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Evaluation of Layered Double Hydroxide Synthesised from a Green Biogenic Precursor for Phosphate Removal: Characterisations and Isotherms

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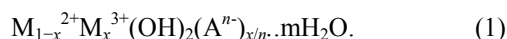
Abstract: CaCr LDH materials were synthesized by the co-precipitation method, using Gastropod shell as a biogenic source of Ca^{2+}. The mineralogical, surficial morphology and elemental composition analysis of the materials showed characteristics typical of hydrotalcite-like materials, composed of Ca, Cr, O, C and Cl. Batch equilibrium adsorption studies showed that phosphate sorption on the LDH reached equilibrium within 5 min with about 98% removal. The sorption of phosphate was well described by the Langmuir isotherm model. The monolayer adsorption capacity of the CaCr LDH for phosphate was 142.86 mg/g. Mechanistic studies of phosphate removal by the LDHs was elucidated via instrumental analysis, *vis-a viz,* SEM-EDX, XRD and FTIR. Results revealed that phosphate was removed via the combination of ion exchange and precipitation. It could be inferred that CaCr LDH synthesised using Gastropod shell as a biogenic source of Ca^{2+} is a suitable adsorbent for phosphate removal from aqua system.

Keywords: Phosphate, Layered Double Hydroxide, Characterisation, Gastropod Shell, Isotherms

1. Introduction

Layered double hydroxides (LDH) are laminar anionic clay materials also known as hydrotalcite compounds and characterized with high exchange capacity [1]. The structure of layered double hydroxides is patterned after the brucite-like structure of Mg $(OH)_2$ which consists of Mg^{2+} octahedrally surrounded by OH^-. LDH chemical composition is described by the formular:

$$M_{1-x}^{2+}M_x^{3+}(OH)_2(A^{n-})_{x/n}.mH_2O. \qquad (1)$$

The M_{1-x}^{2+} M_x^{3+} $(OH)_2$ represents the layer, while $(A^{n-})_{x/n}$·mH_2O represents the interlayer composition. M^{2+} and M^{3+} are divalent and trivalent cations with ionic radius ranging between 0.65 - 0.80 Å and 0.62 – 0.69 Å, respectively. Varying the M^{2+}/M^{3+} ratio alters the charge density and the anion exchange capacity of the LDHs [2]. The net positive charge of the LDH is counterbalanced by the exchangeable interlayer anion A^{n-}, in the interlamellar region which could be any anion such as CO_3^{2-}, NO_3^-, Cl^- with valence n that could be exchanged with other anions [3-4]. m is the amount of water in moles, present in the LDH. M^{2+}, M^{3+}, x, and A^{n-} identities may vary over a wide range, thus giving rise to a large class of isostructural materials with different physicochemical properties [5-6]. The stability of the structure is ensured by the hydrogen bonds between the hydroxyl groups of octahedral sheets and the intercalated species, anions and water molecules [7]. Due to the high ion-exchange properties of the interlayer anions, LDHs have attracted high research interests as promising materials for the selective uptake of polyatomic anions including phosphate from aqueous system [8]. In the present studies, CaCr LDH synthesised using Gastropods shell (a biogenic precursor) as Ca^{2+} source was evaluated for phosphate removal from a synthetic feed phosphate wastewater in a

batch sorption process. The characteristics and isotherms of the sorption process were examined and reported.

2. Materials and Methods

2.1. Preparation of Gastropod Shell Powder

The Gastropod (*A. achatina*) shell used was obtained from an open market in Ondo State, Nigeria. The shell was washed with tap water and rinsed thoroughly with deionized water, dried in the oven at 90°C for 24 h and crushed using a laboratory ceramic mortar and pestle. The crushed shell was made into powder and sieved with mesh of known size.

2.2. Synthesis of CaCr LDH Samples

The LDH samples were prepared via the co-precipitation method as described by [9], using gastropod shell powder as the source of Ca (M^{2+}) and $CrCl_3$ as the source of Cr (M^{3+}), at varying molar ratios (M^{2+}/M^{3+}) of 1:1, 2:1 and 4:1. $CaCl_2$ solution was prepared by dissolving 50 g of gastropod shell powder in 350 ml of dilute HCl. The mixture was vigorously stirred and left to stand for 24 h. 500 ml of the $CaCl_2$ solution was added to 47.62 g, 23.81 g and 11.90 g of $CrCl_3$ giving a Ca: Cr solution mixture of mass ratios of 1:1, 2:1 and 4:1, respectively. The mixture was thoroughly stirred and 2 M NaOH / Na_2CO_3 solution was added drop-wise as precipitant. The precipitate formed was allowed to gelate in the mother liquor for 24 h at room temperature and washed with deionized water repeatedly. The precipitate was collected and dried to constant weight at 80°C. The synthesized LDH samples were labeled LDH_1, LDH_2 and LDH_4, the subscript denotes the Ca: Cr mass ratio used in the synthesis.

2.3. Characterization of Synthesised CaCr LDH Samples

The crystallinity and mineralogical analysis of the samples were recorded on a Rigaku (RINT 2100) X-ray diffractometer (XRD) with a graphite monochromator and a Ni-filtered Cu *Kα* radiation (λ= 0.15406 nm). The measurement was run in the 2θ range from 2° to 90° at a step size of 0.02 and counting time of 1 s per step. The divergence slit size was 0.0573°, while the operating voltage and current were 45 kV and 40 mA, respectively. The data were processed using PAN analytical X'PERT software. The surface physiognomies and elemental composition were analyzed using a Scanning Electron Microscope (JEOL: JSM - 6301F) equipped with Energy Dispersive analysis of X-ray (Oxford INCA 400, Germany). The samples were coated with gold before analysis with the aid of a sputter coater. Operating conditions were: accelerating voltage = 15 kV, current = 12 mA, working distance = 10 mm and magnification up to 100,000 x. The surface functional groups were determined using Fourier Transform Infrared (FTIR) spectrophotometer (Thermo Scientific, USA*)*. Sample pellet was prepared by mixing 1 mg of the sample powder with 250 mg of KBr (AR grade) and pressing at 10,000 psi using a hydraulic press. The measurement covered the range from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1}

