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Kinetics of Phosphate Adsorption by Ca/Cr Layered Double Hydroxide

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Abstract:

Kinetics of phosphate adsorption by Ca/Cr Layered double hydroxide (LDH) in a batch reactor was investigated in this study. The kinetic experiments indicated that the sorption of phosphate from the synthetic feed solution by the synthesised LDH was very fast, with over 98% removal being achieved within 5 min of contact. Kinetic modeling of the sorption process to different kinetic models (pseudo first order, pseudo second order, Elovich and intraparticle diffusion) showed that the pseudo-second order model best described the process. Studies of effect of hydrochemistry on the sorption process such as initial solution pH, ionic strength and organic load contamination interference, indicated nominal effect on the amount of phosphate removed by the LDH. Overall, the study indicated that chemisorption and precipitation are active contributory mechanisms to the sorption of phosphate by Ca/Cr LDH from solution.

Keywords: Adsorption Kinetics, Chemisorption, Layered Double Hydroxide, Phosphate Removal, Precipitation.

INTRODUCTION

With large quantities of phosphates being used for various industrial processes, most especially fertilizer production, which invariably generates large volumes of phosphate-bearing waste effluents, its removal from waste effluents is of prime importance to prevent inherent problems associated with its discharge in the environment. Phosphate effluents treatment is achieved via ion-exchange, chemical precipitation, physical, biological, adsorption or crystallization [Jiang and Wu, 2010; Zhou *et al.,* 2011]. Adsorptive treatment is more appealing because of cost effectiveness, simplicity of design, ease of operation and a remarkable high possibility of phosphate recovery for reuse. Recently, arrays of materials with high amounts of calcium, aluminium and iron compounds are being investigated as adsorbents for phosphate due to their strong affinity to phosphorus binding [Vohla *et al.,* 2011; Adelagun *et al.,* 2017]. Layered double hydroxides (LDHs) also called anionic clays are widely used as adsorbents and anion exchangers with huge selectivity for phosphate removal from aqueous system [Novillo *et al.,* 2014]. LDHs materials exhibit unique characteristics such as permanent layer positive charge, water resistant structure, large surface area, good thermal stability, high anion exchange capacity and remarkable regeneration efficiency when compared with other anion exchangers [Ishikawa *et al.,* 2007; Ryu *et al.*, 2010]. LDHs are very simple and economical to prepare in the laboratory. Methods of preparation include, co-precipitation method, using urea ($CO(NH_2)$) and Na_2CO_3 as precipitant, reconstruction method also called “memory effect”, hydrothermal method and anion exchange method [Patzko *et al.,* 2005; Ishikawa *et al.,* 2007].

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` Dynamics of adsorption are usually explained by kinetics which describes adsorbate uptake controlled by its residence time at the solid-solution interface and mass transfer properties of the adsorbent [Chen and Wang, 2004; Itodo *et al.,* 2013]. The import of sorption kinetics is provision of useful insights into the reaction pathways and the prevailing mechanism of the sorption process [Ololade *et al.,* 2015]. Batch kinetic studies are conducted in order to elucidate the rate at which sorption is taking place which is useful in designing batch sorption system. Due to the high ion -exchange properties of LDHs for the selective uptake of polyatomic anions including phosphate from aqueous system, the studies was aimed at assessment of kinetics of phosphate removal from a synthetic feed phosphate wastewater in a batch sorption process by CaCr LDH. The work is premised on appropriate technology and green chemistry, which involves the use of gastropod shell, a biogenic precursor as the source of Ca^{2+} in the synthesis of the LDH material. Kinetic studies are usually undertaken by evaluating the effect of initial sorbate concentration, sorbent dosage, sorbent particle size, agitation speed, pH and / or temperature on the adsorption process. In this study, series of kinetic experiments were conducted. Adsorption models were used to describe the experimental results. Effects of process variables (pH, ionic strength and organics contamination) on the sorption process were also investigated and reported.

