C for 6h to obtain mixed oxides. These mixed oxides were labeled with respect to their precursors as LDH1 (O), LDH2 (O), LDH3 (O), LDH4 (O) and LDH5 (O), respectively as shown in box below:

Precursor LDHs	Ni:Mg:Al molar ratio	LDHs derived mixed oxides
LDH1	0:3:1	LDH1 (O)
LDH2	1:2:1	LDH2 (O)
LDH3	1.5:1.5:1	LDH3 (O)
LDH4	2:1:1	LDH4 (O)
LDH5	3:0:1	LDH5 (O)

## 2.3 Characterization techniques

### 2.3.1 Powder X-ray diffraction (PXRD)

The powder X-ray diffraction (XRD) is an analytical technique primarily useful for identification of crystalline nature of the material along with the crystal structure and phase composition. It also provides valuable information on atoms arrangements within the crystal and unit cell dimensions. The powder XRD patterns were recorded on a Rigaku Multiflex instrument using a nickel-filtered  $\text{CuK}\alpha$  ( $\lambda = 0.15418$  nm) radiation source set at 30 kV and 15 mA with step of  $0.05^\circ$  and a scintillation counter detector. The intensity data were collected over a  $2\theta$  range of  $5\text{--}70^\circ$ .

The crystallite size was calculated using the Scherrer equation,

$$D = B\lambda/\beta_{1/2} \cos \theta \quad (2.1)$$

where,  $D$  is the average crystallite size,  $B$  is the Scherrer constant (0.89),  $\lambda$  is the wavelength of the X-ray beam,  $\beta_{1/2}$  is the fullwidth at half-maximum (FWHM) of the diffraction peak and  $\theta$  is the diffraction angle.

The relative crystallinity (%) of the samples were determined by integrating the XRD peaks using the following formula,

$$\text{Relative Crystallinity (\%)} = (A_S \times 100)/A_R \quad (2.2)$$

where,  $A_R$  = Integrated area of the reference material under the peaks between a set of  $2\theta$  limits and  $A_S$  = Integrated area of the sample under the peaks between the same set of  $2\theta$  limits as that of the reference.

### 2.3.2 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy is a flame technique useful for detection of metal ions in sample solution based on emission spectroscopy. The technique uses the inductively coupled plasma to excite elements within the sample and emit electromagnetic energy of wavelength typical of a particular element. The analyses were

performed using Perkin Elmer inductively coupled plasma optical emission spectrophotometer (ICP-OES) of model Optima 2100 DV. The solutions were prepared by digesting the samples of interest in (1:1) dilute HCl solution.

### 2.3.3 Atomic absorption spectroscopy (AAS)

The atomic absorption spectroscopy is a useful analytical technique for determination of chemical compositions within the sample solution through absorption of light with specific wavelength by gaseous free atoms. The analyses were obtained on Thermo Scientific atomic absorption spectrometer (Model: AAS-ICE 3500).

### 2.3.4 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is an important analytical tool mainly useful in identification of functional groups of a compound based on vibrational spectroscopy of the bonds. The IR spectra were recorded on an FTIR spectrophotometer, Model Nicolet Impact I-410. The analyses were performed by pelletizing the samples with KBr in the wavelength ranges of 4000–500  $\text{cm}^{-1}$ .

### 2.3.5 Thermogravimetric analysis (TGA)

The thermogravimetric analysis is a method which provides information on the thermal stability of materials. TGA measures either the weight loss or gain of a material due to the loss or decomposition of volatile compounds as a function of increasing temperature or time in an inert atmosphere. The TGA curves were obtained on a Shimadzu thermal analyzer (Model TGA-50). The samples were heated from ambient temperature to 700 °C under  $\text{N}_2$  flow with the heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.3.6 Scanning electron microscopy (SEM)

Scanning electron microscopy is an analytical technique used to study the surface topography of materials. The SEM images were recorded on JEOL Scanning Electron Microscopes (JSM 6390 LV) operating at an accelerating voltage of 15 kV.

### 2.3.7 *Transmission electron microscopy (TEM)*

Transmission electron microscopy (TEM) is a useful characterization technique for materials. A high energy electron beam is subjected to interact with the sample by transmitting it through the thin sample specimen and thus create an image of the sample material. The TEM images were recorded on an FEI–Technai (G2 20 S-TWIN) instrument operating at an accelerating voltage of 200 kV. Prior to the analysis, the samples were dispersed in ethanol and coated on a copper grid using a very dilute suspension.

