PROJECT COMPLETION REPORT

1. **Title of the Project:** Photocatalytic Degradation of Organic pollutants in water using LDH and zeolite nanoparticles
2. **Principal Investigator**: Dr Rasna Devi
3. **Mentor:** Prof. Ramesh Chandra Deka
4. **Implementing Institution and other collaborating Institution(s):** Tezpur University
5. **Date of Commencement:** 03/01/2018
6. **Planned Date of Completion:** 02/01/2021
7. **Actual Date of Completion:**02/01/2022
8. **Objectives as stated in the project proposal:**

The objectives of the proposed were set as follows

(i) Synthesis of nano layered double hydroxides and bimetallic nano layered double hydroxides by synthesizing nano hydrotalcite alone or modification with photoactive metals such as Ti, Zn, Fe etc. and metal oxides e.g TiO_2 either in nano form or bulk form.

(ii) Synthesis of nano zeolites alone and modified nanozeolites by incorporating and impregnating photoactive metals either in nano form or bulk form in nanozeolites.

(iii) Characterization of the synthesized materials with different techniques such as XRD, FTIR, UV, SEM, TEM and N_2 adsorption desorption method.

(iv) Utilization of the materials for photocatalytic degradation of some important industrial pollutants such as phenolic derivatives, benzenes, dyes such as Methylene blue, Congo red, Methyl orange and Rhodamine B under visible and ultra violet light sources.

(v) Utilization of the synthesized materials for organic transformation of alcohol to aldehyde and amines to imines under classical and photocatalytic pathway under both visible and UV light sources.

(iv) The proposed reaction schemes will be monitored through various characterization techniques such as UV-visible spectroscopy, HPLC, NMR spectroscopy and GCMS techniques.

(v) Assembling the data and systematic study of the results for future benefit of the processes.

9. **Deviation made from original objectives if any, while implementing the project and reasons thereof:** No deviation was made in this project

10. **Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:** The details of the work are attached as appendix I in separate sheets. The work is reflected in different publications which is also listed as appendix II

11. **Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:**

(a) *Contribution towards synthesis procedure:* A series of visible light active CoZn-LDH nanosheets were synthesized by reverse microemulsion method and characterized by various physicochemical methods. By varying water to SDS ratio, the longitudinal dimensions of the nanosheets were controlled from 300 nm to 1.9 μm and lateral dimensions were controlled from 23-60 nm. Spectroscopic results exhibited well developed LDH layered structure and SDS intercalation in between the layers. The cationic dyes were removed easily compared to anionic dyes under both dark and light irradiation condition. This can be due to attraction of negatively charged LDH layers and positively charged cationic dye molecules which made the adsorption process faster. In future, aforementioned cationic dyes CV, MB or RhB can be considered for kinetic study and photocatalytic study with other LDHs as well.

The study can be extended to other layer double hydroxides like CoCr-LDH and CoNi-LDH in the future and can be explored by synthesis by hydrothermal method or solvothermal method. It is obvious that most of the cationic dyes are adsorbed to the LDH surface and thus can be removed from the solution either by degradation or removal method. Therefore, optimization of reaction conditions e.g. pH, amount of catalyst, solvent types, reaction time etc. will be beneficial for the future studies. During the synthesis of CoZn-LDH by microemulsion method, water to SDS ratio plays important role in controlling dimension of the nanomaterials.

(b) *Contribution towards novel reaction procedure:* In this reverse emulsion method, only proper mixing of the reaction is required and simple ageing of the precipitate is required. The method is novel from the point of view that no high temperature reaction is required for prolonged time similar to autoclave reactions. Again, no other exfoliation process or any sophisticated stirring equipment is needed. The procedure involves simple stirring in magnetic stirrer.

(c) *Contribution towards hazard removal:* The synthesized CoZnLDH nanosheets were utilized for photocatalytic removal of a series of important dye pollutants namely rhodamine B (RhB), crystal violet (CV), methylene blue (MB); bromocresol green (BG), bromothymol blue (BTB), rose bangle (RB), congo red (CR) and methyl orange (MO) from their aqueous solutions. The dye removal experiments were performed both under dark and visible light irradiation. Light irradiation showed remarkable enhancement of removal percentage of dyes from their aqueous solutions. Cationic crystal violet showed rapid removal in presence of CoZnLDH11 and showed 97 % removal in 80 minutes. The catalytic dye removal experiments were monitored through UV-visible spectrophotometer to analyze concentrations of the solutions and to obtain percentage removal of the dye from the solutions.

The study contributes to understanding the reaction of most of the common dyes in aqueous solution in presence of LDH catalyst. Since, cationic crystal violet 97% removal in 80 minutes and the best dye in this study, it can be understood that adsorption of cationic dye in the anionic LDH layer favours the speed of the reaction.

12. Conclusions summarizing the achievements and indication of scope for future work:

In conclusion, a series of visible light active CoZn-LDH nanosheets were synthesized by reverse emulsion method and characterized by various physicochemical methods. By varying water to SDS ratio, the longitudinal dimensions of the nanosheets were controlled from 300 nm to 1.9 μm and lateral dimensions were controlled from 23-60 nm. Spectroscopic results exhibited well developed LDH layered structure and SDS intercalation in between the layers. The cationic dyes were removed easily compared to anionic dyes under both dark and light irradiation condition. This can be due to attraction of negatively charged LDH layers and positively charged cationic dye molecules which made the adsorption process faster. In future, aforementioned cationic dyes CV, MB or

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13. New Observations:

(a) During the synthesis of CoZn-LDH by microemulsion method, water to SDS ratio plays important role in controlling dimension of the nanomaterials.

(b) The formation of the nanosheets depend on the size of the micelle formed. The possibility of nanosheet formation increases as the SDS amount decreases

(c) Cationic dye crystal violet dye can be removed quite rapidly with CoZn-LDH

14. Innovations:

(a) The BET surface area can be controlled by keeping the same molar ratio of both the salts (Zn and Co) during LDH synthesis
(b) In case of light experiments, the effect of power of light source was first investigated by taking three different power sources namely 20 Watt 240V LED lamp, 100 Watt 230V tungsten bulb and 200 Watt 250V tungsten bulb. The dye removal percentage of all dyes at 180 minutes follow the trend RB~MO~BTB<RB<CR<RhB<MB<CV. Thus, light irradiation has great effect over the speed of the removal process and display double and triple the percentage of dye removal compared to dark condition within same reaction time.

15. Application Potential:

a. Immediate: Since visible light irradiation gave high removal of the dyes, immediate potential of the study would be application of the process in sunlight.

b. Long Term: Optimization of metals having particular band gap and the dye can be done to get maximum removal of the dye.

16. S&T benefits accrued:

a. List of Research publications

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
	(i) R. Devi, P. Begum, P. Bharali and R. C. Deka,	Comparative Study of Potassium Salt-Loaded MgAl Hydrotalcites for the Knoevenagel Condensation Reaction	ACS Omeg	6	7086 – 7095.	2018
	(b) R. Devi*, D. Bharali and R. C. Deka,	Synthesis of LDH for Photocatalytic Removal of Toxic Dyes from Aqueous Solutions, in Materials Modelling for Macro to Micro/Nano Scale Systems,	In *Materials Modelling for Macro to Micro/Nano Scale Systems*, S. B. Singh, P. Ranjan and A. K. Haghi edn., Apple Academic Press publishing,	Chapter 5		2021
	(d) R. Devi and D. Talukdar,	introduction to zeolites and its application in methylation of toluene,	in *Modern Trends in Chemistry*, D. K. Jha edn., Purbayon publication, Guwahati, India,	Chapter 3	83-127.	2020

b. Manpower trained on the project

i) Ph.D. produced : No

ii) Other Technical Personnel trained : MSc project students were trained

c. Patents taken, if any : No

17. Financial Position:

S No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
1.	Salaries/ Manpower costs	19,80,000/-	13,20,000/-	44.066
2.	Equipment	2,00,000/-	1,43,577/-	4.793
3.	Supplies & Materials	4,00,000/-	2,74,514/-	9.164
4.	Contingencies	75,000/-	50,000/-	1.669
5.	Travel	75,000/-	12,956/-	0.432
6.	Overhead Expenses	2,65,500/-	1,99,987/-	8.863
7.	Others, if any			
	Total	29,95,500/-		**100%**

18. Procurement/ Usage of Equipment

a)

S No	Name of Equipment	Make/ Model	Cost (FE/ Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance/ breakdown
1	UV cuvette	Quartz Cuvette,Glass,3.5ml,two sides quartz,10mm path length (1 number)	0.0400 lakh		2	Maintained till date
2	UV cuvette	Quartz Cuvette,Glass,3.5ml, all sides quartz,10mm path length (1Number)	0.10000 lakh		10	Maintained till date
3	Autoclave	Autoclave Digester, 200ml (2 N)	0.3000		15	Maintained till date
4	LED Digital Magnetic Stirrer With Hot Plate ,Cat:E11231, Abdos	Cat:E11231, Abdos	0.2300		11.5	Maintained till date
5	Magnetic Stirrer	Model: PC420D, Make: Corning	0.0660		3.3	Maintained till date
6	Magnetic Stirrer	Remi	0.5014		25.07	Maintained till date
7	Temperature controller for oil bath		0.0700		3.5	Maintained till date
8	UV Chamber	Relitech	0.0600		3	Maintained till date

b) Plans for utilising the equipment facilities in future: For research purposes of remaining work of this project as well as any permitted research work in the institution

Name and Signature with Date

a. Rasna Devi 30/05/2022

(Principal Investigator)

b. RDeka 30/5/2022

(Mentor)

Appendix I

Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs

Method adopted

Synthesising LDH nanosheets: The LDH nanosheets were synthesized by a reverse microemulsion method[i]. In this method, a transparent emulsion (w/o) was prepared by mixing 3.2 g Sodium Dodecyl Sulphate, 2.2 ml water and 100 ml isooctane with the aid of co surfactant 1-butanol (3 ml). After this, 0.002 mol $Zn(NO_3)_2.6H_2O$, 0.004 mol $Co(NO_3)_2.6H_2O$ and 2.4 g urea were added to the microemulsion. The whole mixture was then aged in a preheated oil bath at 100 °C for 24 h under reflux condition. Finally, the precipitate was filtered, washed with ethanol water mixture (1:1) and dried in air oven at 50 °C for 24h to get the final LDH nano sheets. The LDH crystals were washed with ethanol-water mixture and dried in air oven to get the final LDH. The resulting sample is named as CoZnLDH11 in accordance to water to surfactant mole ratio in the mixture which is 11 in CoZnLDH11. Similarly, CoZnLDH30 and CoZnLDH61 were synthesized by taking 1.44g and 0.720g SDS respectively following the aforementioned procedure.

Synthesising LDH by Co-precipitation method:

(i) Preparation of MgAl Hydrotalcite and MgAl(O)Mixed Oxide: Magnesium aluminum carbonate ($MgAl\text{-}CO_3$)hydrotalcite was prepared by followingNyambo et al.In this method, solution A was first prepared by dissolving 38.46g $Mg(NO_3)_2{\cdot}6H_2O$ (0.15 mol) and 18.75 g $Al(NO_3)_2{\cdot}9H_2O$ (0.05 mol) in 125 mL deionized water. Solution B was the prepared by dissolving 14 g NaOH (0.35 mol) and 15.9 g Na_2CO_3 (0.1 mol) in 145 mL of deionized water. Followed by this, solution A was addeddropwise over 1 h to solution B at pH 10−12 with vigorous stirring. Thesolution was kept stirring vigorously for another 1 h and thewhite precipitate formed was then aged for 24 h at65 °C. The precipitate formed was cooled to room temperature, filtered, and washedseveral times with deionized water until the filtrate becomesneutral. Finally, the precipitate was dried at 80 °C for 15 h to get the LDH and calcined at 450 °C for 6 h to obtain MgAl(O) support.

(ii) Preparation of Potassium Salt-Loaded MgAlHydrotalcites: The potassium salt-modified hydrotalcites(HTs) containing same amount of potassium ions(8% w/w)were prepared by a wet impregnation method reported earlier.In this method, a solution of the metal salt containing 1 mmolsalt (except for K_2CO_3, where 0.5 mmol was taken) in 8mL deionized water was stirred with 500 mg calcinedhydrotalcite for 24 h and the slurries were dried at 80 °C for 15h to obtain the loadedcatalysts. The samples were denoted asKNO_3/HT, KOH/HT, K_2CO_3/HT, $KHCO_3$/HT, and KF/HT.Following the same procedure, 10−40% KOH/HT wasprepared by taking an appropriate quantity of KOH and thesupport.