2.4. Adsorption Isotherm Study

Phosphate adsorption isotherms were carried out using solid samples of CaCr LDH in a batch system at room temperature. A stock solution (300 mg/l) of synthetic feed phosphate wastewater was prepared by dissolving 0.43 g of KH_2PO_4 (AR grade) in 1000 ml distilled water and working solutions of varying concentrations (25-300 mg/l) were prepared from the stock by serial dilution. The equilibrium isotherm study of the process was evaluated by contacting 50 ml of phosphate solution of concentration (25 - 300 mg/l) with 0.1 g of the sample and agitated at 200 rpm on a thermostatic shaker. After equilibration, suspensions were withdrawn using a syringe, centrifuged at 5000 g for 10 min, filtered through a 0.22 μm glass fiber filter. Residual phosphate in the supernatant was analyzed by the molybdenum-blue ascorbic acid method using a UV–VIS spectrophotometer at 801nm. The amount of phosphate sorbed per unit mass of the adsorbent (in mg/g) was calculated by using equations:

$$q_{e} = \frac{c_o - c_e}{m} \times v \qquad (2)$$

$$R\ (\%) = 100 \times \frac{c_o - c_e}{c_0} \qquad (3)$$

Where, q_e = amount of PO_4^{3-} sorbed per gramme of LDH (mg/g), v = volume of PO_4^{3-} solution (dm^3), m = mass of LDH (mg), c_o = initial concentration of PO_4^{3-} in mg/l, c_e = final residual PO_4^{3-} concentration (mg/l). The phosphate - laden residue obtained after phosphate uptake was washed with deionized water and dried in a desiccator for further analysis. The kinetics of the adsorption process and studies of process variables (pH, presence of co-existing ions and organic load) shall be reported in a forth-coming paper.

3. Results and Discussion

3.1. Characterisation of Synthesised LDH Samples

The XRD patterns of the prepared LDHs in Figures 1-3 shows diffract graph of hydrocalumite- like materials. Sharp and intense symmetric peaks at low 2θ values and relatively less intense and symmetric basal reflections at higher 2θ values, characteristics of LDH-materials indicates the presence of Ca-Cr LDHs in the prepared materials [10-11]. Notably, the diffract graph of LDH1 sample differs from that of LDH2 and LDH4 samples in peak positions, intensities and basal lattice positions. Major diffractions peaks, d003 and d006 were reflected at 2θ values of 10.60° and 23.03° with d-spacings of 8.34 Å and 3.86 Å, respectively for LDH2 sample, while for LDH4 sample these peaks were reflected at 10.86° and 22.95° with d- spacing of 8.15 Å and 3.87 Å, respectively. These peaks were notably absent in the diffract graph of LDH1 sample. Other major characteristics reflections of hydrocalumite – like materials shown by LDH_2 sample were peaks of d009 and d015 reflected at 2θ values of 35.88° and 39.27° with the d-spacing 2.50 Å and 2.29 Å,

respectively. LDH$_4$ sample reflected other major peaks, d$_{009}$, d$_{015}$ and d$_{110}$ at 2θ values of 35.81°, 39.24° and 62.48° with the d-spacing of 2.52 Å, 2.29 and 1.48, respectively. Furthermore, the patterns of the sharpness and intensity of the peaks indicated an increase in the crystallinity of the samples with increase in the Ca / Cr ratio from LDH$_1$ to LDH$_4$ (Figures 1-3) [6, 12]. Uncharacteristic LDH peaks observed in the diffractogram were attributed to the presence of impurities in the biogenic precursor. FTIR spectrum of the samples (Figures 4-6) is typical of hydrocalumite materials which are characterized by broad adsorption bands around 3450-3520 cm^{-1} attributed to v_{OH} stretching vibration of brucite- like layers [5].
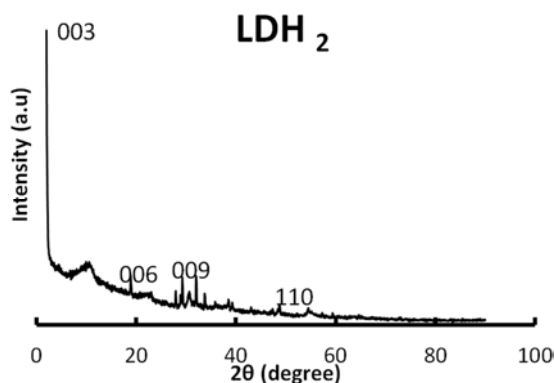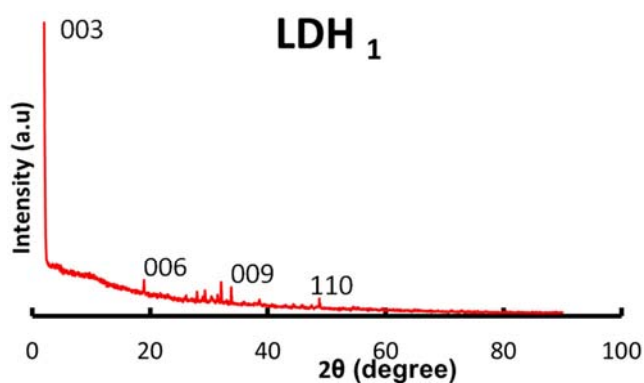
Figure 2. *XRD pattern of LDH$_2$.*
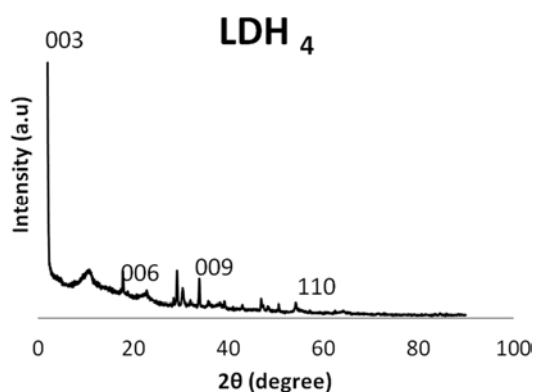
Figure 1. *XRD pattern of LDH$_1$.*

