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Zn-Al Layered Double Hydroxides for Phosphate Removal: Synthesis and Application

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Abstract: Excess phosphate content discharged from various human activities into water bodies often results in Eutrophication. Eutrophication leads to water pollution and degrades the water quality. One of the feasible and economical solutions for the removal of phosphates is Layered Double Hydroxide (LDH) structures. LDHs are a type of anionic clay whose structure is made up of brucite-like layers. The present study deals with the synthesis of Zn-Al LDH by the co-precipitation method. The synthesized Zn-Al LDH was characterized by instrumentation like XRD, TG–DTA, SEM- EDS and FTIR. These analyses confirmed the formation of LDH structure. Different batch experiments were conducted by varying the dosage and contact time. The results of the batch experiments showed that 0.9g was the optimum dosage for phosphate removal and the reaction reached equilibrium at 40min. The maximum removal efficiency was found to be 94.69%.
Index terms: Eutrophication, Zn-Al LDH, phosphate, synthesis, co-precipitation, optimum dosage.

1. Introduction

In surface water bodies, increase in nutrient concentration results in reduction of dissolved oxygen levels in water. This reduction in dissolved oxygen levels which is a result of increased algal growth and decomposition of dead algae will reduce the food for other aquatic life also. This process of eutrophication is known to cause negative impact on ecosystem. As a result of eutrophication excess phosphate is present in water bodies, which is cause of concern if present in excess quantities[1].

Already many conventional techniques for removal of phosphate in water are in practice which may be classified as physical methods like sedimentation, flotation and filtration, chemical methods like precipitation, ion exchange and adsorption and biological methods like bacteria, algae and plants. However, these methods, especially physical and biological methods require high initial investments, resulting in higher energy consumption and larger amounts of sludge is produced. It is difficult to recover P from the sludge [2].

Hence there is a need for efficient and achievable ideas that can remove the phosphate from the water. Layered Double Hydroxides (LDHs) are the potential material to overcome the problems caused due to the presence of phosphates in the water. As reported by earlier researchers Zn-Al containing LDH and their calcined products with high adsorption selectivity are good candidates that can be used for removal of phosphate anions via co-precipitation method. Zn-Al LDH exhibit high selectivity towards phosphate ions. The efficiency of removal of phosphate using Zn-Al LDH are higher than other LDH [3].

LDHs are a type of anionic clay whose structure is made up of brucite-like layers. The positively charged sheets of LDHs are generated by isomorphous substitution of some of the divalent M^{2+} cations which are present in the brucite-like layers by trivalent M^{3+} cations. The intercalation of anions inside the hydrated interlayer galleries between the sheets will balance the positive charge. They are represented by general formula $[M^{2+}_{1-x}M^{3+}_{x}\ (OH)_{2}]^{x+}(A^{n-})_{x/n}yH_2O$, where x is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$. The applications of LDHs includes their usage as additives in water treatment, sensors, polymers, cosmetics, in biology and medicine, in catalysis and in environmental remediation [4]–[6].

Many properties like low toxicity, anion exchange capacity, large surface area per unit of mass, large porosity, thermally stable and a range of divalent and trivalent cationic combinations make them suitable sorbent materials [7]–[9].

LDH materials offer several advantages, such as versatility of their chemical composition, low cost, a wide range of preparation variables, their easily manipulated properties, unique anion exchange and intercala-

tion properties, colloidal and thermal behaviour, chemical stability, they can be easily synthesized in the lab and they are eco-friendly [7]–[9].

Commonly used methods of synthesis of LDHs are precipitation, sol-gel and reconstructions methods whereas complex products of LDHs are synthesized by co-precipitation and anion exchange. To modify the some properties of materials, post-synthesis treatments like hydrothermal and solvothermal methods are used. For preparation of LDHs consisting different M^{2+} and M^{3+} metal cation and different kinds of anionic species including organic, inorganic or biomolecules, co-precipitation is the most feasible method as it provides liberty over different synthetic parameters such as the concentration of metallic salt, pH of reaction medium and choice for different anionic species [10].