Data Collected

(a) Utilization ofCoZnLDH nanosheets

The powder x-ray diffraction patterns of CoZnLDH61, CoZnLDH30, CoZnLDH11 and CoZnLDH11a are depicted in figure 1(a). The peaks at 2θ positions 5.56, 8.49, 11.66, 21.63, 32.84, 34.90 and 59.21, 60.11 can be assigned to (003), (006), (009), (018), (012), (013), (110) and (113) plans respectively of CoZnLDH structure[ii]. Shifting of peak position of (006) plan from normal 2θ value 18 to 8.49 is a direct indication of intercalation of SDS in between

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LDH layers[iii-v]. The shifting of 2θ positions to lower value can be understood from Bragg's diffraction formula $n\lambda/2d = \mathrm{Sin}\theta$. As the 'd' value increases due to intercalation of long chain SDS molecules in the interlayer region, the $n\lambda/2d$ value decreases thus lowering 2θ value. It is also observed that the peak positions of all samples are not altered which indicates that increase or decrease of SDS content in the reaction mixture does not drastically hamper the nucleation process. Interestingly, the (006) plan is prominent only in sample CoZnLDH11a which may be due to resistance of the LDH structure due to low temperature drying at 45 ºC.

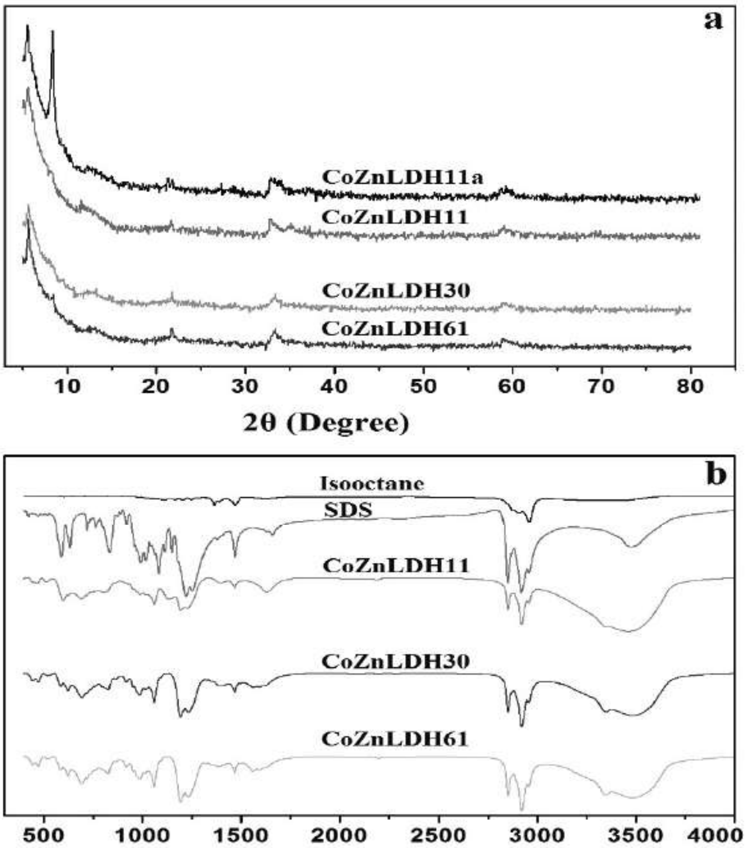

Figure 1: The powder x-ray diffraction pattern (a) and FTIR pattern (b) of CoZn-LDHs

The FTIR spectra of synthesized CoZnLDH showed characteristic vibrations for typical LDH layered structure as depicted in figure 1(b). Vibration at around 3468 cm^{-1} can be assigned to O–H stretching vibrations of surface –OH groups and interlayer water molecules[vi]. Another weak band centered at 3350 cm^{-1} is due to hydrogen bonded water molecules. The band at around 1632 cm^{-1} is due to bending mode of interlayer water molecules. The weak vibration at around 2957 cm^{-1} can be assigned to asymmetric C-H stretching of terminal $–CH_3$ groups[vii]. The absorptions at around 2921 cm^{-1} and 2852 cm^{-1} are C–H asymmetric stretching and symmetric stretching vibrations respectively of $–CH_2$ groups due to the presence of SDS. The corresponding bending vibration of $CH_2–$ is found at around 1469 cm^{-1} [viii]. Again, weak vibration at 1396 cm^{-1} corresponds to asymmetric stretching mode of CO_3^{2-} ion. The weak intensity of this band at 1396 cm^{-1} can be attributed to the fact that interlayer space has been occupied by dodecylsulphonate anion instead of atmospheric CO_3^{2-} [ix]. Vibrations at around 1230 cm^{-1} and 1195 cm^{-1} are observed due to $O–SO_3$ asymmetric vibrations while bands at around 1061 cm^{-1} and 992 cm^{-1} appeared for $O–SO_3$ symmetric vibrations[x]. The appearance of two bands instead of one for $O–SO_3$ asymmetric vibrations in the range 1230 cm^{-1} -1195 cm^{-1} directly shows that the T_d symmetry of free sulphate group has changed to C_{3v} symmetry in

LDH and there is no more interaction of sulphonate group with LDH surface; otherwise, the C_{3v} symmetry would have been further lowered to C_{2v} symmetry causing the asymmetric stretching band to split into three bands instead of two[xi]. The bands ranging from 400 cm^{-1}-850 cm^{-1} arise due to M-O and M-OH vibration of LDH lattice. All the spectral patterns resemble previous literature reports.

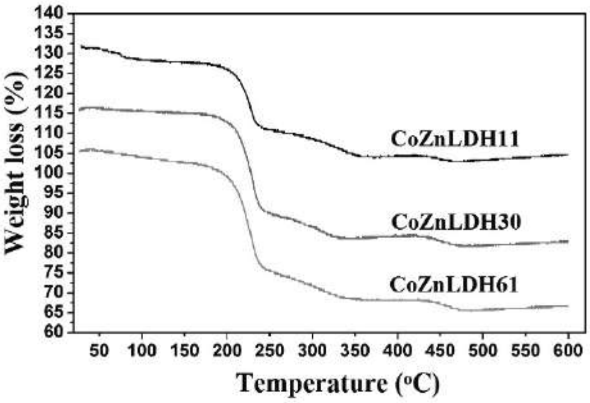

Figure 2: The thermogravimetric analysis of CoZn-LDHs

The thermal stability graphs of SDS-LDH samples are obtained from thermogravimetric analysis which is presented in figure 2. The decomposition of CoZnLDH11 can be divided into four steps[xii]. In the first step, evaporation of physically adsorbed water take place within temperature range 29 °C-94 °C contributing 4 % weight loss of total weight loss. In the range 94 °C-245 °C, loss of interlayer water molecules and collapse of SDS chains take place loosing 17 % weight in second step. Again, dehydroxylation from LDH layers occur within the range 245 °C-357 °C causing 7 % weight loss in the third step. However, we observed only 1 % weight loss in step four within 425 °C-478 °C which may be due to loss of few CO_2 molecules adsorbed onto the LDH surface from air. On the other hand, CoZnLDH30 and CoZnLHD61 showed three distinct degradation steps instead of four. It is observed that the loss of physically adsorbed water, loss of interlayer water molecules and decomposition of SDS chains occur in single step within 26 °C-278 °C (26 % wt. loss) for CoZnLDH30 and 26 °C-246 °C (31 % wt. loss) for CoZnLHD61. Following this, dehydroxylation occur in the range 278 °C-332 °C (7 % wt. loss) and 246 °C-350 °C (7 % wt. loss) for CoZnLDH30 and CoZnLHD61 respectively in the second step. Again, partial loss of CO_2 can be considered in the range 418 °C-482 °C (3 % wt. loss) and 428 °C-481 °C (3 % wt. loss) for CoZnLDH30 and CoZnLHD61 respectively. The total weight loss of the samples follows the trend: CoZnLDH11 (29 %) < CoZnLDH30 (34 %) < CoZnLDH61 (41 %); which can be due to retention of more water molecules from CoZnLDH11 to CoZnLDH61 as a result of decrease of SDS content in the same trend.

Figure 3(a-f) shows the FESEM images of prepared LDH in the magnification range 3.00KX to 30.00KX. We can see that CoZnLDH11 shows randomly oriented, non-uniform, curved nanoflakes which lie vertically and horizontally on top of each other forming intercrossing bridges between the walls (figure 3; a & d). The lateral dimension of the nanoflakes ranges form 300-900 nm while longitudinal dimension is around 28-30 nm. Again, CoZnLDH30 shows vertically oriented, curved nanosheets having lateral dimension 800 nm-1.5 μm and longitudinal dimension 23-60 nm (figure 3; b & e). The nanosheets are joined at the ends or intercross one another forming zigzag sheet morphologies. The CoZnLDH61 (figure 3; c & f) shows zigzag nano sheets similar to CoZnLDH30. These nanosheets grow either parallel to each other or perpendicularly between sheets. Here, lateral dimension of the sheets ranges from 260 nm -1.9 μm while longitudinal dimension is around 30-40 nm.

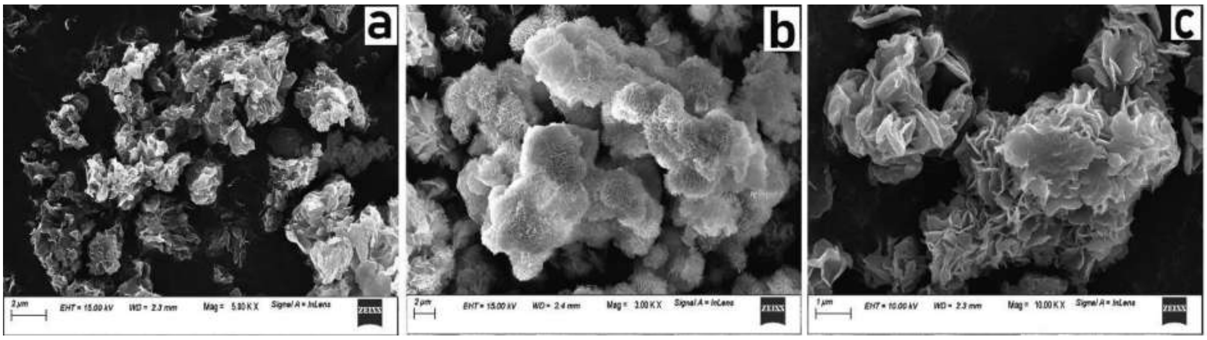

Figure 3: The SEM images of CoZn-LDH11 (a & d), CoZn-LDH30 (b & e) and CoZn-LDH61 (c & f)

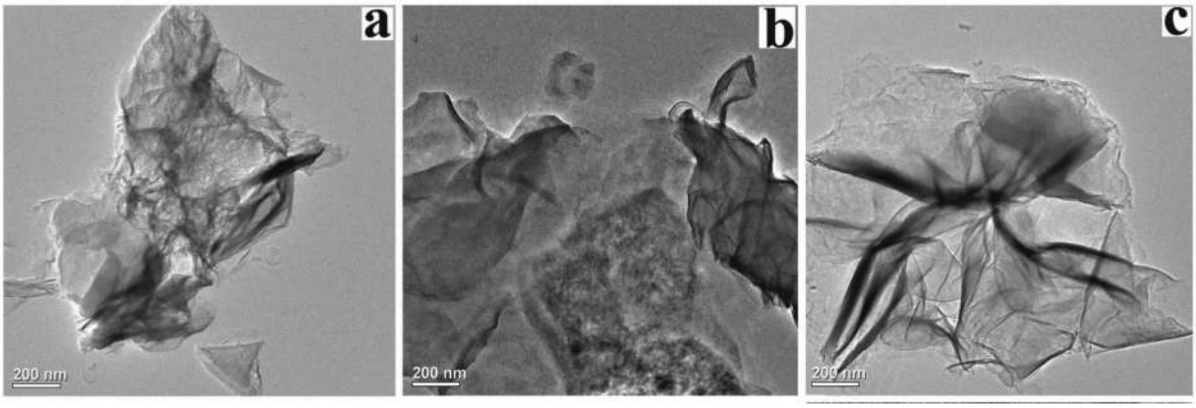

Figure 4: The TEM, HRTEM and SAED images of CoZn-LDH11 (a, d, g), CoZn-LDH30 (b, e, h) and CoZnLDH61 (c, f, i)

The TEM, HRTEM and SAED images of CoZnLDH11, CoZnLDH30 and CoZnLDH61 are presented in figure 4(a-i). The TEM micrographs of all three samples showed two-dimensional sheet like morphologies which are nearly transparent to the electron beam indicating formation of ultrathin LDH nano sheets[xiii]. Since the lateral dimension is quite larger than the longitudinal dimension, nanosheets are intercrossed and folded with one another in their self-assembly. The SAED pattern of all these samples showed diffraction rings with small and indistinct bright spots showing polycrystalline nature of the catalysts with low crystallinity. The interplanar distances calculated by inverse FFT method from HRTEM images are found to be in the order CoZnLDH11 < CoZnLDH30< CoZnLDH61. This shows that the concentration of surfactant has some effect over the size of LDH; as the amount of SDS lowered in the mixture, the interplanar distance also decreases in the same trend.