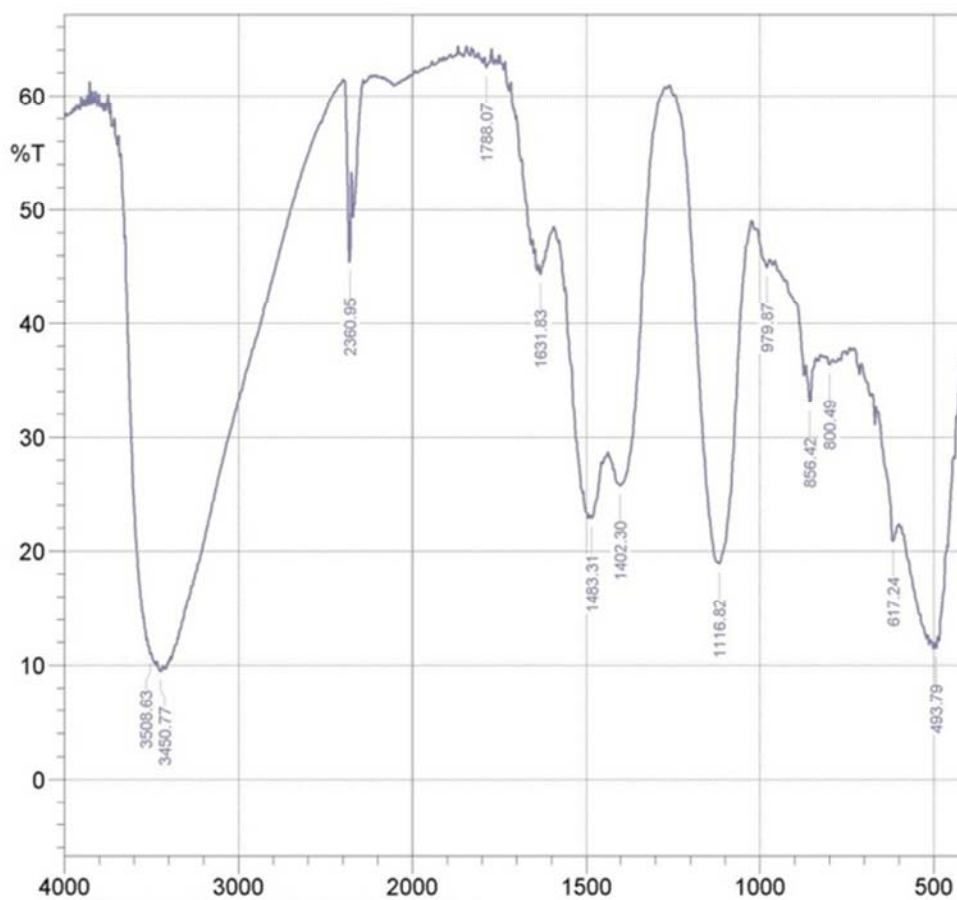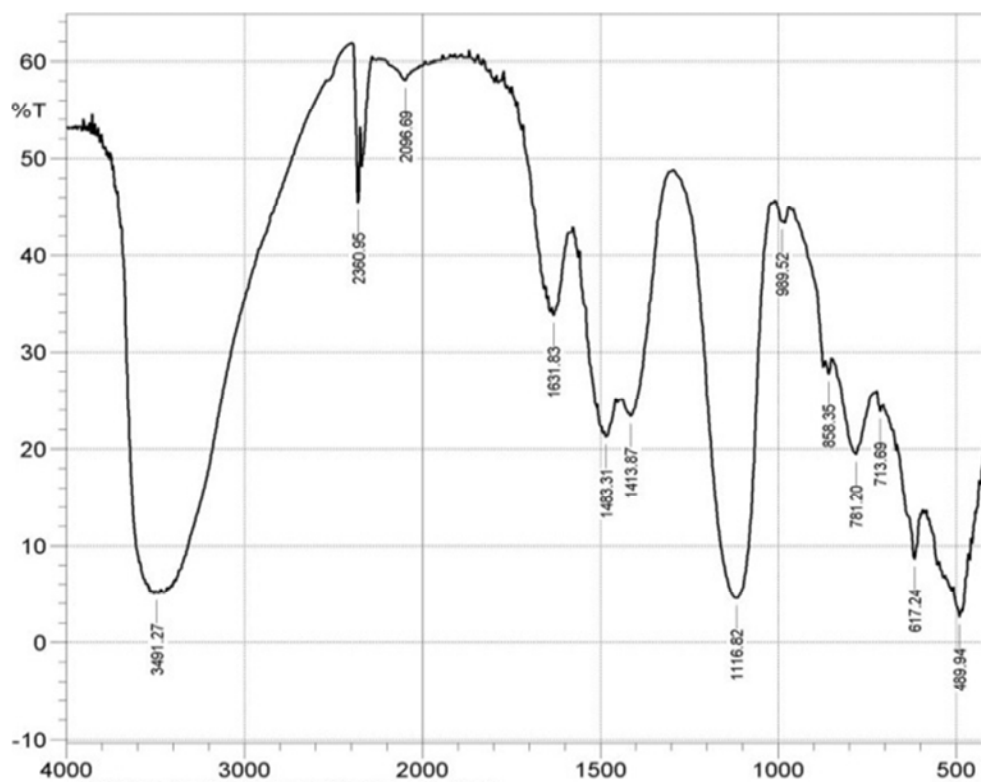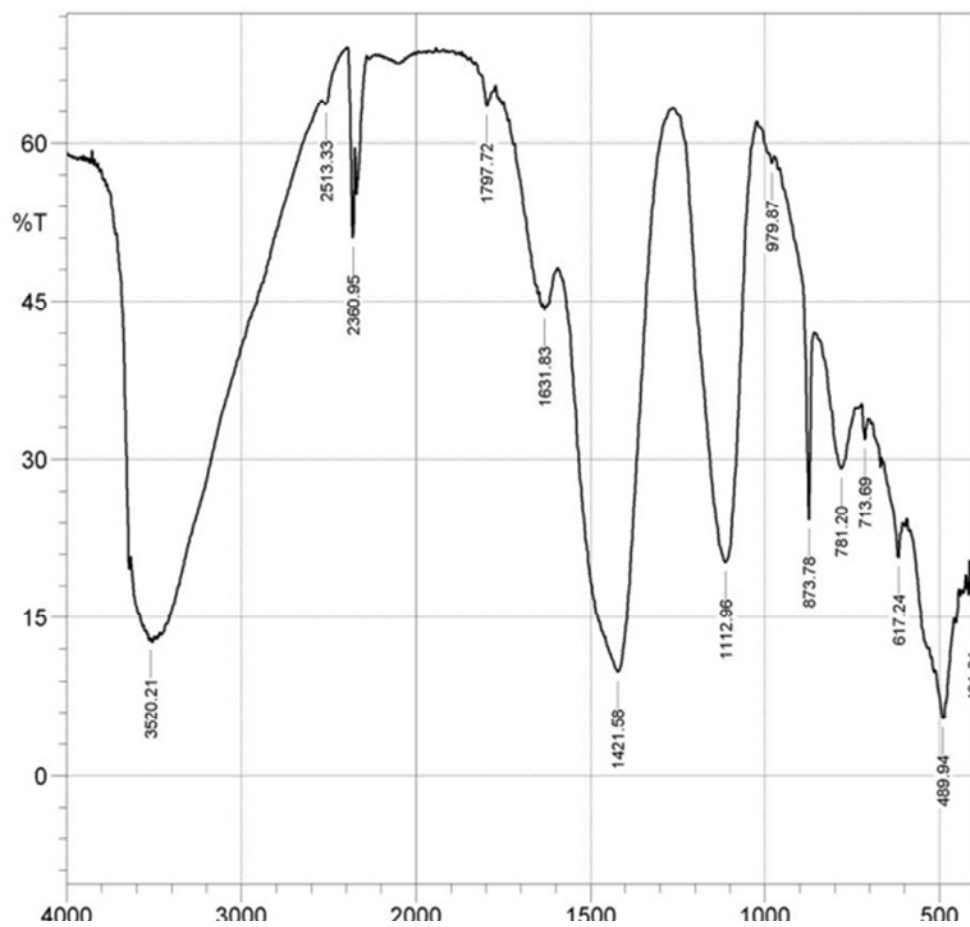**Figure 3.** *XRD pattern of LDH$_4$.*