Hence present study involves synthesis of the Zn-Al LDH by co-precipitation method and characterising it by X-Ray Diffraction (XRD), Thermal Analysis (TG-DTA), Fourier-transform infrared spectroscopy analysis (FT-IR) and Scanning electron microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS). Treatment experiments are carried out for removal of the phosphate with respect to dosage of LDH and contact time.

2. Materials and Methodology

A. Materials

Chemicals used in present study are sodium carbonate (Na_2CO_3) (Avra, 98%), sodium hydroxide (NaOH) (Avra, 98%), zinc nitrate ($Zn(NO_3)_2.6H_2O$) (AVRA, 98%), aluminium nitrate ($Al(NO_3)_3.9H_2O$) (Avra, 98%), potassium di-hydrogen phosphate(KH_2PO_4), phenolphthalein indicator, molybdate vanadate reagent.

B. Synthesis of LDH

Solution A = Sodium carbonate (Na_2CO_3) + Sodium hydroxide (NaOH)

SolutionB = Zinc nitrate ($Zn(NO_3)_2.6H_2O$) + Aluminium nitrate ($Al(NO_3)_3.9H_2O$)

The LDH was synthesized in the range of pH from 9 to 11. Two solutions, 0.09M of Na_2CO_3 and 1.6M of NaOH were added with 100ml of distilled water in the beaker and stirred. Then 0.6M of $Zn(NO_3)_2.6H_2O$ and 0.2M of $Al(NO_3)_3.9H_2O$ were added with 100ml of distilled water in another beaker and stirred. Above solutions were placed in two different burettes, i,e. solution A in burette A and solution B in burette B. These two solutions were added drop wise and simultaneously to the beaker containing 250ml of distilled water which was placed on magnetic stirrer and stirred continuously by maintaining pH at 9 to 11. After this process, solution was filtered and washed with 100mL of distilled water and then oven dried for 10hrs. Then characterization of sample was done by XRD, SEM, EDS, TG-DTA, and FTIR analysis [11]–[13].

C. Determination of phosphate

After characterization of LDH, treatment of phosphate was done using synthesized LDH and thereby treatment efficiency eas evaluated. Determination of phosphate was done by colorimetric method [14]. The spectrophotometric measurements were carried out at 470 mm. Standard phosphate solutions (0.5 mg/L to 70 mg/L) were prepared. 35 mL of standard solution was taken along with a drop of phenolphthalein indicator in it, followed by addition of 10 mL of vanadate molybdate reagent and diluted upto 50 mL. The reactants were mixed and allowed to develop the yellow colour. The absorbance was measured at 470 nm. Calibration curve of concentration versus absorbance was plotted to find the concentration of the samples

D. Analytical Instruments

Instruments used during the experimentation were magnetic stirrer (REMI-2L), pH meter (Systronics - µ pH system 362). XRD (D8 QUEST, Horizontal Goniometer), SEM-EDS (JEOL make, JSM-IT500LA), FTIR (Spectrum 2 FT-IR/ SP 10, PerkinElmer, Singapore pvt .ltd), TG-DTA (SDT-Q600) instruments used for characterization. Orbital shaker, spectrophotometer (LABINDIA ANALYTICAL - UV 3000+).

E. Batch Experiments

All the experiments were carried out with one control and samples in duplicate. Initial concentration of the solution was 75mg/L and volume was 50mL. The pH of the phosphate solution was 6 and pH solution after

treatment was found to be 7. The first set of experiment was done with varying dosage of 0.1g, 0.2g, 0.5g, 0.7g, 0.9g for 30min. In the second set of experiments, the experimentation was carried out varying contact time from 0 to 60 min with time interval 10min. The thorough mixing of solution during the experiment was done using orbital shakers. After that the solution was filtered and was analyzed for phosphate concentration.