### 2.3.8 *Brunauer–Emmett–Teller (BET) analysis*

The Brunauer–Emmett–Teller (BET) method is based on the multilayer adsorption of gaseous molecules on solid surface using non-corrosive inert gases like nitrogen, argon etc. as adsorbates. The BET method is widely used to determine the specific surface area and porosity of a solid material. The analyses were performed on Quantachrome Instruments (Model: NOVA 1000e) using nitrogen gas. All the BET values in this study were measured within a precision of  $\pm 5\%$ . The pore size and pore volume are determined following the Barrett–Joyner–Halenda (BJH) method in the same instrument.

### 2.3.9 *Ultraviolet-visible (UV-visible) spectroscopy*

The Ultraviolet-visible (UV-visible) spectroscopy is a useful analytical technique based on electronic transitions to identify the conjugated double bonds and aromatic conjugation within a molecule. The UV-visible spectra were recorded on Shimadzu Corporation UV-visible spectrophotometer (UV–2550).

### 2.3.10 *Diffused reflectance ultraviolet-visible (DRUV-vis) spectroscopy*

Diffuse reflectance ultraviolet-visible (DRUV-vis) spectroscopy is a spectroscopic technique used to characterize materials in the powder form with the advantage of the enhanced scattering phenomenon. Moreover, the light scattering effects in the absorption spectra of the samples dispersed in liquid media can be avoided using DRS [2,3]. The DR spectra of the samples were collected on Shimadzu Corporation UV-visible spectrophotometer (UV–2450).



### 2.3.11 Raman spectroscopy

Raman spectroscopy is a technique based on inelastic scattering of monochromatic light which provides information on the vibrational, rotational and other low frequency transitions in a system. It is useful in identification of a molecule providing chemical fingerprint. Raman spectra of the samples were collected on a laser micro Raman system (make: Horiba Jobin Yvon, model: LabRAM HR) at room temperature with an excitation wavelength of 633 nm.

### 2.3.12 Nuclear magnetic resonance (NMR) spectroscopy

The nuclear magnetic resonance (NMR) spectroscopy is a technique associated with the magnetic properties of certain atomic nuclei. NMR spectroscopy helps to determine the differences in the magnetic properties of various nuclei present and also their positions within the molecule. The NMR spectroscopy also provides information on different kinds of environment within the molecule by detecting the presence of atoms in the neighboring groups. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL NMR spectrometer (ECS-400) taking  $\text{Me}_4\text{Si}$  as the internal standard in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  solvents.

## 2.4 Typical procedures of catalytic reactions

### 2.4.1 Adsorption study of organic dye pollutants

#### 2.4.1.1 Adsorption of methyl orange (MO) over various ternary NiMgAl LDHs

Adsorption experiments were carried out in a batch mode by the addition of 5 mg LDHs to a series of 20 mL MO solution of various initial concentrations ranging from 10–70 mg/L for 180 min at room temperature and optimum pH of 6. The effect of contact time, adsorbent dosage, initial dye concentration and pH of the dye solution on MO removal was also investigated. The pH of the MO solutions was adjusted by using 0.1 M NaOH and 0.1 M HCl solutions. The adsorption kinetics was investigated by withdrawing the dye samples at a particular time intervals for analyzing the concentration of residual dye solutions. For analyzing adsorption isotherm, experiments were carried out by using adsorbent amount of 5 mg with different initial dye concentrations (ranging from 10–70

mg/L) until a stage of equilibrium get reached. Each experiment was carried out twice to avoid error in data evaluation. The concentration of the residual MO in the sample solutions were analyzed using the UV-visible spectrometer at 464 nm. The dye uptake/removal (%), adsorption capacity at equilibrium ( $q_e$ ) and adsorption capacity at time  $t$  ( $q_t$ ) were calculated by using the following mass balance equations.

$$\text{dye uptake/removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (2.3)$$

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2.4)$$

$$q_t = \frac{(C_o - C_t) V}{m} \quad (2.5)$$

where,  $C_o$  (mg/L) is the initial dye concentration,  $C_e$  and  $C_t$  (mg/L) are the concentrations of dye at equilibrium and time  $t$ ,  $V$  is the volume of the dye solution used (L) and  $m$  is the mass of adsorbent used (g).