We again obtained specific surface area, pore volume as well as pore size distribution curves of the synthesized CoZn-LDHs by BET method using N_2 adsorption desorption isotherms. The CoZnLDH11 exhibits BET surface area 111.909 m^2/g while CoZnLDH30 and CoZnLDH61 showed 113.739 m^2/g and 121.242 m^2/g respectively. Comparable surface area of all three samples can be attributed to the use of similar ratio of salt mixtures and presence of similar environment during synthesis procedure. According to IUPAC classification, all three LDHs shows type IV isotherm and H3 hysteresis loop indicating the existence of mesoporous structure. Again, H3 hysteresis loop corresponds to slit-shaped pores which are formed due to non-rigid aggregates of sheet like or plate like particles[xiv]. The CoZnLDH11 shows pore radius 20.254 **Å** and pore volume 0.656 cc/g while CoZnLDH30 shows pore radius 50.199**Å** and pore volume 0.166 cc/g. On the other hand, CoZnLDH61 have pore radius 15.300 **Å** with 0.191 cc/g pore volume. The pore size distribution curves (figure 6d) are unimodal and multimodal in the region 10-70 **Å** that confirm presence of mesopores in the structure.

The catalytic activity of CoZnLDH nanosheets were evaluated by removal of a series of cationic dyes i. e, rhodamine B (RhB), crystal violet (CV) and methylene blue (MB); and a series of anionic dyes i. e bromocresol green (BG), bromothymol blue (BTB), rose bangle (RB), congo red (CR) and methyl orange (MO) from their aqueous solutions. The reaction conditions were controlled by performing the reactions in presence of catalysts and in absence of catalysts under dark as well as under visible light irradiation. Dark reactions were performed in presence of catalysts following the method mentioned in section 2.4. For a typical dark reaction, 10 mg CoZnLDH11 was added to 20 ml of 0.02M MB solution in a dark chamber under continuous stirring condition and concentrations were recorded at specific time intervals. Concentration recorded prior to addition of catalyst was termed as initial concentration. The results are summarized in figure 5. The catalyst could not remove BTB and BG at all within 4h while other dyes namely RhB, MB, RB, CR and MO were removed from low to moderate range (17-44 %). Interestingly, removal of CV gradually increases up to 120 minutes showing 86 % removal which then slowly increases upto 4h showing 92 % removal. This can be attributed to less availability of active surface area of CoZnLDH for the dye molecules to get adsorbed onto the surface and less concentration of dye in the aqueous solution than the initial stage. Thus, we can consider cationic dye CV as the optimized dye for further study.

Followed by dark reactions, we investigated the catalyst study by taking the three catalysts i.e., CoZnLDH11, CoZnLDH30 and CoZnLDH61 for removal of CV under dark. The results are depicted in figure 6a. The CoZnLDH11 and CoZnLDH61 followed the same trend and showed 93 % removal within 5h. On the other hand, increase of dye removal (%) by CoZnLDH30 is somewhat lower than CoZnLDH11 and CoZnLDH61 throughout the time. However, as the time increases the removal is comparable and gives 90 % removal in 5h. After 24h reaction time, 97 % removal was observed for CoZnLDH11 and CoZnLDH61 while 94 % was observed for CoZnLDH30. Thus, CoZnLDH11 was chosen as optimized catalyst for further reactions.

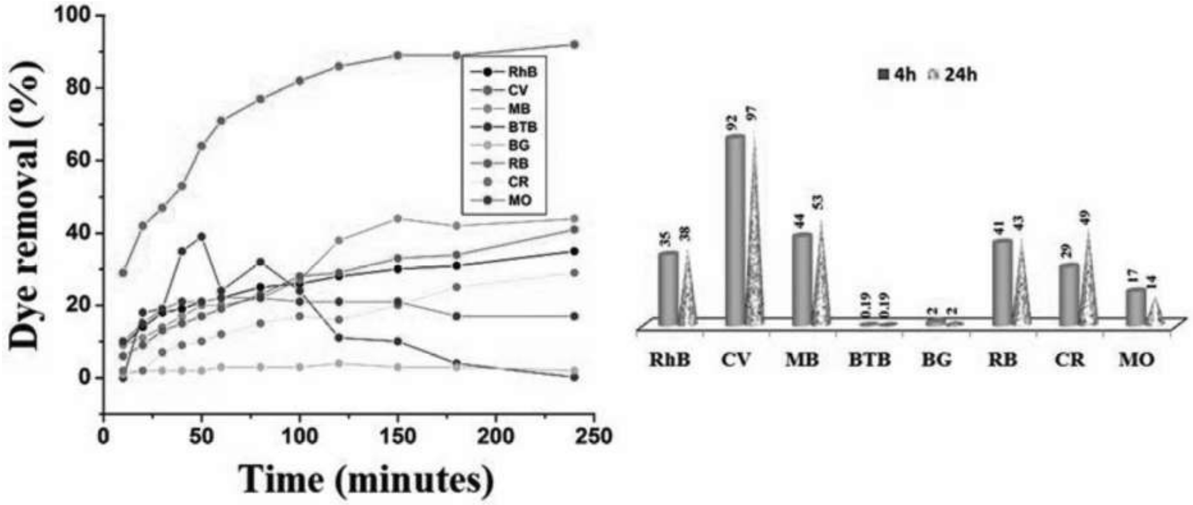

Figure 5: Adsorption of cationic and anionic dyes under dark in presence of CoZnLDH11 (Conditions: C_o = 0.02M, $V_{solution}$ = 20 mL, catalyst amount = 10 mg)

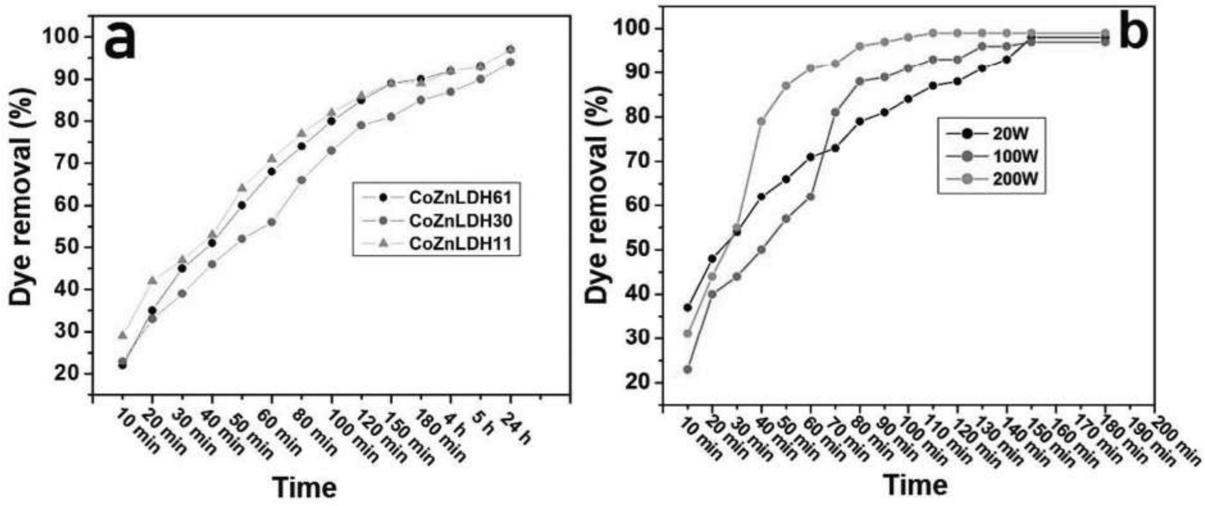

Figure 6: Optimization of (a) catalysts and (b) power source under visible light irradiation (Conditions: Co = 0.02M, $V_{solution}$ = 20 mL, catalyst amount = 10 mg)

In case of light experiments, the effect of power of light source was first investigated by taking three different power sources namely 20 Watt 240V LED bulb, 100 Watt 230V tungsten bulb and 200 Watt 250V tungsten bulb. For this purpose, 10 mg of previously optimized catalyst CoZnLDH11 was added to 20 ml of 10 ppm crystal violet solutions and exposed to light irradiation. Samples were collected at a time interval of 10 minutes and analyzed through UV-Visible spectrophotometer. The results are summarized in figure 6b. We observed that 97-99 % removal was obtained in 180 minutes. This is quite faster than dark reaction which took 24h for removal of 97 % CV. With 20 Watt LED light, the removal increase gradually giving 93 % in 140 minutes which then increase slowly upto 180 minutes showing 98 % removal. When 100 Watt power source was used, 93 % removal was observed in 110 minutes and then 97 % in 150 minutes. As expected, when 200 Watt bulb was used the reaction became faster giving 99 % removal in 110 minutes. This shows that as the power of the irradiated light increases, the removal becomes faster. We therefore used 200 Watt bulb for further investigations.

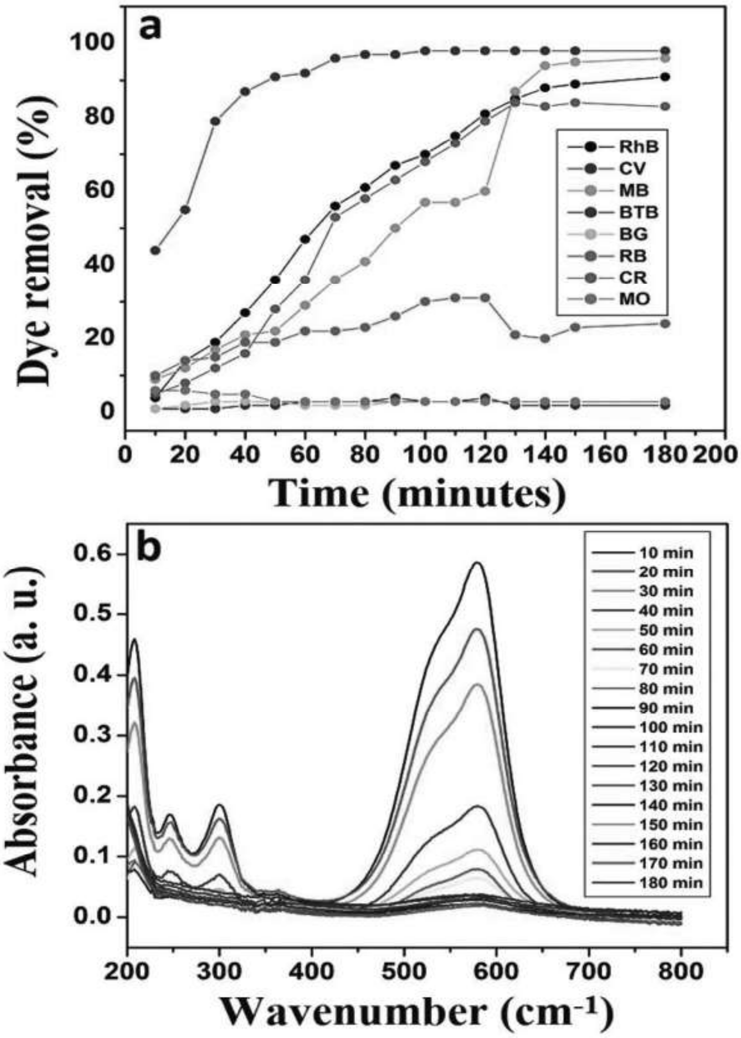

Figure 7: Adsorption of crystal violet dye under visible light by CoZnLDH11 (Conditions: $C_o = 0.02M$, $V_{solution} = 20$ mL, catalyst amount = 10 mg, power source = 200 Watt 250V tungsten bulb)

Figure 7 (a-b) depicts UV-visible adsorption spectra of all dyes over CoZnLDH11 nanosheets under visible light irradiation for 300 minutes. Similar to dark reactions, CoZnLDH11 could not remove BG, MO and BTB under light irradiation. Again, the removal of RB was low (25 % in 180 min) and comparable to dark reaction. On the other hand, removal percentage of MB gradually increases till 140 minutes and display 94 % removal in 140 minutes which is double as compared to dark condition which showed 44 % removal in 150 minutes. The removal became slower beyond 140 minutes and resulted 96 % removal in 180 minutes. Similarly, RhB displays 88 % removal in 140 minutes which is about three times faster compared to dark condition. Within 180 minutes 91 % RhB was removes. Again, 83 % CR was removed in 180 minutes which is more than three times faster in comparison to dark condition. In case of CV, 91 % removal was achieved within 50 minutes which is one fifth of the time taken in dark reaction (91% removal in 300 minutes) for the same removal percentage. The increase was rapid till 60 minutes, which then slowly increases beyond 60 minutes and gives 97 % dye removal in 80 minutes and then 98 % in 180 minutes. From figure 8a the dye removal percentage of all dyes at 180 minutes follow the trend RB˜MO˜BTB<RB<CR<RhB<MB<CV. Thus, light irradiation has great effect over the speed of the removal process and display double and triple the percentage of dye removal compared to dark condition within same reaction time.