3. Results and Discussions

A. Characterization

The XRD patterns of the synthetized LDH is presented in Figure 1. Hydrotalcite –like compounds were observed for Zn–Al samples. Peaks were found at different 2θ values. Highest peak observed at approximately 2θ = 11.67° corresponds to characteristic peak of the layered structures. The highest peak of XRD results is matching with the JCPDS card number 380486 with the chemical formula $Zn_6Al_2(OH)_{16}CO_3.4H_2O$. Thus XRD of the synthesized Zn-Al LDH showed patterns that were typical for LDH. [11]

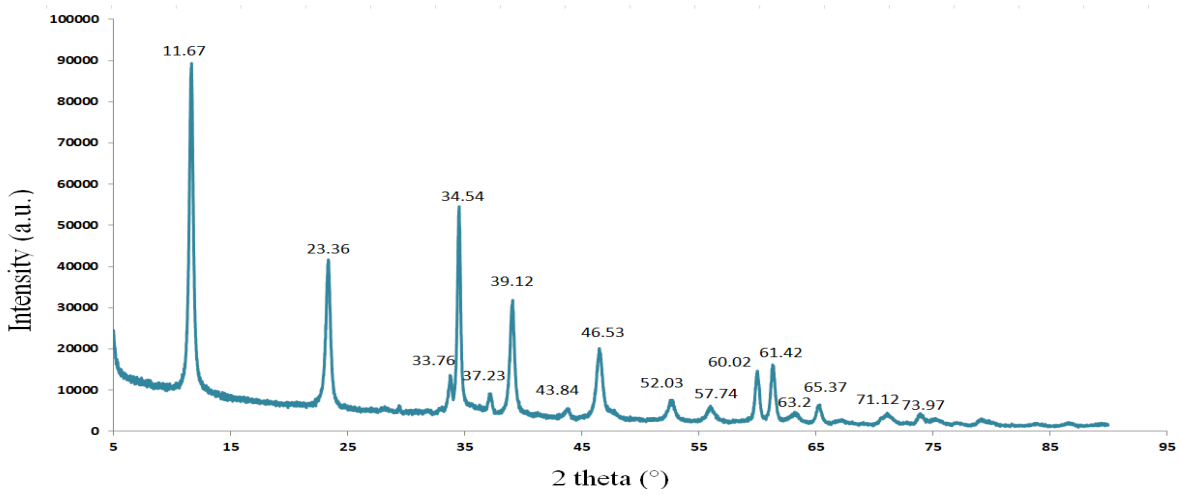


Fig 1: Showing the XRD pattern of synthesized LDH

The TG–DTA profiles are shown in Figure 2 and Figure 3. It was observed that Zn–Al samples showed weight loss occurred in three stages. The weight loss occurred in the range of 23.26 ºC - 44.74ºC in the first step which corresponds to removal of adsorbed and interlayer water. At a temperature range between 44.74ºC and 224.84 ºC the second decomposition occurred which corresponds to dehydroxylation and removal of interlayer anions from hydrotalcite. The third thermal decomposition occurred at a temperature range for dehydroxylation or decarbonation between 892.16ºC and 992.07ºC. [11]

At the temperature range upto 23.26 to 562.04°C, which corresponds to rehydration of LDH, and this rehydration shows up on DTA curve as an exothermic. From 562.04 to 992.07°C, a second DTA effects occurs, which corresponds to dehydration of the LDH. This process is endothermic. [11]