#### 2.4.1.2 Adsorption of various anionic and cationic dyes over CuMgAl LDHs

Batch adsorption experiments were carried out by mixing 5 mg of the adsorbent with 20 mL of 20 mg/L dye solution at room temperature and pH of 6 for 180 min. The adsorbent was separated by centrifugation and the concentration of the residual dye in the sample solutions was analyzed using the Shimadzu Corporation UV-visible spectrometer (UV-2550) at their respective absorbance maximum. The effect of various parameters such as contact time, adsorbent dosage, initial dye concentration and pH of the dye solution on adsorption process was also investigated. The pH effect was studied over a wide range of pH (2–10) by adjusting the dye solutions using 0.1 M NaOH and 0.1 M HCl solutions. The adsorption kinetics was investigated by withdrawing the dye samples at a particular time intervals of 5, 10, 20, 30, 60, 90, 120 and 180 min. The adsorption isotherm was carried out using a constant amount of the adsorbent of 5 mg and 20 mL of dye solutions with different initial concentrations (ranging from 10–70 mg/L). The dye removal (%), adsorption capacity at equilibrium,  $q_e$  (mg/g) and adsorption capacity at time  $t$ ,  $q_t$  (mg/g)

were calculated according to the equations, 2.3, 2.4 and 2.5 respectively. For data consistency, each experiment was carried out twice.

#### 2.4.1.3 Adsorption of congo red (CR) over NiAl LDHs

Adsorption experiments were carried out with 20 mL of a series of congo red (CR) solutions of various concentrations ranging from 10 to 60 mg/L and 10 mg of LDH as adsorbent at 25 °C and pH 6. The adsorption process was monitored using UV-visible spectrophotometer at maximum wavelength ( $\lambda_{\max}$ ) of 497 nm at a particular time intervals (from 5 to 180 min) and the equilibrium time attained was 90 min. The dye removal (%), adsorption capacity at equilibrium ( $q_e$ ) and adsorption capacity at time  $t$  ( $q_t$ ) were calculated by using the equations, 2.3, 2.4 and 2.5 respectively.

#### 2.4.1.4 Adsorption kinetics study

The adsorption kinetics was evaluated with pseudo-first and second order kinetic model for understanding the characteristics of the adsorption process. The linear form of pseudo-first order kinetic model is given by the equation as [4],

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2.6)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) are the adsorption capacity at equilibrium and at time  $t$ , respectively,  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant. The values of  $k_1$  and  $q_e$  were calculated from the linear plots of  $\log (q_e - q_t)$  versus  $t$ .

The linear form of pseudo-second order kinetic model is given by the equation as [5],

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.7)$$

where,  $k_2$  ( $\text{g/mg} \cdot \text{min}$ ) is the pseudo-second order rate constant. The values  $k_2$  and  $q_e$  were calculated from the linear plots of  $t/q_t$  versus  $t$ .

The diffusion mechanism of the adsorption process was investigated by the intraparticle diffusion kinetic model using the following equation [6],

$$q_t = k_i t^{1/2} + C \quad (2.8)$$

where,  $k_i$  ( $\text{mg/g}\cdot\text{min}^{1/2}$ ) is the intraparticle diffusion rate constant and  $C$  is the intercept. The values of  $k_i$  and  $C$  were calculated from the slope and intercept of the plots of  $q_t$  versus  $t^{1/2}$ . The intercept,  $C$  is related to the boundary layer thickness.

#### 2.4.1.5 Adsorption isotherm study

The adsorption isotherms were analyzed by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The Langmuir adsorption isotherm is based on the monolayer coverage that takes place at specific homogeneous adsorbent site. The linearized form of the Langmuir isotherm is expressed as [7],

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \quad (2.9)$$

where,  $C_e$  represents the equilibrium concentration of dye ( $\text{mg/L}$ ),  $q_e$  ( $\text{mg/g}$ ) and  $q_m$  ( $\text{mg/g}$ ) are the equilibrium and maximum adsorption capacity, respectively,  $k_L$  is the Langmuir constant. The values of  $q_m$  and  $k_L$  can be calculated from the slope and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$ , respectively. The favorability of the adsorption process can be predicted from the value of dimensionless constant separation factor or equilibrium parameter,  $R_L$  which is given by the equation,

$$R_L = \frac{1}{1 + k_L C_0} \quad (2.10)$$

where,  $k_L$  is the Langmuir adsorption constant and  $C_0$  is the initial dye concentration. For a favourable process,  $R_L$  value lies between 0 and 1 ( $0 < R_L < 1$ ) and while for irreversible, linear and unfavourable case,  $R_L = 0$ ,  $R_L = 1$  and  $R_L > 1$ , respectively.