In conclusion, a series of visible light active CoZn-LDH nanosheets were synthesized by reverse emulsion method and characterized by various physicochemical methods. By varying water to SDS ratio, the lateral dimensions of the nanosheets were controlled from 300 nm to 1.9 μm and longitudinal dimensions were controlled from 23-60 nm. Spectroscopic results exhibited well developed LDH layered structure and SDS intercalation in between the layers. The cationic dyes were removed easily compared to anionic dyes under both dark and light irradiation condition. This can be due to attraction of negatively charged LDH layers and positively charged cationic dye molecules which made the adsorption process faster. In future, aforementioned cationic dyes CV, MB or RhB can be considered for kinetic study and photocatalytic study with other LDHs as well.

(b) Utilization of potassium modified bulk MgAl-LDH

Powder X-ray diffraction patterns of parent hydrotalcite and potassium salt loaded hydrotalcites are presented in Figure 1. Reflections at 2θ values of 11.5, 23.05, 34.7, 38.35, 45.95, 60.5 and 61.75° corresponding to (003), (006), (102), (105), (108), (110) and (113) planes respectively, indicates the formation of highly crystalline layered structure of hydrotalcite which corroborates well with literature reports.[xv] Again all potassium salt loaded samples show strong peaks for (003) and (006) planes which clearly shows the presence of hydrotalcite phase; this confirms rehydration and reconstruction of hydrotalcite phase after loading. However, shifting of 2θ positions to slightly higher or lower values and diminished intensity of loaded samples can be attributed to the presence of potassium salts on hydrotalcite structure. It has been observed from Figure 1 that the salts KOH, $KHCO_3$ and K_2CO_3 are well dispersed over the support while KF and KNO_3 loaded samples showed some additional diffraction lines in the XRD pattern. Hence, preferred catalyst can be chosen among KOH, $KHCO_3$ and K_2CO_3 in terms of phase stability. This observation was further investigated through crystallinity study which did not follow the similar trend. The crystallinity study revealed that the highest crystallinity after loading was achieved for KOH/HT and the lowest was for $KHCO_3$/HT (Figure S1, Supporting Information). It shows that although $KHCO_3$ disperse better than KF and KNO_3 onto the host, it decreases the crystallinity of the overall catalyst. Thus, crystallinity loss is dependent on the nature of the salt but not upon dispersion. Thus, observing both crystallinity and phase stability we can observe that KOH/HT is stable and highly crystalline catalyst amongst KOH, $KHCO_3$ and K_2CO_3. Therefore, KOH/HT is chosen as the preferred salt from XRD. We have also calculated crystallite sizes, unit cell parameters (a), and basal spacing between the layers (d) which are summarized in Table 1. Peaks for (003) and (006) reflections were considered to calculate basal spacings between the layers. Peak for (110) reflection was used to calculate unit cell parameter 'a' according to the formula 'a' = 2d while (003) plane was used to calculate 'c' according to the formula 'c' = 3d.[xvi] Comparison of the original hydrotalcite to the loaded hydrotalcites shows that the basal spacings and unit cell parameters increase after loading. Increase of basal spacings and unit cell parameters further support increase of Mg (+2) ions gradually in the LDH indicating interaction of some Al(+3) ions with potassium salts and decrease of coulombic interaction between interlayer anions and brucite-like layers.[xvii,xviii] The increase of both 'd' and 'a' are larger for KOH/HT, K_2CO_3/HT and KNO_3/HT (d_{003}=7.80-7.93; d_{006}=3.88-3.91; a=3.06 -3.07) than KF/HT and $KHCO_3$/HT (d_{003}= 7.70-7.73; d_{006}= 3.85-3.86; a=3.05-3.06).

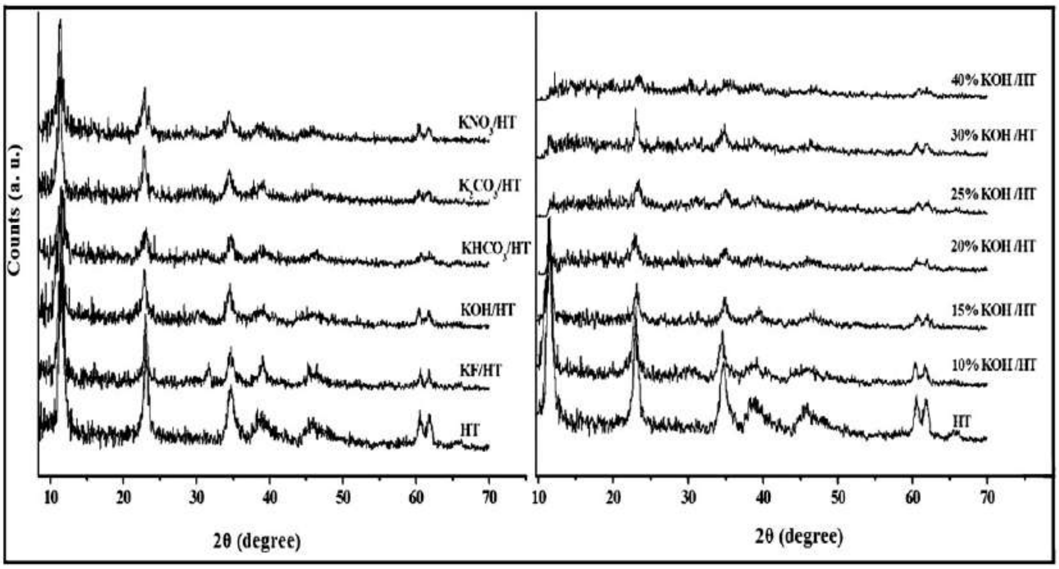

Figure 1. Powder x-ray diffraction pattern of potassium loaded hydrotalcites

Thus, a stability order of the salts over the support can be understood from overall results of X-ray diffraction study which follows the trend KOH/HT ~ K_2CO_3/HT > $KHCO_3$/HT > KF/HT ~ KNO_3/HT. Hence, among the studied salts over hydrotalcite support KOH is chosen as the preferred salt. Smaller crystallite size of KOH/HT in comparision to the others is again in favour of its selection as preferred catalyst for base catalyzed reaction.[xix] Following these results we have loaded KOH amount of 15-40% (w/w) by identical impregnation method to gain better understanding of the effect of the salt over the support.

Figure 1 shows that hydrotalcite layered structure preserve up to 20 % loading of KOH and collapse above it where the reflection for (003) plane was completely destroyed for 25-40% loaded samples. However, crystallinity loss was quite higher for 15-40% loaded samples. When 15% KOH was loaded, crystallinity loss was increased seven times more in comparison to 10 % loaded sample. Therefore, KOH loading beyond 10% is believed to be not effective over hydrotalcite support. Hence, 10% KOH/HT has been conceded as the best catalyst in this study.

Table 1. Calculation of lattice parameter and basal spacings for potassium salt loaded hydrtalcites

Sample	(003) reflection, 2θ (°)	d_{003} (Å)	(006) reflection, 2θ (°)	d_{006} (Å)	(110) reflection, 2θ (°)	d_{110} (Å)	a (Å)	c (Å)	Crystallite size (003)
HT	11.50	7.70	23.05	3.85	60.50	1.53	3.06	23.10	128.09
KF/ HT	11.50	7.70	23.00	3.86	60.60	1.52	3.05	23.10	135.56
$KHCO_3$/HT	11.45	7.73	23.10	3.85	60.55	1.52	3.05	23.19	153.65
K_2CO_3/HT	11.35	7.80	22.70	3.91	60.35	1.53	3.06	23.40	135.70
KNO_3/ HT	11.35	7.80	22.90	3.88	60.20	1.53	3.07	23.40	164.93
KOH/ HT	11.15	7.93	22.85	3.89	60.35	1.53	3.06	23.79	82.31

The TGA and DTA results obtained from thermal analysis of uncalcined samples between temperature range 20 °C-500 °C shows four decomposition steps which are typical for hydrotalcite like compounds (Figure S2, Supporting Information). The first weight loss step in the temperature range 20-90 °C corresponds to the loss of physically adsorbed water on the surface which is found to be in the ranges of 1-12% of the total weight loss (Table P1, Supporting Information). In the second step, 12-15% weight loss takes place in the range of 80 °C-250 °C due to the loss of interlayer water molecules. We have observed that the weight loss steps of all loaded samples are similar to the parent hydrotalcite except the step for interlayer water loss. For HT, KF/HT and KNO_3/HT, interlayer water loss takes place only in single step while it takes place in several steps for KOH/HT, $KHCO_3$/HT and K_2CO_3/HT. This shows that the water molecules may be linked in different environment in presence of different guest molecules. In the third step i.e. 250 °C-415 °C, dehydroxylation and partial loss of carbon dioxide takes place showing 13-22% weight loss. It is noteworthy that dehydroxylation becomes slower after loading of the salts and collapse of the brucite layers starts at low temperature in comparison to the parent hydrotalcite. Besides, dehydroxylation is the fastest in case of KNO_3/HT and slowest in case of KOH/HT which in turn confirms that HT phase is thermally less stable in presence of KNO_3 salt and more stable in presence of KOH. In the fourth weight loss step, loss of carbon dioxide from the samples takes place in the temperature range of 395 °C - 518 °C showing a weight loss of 2-4%. Thus, TGA analysis reveals that hydrotalcite layer collapse earlier for KNO_3/HT and KF/HT in comparison to the other three i.e. KOH/HT, $KHCO_3$/HT and K_2CO_3/HT which gives thermal stability order of the loaded salts as KNO_3/HT < KF/HT< $KHCO_3$/HT < K_2CO_3/HT < KOH/HT. Thus, TGA analysis also reveals that KOH/HT is the most thermally stable catalyst and the preferred catalyst in our study.

The FTIR spectra of prepared hydrotalcites are presented in Figure 2. Characteristic bands for hydrotalcite at around 3450, 1640, 1380, 860, 661 and 510 cm^{-1} clearly indicates the presence of interlayer water molecules, hydroxyl groups in the brucite-like layers, carbonate ions in the interlayer galleries and Mg–O and Al–O bonds in all samples. Again, band at around 3600-2800 cm^{-1} for KOH/HT, K_2CO_3/HT and $KHCO_3$/HT samples are broader in comparison to KNO_3/HT and KF/HT which may be due to large water content of these samples in the surface as well as in the interlayer spaces. This again correlates well with thermogravimetric analysis of the samples confirming high water content of these samples in the interlayer spaces.

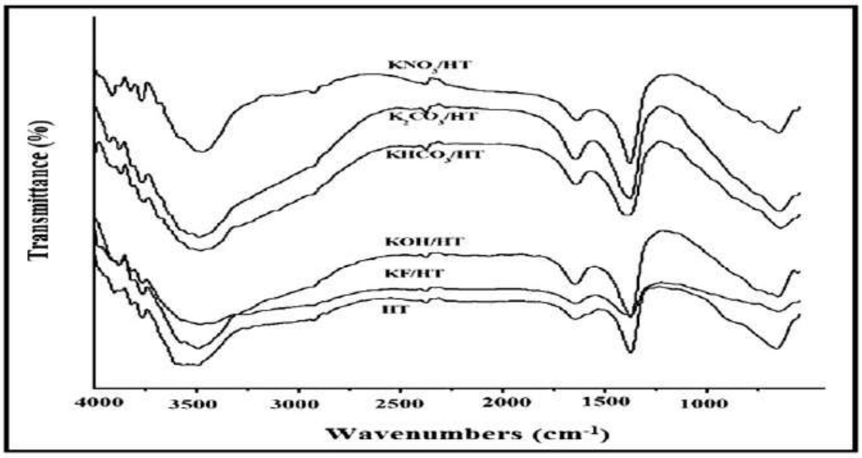

Figure 2. FTIR patterns of hydrotalcites loaded with potassium salts.