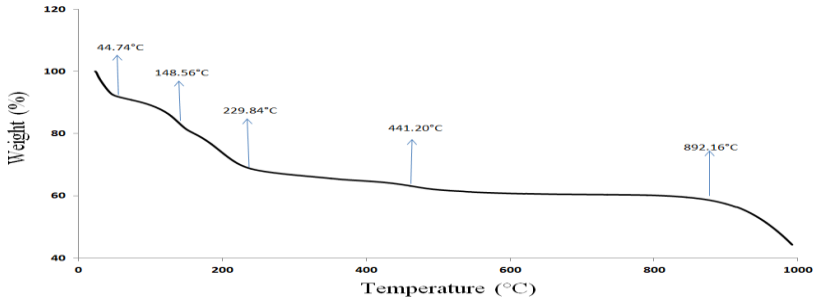


Fig 2: TGA curve of synthesized LDH

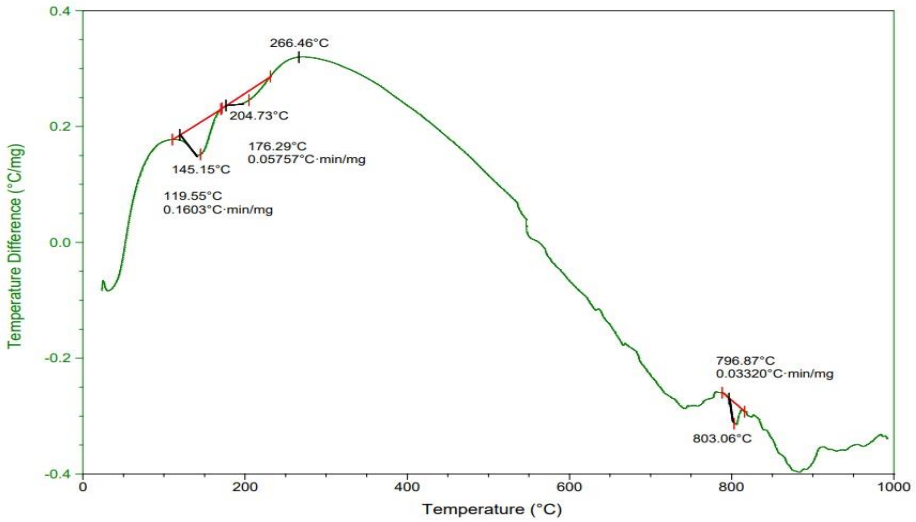


Fig 3: DTA curve of Synthesized LDH

The SEM micrograph of the sample prepared with Zn-Al sample is shown in the Figure 4. The micrograph of Zn-Al indicated homogeneous morphology of hexagonal shape primary particles. The SEM image of Zn-Al showed amorphous plates – like particles with multifarious shapes as well. All of these results are in good agreement with XRD results of Zn-Al-CO_3 LDH.

The energy dispersive spectrograph in Figure 5, shows the presence of elements used in the synthesis of the layered double hydroxides such as zinc, aluminium. carbon, oxygen and the values measured in atomic and mass % are listed in the table [15].

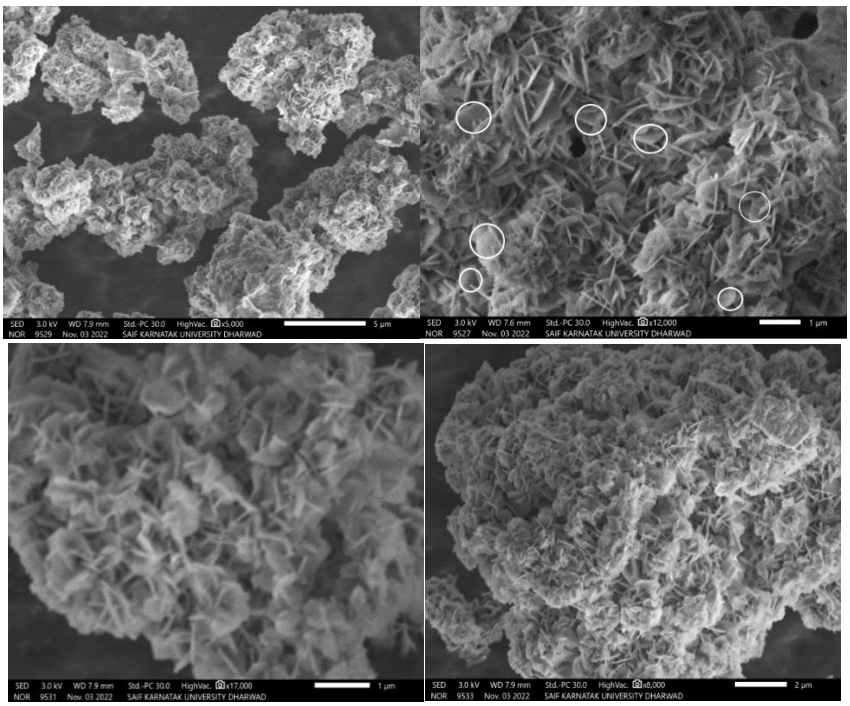
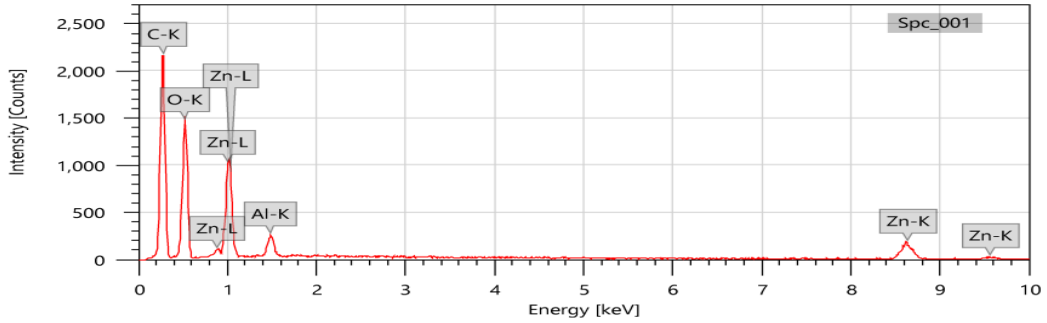