The Freundlich adsorption isotherm is related to the multilayer adsorption on heterogeneous surfaces. The linearized form of Freundlich isotherm is expressed as [8],

$$\log q_e = \frac{1}{n} \log C_e + \log k_F \quad (2.11)$$

where,  $k_F$  and  $n$  are Freundlich constants that related to the adsorption capacity and adsorption intensity, respectively.

The linearized form of D–R isotherm equation is expressed as [9],

$$\ln q_e = \ln q_o - k_{DR} \varepsilon^2 \quad (2.12)$$

where,  $k_{DR}$  is a constant related to the mean energy of adsorption ( $\text{mol}^2/\text{kJ}^2$ ) and  $q_o$  is the sorption capacity ( $\text{mg}/\text{g}$ ). The Polanyi potential,  $\varepsilon$ , can be calculated from the following equation,

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (2.13)$$

where,  $R$  is the universal gas constant ( $\text{J}/\text{mol}\cdot\text{K}$ ) and  $T$  is the absolute temperature ( $\text{K}$ ). With the D–R isotherm model, from  $k_{DR}$  values the mean adsorption energy ( $E$ ) can be calculated using the equation,

$$E = \frac{1}{\sqrt{2k_{DR}}} \quad (2.14)$$

The mean adsorption energy ( $E$ ) implies the energy change due to the transfer of one mole of the ion in solution from infinity to the solid surface [10]. The value of  $E$  between 1–16  $\text{kJ}/\text{mol}$  prevails physical adsorption and the value more than 16  $\text{kJ}/\text{mol}$  prevails chemisorptions [11,12].

#### 2.4.1.6 Adsorption thermodynamics study

The change in free energy ( $\Delta G^\circ$ ) of adsorption in terms of reaction thermodynamics can be calculated using the following equation [13–15]:

$$\Delta G^\circ = -RT \ln k \quad (2.15)$$

where,  $k$  is thermodynamic equilibrium constant without units, determined from the isotherm equation to find  $\Delta G^\circ$  values at different temperature. It is known that  $\Delta G^\circ$  is the function of change in standard enthalpy ( $\Delta H^\circ$ ) as well as change in standard entropy ( $\Delta S^\circ$ ) of adsorption:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.16)$$

Substituting the eq (2.15) into eq (2.16), gives van't Hoff equation and is expressed as [16],

$$\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (2.17)$$

Thus, the values of both  $\Delta S^\circ$  and  $\Delta H^\circ$  of the adsorption process can be obtained from the plot of  $\ln k$  versus  $1/T$ .

## 2.4.2 Photocatalytic degradation of organic pollutants

### 2.4.2.1 Photocatalytic degradation of phenol and its compounds using ZnFe LDH

In order to regulate the photocatalytic activity of the synthesized catalyst, the degradation of phenol and its derivatives was carried out using both visible and UV light source. For a typical run, 10 mg of catalyst was added to 20 ml of phenolic solution with initial phenol concentration of 5mM, and then the reaction mixtures were allowed to stir magnetically at room temperature. The visible light source used was 250 W tungsten lamp and UV light source was 125 W medium pressure mercury lamp. The light source was kept about 16 cm away from the reaction vessel in order to minimize the heat generated from the lamp. All reactions were carried out in dark for 30 min prior to expose under light in order to reach an adsorption-desorption equilibrium. The concentration of the residual phenolic solutions was monitored at different time intervals on a UV-visible spectrophotometer by withdrawing 2 mL of the aliquots. The degradation (%) of the organic pollutants are determined by using the following equation,

$$D = \frac{(C_o - C_t)}{C_o} \times 100\% \quad (2.18)$$

where,  $C_o$  is initial concentration and  $C_t$  is final concentration of organic pollutants. Blank experiments were also performed in absence of catalyst under similar reaction conditions. The effect of various reaction parameters such as catalyst amount, concentration of phenols, and pH was also studied to get an optimized condition for the degradation process. All the experiments were done in duplicate for accuracy.