MATERIALS AND METHODS

Adsorbent preparation

All reagents/chemicals used were of analytical grade obtained from AR and BDH chemical companies and used without pretreatment. Solutions of $CaCl_2$ derived from gastropod shell were obtained as earlier described [Adelagun *et al.,* 2017]. The LDH samples were prepared via the co-precipitation method using gastropod shell powder as the source of Ca (M^{2+}) and $CrCl_3$ as the source of Cr (M^{3+}). Mixed solution of $CaCl_2$ and $CrCl_3$ of molar ratio of 2:1 was prepared and stirred to give an even mix. 2 M NaOH/Na_2CO_3 solution was added drop-wise as precipitant to the mixture. The resulting slurry was left for 24 h in the precipitant to gelate. The gelatinous precipitate was then thoroughly washed with deionized water repeatedly, filtered and dried to constant weight at 80°C in the oven.

Determination of pHpzc of the adsorbent

The point of zero charge (PZC) of the adsorbent was determined using the batch equilibrium procedure described by Milonjic *et al.,* (1981) viz: to a series of 100 ml conical flasks, 45 ml of 0.1 M KNO_3 solution was transferred. The initial pH values of the solutions were roughly adjusted between 2, 4, 6, 8, 10 and 12 by adding either 0.1 M HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 ml by adding KNO_3 solution. The pH0 of the solutions were then accurately noted using a pH meter (Hanna pH 211 microprocessor). 1 g of the adsorbent was added to each flask and immediately securely capped. The suspension was then manually agitated for 24 hours. The pH values (pH_f) of the supernatant liquid were noted. The difference between the initial and final pH ($\Delta pH = pH_0 - pHf$) values was plotted against the pH_0. The point of intersection of the resulting curve on pH0 gave the PZC.

Batch kinetic studies

The adsorption kinetic experiment was conducted in a batch process at room temperature. Phosphate stock solution (300 mg/L) was prepared by dissolving 0.43 g of KH_2PO_4 in 1000 ml distilled water and working solutions of different orthophosphate concentrations: 25, 50, 100, 200, and 300 mg/l, were prepared, as required, from the stock by serial dilution. To a 1000 ml of the synthetic phosphate solution of concentrations (25 - 300 mg/l), 2 g of the adsorbent was added and stirred using a magnetic stirrer at 200 rpm. Solution samples were withdrawn at intervals between 0-3 h of sorption 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 (UV-1601, Shimadzu) at 801 nm. The amount of phosphate sorbed per unit mass of the adsorbent (mg/g) was calculated by using the mass balance equation:

$$q_e = \frac{c_o - c_e}{m} \times v \qquad (1)$$

$$R\,(\%) = 100 \times \frac{c_o - c_e}{c_0} \qquad (2)$$

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-} (mg/l), c_e = final residual PO_4^{3-} concentration (mg/l).

Process variables optimization studies

Determination of effect of initial solution pH on the sorption was assessed by adjusting the initial pH of the adsorbate (phosphate) of fixed concentration between pH values of 7 and 12, using 0.1M HCl and 0.1M NaOH. 0.1 g of the adsorbent was contacted with 50 ml of known orthophosphate concentration (40 mg/l) at a specified pH and agitated at 200 rpm for 2 hours. Samples 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 determined as mentioned earlier. Also residual pH of the solution was determined at the end of the sorption process. The influence of organics contaminations interference studies was simulated by the addition of humic acid (HA) of concentrations that range between 5 and 80 mg/l, while effects of ionic strength on the sorption process was tested in NaCl solutions (%): 0, 0.125, 0.25, 0.5, 1.25 and 2.5, equivalent to ionic strengths (mol/L) of 0, 0.02125, 0.0425, 0.085, 0.2125 and 0.425). Each analysis was run in triplicate.

RESULT AND DISCUSSION

Sorption Kinetics Studies

The time-concentration profile of phosphate uptake from solution by the adsorbent at different initial concentrations is presented in Fig. 1. The results obtained showed that phosphate uptake rate by the adsorbent from solution was very fast and initial concentration dependent. This suggests a rapid initial transfer into the near surface boundary layer of the adsorbent. Phosphate uptake greater 97 % was achieved within the first 5 min of sorption for all initial concentrations. It was seen that the equilibrium time required for the sorption of phosphate on the surface of the adsorbent was almost 30 min and the removal rate was about 98% at this time. Complete adsorption equilibrium was almost attained within 30 min by the adsorbent, with minimal sorption being achieved after this time. No significant decrease in residual phosphate concentration was observed with further increase in retention time after 2 h (Fig. 1). So, all the further adsorption experiments were conducted at 2 h contact time.