Nitrogen adsorption desorption measurements were carried out to investigate the surface area, pore sizes and pore volumes of the materials. Table 2 shows textural properties of the parent hydrotalcite and potassium salt loaded hydrotalcites. The parent hydrotalcite exhibits BET surface area of 207 m^{2}g^{-1}. Introduction of potassium species decreases the BET surface area of all the samples. The surface area of hydrotalcite loaded with K_2CO_3 is lost to the greater extent in comparison to the other four salts and decreases up to 90 m^{2}g^{-1}. This is due to the blockage of pores and interlayer spaces of hydrotalcite by CO_3^{2-} anions of K_2CO_3 salt thus preventing N_2 molecules to adsorb onto the surface. This observation has been further confirmed by the pore volume calculation of the samples which shows that the pore volume of K_2CO_3/HT is the smallest and decreases from 0.23 cm^{3}g^{-1} of parent hydrotalcite to 0.19 cm^{3}g^{-1} of the loaded one. On the other hand, surface areas of KNO_3/HT and KF /HT are 201 m^{2}g^{-1} and 197 m^{2}g^{-1} respectively. This can be expected for low water content of these materials as described in TGA and DTA analysis. We have found intermediate values of surface areas for the samples KOH/HT and $KHCO_3$/HT. This can be attributed to the high water content in these samples. On the other hand KOH/HT sample shows the largest pore volume and pore diameter with comparable surface area as that of the parent hydrotalcite. Thus, surface areas and pore sizes of loaded hydrotalcites, other than K_2CO_3 salt are not abruptly affected after loading the salts. The N_2 adsorption-desorption measurements showed that all hydrotalcites exhibit type II isotherm and H3 hysteresis loops characteristics of both monolayer and multilayer adsorption and typical for aggregated powders like clays or cements having no uniform pore structures (Figure S3, Supporting Information).[xx,xxi] Type H3 hysteresis loops are generally found for non-rigid aggregates of plate-like particles or assemblages of slit-shaped pores in the sample. It has again been confirmed from the pore size distribution curves of the samples which show broad range of pore sizes in the samples. However, narrow pore size distribution centered at pore radius of 20 Å and large pore volume of KOH/HT has led us to select it as the optimum sample in this study.

The SEM images of parent hydrotalcite and KOH/HT in magnification of X5500 and X4000 are shown in Figure 3. The parent hydrotalcite has crystal sizes in nanometer ranges with homogeneous shapes of the crystals. On loading KOH onto it, particle size decreases showing layers of agglomerated sheets in the ranges of 1-2 micrometer.

Table 2. Textural properties of potassium salt loaded hydrotalcites

Entry	Sample	BET area (m^{2}g^{-1})	Pore volume (cm^{3}g^{-1})	Pore diameter (nm)	Base Strengths (H_-)	Total basicity (mmolg^{-1})	Soluble basicity (mmolg^{-1})
1	HT	207	0.23	3.30	$9.6 < H_- < 11.1$	0.12	0.00[a] 0.00[b]
2	KF /HT	197	0.32	3.38	$12.7 < H_- < 15$	0.18	0.02
3	$KHCO_3$/HT	184	0.25	3.95	$9.6 < H_- < 11.1$	0.18	0.03
4	K_2CO_3 /HT	90	0.19	3.99	$12.7 < H_- < 15$	0.23	0.05
5	KNO_3/ HT	201	0.32	3.66	$12.7 < H_- < 15$	0.19	0.00
6	KOH /HT	185	0.36	4.00	$12.7 < H_- < 15$	0.22	0.03

[a] Hydrotalcite, [b]Reconstructed hydrtalcite obtained by immersion of MgAl mixed oxide in water for 24 h

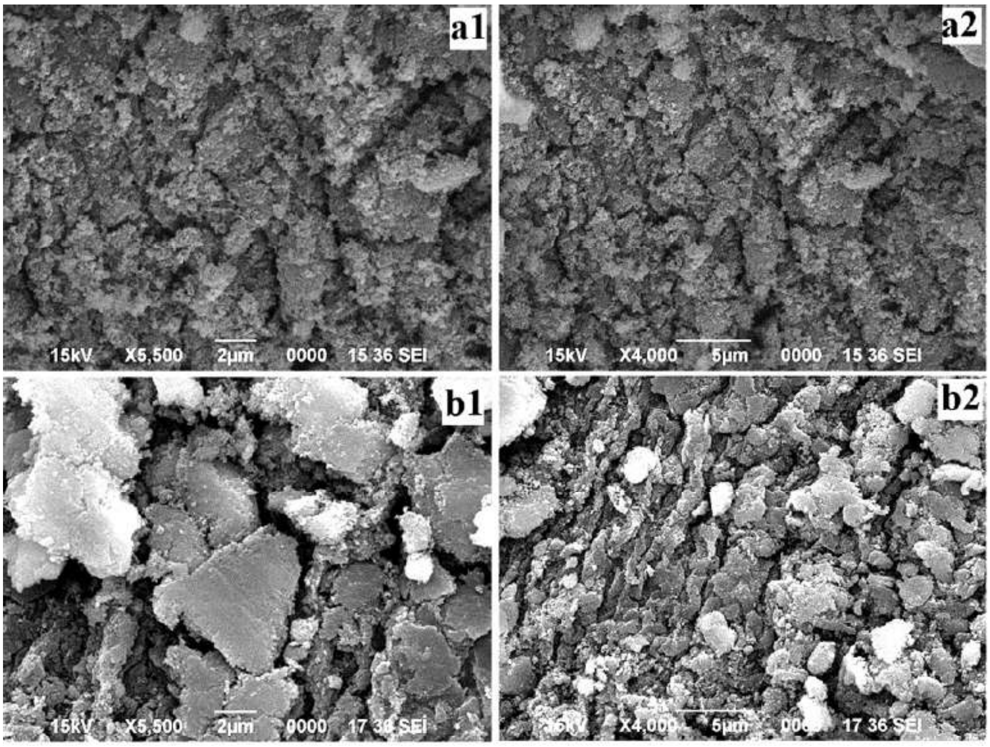

Figure 3. Scanning electron micrographs of (a) HT and (b) KOH/HT at two different resolutions.

The results of base strengths of all hydrotalcites which were determined by Hammett indicator method are summarized in Table 2. Hydrotalcites loaded with KF, K_2CO_3, KNO_3, and KOH after drying at 80 °C for 15 h showed colour change in presence of Tropaeolin-O ($H_- = 11.1–12.7$) indicator and could not change the colour of 2,4-dinitroaniline ($H_- = 15$). Therefore, they showed similar base strength in the range $12.7 < H_- < 15$. On the other hand, the unloaded parent hydrotalcite and $KHCO_3$/HT showed colour change with Phenolphthalein ($H_- = 8.0\text{-}9.6$) while no change was observed with Tropaeolin-O ($H_- = 11.1–12.7$). Thus their base strengths lies in the range $9.6 < H_- < 11.1$. Total basicity measurement of the samples shows that the number of total basic sites for K_2CO_3/HT and KOH/HT are higher than the other samples. This is reflected in the catalytic activities shown in Table 4 that the conversions for KOH/HT and K_2CO_3/HT are higher than the other catalysts. On the other hand, the total number of basic sites of all the catalysts is relatively low as compared to calcined hydrotalcites reported in literature. However, it is quite obvious from the results that although the number of total basic sites is not quite high, uncalcined hydrotalcites also can fairly catalyze Knoevenagel condensation reaction with its moderate base strengths. Thus, loading of alkali metal compounds over hydrotalcites would be acknowledged to catalyze some mild base catalyzed organic reactions such as Knoevenagel condensation reaction, Nitroaldol condensation reaction, Aldol condensation etc. Soluble basicities of all the samples are low, where no soluble base was found at all for KNO_3/HT. This again indicates more interaction of KNO_3 with host hydrotalcite structure thus preventing their loss as soluble base.

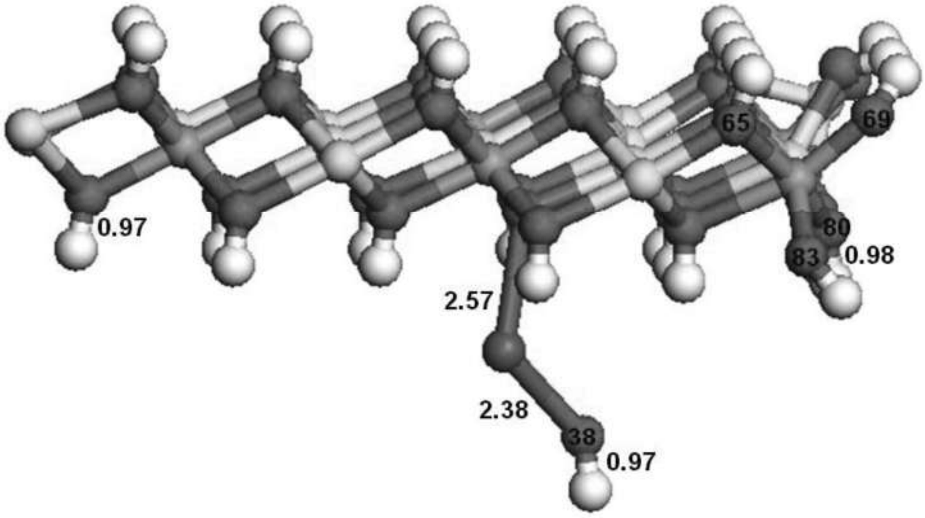

Figure 4. Optimized structure for most stable geometry of $Mg_3Al(OH)_8KOH$. The green balls represent Magnesium, pink represent Aluminium, purple represent Potassium, red represent oxygen and the grey balls represent Hydrogen atoms in the optimized geometry. The Oxygen atoms having larger values of f(-) (higher basicity) are numbered and the bond lengths are in Å.

Table 3. The values of Fukui functions with respect to Mulliken and Hirshfeld charges of the basic oxygen atoms of the metal oxide

	Fukui function (f_O^+)		Fukui function (f_O^-)		Relative electrophilicity (f_O^+/f_O^-)		Relative nucleophilicity (f_O^-/f_O^+)	
Atom	MPA	HPA	MPA	HPA	MPA	HPA	MPA	HPA
O 38	0.026	0.025	0.019	0.027	1.37	0.93	0.73	1.08
O 65	-0.001	0.006	0.002	0.005	-0.50	1.20	-2.00	0.83
O 69	0.021	0.022	0.021	0.022	1.00	1.00	1.00	1.00
O 80	0.004	0.006	0.002	0.006	2.00	1.00	0.50	1.00
O 83	0.017	0.019	0.017	0.020	1.00	0.95	1.00	1.05

We again calculated the reactivity of the O-atoms using density functional based reactivity descriptor, Fukui function. Fukui functions, f_O^+ and f_O^- are evaluated using Hirshfeld population analysis (HPA) and Mulliken population analysis (MPA) schemes to locate the nucleophilic and electrophilic sites, respectively. Though an analytical expression for the Fukui function is not available, it is usually calculated using finite difference approximation which is called condensed Fukui function. The condensed Fukui function of an atom 'O' in a molecule with N electrons at constant external potential, $v(\vec{r})$ can be expressed as:

$$f_O^+ = \frac{1}{\Delta N}\left[\rho_O(N_o + \Delta N) - \rho_O(N_o)\right] \qquad \text{(for nucleophilic attack)}$$

1(a)

$$f_O^- = \frac{1}{\Delta N}\left[\rho_O(N_o) - \rho_O(N_o - \Delta N)\right] \qquad \text{(for electrophilic attack)}$$

(1b)

where, $\rho_O(N_o)$, $\rho_O(N_o + \Delta N)$ and $\rho_O(N_o + \Delta N)$ are charge densities on atom O of the system with N_o, $N_o + \Delta N$ and $N_o - \Delta N$ electron systems, respectively. In conventional

Fukui function computations, a value of 1.0 is used for ΔN. In the present calculation, we have used a value of 0.1 for ΔN. The values of Fukui functions are given in Table 3. We have calculated the fukui functions (f_O^+ and f_O^-), relative electrophilicity (f_O^+/f_O^-) and relative nucleophiliciry (f_O^-/f_O^+) for those oxygen atoms in the hydrotalcite system having higher values of these reactivity parameters. In general, it is observed that for a particular atom in a molecule, the increase in f_O^- values is the indication of high basicity. From Table 3, it has been seen that the highest f_O^- value is obtained for the oxygen atom number 38, which is the one attached to the Potassium atom. Relative electrophilicity, (f_O^+/f_O^-) and relative nucleophilicity, (f_O^-/f_O^+) are better reactivity parameters to locate the preferable site for nucleophilic and electrophilic attacks, respectively in a chemical system.[xxii,xxiii] The basicity of a system increases with the increase of (f_O^-/f_O^+) ratio. Thus, the oxygen attached to the potassium having highest value of relative nucleophilicity (f_O^-/f_O^+) will be the most basic site. From this calculation we have inferred that the O-atom attached to the K-atom have highest values of f_O^- as well as f_O^-/f_O^+. Therefore, we can conclude that O38 is the most basic site in the hydrotalcite system. The optimized structure of the hydrotalcite is shown in Figure 4. The oxygen atoms for which the reactivity parameters have been evaluated are marked and these are the atoms having higher basic character in the system.