Fig 4: SEM images of synthesized LDH at different magnifications (5000X, 8000X, 12000X, 17000X)



Items	Value
measurement conditions	
Acceleration voltage	20.00 kV
Probe current	-
Magnification	x 1000
Process time	T3
Measurement detector	First
Live time	30.00 seconds
Real time	30.57 seconds
Dead time	2.00
Count rate	1861.00 CPS

Display name	Standard data	Quantification method	Result Type
Spc_001	Standardless	ZAF	Metal

Element	Line	Mass%	Atom%
C	K	46.06±0.17	57.68±0.22
O	K	41.46±0.34	38.98±0.32
Al	K	1.41±0.04	0.78±0.02
Zn	K	11.08±0.24	2.55±0.06
Total		100.00	100.00
Spc_001			Fitting ratio 0.0413

Fig 5: EDS of synthesized LDH

The FTIR spectra of the LDH in Figure 6 shows a typical Zn-Al hydrotalcite like material showing broad intense band at 3470 cm^{-1} (OH stretching vibrations from structural hydroxyl groups and interlayer water molecules) band at 1360cm^{-1} (OH bonding made of water molecules) for Zn-Al. In addition band at 551cm^{-1} show the presence of CO_3^{2-} in the interlayer [16], [17].

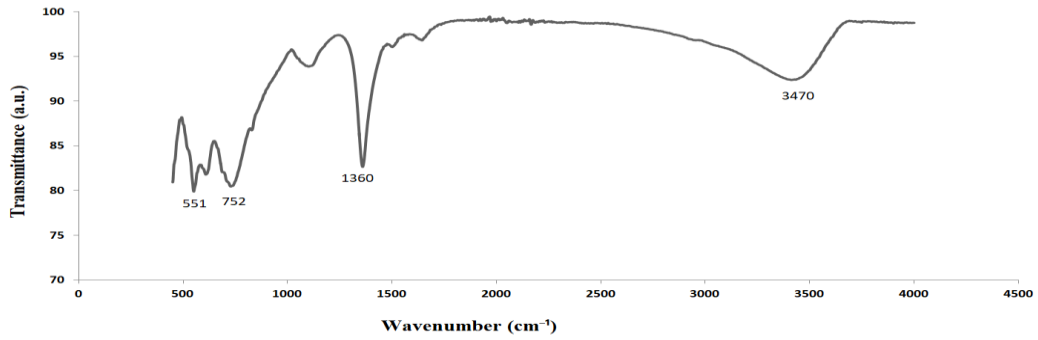


Fig 6: FTIR image of synthesized LDH

B. Water treatment for removal of phosphate

Effect of LDH dosage: The graph of concentration of phosphate with respect to dosage of LDH in shown in Figure 7 and the graph of percentage reduction of phosphate versus dosage of LDH is shown in figure 8. The percentage removal of phosphate increased with increasing amount of dosage. The maximum phosphate reduction of 89.24% was observed at 0.9g of LDH dosage.