Figure 4. *FTIR Spectra of LDH$_1$.*

Figure 5. *FTIR Spectra of LDH₂.*

Figure 6. *FTIR Spectra of LDH₄.*

The bending vibration of the interlayer water $\delta_{\text{H-OH}}$ was found at 1631 cm^{-1}. The bands at 1413 cm^{-1}, 1116 cm^{-1}, and 617 cm^{-1} were attributed to CO_3^{2-}, due to asymmetric stretching, symmetric stretching and bending modes, respectively [3, 13-14]. The weak band around 750-800 cm^{-1} was attributed to M-O-M vibration in the brucite–like layer while the bands around 480-500 cm^{-1} corresponded to M-OH stretching and bending vibrations. Characteristic IR band of chromate was recorded at 856-880 cm^{-1}. SEM / EDX techniques were utilized to determine the LDHs surficial morphology and elemental chemical composition as a function of preparation adopted for the materials. SEM images of the samples presented in Figures 7-9 showed that the samples were composed of agglomerates of tiny hexagonal crystals fused together. The results obtained via EDX analysis indicated the presence of Ca, Cr, Cl and O in all the samples (Figures 10-12). Furthermore, the results showed that the M^{2+}/M^{3+} molar ratios of the samples are smaller than that of the starting solutions (Table 1) which is an indication of incomplete reaction between Ca^{2+} and Cr^{3+}.
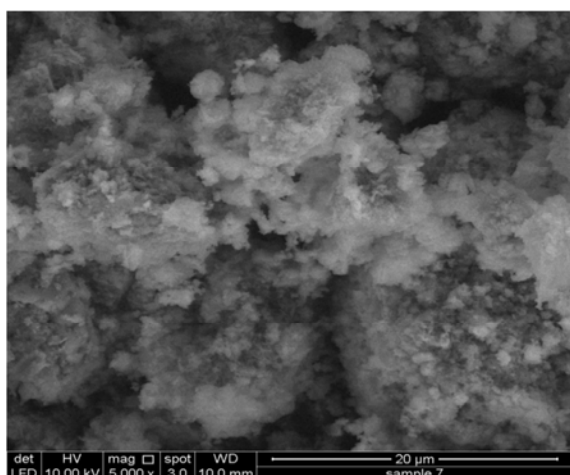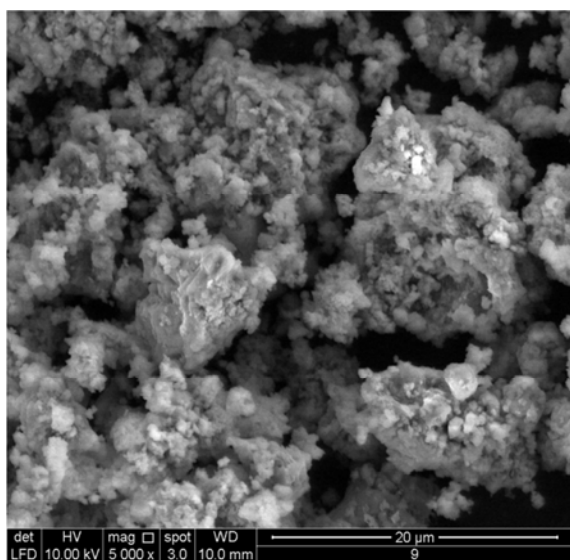

Figure 9. SEM images of LHD$_4$.

Figure 7. SEM images of LHD$_1$.

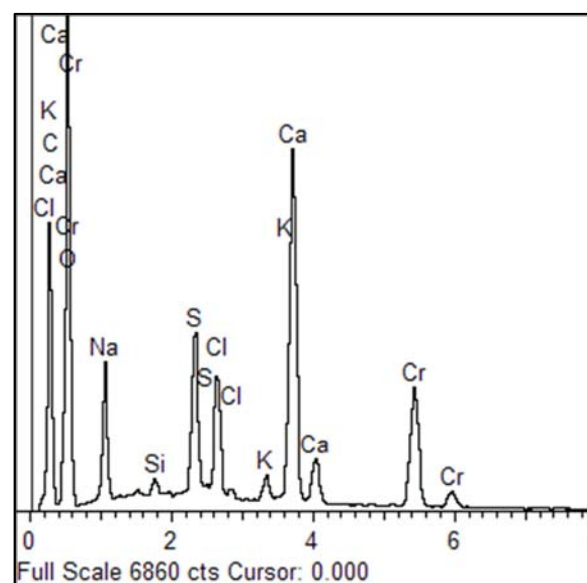*Figure 10. EDX spectra of LDH$_1$.*

Figure 8. SEM images of LHD$_2$.

Figure 11. EDX spectra of LDH$_2$.

Figure 12. *EDX spectra of LDH4.*

Table 1. *Molar ratios of Synthesised LDHs Samples by EDX Analysis.*

Samples	Ca^{2+} (%)	Cr^{3+} (%)	Solid Molar Ratio (M^{2+}/M^{3+})	Solution Molar Ratio (M^{2+}/M^{3+})
LDH$_1$	5.84	6.74	0.87	1:1
LDH$_2$	4.84	2.63	1.08	1:2
LDH$_4$	10.92	3.38	3.23	1:4

3.2. Adsorption Studies of Phosphate Removal by LDH Samples
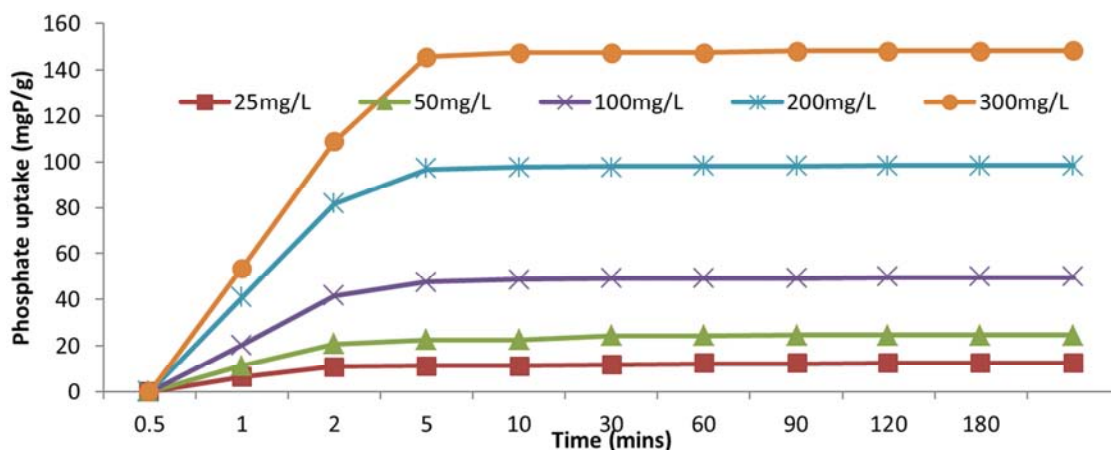
3.2.1. Effect of CaCr Molar Ratio