The catalytic activities of the parent and potassium salt loaded hydrotalcites were evaluated for liquid phase Knoevengael condensation reaction (Scheme 1) at room temperature with variety of aldehydes. The conversion of reactants to the products in an organic reaction is mainly influenced by parameters such as solvent, temperature, effect of substituted groups in the substrates, amount of catalysts etc. Taking these points into consideration, we have optimized the reaction conditions by varying the conditions. At first, the reaction was at room temperature without any catalyst by taking malononitrile and p- nitrobenzaldehyde as model reactants and methanol as solvent. To our expectation, no formation of the product was observed. Therefore, we have performed all other reactions in presence of catalysts i. e with modified hydrotalcites and rehydrated hydrotalcite under the same reaction conditions. The results are summarized in Table 4. Reaction with rehydrated hydrotalcite is comparatively slower than the loaded hydrotalcite (entry 2, Table 4). It has been observed that the reaction in methanol is not selective with all the catalysts and conversions are lower than reported methods. However, KNO_3/HT and KF/HT (entries 3 & 4, Table 4) catalysts show better results than the other catalysts in terms of selectivity and it can be correlated to their larger surface areas than the other loaded catalysts. This can be correlated again from TGA results described above that due to low water content in KNO_3/HT and KF/HT, aprotic environment of the catalyst makes the aldol type intermediate to dehydrate easily thus showing better selectivity of the Knoevenagel product in comparison to KOH/HT, $KHCO_3$/HT and K_2CO_3/HT(entries 5-7, Table 4), where more interlayer water content of these catalysts offers protic environment in the catalysts thus stabilizes the intermediate aldol type product before the dehydration step. However, low conversions of the product with KNO_3/HT and KF/HT catalysts can be attributed to the interaction of the salts with the support forming new phases and thus reducing active sites of the catalysts (XRD). On the other hand, the preferred catalyst of this study i.e. KOH/HT (entry 7, Table 4) showed the highest conversion, largest pore volume, longest pore diameter and good selectivity within 30 minutes and therefore the reaction was further carried out with this catalyst to optimize the reaction conditions. High conversion of KOH/HT also supported by its small crystallite sizes (Table 1) which favors the active hydroxyl groups to take part in the reaction [45].

Scheme 1.

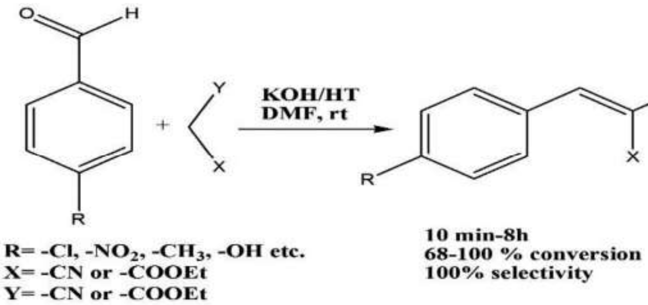

Table 4. Knoevenagel condensation reaction with different potassium salt loaded hydrotalcites at room temperature

Entry	Sample	Time (min)	% Conversion[a]	% Selectivity[a]
1	No catalyst	30	0	-
2	HT[b]	30	41	90
3	KNO_3 /HT	30	57	91
4	KF / HT	30	42	90
5	K_2CO_3 /HT	30	63	69
6	KOH /HT	30	66	81
7	$KHCO_3$/HT	30	61	76
8	KOH[c]	30	0	0

Conditions: p-nitrobenzaldehyde (1 mmol), malononitrile (1 mmol), methanol (3 mL), catalyst amount: (25 mg, 8w% of Potassium ion), reaction temperature: room temperature, [a]Obtained from ^{1}H NMR analysis of the crude reaction mixture, [b]Reconstructed hydrotalcite obtained by immersion of MgAl mixed oxide in water for 24 h, [c]Reaction with KOH salt (8w% of 25 mg)

Following this study, we have investigated the effect of solvents with 10 % KOH/HT at room temperature by taking six different solvents of different polarity. It is observed that solvents play a significant role on both conversions and selectivities. When aprotic polar solvents were used (entries 2, 4 and 5, Table 5), 81-99 % conversion was observed giving 100 % selectivity of the product within 15 minutes. On the other hand, when protic polar solvent methanol was used, the reaction was slow and both conversion and selectivity was poor (entry 3, Table 5). Non-polar solvents like toluene and diethyl ether (entries 1, 6) takes longer reaction time than polar solvents giving 61-99 % conversion and 100 % selectivities within hours. It is noteworthy to mention that in this study DMF is superior to the most commonly used solvent toluene for Knoevenagel condensation reaction in presence of hydrotalcite catalysts. It can be attributed to the fact that the reactants are miscible well in a polar environment and the catalyst mix homogeneously in the reaction mixture during vigorous stirring condition. Thus interaction of the catalyst with reactants becomes feasible in DMF in comparison to non-polar solvent toluene or diethyl ether. Therefore, it is clear from Table 5 that DMF is the best choice in terms of conversion, selectivity and reaction time and 10% KOH/HT can be chosen as the optimum catalyst with DMF.

Table 5. Effect of various solvents on Knoevenagel condensation reaction at room temperature

Entry	Solvent	Time (min)	% Conversion[a]	% Selectivity[a]
1	Toluene	40	99	100
2	DMF	15	99	100
3	MeOH	30	66	81
4	Acetonitrile	15	81	100
5	DCM	15	99	100
6	Diethyl ether	4h	61	100

Conditions: p-nitrobenzaldehyde (1 mmol), malononitrile (1 mmol), solvent (3 mL), catalyst (25 mg); Catalyst: 10% KOH/HT, [a]Obtained from ^{1}H NMR yield of the crude reaction mixture.

We then next used 10% KOH/HT for Knoevenagel condensation reaction with various aldehydes bearing electron donating and electron withdrawing groups, active methylene compounds (malononitrile and diethyl malonate) and DMF at room temperature. The results are summarized in Table 6. Knoevenagel condensation reaction has been reported previously with hydrotalcite like catalysts such as rehydrated Mg-Al hydrotalcite, metal loaded Mg-Al hydrotalcite in different reaction media and optimized reaction conditions.[xxiv] At this time, rehydration and loading have been done in the same step and found an efficient catalyst for this reaction. Aldehydes with both electron donating and electron withdrawing groups reacted efficiently with malononitrile under similar reaction condition to give 99 % conversions and 100 % selectivity of the corresponding olefins (entries 5, 7). Aldehydes containing electron withdrawing groups in ortho and para positions do not have much effect over the reaction time (entries 2, 5; Table 6) and reacted faster than aldehydes bearing electron donating groups (entry 7, 8). On the other hand unloaded catalyst takes comparatively longer reaction time than loaded catalysts and gives 99% conversion and 100% selectivity within 1.5 h (entry 3, Table 6). It may be due to presence of potassium salts and improved basicity of the loaded catalysts thus completing the reaction within short time. Heterocyclic aldehyde i.e 2-furaldehyde also reacted faster giving 99% conversion within 15 minutes. However, reaction with aliphatic aldehydes and aldehydes with big molecular size are comparatively slower than simple aldehydes showing moderate yield (52-65%, Entry 12-13) within 5h. With diethyl malonate as active methylene compound, the acidity of the acidic protons decreases due to two ester groups thereby increasing reaction time for all substrates and giving 70-90% conversion and 100 % selectivity within 4-8 hours. Polycyclic aromatic aldehyde such as 1-naphthaldehyde also reacted efficiently giving high conversion to the product. It is observed that uncalcined KOH/HT with base strength in the range $12.7 < H_– < 15$ shows comparable results to calcined mixed oxide catalyst i.e 21w % MgO-ZrO_2[xxv] and 10.3% K-MgAl(O)[xxvi] having base strength $26.5 \leq H_– < 33.0$ (footnote *b* and *c*, Table 6). This can be understood as high BET surface area of KOH/HT compared to other two made the reaction comparable to each other. We have also evaluated the efficiency of the catalyst by performing the reaction between malononitrile and 4-chlorobenzaldehyde for four repetitive cycles. It is observed that the catalyst is active even at the fourth cycle of the reaction and which gives 99 % conversion and 100 % selectivity within 15 minutes (entry 20, Table 6). On the whole, potassium hydroxide loaded MgAl-hydrotalcite acts as an efficient solid base catalyst for Knoevenagel condensation reaction at room temperature.

Table 6. Knoevenagel condensation reaction of different aldehydes and active methylene compounds with 10 % KOH/HT

Entry	R	X	Y	Time (min)	% Conversion[a]	% Selectivity[a]
1	Ph	CN	CN	30	99	100
2	4-$NO_2C_6H_4$	CN	CN	15	99	100
				15	97[b]	
				10	99[c]	
3	4-$NO_2C_6H_4$	CN	CN	40	99[d]	100
4	4-$NO_2C_6H_4$	CN	CN	90	99[e]	100
5	2-$NO_2C_6H_4$	CN	CN	15	99	100
6	4-ClC_6H_4	CN	CN	10	99	100
7	4-$CH_3C_6H_4$	CN	CN	60	99	100
8	4-OHC_6H_4	CN	CN	60	99	100
9	1-Naphthyl	CN	CN	60	99	100
10	2-Furaldehyde	CN	CN	15	99	100
11	Propionaldehyde	CN	CN	90 min	99	100
12	Isobutyraldehyde	CN	CN	5h	52	100
13	Cinnamaldehyde	CN	CN	5h	65	100
14	4-$NO_2C_6H_4$	COOEt	COOEt	240	99	100
15	2-$NO_2C_6H_4$	COOEt	COOEt	240	99	100
16	4-ClC_6H_4	COOEt	COOEt	240	99	100
17	4-$CH_3C_6H_4$	COOEt	COOEt	480	82	100
18	4-OHC_6H_4	COOEt	COOEt	480	77	100
19	1-Naphthyl	COOEt	COOEt	480	68	100
20	4-ClC_6H_4	CN	CN	15	99[f]	100

Conditions: aldehyde (1 mmol), active methyl compound (1 mmol), DMF (3 mL), 10% KOH/HT (25 mg); [a]Obtained from ^1H NMR yield of the crude reaction mixture, [b]Aldehyde (2 mmol), Active methylene compound (2 mmol), 21 w% MgO-ZrO_2 (20 mg), DMF (1 mL), [c]Aldehyde (2 mmol), Active methylene compound (2 mmol), 10.3% K-MgAl(O) (20 mg), DMF (1 mL), [d]Reaction with rehydrated hydrotalcite, [e] Reaction with as prepared hydrotalcite after drying at 80 °C for 15 h., [f] 4th run with recovered catalyst

Following this, the leaching of potassium species into solution was tested by flame photometry study. For this purpose, the reaction was performed with 2mmol p-nitobenzaldehyde, 2mmol malononitrile and 100mg of 10% KOH/HT in DCM solvent. After completion of the reaction, 10 ml water was added to dissolve the leached out potassium and to separate organic portion. We observed that 0.355 mg K was leached out from 100 mg catalyst which is quite low in comparison to the loading amount. Thus, leaching of small amount of potassium does not affect the of the overall reaction speed and conversion.