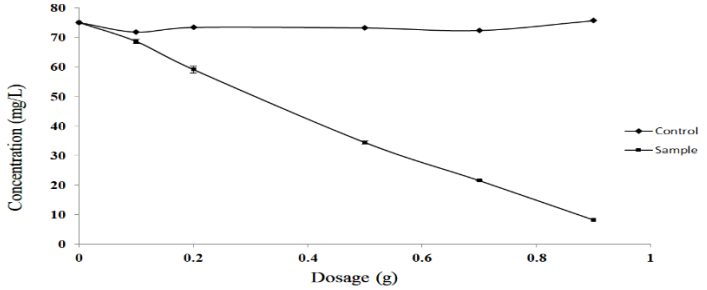


Fig 7: Variation of phosphate with respect to dosage of LDH

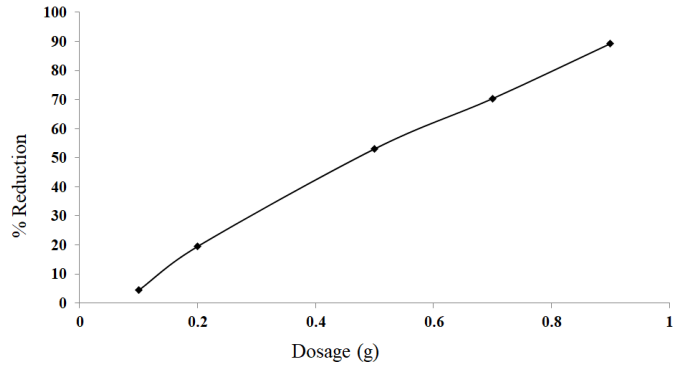


Fig 8: Percentage reduction of phosphate with respect to dosage of LDH

Effect of Contact time: As the maximum phosphate reduction was observed at 0.9g dosage, it was selected for the next experiment to determine variation of phosphate at different contact time. The percentage removal of phosphate is noted at 10min, 20min, 30min, 40min, 50min and 60min. The graph plotted between concentrations of phosphate with respect to contact time in shown in Figure 9. The graph plotted between percentage phosphate reduction and contact time is shown in Figure 10. As the contact time increases, the phosphate reduction increases rapidly and reaches equilibrium at 40min with 90% phosphate reduction. The maximum phosphate reduction of 94.69% is observed at 60min.[16]