#### 2.4.2.2 Photocatalytic degradation of methylene blue and rhodamine B using ZnFe LDH

The photocatalytic activity of the synthesized catalyst was carried out for degradation of methylene Blue (MB) and rhodamine B (RhB) under both UV and visible light irradiation. In a typical run, 5 and 10 mg of the catalyst was suspended to 50 mL dye solution of MB and RhB, respectively with initial dye concentration of 10 mg/L under light irradiation. The UV light source used was 125 W medium pressure mercury lamp and visible light source was 250 W tungsten lamp. A distance of 16 cm was maintained between the light source and solution in order to reduce the heat eliminated from the light source. Prior to exposure to light irradiation, all the experiments were carried out in dark for 30 min in order to achieve adsorption-desorption equilibrium. The experiment was also performed blank under similar conditions without using catalyst for both MB and RhB. The samples were withdrawn at a particular time intervals, centrifuged to separate the catalyst and monitored on a UV-visible spectrophotometer at maximum absorbance of 663 and 554 nm for MB and RhB, respectively. The degradation (%) of organic pollutants was determined by using the following equation 2.18.

#### 2.4.2.3 Reaction kinetics study

The reaction kinetics for photocatalytic degradation of organic pollutants was analyzed by using Langmuir–Hinshelwood first order kinetics and the equation is expressed as,

$$\ln(C_o / C) = k_{app}t \quad (2.19)$$

where,  $C_o$  and  $C$  are the concentration of phenolic compounds at time 0 and  $t$ , respectively; and  $k_{app}$  is the apparent rate constant in  $\text{min}^{-1}$ .

### 2.4.3 Nitro-aldol condensation reaction

#### 2.4.3.1 Nitro-aldol condensation reaction under mild condition

The nitro-aldol condensation reactions were performed under the solvent free conditions by taking 1 mmol of the aldehyde, 10 mmol of the nitromethane and 10 mg of the catalysts. For a comparative study, all reactions were carried out for 36h and the reaction conditions were optimized by varying the substituent, temperature and the amount of catalysts. The reactions were monitored via thin layer chromatography and % conversions were obtained from  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses of the crude reaction mixture. To evaluate the catalytic activity more clearly, the turnover frequency (TOF) of the catalysts was calculated using the general equation,

$$\text{TOF} = \text{TON} \times \frac{1}{\text{Time (h)}} \quad (2.20)$$

where, TON refers to the turnover number. For the turn over number calculations, the number of active or basic sites was calculated by basicity measurements. In this method, a suspension of the 15 mg catalyst in a 2 mL toluene solution of phenolphthalein (0.1 mg/mL) was stirred for 30 minutes and titrated with a toluene solution of benzoic acid (0.01 M). The aqueous soluble amount of basic sites was determined by the acid–base titration method reported previously.

#### 2.4.3.2 Nitro-aldol condensation reaction under microwave condition

The catalytic performance of the catalysts was tested for nitro-aldol condensation reaction. All the reactions were carried out in scientific microwave reactor “Catalyst System Scientific Microwave systems” with power output 700 watt (2450 MHz) and having power levels from 140 to 700 watt and automatic temperature sensors with flexible probe upto 600 °C. In a typical reaction procedure, to a mixture of 1 mmol of the aldehyde and 10 mmol of the nitromethane, 10 mg of the catalysts was added in a long necked microwave flask under refluxing condition. The progress of the reactions was monitored by thin layer chromatography. The product was purified by thin layer chromatography technique and analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques. All reactions were carried out



under solvent free MW condition with MW power 280 Watt (40% of 700 Watt) and 50 °C. The reaction conditions were optimized by MW power (%) amount of catalysts and varying substituent. The conversions were calculated from  $^1\text{H}$  NMR analyses of the crude reaction mixture.

## 2.5 Computational details

Electronic structures of all the species involved in Phenol + OH reaction were optimized using B3LYP functional method [17–19] along with 6-31+G (d,p) basis set. Vibrational frequencies calculations were carried out using the same level of theory at which the optimization was made. All the stationary points have been identified by the real positive vibrational frequencies, corresponding to stable minima, except the transition state structures. They were characterized by only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculation [20] was also performed to confirm that the transition state properly connected the reactants and products and the transition was smooth. All the DFT calculations are performed using GAUSSIAN 09 program package [21].

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