CHAPTER 6

CONCLUSIONS AND FUTURE SCOPES

One of the major objectives of the present work was to synthesize and characterize transition metal based-LDHs with activity measurements for environmental remediation as adsorbent and photocatalysts towards the efficient removal of various organic contaminants such as dyes, phenol and chlorophenols from aqueous solution. Another important objective was to develop a green and environmentally benign catalyst for base catalysed organic reaction such as nitro-aldol condensation (Henry) reaction under mild and microwave conditions. The LDH derived mixed oxides have been employed as the base catalyst for the above mentioned organic transformation.

This chapter presents overall conclusion of the thesis work with concluding remarks drawn from each chapter. The possible future scopes of the present work have also been highlighted.

6.1 Concluding remarks and outlook

In context of the objective of the present investigation, the thesis is comprised of total six chapters.

Chapter 1 presented a brief overview on transition metal-based LHDs highlighting their synthesis, properties and applications for waste water treatment and base catalysed organic transformations. Extensive literature reviews in perspective of the application of LDHs have been included and the objectives of the present work were highlighted at the end of the chapter.

Chapter 2 emphasized the details of materials and characterization techniques used for the entire work. The procedures of all the experimental works were described in this chapter.

Chapter 3 dealt with the results and discussion part describing the characterization of various binary and ternary LDHs with their applications for adsorption of organic dye pollutants. The chapter was divided into three sections depending on the alterations of transition metal/method in the syntheses of LDHs. A co-precipitation method was employed to synthesize NiMgAl LDHs with variable compositions. The adsorption activities of the synthesized LDHs were investigated for removal organic dye pollutants. The presence of Ni greatly influenced the structural as well as the adsorption capacity of the LDH samples. The ternary LDH3 with Ni/Mg molar ratio of 1:1 displayed efficient adsorption activity for removal of anionic methyl orange (MO) from aqueous solution with % dye uptake of 97% and maximum adsorption capacity (q_m) of the adsorbent was 127.9 mg/g at pH 6. The effects of various reaction parameters such as contact time, adsorbent dosages, initial dye concentration and solution pH on the adsorption process were studied. The adsorption kinetics followed pseudo-second order kinetic model and Langmuir adsorption model displayed better fitting with the adsorption data, indicating a monolayer adsorption process. Moreover, D–R isotherm model showed physical nature of the adsorption process.

Another series of LDHs were synthesized by simple alteration of divalent metal with transition metal such as Cu in the syntheses. A simple co-precipitation method was employed for the synthesis of CuMgAl LDHs with varying molar ratio of Cu/Mg. The Cu content enhanced the adsorption efficiency of the LDHs for the removal anionic dye from aqueous solution with efficient activity for Cu rich LDH (CuMgAl 4). The study also showed that the anionic dyes were adsorbed in higher amount compared to the cationic dyes over the LDH surface, which could be attributed to the electrostatic attraction between the positive surface site of LDH adsorbents and anionic dye molecules at pH 7. Moreover, the adsorbent showed multicyclic adsorption activity and also selectively removed dye from a mixture of anionic and cationic dyes.

We also studied the effect of ultrasound irradiation on adsorption efficiency of NiAl LDH. A sonochemical method had been employed for the synthesis of LDH materials under various ultrasonic irradiation times. The synthesized materials were employed as adsorbent for the adsorptive removal of congo red (CR) from aqueous solution. The ultrasonic irradiation time, contact time, adsorbent dosage and initial dye concentration had great impact on the adsorption process. NiAl-LDH synthesized at 1h ultrasonic irradiation time (NiAl-S_1 LDH) displayed enhanced adsorption efficiency for removal of CR with maximum adsorption capacity of 120.5 mg/g at pH 6. The thermodynamic study revealed that the adsorption of CR on NiAl-S_1 LDH is feasible, spontaneous and endothermic in nature.

Chapter 4 described the results and discussion part of the characterization of ZnFe LDH with their catalytic application for photodegradation of organic pollutants. This chapter was divided into two sections based on the alterations of their catalytic application. ZnFe LDH with Zn/Fe molar ratio of 3 was synthesized via the simple co-precipitation method. The photocatalytic degradation of various phenolic compounds, such as phenol and chlorophenols under visible and UV light irradiations were studied over ZnFe LDH. The enhanced photocatalytic activity was achieved for degradation of phenol and its compounds using visible light irradiation. The photodegradation process had been influenced by various parameters, such as catalyst amount, initial concentration of phenolic compounds and pH. The kinetics of the photodegradation process had well been described with Langmuir-Hinshelwood first order kinetics for all the phenolic compounds. The degradation proceeds via the attack of hydroxyl radical on the aromatic phenol ring with the formation of various transient states followed by the aromatic ring opening led to the formation of corresponding aliphatic acids and finally mineralization of the toxic organic contaminants. Moreover, the phenolic degradation was well supported by the theoretical study. The photocatalyst showed good reusability upto four cycles for degradation of phenol.