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Appendix II

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
1	R. Devi, P. Begum, P. Bharali and R. C. Deka,	Comparative Study of Potassium Salt-Loaded MgAl Hydrotalcites for the Knoevenagel Condensation Reaction	ACS Omega	6	7086 – 7095.	2018
2	R. Devi*, D. Bharali and R. C. Deka,	Synthesis of LDH for Photocatalytic Removal of Toxic Dyes from Aqueous Solutions, in Materials Modelling for Macro to Micro/Nano Scale Systems,	In *Materials Modelling for Macro to Micro/Nano Scale Systems*, S. B. Singh, P. Ranjan and A. K. Haghi edn., Apple Academic Press publishing,	Chapter 5		2021
3	R. Devi and D. Talukdar,	introduction to zeolites and its application in methylation of toluene,	in *Modern Trends in Chemistry*, D. K. Jha edn., Purbayon publication, Guwahati, India,	Chapter 3	83-127.	2020
4	**R. Devi*** and R. C. Deka,	Synthesis of CoZnLDH nanosheets by reverse microemulsion method for photo adsorption of Dyes	Journal of material Chemistry,	(Communicated)		

Presented Oral

1. **Organix-2018**, an International Conference in Chemistry, from 20-21st Dec, **2018**, Department of Chemical Sciences, Tezpur University, Assam, India
2. **Regional seminar on Science for Sustainable Development (SSD-2019)**, 9th January, **2019**, Department of Chemistry, B. Borooah College, Guwahati, Assam, India
3. **International Conference on Emerging Trends in Chemical Sciences (ETCS)**, from 13-15 Feb **2020**, Department of Chemistry, Gauhati University

WOS-A Project Outcome

1. **Name of PI:** RASNA DEVI

2. **Host Institute Name:** TEZPUR UNIVERSITY

3. **WOS-A Project Ref. No.:** SR/WOS-A/CS-43/2017 (G)

4. **Title of project:** PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS IN WATER USING LDH AND ZEOLITE NANOPARTICLES

5. **Abstract of project outcome (in 500 words):** Synthesis of CoZnLDH nanosheets have been successfully carried out with a reverse emulsion technique using isooctane, sodium dodecyl sulphate (SDS) and water. The Zn in LDH act as photoactive metal in the structure. Herein, three different LDHs namely CoZnLDH11, CoZnLDH30 and CoZnLDH61 were synthesized by varying water to SDS molar ratio 11, 30 and 61 respectively. Followed by this, characterization of the synthesized LDH have been completed with different techniques i. e XRD, FTIR, SEM, TEM, TGA and N_2 adsorption desorption methods which showed well developed layered double hydrotalcite and nanosheet structure having intercalated SDS in between the layers The synthesized CoZnLDH nanosheets were utilized for photocatalytic removal of a series of important dye pollutants namely rhodamine B (RhB), crystal violet (CV), methylene blue (MB); bromocresol green (BG), bromothymol blue (BTB), rose bangle (RB), congo red (CR) and methyl orange (MO) from their aqueous solutions. The dye removal experiments were performed both under dark and visible light irradiation. Light irradiation showed remarkable enhancement of removal percentage of dyes from their aqueous solutions. Cationic crystal violet showed rapid removal in presence of CoZnLDH11 and showed 97 % removal in 80 minutes. The catalytic dye removal experiments were monitored through UV-visible spectrophotometer to analyze concentrations of the solutions and to obtain percentage removal of the dye from the solutions. As expected, the fruitful outcome from the work includes publications in journals like ACS Omega, book chapters as well as abstract presentations in seminars, workshops etc. which is being listed in the project completion report.

    Again, we have synthesized a series of potassium salt loaded MgAl-hydrotalcites by wet impregnation of KNO_3, KF, KOH, K_2CO_3 and $KHCO_3$ salts over calcined MgAl-hydrotalcite (Mg: Al = 3:1). The samples were characterized by XRD, FTIR, TG-DTA, SEM and N_2 absorption-desorption techniques to investigate their structural properties. The results showed formation of well-developed hydrotalcite phase and reconstruction of layered structure after impregnation. The prepared hydrotalcites possess mesopores and

Forwarded
30/5/2022

micropores having pore diameters in the range of 3.3-4.0 nm and BET surface area 90-207 m^2/g. Base strengths calculated from Hammett indicator method were found increasing after loading salts where KOH loaded hydrotalcite showed base strength in the range of $12.7 < H_- < 15$ which was found to be the preferred catalyst. Subsequently, KOH loading was increased from 10-40 % (w/w) and catalytic activity was evaluated for Knoevenagel condensation reaction at room temperature. DFT calculations show that amongst all the oxygen atoms present in the hydrotalcite, the O-atom attached to the K-atom has the highest basic character. In this study, 10 % KOH loaded hydrotalcite showing 99 % conversion and 100 % selectivity was selected as the preferred catalyst in terms of base strength, stability and catalytic efficiency.

We have synthesized nano zeolites and molecular sieves like MCM 41, SBA 15 and KIT 6 which are not yet fully characterized. We have characterized these materials by XRD, IR and TGA methods. Meanwhile the applications of these catalysts in real industrial problems are yet to be explored.

6. Publication list from project (only in SCI Journal):

(i) R. Devi, P. Begum, P. Bharali and R. C. Deka, Comparative Study of Potassium Salt-Loaded MgAl Hydrotalcites for the Knoevenagel Condensation Reaction, ACS Omega 2018, 3, 6, 7086 –7095.

(ii) R. Devi*, D. Bharali and R. C. Deka, Synthesis of LDH for Photocatalytic Removal of Toxic Dyes from Aqueous Solutions, in Materials Modelling for Macro to Micro/Nano Scale Systems, S. B. Singh, P. Ranjan and A. K. Haghi edn., Apple Academic Press publishing, 2021, Chapter 5.

(iii) R. Devi* and R. C. Deka, Synthesis of CoZnLDH nanosheets by reverse microemulsion method for photo adsorption of Dyes (Communicated)

(iv) R. Devi and D. Talukdar, introduction to zeolites and its application in methylation of toluene, in Modern Trends in Chemistry, D. K. Jha edn., Purbayon publication, Guwahati, India, 2020, Chapter 3, pp 83-127.

7. Link project achievements with National Missions (if any):

8. Please mention details if you got regular job: No

9. Final settlement of project (please tick appropriate):

(i) Done [✓]

(ii) Final grant yet to be received from DST [✓]

(iii) Unspent balance refund to DST [✓]

bharatkosh.gov.in
Government of India Receipt Portal

RECEIPT

Transaction Ref.No. 0207210004802 Dated: Jul 6 2021 12:07AM

Received from M/S. TEZPUR UNIVERSITY with Transaction Ref.No. 0207210004802

Dated Jul 6 2021 12:07AM the sum of INR 2361 (Two Thousand Three Hundred Sixty-One Only) through Internet based Online payment in the account of

Interest receipt on unspent balances (DSIR), , DST-WOS RASNA DEVI REFUND OF INTEREST.

Printed On: 11-01-2022 01:29:09

Courtesy :- Controller General of Accounts

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oll free No.1800 118 111)

RN No. (for Departmental Use)	258298111119000031148	
	Beneficiary (PAO) IFSC Code :	RBISOMBPA04
	Beneficiary (PAO) Account Type :	Current Accout
	Remitter's Bank Name :	STATE BANK OF INDIA
	Remitter's Bank A/C No. :	30448821505
	Remitter's Bank IFSC Code :	SBIN0000195
	Payment Period/ Frequency :	No Restriction

Note : Please provide this URN No. at the Remarks column at the NEFT/ RTGS slip. Officials at Bank's counter himself/ herself need to ensure that the remitter Bank A/c no & the depositor being used for the NEFT/ RTGS instruction is same as what is printed on this deposit slip. Any error in entry of this A/c no. will lead to non-delivery of services expected in lieu of this payment to Government of India.

Remitter Name	Department / office from whose books the demand emanated	Full particulars of the nature of remittance and/or authority (if any)	Amount	Head of Account	Beneficiary Name (PAO)& Code	Remarks
Tezpur University	Pr.A.O.,DEPARTMENT OF SCIENCE AND TECHNOLOGY, (H.Q), TECH. BHAWAN, NEW DELHI - 16 (258298)	interest receipt on unspent balances,REFUND OF UNSPENT BALANCES DST	2,851.00	004901800000000-MISCELLANEOUS INTEREST RECEIPTS	PAO(DST), New Delhi (058296)	BEING INTEREST REFUNDED
				Total :	2,851.00	

(In words) **Rupees** : Two Thousand Eight Hundred Fifty-One Only

For Bank's Usage	
NEFT Request Received Date	
Transaction Amount	
NEFT Charges	
NEFT UTR No	
Deposit Slip Creation Date	11/11/2019 (This Deposit Slip is Valid for 15 Days till 26/11/2019)

Note : [illegible] UTR Number at the Track your Payment / Payment history [illegible] available at NTRP, as soon as you complete the NEFT/RTGS payment and [illegible] UTR Number from your Bank. [illegible] to do so, the system will not be able to generate the transaction receipt. Remark: This Dep[illegible] is valid for 15 days from the date of cre[illegible] of deposit [illegible] at NTRP, please make sure to do the NEFT/RTG[illegible] within 15 days, else the NEFT [illegible] not be accepted and treated as invalid.

Courtsey :- Public Financial Management System

Dy Registrar (Finance)
Tezpur University

Finance Officer
Tezpur University

bharatkosh.gov.in

Government of India Receipt Portal

RECEIPT

Transaction Ref.No. 0312210016271 Dated: Dec 6 2021 11:12PM

Received from M/S. TEZPUR UNIVERSITY with Transaction Ref.No. 0312210016271

Dated Dec 6 2021 11:12PM the sum of INR 2713 (Two Thousand Seven Hundred Thirteen Only) through Internet based Online payment in the account of

interest receipt on unspent balances, , DST-RASNA DEVI.

Disclaimer:- This is a system generated electronic receipt, hence no physical signature is required for the purpose of authentication

Printed On: 11-01-2022 01:30:25

Courtesy :- Controller General of Accounts

Declaration for House Rent Allowance

This is to certify that I, Ms/Dr RASNA DEVI (PI of WOS-A Project) am eligible for HRA as neither I nor my spouse is living in Government Accommodation.

The HRA rate as per GoI norms based on class of cities is (please tick appropriate):

1. Class X (24%) [ ]
2. Class Y (16%) [ ]
3. Class Z (8%) [✓]

Rasna Devi
Signature of PI

6/11/2019
Signature of Mentor with stamp

Professor
Department of Chemicals Sciences
Tezpur University
Tezpur - 784028

Head of the Institution
(Signature with stamp)

Registrar I/C
Tezpur University
Napaam, Tezpur

Declaration for House Rent Allowance

This is to certify that I, Ms/Dr RASNA DEVI am eligible for HRA as neither I nor my spouse is living in Government Accommodation.

The HRA rate as per GoI norms based on class of cities is (please tick appropriate):

1. Class X (24%) [ ]
2. Class Y (16%) [ ]
3. Class Z (8%) [✓]
4. Not Applicable [ ]

Rasna Devi
Signature of PI

BDeka 18/6/2021
Signature of Mentor with stamp

Professor
Department of Chemicals Sciences
Tezpur University
Tezpur - 784028

18/6/21
Head of the Institution
(Signature with stamp)

कुलसचिव
तेजपुर विश्वविद्यालय
Registrar
Tezpur University

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2019-2020………… in respect
non-recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Non-recurring grant**
5. Grants position at the beginning of the Financial year
   - (i) Cash in Hand/Bank: **58,116/-**
   - (ii) Unadjusted advances: **Nill**
   - (iii) Total: 58,116/-
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
58,116 /-	**1700 /-**	**3393 /-**	**-**	**-**	**0.00/-**	**56,423/-**	**0.00/-**	**56,423.00/**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	1,43,577	1,43,577

Details of grants position at the end of the year

(i) Cash in Hand/Bank **56423.00/-**
(ii) Unadjusted Advances: **Nill**
(iii) Total 56423.00/-

Devi
Signature of PI
Date 02/12/2021

Signature 27/11/2021
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature 28/11/21
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 02/12/2021

Place: Tezpur University

Signature of PI
Date 02/12/2021

Signature 27/11/2021
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature 28/11/21
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2020-2021 in respect ………… **non-recurring** GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Non-recurring grant**
5. Grants position at the beginning of the Financial year
   - (i) Cash in Hand/Bank: **56,423/-**
   - **(ii)** Unadjusted advances: **Nill**
   - (iii) Total: 56,423/-
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
56,423 /-	**1945/-**	**1945/-**	**-**	**-**	**0.00/-**	**56,423/-**	**0.00/-**	**56,423.00/**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	**Nill**	**Nill**

Details of grants position at the end of the year

(i) Cash in Hand/Bank **56423.00/-**
(ii) Unadjusted Advances: Nill
(iii) Total 56423.00/-

Signature of PI
Date 02/12/2021

Signature
Name………. Chief Finance Officer
(Head of the Finance)/ (With seal)
Date **Finance Officer**
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date **Registrar**
Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 02/12/2021
Place: Tezpur University

Signature of PI
Date 02/12/2021

Signature 27/12/2021
Name……. Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR.........2020-2021............ in respect **of recurring** GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ......**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No... **SR/WOS-A/CS-43/2017**
3. Principal Investigator......**Dr Rasna Devi**
4. Whether recurring or non-recurring grants...... **Recurring**
5. Grants position at the beginning of the financial year
   (i) Cash in Hand/Bank: **22,292/-**
   (ii) Unadjusted advances: **Nill**
   (iii) Total: 22,292/-
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received 2018-2019 years [figure as at Sl. No. 5 (ii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year 2020-2021			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
22,292/-	**768 /-**	**768/-**	**SR/wosA/CS-43/2017**	**18/05/2020**	**10,00,000/-**	**10,22,292 /-**	**9,72,549/-**	**49,743/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
256201	**716348**	**Nill**	**9,72,549/-**

Details of grants position at the end of the year

(i) Cash in Hand/Bank **49,743/-**
(ii) Unadjusted Advances : **Nill**
(iii) Total 49,743/-

Signature of PI
Date 02/12/2021

Signature
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date **Finance Officer**
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date **Registrar**
Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 02/12/2021