In order to assess the effect of molar ratio (M^{2+}: M^{3+}) on phosphate removal, the prepared LDHs of varying molar ratios (1:1, 2:1, 4:1) were subjected to the adsorption assays. It was observed that the amount of phosphate removed by the samples increased with increasing molar ratio. While about 90% and 95% removal was observed with LDH$_1$ and LDH$_2$ samples, respectively, about 98% removal occurred with

LDH$_4$ sample. The partial substitution of Cr^{3+} for Ca^{2+} causes an increase in the net positive charge as a result of differences in the ionic radius of the cations [15]. This causes a phase change leading to increase in its adsorption capacity. The sorption capacity of the LDHs increases with increasing Ca^{2+} and reduced Cr^{3+} contents. Substances with high Ca contents have shown to have high affinity for phosphate [16]. The marginal similarities in the amount of phosphate removed (90, 95, 98%) by the LDHs suggest that the type of metal (especially divalent) influences the sorption capacity of the LDHs more than net positive charge. The Ca-Cr of molar ratio 2 (LDH$_2$) appeared optimal for phosphate uptake from aqua system and was used for subsequent studies.

3.2.2. Effect of Initial Phosphate Concentration

The effect of initial phosphate concentration on phosphate uptake by LDH$_2$ was assessed at varying initial phosphate concentrations (25-300 mgP/l), by contacting 0.1g of LDH with 50 ml of 40 mgP/l phosphate solution, pH of 5.5, for 2 hr. The amount of phosphate removed by the adsorbent increased with increase in contact time for all initial phosphate concentrations studied, with a phosphate uptake of > 98% within the first 5 mins of contact, after which equilibrium gradually sets in (Figure 13). The initial rapid uptake was ascribed to the difference in concentration between the solute concentration in solution and that at the surface of the adsorbent present at the commencement of the sorption process. Furthermore, the result (Figure 13) revealed that phosphate uptake increases with increase in initial phosphate concentration. The magnitude of phosphate removed by the adsorbent varied with the initial phosphate concentrations. The increased removal observed at higher initial concentration is as a result of the increase in the driving force of overcoming all mass transfer resistance between adsorbent moieties and the adsorbate [11, 17]. Consequently, an increase in the initial phosphate concentration led to increase in the amount of phosphate removed per gram of the LDH$_2$.

Figure 13. *Phosphate uptake by LDH$_2$ as a function of initial phosphate concentration.*

3.2.3. Adsorption Equilibrium Isotherm Studies

In adsorption process, equilibrium is established when the concentration of the adsorbate in the bulk solution is in

dynamic balance with that at the interface of the adsorbent. Adsorption isotherms are mathematical models characterized by certain constants whose values express the surface properties and affinity of the adsorbents for the adsorbates

[18-19]. The adsorption equilibrium experimental data of phosphate removal by LDH_2 from aqueous solution were modeled using adsorption isotherms of Langmuir, Freundlich, Temkin and Harkins-Jura. The Langmuir isotherm model assumes a monolayer adsorption on specific homogeneous sites within the adsorbent and that there is no significant interaction among the adsorbed species. The Freundlich isotherm model regarded as an empirical equation, indicates non-uniformity of the adsorbent surface, is also used to describe chemisorption on a heterogeneous surface. The Temkin isotherm model takes into account the interactions between adsorbent and adsorbate and is based on the assumption that the free energy of adsorption is simply a function of surface coverage. Halsey isotherm model is be used to evaluate the multilayer adsorption system for adsorption at a relatively large distance from the surface. The non- linear expression of these models is given as:

$$\text{Langmuir: } qe = \frac{q_m\, b c_e}{1 + b c_e} \qquad (4)$$

$$\text{Freundlich: } q_e = k_f c_e^{1/n} \qquad (5)$$

$$\text{Temkin: } q_e = B_T\, lnA\ C_e \qquad (6)$$

$$\text{Halsey } q_e = e^{\frac{lnk - lnc_e}{n}} \qquad (7)$$

Where, ce is the concentration of the phosphate at equilibrium (mg/L), qe is the amount of phosphate sorbed at equilibrium per unit mass of LDH_2 (mg/g), q_m is the monolayer sorption capacity at equilibrium (mg/g) and b is the Langmuir constant (dm^3/g). The constant, k_f, is the Freundlich constant and n is the sorption intensity, B_T (J/mol) corresponds to the heat of adsorption, is the Temkin isotherm constant and A (l/g) is the equilibrium binding constant, corresponding to the maximum binding energy. Details of the values of the isotherm parameters obtained from the plots (Figure 14) of the experimental data of adsorption equilibrium study to the aforementioned isotherm equations are presented in Table 2.
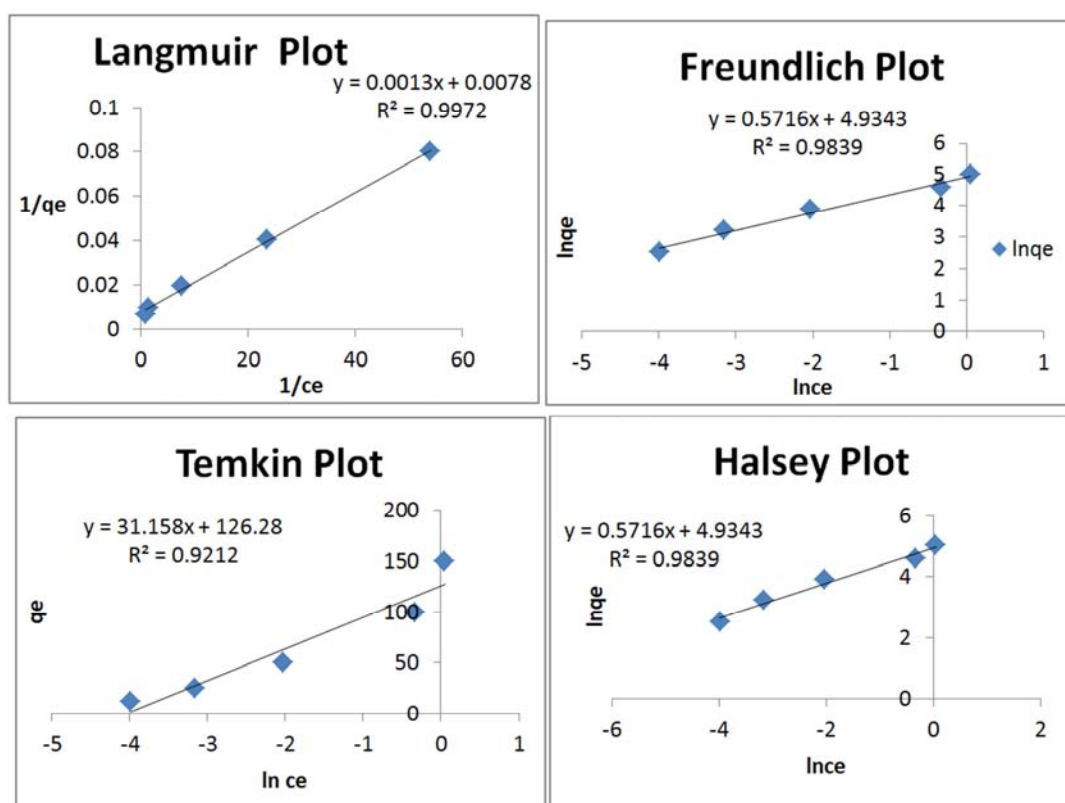

Figure 14. Equilibrium Isotherms Models Plots for the Removal of Phosphates by LDH_2.