Moreover, for enhancing the scope of ZnFe LDH as efficient photocatalyst, degradation of various dye pollutants in aqueous solution had been studied under both UV and visible light irradiations. The catalyst exhibited efficient activity towards the photodegradation of methylene blue (MB) and rhodamine b (RhB) in aqueous solution with 100% degradation in 120 and 240 min, respectively. The effects of various reaction parameters such as light irradiation time, catalyst amount, initial dye concentrations and solution pH on the photodegradation process had been studied to effectively utilise the catalyst. The degradation kinetics followed first order kinetics for both MB and RhB. Moreover, the catalyst retained its activity upto five cycles without any major difference in the activity for degradation of both dyes.

Chapter 5 presented the results and discussion part of the characterization of mixed metal oxides derived from LDHs with their catalytic activities for base catalysed nitro-aldol (Henry) reaction under mild and microwave conditions in two different sections. We had successfully synthesized ternary LDHs by partially substituting Mg^{2+} cation with M^{2+} ($M^{2+} = Ni^{2+}$ or Co^{2+}) cations in MgAl LDH and calcined at 450 °C to obtain mixed metal oxides. The main purpose of this study was to observe the influence of divalent metal (M^{2+}) cations on structural and catalytic properties of MgAl LDH and thus on their derived mixed metal oxides. NiMgAl mixed oxide exhibited the efficient catalytic activity for nitro-aldol condensation reaction at room temperature and under solvent free condition. The effect of calcination temperatures on the reaction had also been studied. The enhanced catalytic activity of the mixed oxide was attributed to the high BET surface area and turn over frequency. Various reaction parameters such as catalyst dosages, temperature and substituent effects were studied thoroughly in order to achieve an optimised condition for the reaction. The catalyst retained its activity upto 4^{th} cycle without any significant loss in the activity.

Again, to observe the effect of Ni on structural and catalytic activity of brucite-like LDH, a series of NiMgAl LDHs had been synthesized via the co-precipitation method with varying composition of Ni keeping the molar ratio of (Ni+Mg)/Al at 3 and calcining the samples at 450 °C to obtain their corresponding mixed metal oxides. The catalytic measurements of the LDH derived mixed oxides were carried out for nitro-aldol condensation reaction under solvent free MW condition. The molar ratio of divalent cations (Ni/Mg) greatly influenced the % conversion of the reaction. The mixed oxide, LDH3 (O) with Ni/Mg molar ratio of 1 in the respective precursor possessed the fast and superior catalytic activity for reaction under MW irradiation with 97% conversion in 7 min. The presence of equivalent amount of divalent metal cations (Ni/Mg = 1) in the brucite-like LDH increased the surface area of the catalyst and consequently, enhanced its activity for nitro-aldol reaction. The effect of various reaction parameters on the catalytic reaction had been studied. The catalyst showed reusability upto 4 cycles with similar catalytic activity in each case.

Chapter 6 described the concluding remarks and major findings of the experimental work along with the possible future scopes that can be explored with importance to the research contributions.

The major findings of the thesis comprise:

- Introduction of Ni in MgAl LDH greatly affects the structural as well as the adsorption capacity of the LDH samples for removal of methyl orange (MO) from aqueous solution.

- Cu content in the brucite-like LDH enhances the adsorption efficiency for the removal anionic dye from aqueous solution with efficient activity for Cu rich LDH (CuMgAl 4).

- The anionic dyes are efficiently adsorbed over the CuMgAl LDH surface which is attributed to the electrostatic attraction between the LDH surface and anionic dye molecules.

- Sonochemically synthesized NiAl-LDH ($NiAlS_1$ LDH) displays enhanced adsorption activity for removal of congo red (CR) from aqueous solution.

- The thermodynamic study reveals the physical and endothermic nature of the adsorption process for removal of CR on $NiAlS_1$ LDH.

- ZnFe LDH shows excellent photocatalytic activity towards the removal of various organic pollutants, such as phenolic compounds and dyes.

- The degradation proceeds via the aromatic ring opening leads to the formation of corresponding aliphatic acids and finally mineralization of the toxic organic contaminants.