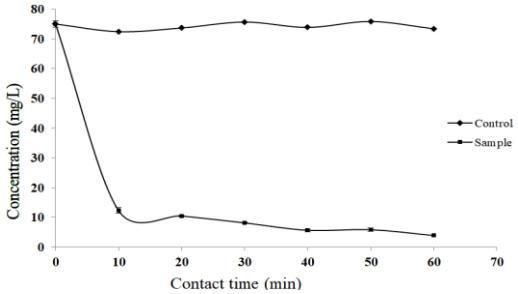


Fig 9: Variation of phosphate with respect to contact time of LDH

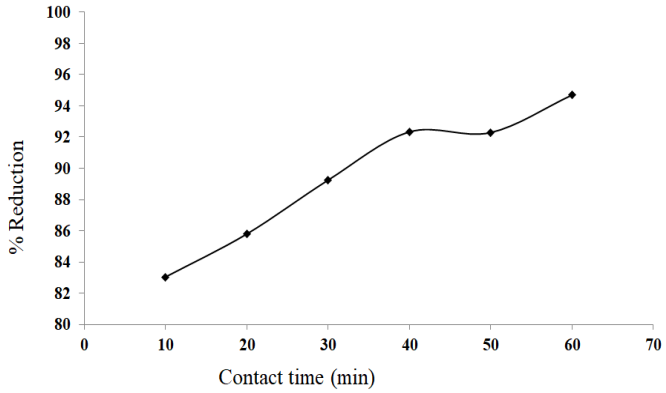


Fig 10: Percentage reduction of phosphate with respect to contact time of LDH

Mechanism: The XRD patterns of Zn-Al LDH before and after treatment are illustrated in Figure 11. Highest Peak observed at approximately 2θ = 11.72° corresponds characteristic peak of the layered structures. The peak at 34.6° is matching with the JCPDS card number 211489, wavelength 1.5418 with the chemical formula $Zn_2(PO_3)_4$. And the another peak at 23.44° is matching with JCPDS card number 760273 with chemical

formula D_3PO_3 (deuterium phosphate). From this result of XRD patterns both before and after treatment, we can infer that carbonate ions are exchanged with phosphate ions [18].

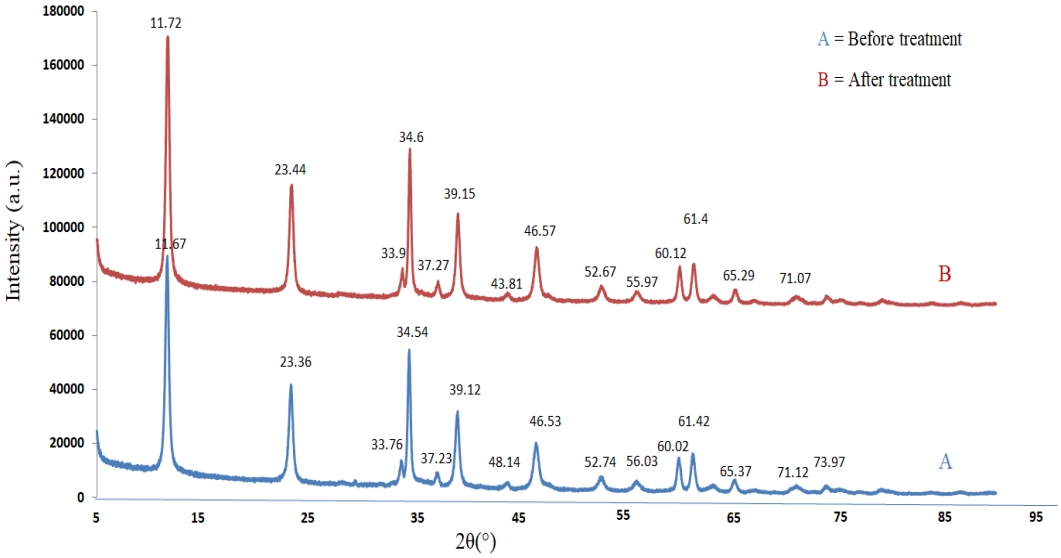


Fig 11: Showing XRD results of LDH before and after treatment.

4. Conclusion

This work proposes the application of LDHs for the removal of phosphate from synthetic water. Synthesizing Zn-Al LDH by co-precipitation method was feasible and showed efficient results at pH 9 to 11. The XRD results confirm that the synthesis method proposed was efficient to obtain crystalline Zn-Al LDH material. The thermal analysis showed that at higher temperature weight loss is less, hence LDH structure is not collapsed. In treatment part, phosphate removal experiments indicated that, the percentage reduction of phosphate increases with increase in dosage of phosphate. When using a dosage of 0.9 g in synthetic water, LDH reached a phosphate reduction at 89.24%. When phosphate reduction experiments were conducted with respect to contact time using 0.9 g of Zn-Al LDH, the reaction reached equilibrium at 40min and maximum reduction was observed to be 94.69 % at 60min, On the basis of above results, it can be concluded that Zn-Al LDHs could be used as a potential material for phosphate removal in water.

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Conflict of Interest

The authors have declared no conflict of interest.

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