The Langmuir monolayer adsorption capacity (q_m) of LDH_2 for phosphate was 142.86 mg/g. The magnitude of b (0.634 L/mg) showed high binding energy of phosphate sorption on the LDH_2. The low value of the Freundlich constant, n, (1.75), is an indication of a favourable process, while the high value of K_f (138.93 mg/g) is a pointer to the high affinity of the LDH_2 samples for phosphates. Values of the Temkin parameters obtained were high (B_T = 31.15 kJ/mol, A= 4.051 L/g), indication of high sorption energy and maximum binding energy, respectively. From the plots, the adsorption curves relating the solid and liquid phase concentration of phosphate at equilibrium to the Langmuir, Freundlich, Temkin and Halsey isotherm equations are given as:

$$\text{Langmuir: } q_e = \frac{141.86 c_e}{1 + 0.634 c_e} \qquad (8)$$

$$\text{Freundlich: } q_e = 138.93 C_e^{0.571} \qquad (9)$$

$$\text{Temkin } q_e = 31.15 ln 4.05 C_e \qquad (10)$$

$$\text{Halsey } q_e = e^{\frac{ln138.93 - lnc_e}{1.7513}} \qquad (11)$$

Evaluation of the fittings of the isotherm models to the experimental data was tested using the linear coefficient of determination (R^2) and the non-linear chi-square (x^2). The linear coefficient of determination, (R^2) indicates the percentage of variability in the dependent variable that has been explained by the regression line. The value of R^2 varies between zero and one. A value of one indicates that 100% of the variation of the amount of phosphate sorbed has been explained by the regression line. The linear coefficient of determination was estimated using equation:

$$r^2 = \frac{S^2_{xy}}{S_{xx}S_{yy}} \qquad (12)$$

Where S_{xx} is the sum of square of x, S_{yy} is the sum of squares of y and S_{xy} is the sum of squares of x and y. Furthermore, the non- linear chi-square test is a statistical tool used to determine the best fit of an adsorption system. It is obtained by judging the sum squares differences between the experimental and the calculated data with each squared difference being divided by its corresponding value (calculated from the models). Small value of x^2 is an indication of the suitability of the model to the experimental data, while large number represents variation of the model to the experimental data. Mathematically, it is calculated from the equation:

$$x^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (13)$$

The values of R^2 and x^2 obtained for the isotherm models from their fittings to the experimental data are presented in Tables 2. Comparatively, the Langmuir isotherm model yielded a better fit than the other models with a very high R^2 value (0.997) and negligible low chi- square value (0.0423). Consequent upon the equilibrium isotherm studies, it could be deduced that the sorption of phosphate by LDH_2 was favourable as indicated by high adsorption intensity values (*n and b*) between phosphate and LDH2 which implies a strong bond. Furthermore, sorption of phosphate occurred on monolayer surface of the LDH_2 sample.

Table 2. Calculated Equilibrium Constants for Phosphate adsorption on LDH_2.

Langmuir	Freundlich	Temkin	Halsey	Dubinin –Radushkevich
q_m (mg/g): 142.86	K_f (mg/g): 138.93	B_T *(kJ/mol)*: 31.15	K_H (mg/l): 138.93	qm (mol/g): 76.172
b (L/mg): 0.634	1/n: 0.571	A (L/g): 4.05	n: 0.571	E (kJ/mol): 15.623
R^2: 0.997	R^2: 0.983	R^2: 0.921	R^2: 0.983	K_{DR} (mol^2/kJ^2): 0.002
x^2: 0.0423	x^2: 0.1854	x^2: 2.5427	x^2: 0.6120	x^2: 2.7252; R^2: 0.765

3.2.4. Estimation of Energy of Sorption

The energy of sorption process of phosphate on LDH_2 was estimated by testing the experimental sorption data obtained from the equilibrium isotherm studies with the Dubinin − Radushkevich (D-R) equation expressed as: $lnqe = lnqm - k\varepsilon^2$ (14)

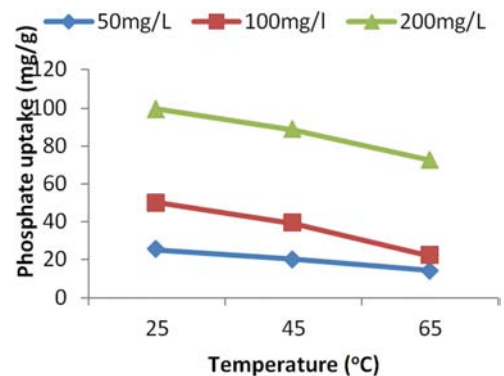$$\text{Where, } \varepsilon = RT(1 + \frac{1}{ce}) \qquad (15)$$

And,

$$E = \frac{1}{\sqrt{2K}} \qquad (16)$$

Where, q_m (mol/g) is the D-R constant representing the theoretical saturation capacity, ε (polanyi potential) is calculated using Eqn. 15. The parameters q_m and *k,* calculated from the intercept and slope of the plots of lnq_e against E^2 were 76.172 mol/g and 0.002, respectively (Table 3). Insight into the type of adsorption process as chemisorption or physisorption was determined by considering the value of the constant E, the mean free energy of adsorption per molecule of the adsorbate when transferred to the surface of the solid from infinity in solution [20]. K is related to the mean adsorption energy *E* (kJ mol^{-1}) as shown in Eqn. 16. If the value of *E* lies between 8 and 16 kJ/mol the sorption process is considered as chemisorption, while values below 8 kJ/mol indicate a physical adsorption process [21]. The *E* (kJ/mol) value of the sorption process was found to be 15.623 kJ/mol. This value is relatively not in the range for physical adsorption, a pointer to the fact that chemisorption was the prevailing mechanism of interaction between phosphate and the LDH_2 surface.