- The substitution of divalent metal cations greatly affects the crystallization as well as on the catalytic activity for nitro-aldol (Henry) reaction.

- The NiMgAl mixed oxide exhibits the highest catalytic efficiency for nitro-aldol reaction at room temperature and under solvent free condition.

- The molar ratios of divalent cations (Ni/Mg) greatly influence the % conversion of the nitro-aldol reaction. The LDH3 (O) mixed oxide with Ni^{2+}/Mg^{2+} molar ratio of 1:1 shows efficient catalytic activity for reaction under MW irradiation.

Thus the present investigation forwards transition metal-based LDHs as one of the possible choices for advanced applications in different fields including catalysis, adsorption, electrochemistry, polymers, biotechnology, biomedicines and so on.

6.2 Future scopes

The present investigation gives a comprehensive preliminary glimpse on transition metal-based LDHs and their application in different field of prospects. However, there are some possibilities for future studies in this domain and the following points may be highlighted as future scopes of the present investigation.

1. LDH derived mixed oxides can be employed for other base catalysed organic transformations such as Knoevenagel condensation, Claisen-Schmidt condensation reaction etc. under mild conditions.
2. Photocatalytic degradation study can be extended for various other organic contaminants.
3. An in-depth study is needed for analysing the products obtained in the photodegradation process which were remained untouched in this limited period of time.
4. A theoretical study can also be attempted to understand the complete degradation mechanisms and degradation pathways for photodegradation of cholophenols and dye pollutants.
5. Fabrication of new catalyst can be done using LDHs as catalyst support with a range of nanoparticles, graphene oxides and carbon dots.

LIST OF PUBLICATIONS

1. **Bharali**, **D.,** Devi, R., Bharali P., and Deka, R. C. Synthesis of high surface area mixed metal oxide from the NiMgAl LDH precursor for nitro-aldol condensation reaction. *New Journal of Chemistry*, 39:172–178, 2015.

2. **Bharali**, **D.** and Deka, R. C. Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide. *Journal of Environmental Chemical Engineering*, 5(2):2056–2067, 2017.

3. **Bharali**, **D.** and Deka, R. C. Preferential adsorption of various anionic and cationic dyes from aqueous solution over ternary CuMgAl LDH. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 525:64–76, 2017.

4. **Bharali**, **D.,** Bharali P., Choudary, B. M., and Deka, R. C. Efficient removal of anionic organic dye pollutants from aqueous solution by NiMgAl layered double hydroxides (Communicated).

5. **Bharali, D.,** Gour, N. K., Choudary, B. M., and Deka, R. C. Experimental and theoretical studies on photocatalytic degradation of phenol and its derivatives using ZnFe layered double hydroxide (Communicated).

6. **Bharali**, **D.,** Bharali P., and Deka, R. C. Effect of Ni on structural properties of NiMgAl-LDH derived mixed oxides and their catalytic activity for nitro-aldol condensation reaction (Under preparation).

LIST OF CONFERENCES ATTENDED

List of Oral/Poster Presented

1. Oral presented in National Conference on Contemporary Developments in Chemical Sciences-2015, Tezpur University, Assam, 23 & 24 November, 2015.

2. Poster presented in National Seminar on Recent Advances in Chemical Research (RACR 14), Rajiv Gandhi University, Arunachal Pradesh, 20 & 21 March, 2014.

3. Poster presented in National Seminar on Recent Trends in Fundamental and Applied Chemical Sciences (RTFACS-14), Dibrugarh University, Dibrugarh, 19–21 November, 2014.

4. Poster presented in International Symposium on Recent Advances in Chemistry, North Eastern Hill University, Shillong, 03–05 March, 2015.

List of Seminar/Conference/Workshop/Symposium attended

1. 13th Orientation Programme in catalysis, NCCR, IIT, Madras from 26th November to 13th December, 2012.

2. Indo-Finnish Symposium on Role of catalysts on production of green fuel, Tezpur University, Assam, 1st February, 2013.

3. Workshop on Spectroscopic Tools and their Applications, Tezpur University, Assam, 6th April, 2013.

4. Science Academics Lecture Workshop on Modern Trends in Chemistry, Tezpur University, Assam, 20–22 November, 2013.

5. Indo-Finnish Workshop on Green Chemistry, Tezpur University, Assam, 13 & 14 December, 2013.

6. 20th National Magnatic Rasonance Society Symposium, Tezpur University, Assam, 2–5 February, 2014.