Furthermore, the time – concentration curves are smooth and continuous thus suggesting the possibility of formation of a monolayer on adsorbent surface [Das *et al.,* 2006]. This confirmed our earlier assumption from the equilibrium isotherm studies of the sorption of phosphate by the synthesised Ca/Cr LDH as described by the Langmuir isotherm model [Adelagun *et al.,* 2017]. Increased uptake efficiency by the adsorbents observed with increase in initial concentration was most likely due to an increment in the driving force at higher concentration. The percentage of removal increased with increased initial phosphate concentration from 99.44% for 25 mg/l P to 99.96 % for 300 mg/l P.

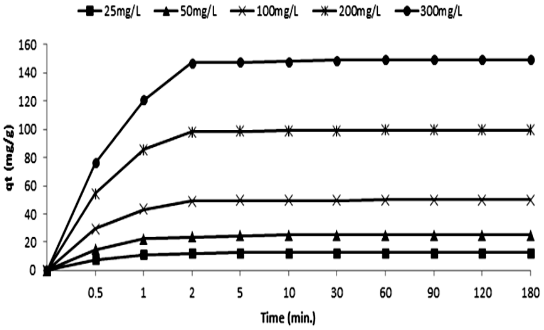

Fig. 1. Time-Concentration Profiles of Phosphate Removal by Ca/Cr LDH Sample

These findings are in agreement with previous studies which indicate fast initial oxyanion adsorptions by LDHs followed by a slower process until reaching complete equilibrium [Das *et al.,* 2006; Zheng *et al.,* 2012; Novillo *et al.,* 2014]. The reason being thus: LDHs possess lamellae that are positively charged and as such, interact strongly with anionic species in solution. Adsorption and ionic exchange are the two mechanisms involved in the anion removal. While the ionic exchange is a diffusion process and slow, the adsorption process is relatively faster due to the strong interactions between the negative ions and the positive external surface [Novillo *et al.,* 2014].

Sorption Kinetic Modeling

Insights into the possible reaction mechanism(s) and estimation of rates of adsorption of the sorption process are obtained via kinetic modeling. The mechanisms believed to be involved during sorption of oxyanions (e.g. phosphate) by LDH materials are, external mass transfer (boundary layer/ film diffusion) between the external surface of the adsorbent particles and the surrounding fluid phase, intraparticle transport and chemisorption (reaction at phase boundaries) [Goh *et al.,* 2008]. Elucidation of the actual mechanism of phosphate sorption by the LDH was assessed using mathematical models. To this end, the experimental data obtained from the kinetic studies were tested with four kinetic models, including pseudo-first order [Lagergren, 1898], pseudo-second-order [Simonin, 2016], Elovich [Ho and Ofomaja, 2005] and intraparticle diffusion [Karaca *et al.,* 2004; Weber and Morris, 1967]. The Elovich model is an empirical equation which considers the contribution of desorption in a system, while pseudo first-order and second-order equations describe the kinetics of the solid–solution system based on mononuclear and binuclear adsorption, with respect to the sorbent capacity [Novillo *et al.,* 2014]. The linear equations of the models are represented as thus:

Pseudo First Order: $$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (3)$$

Pseudo Second Order: $$\frac{t}{q_t} = \frac{1}{k\, q_e^2} + \frac{t}{q_e} \qquad (4)$$

Elovich: $$q_e = A + 2.303 B \log t \qquad (5)$$

Intra particle diffusion: $$q_t = C + k_{id} t^{0.5} \qquad (6)$$

Where q_t and q_e are the amount of phosphate adsorbed at time t and equilibrium, respectively (mg/g), k_1 and k_2 are the first-order and second-order adsorption rate constants (h-1 and g/mg min), respectively, A (mg/g) is the initial sorption rate, and B (mg/g/min) corresponds to the extent of surface coverage and activation energy for chemisorption, kid is the intraparticle diffusion rate constant (mg/g min 0.5), C is a constant that gives idea about the thickness of the boundary layer: the larger the value of C, the greater the boundary layer effect [Cheng *et al.,* 2009].