3.2.5. Effect of Temperature and Evaluation of Thermodynamic Parameters

The effect of temperature on the adsorption capacity of LDH_2 was assessed at varying temperatures of 25, 45 and 65°C. Figure 15 displays the plot of amount of phosphate removed as a function of temperature. The amount of phosphate removed decreases with increase in temperature for all concentrations studied (50, 100, 200 mgP/l). This suggests that lower temperatures are most suitable for phosphate sorption on CaCr LDH, indicating that the interaction between the adsorbate and adsorbent was exothermic in nature.

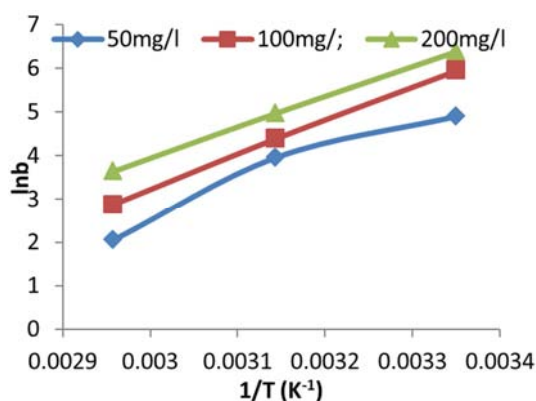
Figure 15. Phosphate Uptake as a Function of Temperature.

Figure 16. Plot of ln b against 1/T for Thermodynamic Analysis.

Temperature dependence of adsorption process is associated with changes in thermodynamic parameters: Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). The Gibbs free energy is the thermodynamic driven energy in chemical reactions, used to determine whether a reaction is spontaneous ($\Delta G > 0$), at equilibrium ($\Delta G = 0$) or not feasible ($\Delta G < 0$). The value of Gibbs free energy is calculated by

using the equation:

$$\Delta G^O = -R\,T\,lnb \qquad (17)$$

$$lnb = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{RT} \qquad (18)$$

Where, R is the universal gas constant, T is temperature (K) and *b* is Langmuir constants. The results obtained for the thermodynamic analysis of the process indicated that the process is thermodynamically spontaneous with negative values obtained for Gibbs free energy ($\Delta G < 0$) and ranged between -12140 and -5760 (Table 3). The enthalpy (ΔH^o) and entropy (ΔS^o) of the process were evaluated using Van't Hoff equation (18). Values of ΔH^o and ΔS^o calculated from the slope and intercept of the linear plots of *ln b* versus 1/T (Figure 16) is presented in Table 3. The negative values of ΔH^o indicated the exothermic nature of the sorption process, while the negative values of ΔS^o indicated decreased randomness at the solid / solution interface during the sorption of PO_4^{3-} on LDH_2.

Table 3. Thermodynamic Parameters Changes of Phosphate Removal by LDH_2 Samples.

T (K)	50mg/l			100mg/l			200mg/l		
	ΔG^O	ΔS^O	ΔH^O	ΔG^O	ΔS^O	ΔH^O	ΔG^O	ΔS^O	ΔH^O
298	-12140			-14716			-15806		
318	-10469	-19.11	-7222	-11607	-20.17	-7801	-12933	-17.01	-6987
338	-5760			-8093			-10229		

3.3. Characterisation of Phosphate - Laden LDH.

Characterisation of the spent LDH samples studies gives an insight into the possible mechanisms of the sorption process which are used to elucidate the interaction between adsorbate and adsorbent for optimization of the operation parameters of an adsorption process. Several studies have opined that anions are adsorbed on LDHs by either anion exchange with the hydroxyl anions in the water solution, electrostatic interaction and/or formation of complex (outer-sphere / inner sphere) [14, 22]. SEM analysis revealed a change in the surface architecture of the spent LDH sample after phosphate sorption (Figure 17). Elemental composition of the spent LDH samples by EDX analysis provided a clear evidence of the sorption of phosphate on the surface of P-laden LDH_2 (Figure 18). Notably, the decrease in the amount of chloride and increase in phosphate content of the spent-LDH_2 sample indicated the possibility of anion exchange between chloride and phosphate ions during the sorption process (Table 4).

Table 4. Elemental composition in the CaCr LDH_2 before and after phosphate uptake.

Element	Before Uptake (%)	After Uptake (%)
C	24.91	23.33
O	45.50	42.68
Na	5.09	1.06
P	0	6.27
S	3.47	1.07

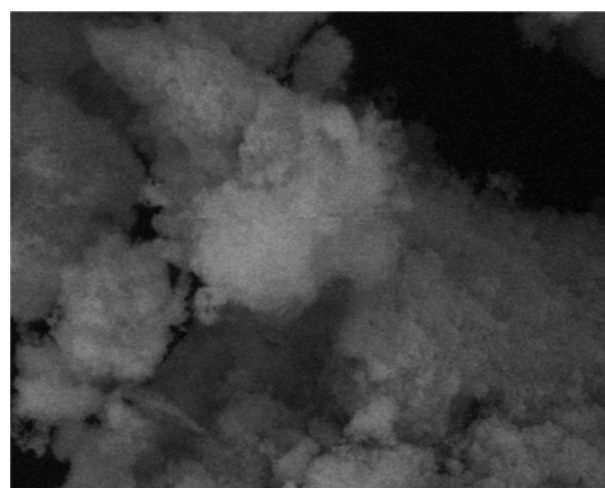| Element	Before Uptake (%)	After Uptake (%)
Cl	2.97	1.10
Ca	11.01	18.69
Cr	7.76	5.80
Total	100	100

Figure 17. SEM image of P- laden LDH_2.

Appraisal of the FTIR spectra of both the spent (Figure 19) and raw LDH_2 samples (Figure 5) indicated the appearance of new peaks in the spectra of the spent sample. Phosphate peaks were reflected at 873 cm^{-1} and 1047 cm^{-1}. The phosphate peak at 1047 cm^{-1} attributed to the bending vibration of adsorbed phosphate was formed as a result of ion exchange between the