Place: Tezpur University

Signature of PI
Date 02/12/2021

Signature 27/12/2021
Name………Chief Finance Officer
(Head of the Finance)/ (With seal)
Date Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]
FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR.........2019-2020............ in respect
of recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ......**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No... **SR/WOS-A/CS-43/2017**
3. Principal Investigator......**Dr Rasna Devi**
4. Whether recurring or non-recurring grants...... **Recurring**
5. Grants position at the beginning of the financial year
   (i) Cash in Hand/Bank: Rs. **23450 /-**
   (ii) Unadjusted advances: **Nill**
   (iii) Total: 23450/-
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl, No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year 2019-2020			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
23450 /-	**661 /-**	**1819 /-**		-	**Nill**	**22,292 /-**	0.00	**22,292/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	-	Nil

Details of grants position at the end of the year
(i) Cash in Hand/Bank **22,292 /-**
(ii) Unadjusted Advances **Nill**
(iii) Total 22,292/-

Signature of PI
Date 02/12/2021

Signature 27/12/21
Name........., Chief Finance Officer
(Head of the Finance)/ (With seal)
Finance Officer
Tezpur University
Date

Signature 28/12/21
Name........ Head of the Organisation
(With seal)
Registrar
Tezpur University
Date

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

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(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 02/12/2021

Place: Tezpur University

Signature of PI
Date 02/12/2021

Signature 27/11/2021
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date Finance Officer
Tezpur University

Signature 28/11/21
Name........ Head of the Organisation
(With seal)
Date Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2017-2018………… in respect
of recurring/non-recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Non-recurring grant**
5. Grants position at the beginning of the Financial year
   (i) Cash in Hand/Bank : **2,00,000/-**
   (ii) Unadjusted advances:
   (iii) Total: **2,00,000/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Gant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
	132/-	**132/-**	**SR/WOS-A/CS-43/2017**	**20/12/2017**	**2,00,000/-**	**2,00,000/-**	**Nill**	**2,00,000/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	**Nill**	**Nill**

Details of grants position at the end of the year
(i) Cash in Hand/Bank **2,00,000/-**
(ii) Unadjusted Advances
(iii) Total **2,00,000/-**

Devi		
Signature of PI	Signature	Signature
Date 13/11/2019	Name……… Chief Finance Officer	Name…….. Head of the Organisation
	(Head of the Finance)/ (With seal)	(With seal)
	Date Finance Officer Tezpur University	Date Registrar Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

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(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

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(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 13/11/2019

Place: Tezpur University

Signature of PI
Date 13/11/2019

Signature
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2017-2018………… in respect
of recurring/non-recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Recurring**
5. Grants position at the beginning of the Financial year
   (i) Cash in Hand/Bank : **9,60,000/-**
   (ii) Unadjusted advances:
   (iii) Total: **9,60,000/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year 2018-2019			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
	343/-	**343/-**	**SR/WOS-A/CS-43/2017**	20/12/2017	**9,60,000/-**	**9,60,000/-**	**2,37,439/-**	**7,22,561/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
75,987 /-	**1,61,452**	-	**2,37,439/-**

Details of grants position at the end of the year

(i) Cash in Hand/Bank **7,22,561/-**
(ii) Unadjusted Advances
(iii) Total **7,22,561/-**

Signature of PI
Date 13/11/2019

Signature
18/11/19
Name……… Chief Finance Officer
(Head of the Finance)/ (With seal)
Finance Officer
Date *Tezpur University*

Signature
19/11/19
Name........ Head of the Organisation
(With seal)
Registrar
Date *Tezpur University*

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

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(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

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(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 13/11/2019

Place: Tezpur University

Signature of PI
Date 13/11/2019

Signature 13/11/19
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature 19/11/19
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR.........2018-2019............ in respect
of recurring/non-recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ......**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No... **SR/WOS-A/CS-43/2017**
3. Principal Investigator......**Dr Rasna Devi**
4. Whether recurring or non-recurring grants...... **Non-recurring grant**
5. Grants position at the beginning of the Financial year
   (i) Cash in Hand/Bank : **2,00,000/-**
   (ii) Unadjusted advances:
   (iii) Total: **2,00,000/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
2,00,000/-	**1,693/-**	**1,693/-**	-	-	**0.00/-**	**2,00,000/-**	**1,43,577/-**	**56,423/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	**1,43,577/-**	**1,43,577/-**

Details of grants position at the end of the year

(i) Cash in Hand/Bank **56,423/-**
(ii) Unadjusted Advances
(iii)Total **56,423/-**

Signature of PI
Date 13/11/2019

Signature
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Finance Officer
Tezpur University
Date

Signature
Name........ Head of the Organisation
(With seal)
Registrar
Tezpur University
Date

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

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(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

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(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

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(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 13/11/2019

Place: Tezpur University

Signature of PI
Date 13/11/2019

Signature
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2018-2019………… in respect
of recurring/non-recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Recurring**
5. Grants position at the beginning of the Financial year
   - (i) Cash in Hand/Bank : **722561/-**
   - (ii) Unadjusted advances:
   - (iii) Total: **722561/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year 2018-2019			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
7,22,561/-	**683/-**	**683/-**	**-**	**-**	**0.00/-**	**7,22,561/-**	**7,00,269/-**	**22,292/-**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
2,05,269	**4,95,000**	-	**7,00,269/-**

Details of grants position at the end of the year
(i) Cash in Hand/Bank 22,292/-
(ii) Unadjusted Advances
(iii) Total 22,292/-

Signature of PI
Date 13/11/2019

Signature
Name……….Chief Finance Officer 18/11/19
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature 19/11/19
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

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(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

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(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 13/11/2019

Place: Tezpur University

Signature of PI
Date 13/11/2019

Signature
Name.......... ~~Chief~~ Finance Officer
(Head of the Finance)/ (With seal)
Date Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2021-2022
…………in respect of **non-recurring**
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Non-recurring grant**
5. Grants position at the beginning of the financial year
   - (i) Cash in Hand/Bank: **56,423/-**
   - **(ii)** Unadjusted advances: **Nill**
   - (iii) Total: **56,423/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Government	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
56,423 /-	**661/-**	**661/-**	-	-	**0.00/-**	**56,423/-** (Deposited to Bharatkosh)	**0.00/-**	**0.00/**

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	**Nill**	**Nill**

Details of grants position at the end of the year

- (i) Cash in Hand/Bank **0.00/-**
- (ii) Unadjusted Advances: Nill
- (iii) Total : 0.00/-

Rasna Devi
Signature of PI
Date 02/05/2022

Signature
13/5/2022
Name……… Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
13/5/22
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

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(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

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(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

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Date: 02/05/2022
Place: Tezpur University

Rasna Devi
Signature of PI
Date 02/05/2022

Signature
Name.......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature 3/5/22
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

GFR 12 – A

[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR………2021-2022………… in respect **of recurring**
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme ……**Women Scientist Scheme A (WOS-A)**
2. WOS-A Reference No… **SR/WOS-A/CS-43/2017**
3. Principal Investigator……**Dr Rasna Devi**
4. Whether recurring or non-recurring grants…… **Recurring**
5. Grants position at the beginning of the financial year
   (i) Cash in Hand/Bank: **49,743 /-**
   (ii) Unadjusted advances: **Nill**
   (iii) Total: **49,743/-**
6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received 2018-2019 years [figure as at Sl. No. 5 (ii)]	Interest Earned thereon	Interest deposited back to the Government	Grant received during the year 2021-2022			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
49,743/-	583 /-	583/-	-	-	Nill	49,743/-	0.00/-	49,743/-

Component wise utilization of grants:

Grant-in-aid–General	Grant-in-aid–Salary	Grant-in-aid–creation of capital assets	Total
-	-	Nill	Nill

Details of grants position at the end of the year

(i) Cash in Hand/Bank 49,743/-
(ii) Unadjusted Advances : Nill
(iii) Total: 49,743 /-

Rasna Devi
Signature of PI
Date 02/05/2022

Signature
Name……. Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name…….. Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **WOS-A** (name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 02/05/2022

Place: Tezpur University

Rasna Devi
Signature of PI
Date 02/05/2022

Signature
Name......... Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name........ Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

(Strike out inapplicable terms)

STATEMENT OF EXPENDITURE

1. Sanction Order No and Date: **SR/WOSA/CS-43/2017 (G) and 20/12/2017**
2. Total Project Cost: **29,95,500 /-**
3. Revised Project Cost (if applicable):
4. Date of Commencement: **03/01/2018**
5. Grant received in each year:
    a. 1st Year: **9,60,000/-**
    b. 2nd Year: **Nill**
    c. 3rd Year: **10,00,000 /-**
    d. Interest, if any: **583 /-**
    e. **Total (a+b+c+d): 19,60,583/-**

STATEMENT OF EXPENDITURE

To be submitted financial year wise

(From 01/04/2020 to 02/01//2022 of the financial year 2021-2022, 01-04-2021 till 31.03.2022)

Sl No. (I)	Sanctioned Heads (II)	Sanctioned Cost (III)	Expenditure Incurred					Total Expenditure IV + V + VI (VII)	Balance as on (date) III – VII = (VIII)	Requirement of Funds up to 31st March next year	Remarks (if any)
			1st Year (3rd Jan 2018 to 31st March 2018) (IV)	2nd Year (1st April 2018 to 31st March 2019) (V)	3rd Year (1st April 2019 to 31st March (2020)	4th Year (1st April 2020 to 31st March (2021) (VI)	5th Year (1st April 2021 to 31st March 2022)				
1.	**Fellowship**	13,20,000/-	1,61,452/-	495000/-	-	6,63,548/-	Nill	13,20,000/-	0,00/-	6,60,000/-	
2.	**Consumables**	3,00,000/-	7,214/-	142286/-	-	1,25,014/-	Nill	2,74,514/-	25,486/-	1,00,000/-	
3.	**Travel**	37,200/-	-	6756/-	-	6,200/-	Nill	12,956/-	24,244/-	-	
4.	**Contingencies**	50,000/-	6,273/-	18727/-	-	25,000/-	Nill	50,000/-	0.00/-	25,000/-	
5.	**HRA**	52,800/-				52,800/-	Nill	52,800/-		52,800/-	
6.	**Equipment**						Nill				
7.	**Overhead expenses**	2,00,000/-	62,500/-	37,500/-	-	99,987/-	Nill	1,99,987/-	13.00/-	65,000/-	
	Interest earned	583/- **(Deposited to Bharatkosh)**									
8.	**Total**	**19,60,000/-**	**2,37,439/-**	**700269/-**	-	**9,72,549/-**	**0.00/-**	**19,10,257/-**	**49,743/-**	**9,02,800/-**	

Rasna Devi

Name and Signature of Principal Investigator:
Date: 02/05/2022

Signature of Competent financial authority: Finance Officer
(with seal) Date: Tezpur University

*** DOS – Date of Start of Project**

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e., Figures in Column (VIII) should not exceed corresponding figures in Column (III)
2. Utilisation Certificate for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.

STATEMENT OF EXPENDITURE

1. Sanction Order No and Date: **SR/WOSA/CS-43/2017 (C) and 20/12/2017**
2. Total Project Cost: **29,95,500/-**
3. Revised Project Cost (if applicable):
4. Date of Commencement: **03/01/2018**
5. Grant received in each year:
    - a. 1st Year: **2,00,000/-**
    - b. 2nd Year: Nill
    - c. 3rd Year: Nill
    - d. Interest, if any: **661 /-**
    - e. **Total (a+b+c+d): 2,00,661/-**

STATEMENT OF EXPENDITURE

To be submitted financial year wise

(From 01/04/2021 to 02/01//2022 of the financial year 2021-2022, 01-04-2021 till 31.03.2022)

Sl No (I)	Sanctioned Heads (II)	Sanctioned Cost (III)	Expenditure Incurred			Total Expenditure IV + V + VI (VII)	Balance as on (date) III – VII = (VIII)	Requirement of Funds upto 31st March next year	Remarks (if any)
			1st Year (3rd Jan 2018 to 31st March 2018) (IV)	2nd Year (1st April 2018 to 31st March 2019) (V)	3rd Year & so on (1st April 2019 to 31st March 2022) (VI)				
1.	Fellowship								
2.	Consumables								
3.	Travel								
4.	Contingencies								
5.	Others, if any	-							
6.	Equipment	2,00,000/-	0.00/-	1,43,577/-	0.00/-	1,43,577/-	56,423/- (Deposited to Bharatkosh)	No	No
7.	Overhead expenses								
	Interest earned	661 /- (Deposited to Bharatkosh)	-			-			
8.	Total	2,00,000/-	-	1,43,577/-	0.00/-	1,43,577/-	0.00/-		

Rasna Devi

Name and Signature of Principal Investigator:

Date: 02/05/2022

Signature of Competent financial authority: __________

(with seal) **Date:** 13/5/2022

Finance Officer
Tezpur University

*** DOS – Date of Start of Project**

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e., Figures in Column (VIII) should not exceed corresponding figures in Column (III)
2. Utilisation Certificate for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.