surface hydroxyl groups on the LDH (M-OH) to give M-O-P, an indication of ligand exchange during the sorption process. The X-ray diffractogram of the phosphate-loaded LDH (Figure 20) was very different from that of the raw sample (Figure 2) as observed by: (i) the broad peak at $2\theta = 25\text{-}50°$, an implication of loss of order in the structure of the layered material after phosphate uptake (ii) significant reduction in the crystallinity of the spent samples, an indication of amorphous nature of the phosphate-laden LDH_2. Mineralogical composition of the phosphate laden LDH_2 sample indicated the formation of whitlockite, hydroxyapatite ($Ca_5(PO_4)_3.OH$) and calcite [23-24]. Calcium - based LDHs are believed to exhibit this phenomenon due to formation of amorphous phosphate salts (precipitates) of Ca on the surface of the LDH sample during the sorption process [1]. The LDH readily releases Ca^{2+} into the liquid phase which leads to the increase in Ca^{2+} concentration observed after P uptake (Table 4) as a result of its high solubility product (5.02×10^{-6}) to precipitate with phosphate [25]. The dissolution phenomenon of the LDHs is responsible for the lost of the layered structure after phosphate uptake (Figure 20). These findings are in conformity with the removal of Ca-based LDHs for removing different P species in other previous studies [11, 25-28]. These findings reveal that the dual combinations of ion exchange and precipitation were the mechanisms of phosphate removal by the LDH sample.
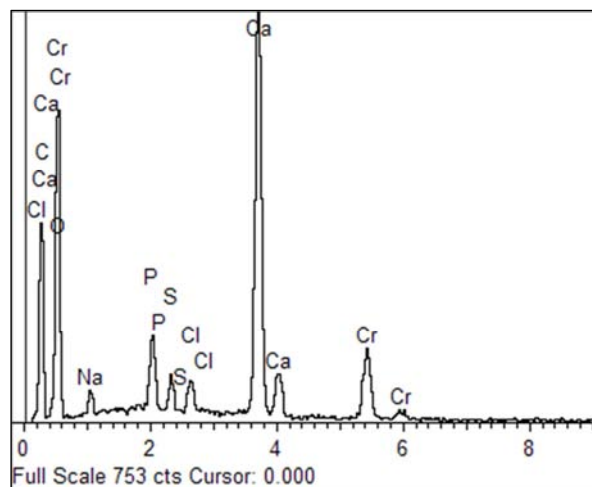

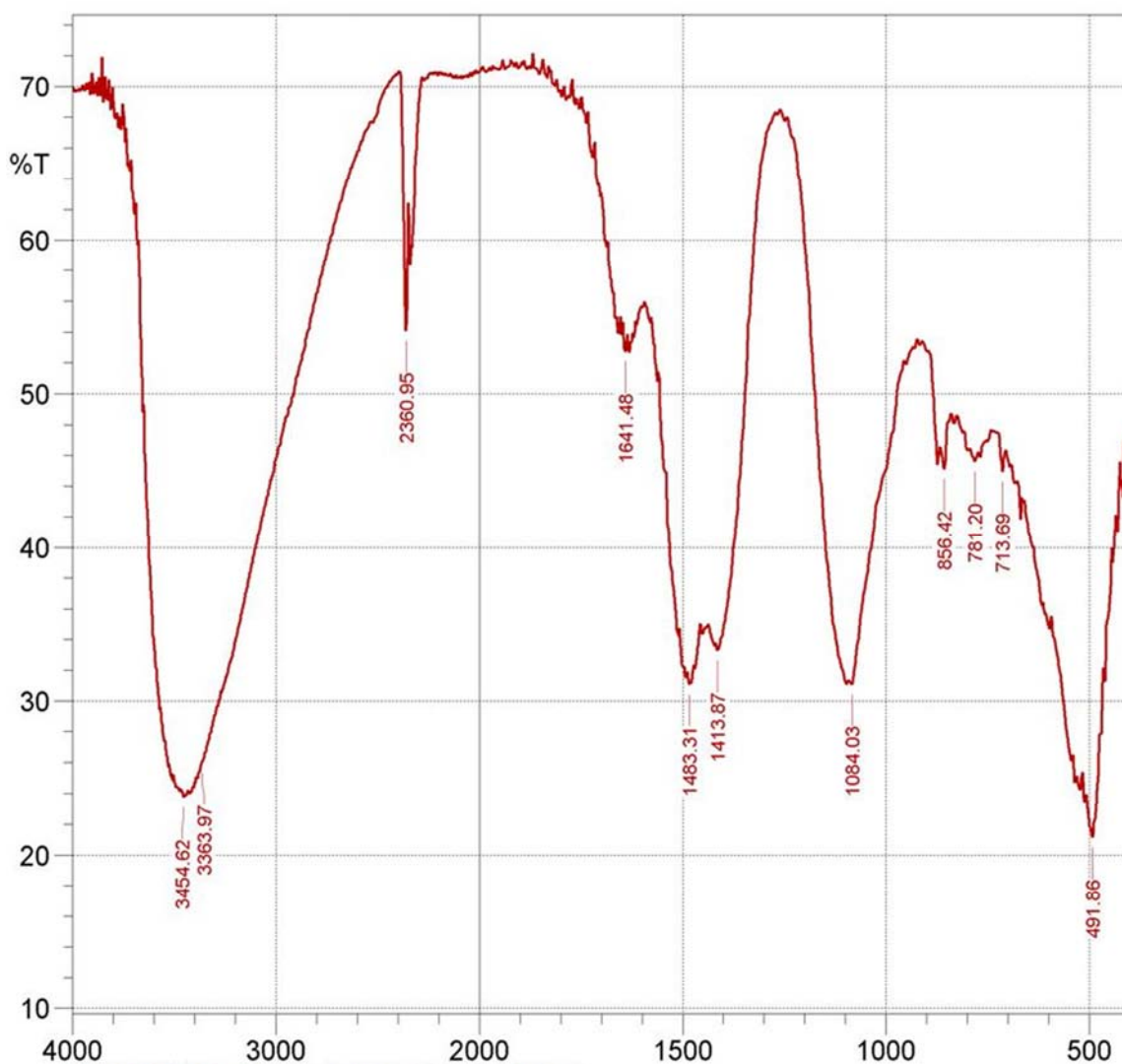**Figure 18.** *EDX Spectra of P- laden LDH₂.*

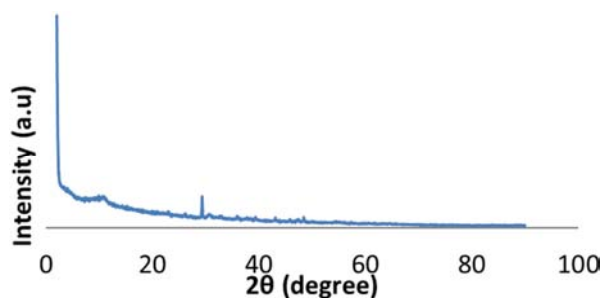**Figure 19.** *FTIR Spectra of P- laden LDH₂.*

Figure 20. *XRD Pattern of P- laden LDH₂.*

4. Conclusion

In conclusion, novel CaCr LDHs were successfully synthesised using Gastropod shell as a biogenic precursor for Ca^{2+} source. The study revealed that the type and amount of divalent cation content in the LDH sample is important in the sorption capacity as adsorbent with the highest Ca content was most suitable for optimum removal of phosphate from aqua system. The experimental data of the sorption process fitted well into Langmuir isotherm model with a maximum monolayer sorption capacity of 142.86 mg/l. Characterisation of the phosphate-loaded LDH revealed the loss of the layered structure as a result of dissolution of Ca^{2+} from the LDH and combination of ion exchange and co- precipitation as mechanisms of the removal process. The findings obtained in this study will further the development of layered double hydroxides for water/ wastewater treatment.

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