The kinetic parameters, namely, rate constants (k_1, k_2), correlation coefficient (R^2), error functions (χ^2) , predicted and calculated equilibrium uptakes (qe_{exp}, qe_1 , qe_2) are presented in Table 1. It can be seen that the correlation coefficients (R^2) of pseudo second-order model are much higher (R^2 = 1.00) than those of first-order model (R^2 =.0.49 - 0.62) and Elovich model (0.46 - 0.56). Also, the theoretical uptakes q_{e2} are in good agreement with the experimental uptakes qe_{exp} for the pseudo second-order model in comparison to the other two models whose value deviated greatly from the experimental values. Furthermore, the error function (θ2) is negligible (< 0.1) for the pseudo second order kinetic model. This suggests that the adsorption kinetics of phosphate by the Ca/Cr LDHs is well described by the pseudo second-order kinetic model. This is a pointer to the fact that the sorption of phosphate onto the LHD occurred probably via chemisorption. This indicated chemisorption or chemical bonding between adsorbent active sites and phosphate prevalence in the adsorption process. These findings are in agreement with previous studies which reported that the phosphate adsorption on LDHs is described by a pseudo-second order mechanism [Hosni and Srasra, 2010; Halajnia *et al.,* 2013; Yu *et al.,* 2015; Li *et al.,* 2016; Hatami *et al.,* 2018].

Ho and McKay, (1998), opined that for a chemically-controlled sorption process, the pseudo second order constant is dependent on the concentration of the sorbate ions in solution and not on the particle diameter or flow rate. Values obtained for the pseudo second order constants: qe and k_2 (Table 1) indicated that while the values of the former (q_e) increased with increase in the initial phosphate concentrations, the values of k_2 were independent of the initial sorbate concentration. This implies that the mechanism of phosphate removal by the Ca/Cr LDH was not solely controlled by chemisorption but involves exchange of electrons in the process of removal.

Table 1: The Kinetic Parameters for Phosphate Uptake by Ca/Cr LDH Samples

Initial conc. (mg/l)		Pseudo 1st order				Pseudo 2nd order				Elovich			
	qe_{exp}	qe_1	K_1	R^2	χ_2	q_{e2}	K_2	R^2	χ_2	B	A	R^2	χ_2
25	12.4437	0.564	0.056	0.493	250.23	12.52	7.68	1	0.001	0.6544	9.639	0.56	0.368
50	24.9505	0.809	0.049	0.5283	716.72	24.94	8.35	1	0.001	1.4251	18.75	0.561	0.77
100	49.701	1.574	0.038	0.6099	147.54	50	7.69	1	0.002	2.9848	37.64	0.479	1.42
200	99.2394	4.175	0.069	0.5216	2164	100	7.14	1	0.006	5.8489	75.52	0.459	3.92

The mechanism of adsorbate transport from the solution phase to the surface of the adsorbent usually occurs in several steps. The steps are: film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface [Zheng *et al.,* 2012]. The slowest of these steps is considered as the rate determining step. In a rapidly stirred batch adsorption process, pore particle diffusion is often the rate limiting step while for a continuous flow system, film diffusion is more likely the rate limiting step. Although there is a high possibility for the pore diffusion to be the rate limiting step in a batch process, the adsorption parameter which controls the batch process for most of the contact time is the intra-particle diffusion [Yin *et al.,* 2011]. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which the components diffuse towards one another. According to the Weber and Morris, (1963) model in Eqn. (6), if a plot of qt versus t 0.5, gives a straight line, it is an indication that the sorption process is controlled by intraparticle/pore diffusion only. However, if there are multi-linear plots, then it implies that two or more steps influenced the sorption process. In order to investigate the rate determining step of the process, the experimental data obtained from the initial concentration optimization were fitted into the intraparticle diffusion equation (Eqn. 6). The results obtained in Figure 2 showed the plots of the amount of phosphate sorbed (qt,(mg/g) by Ca/Cr LDH against t 0.5 ($min^{0.5}$).

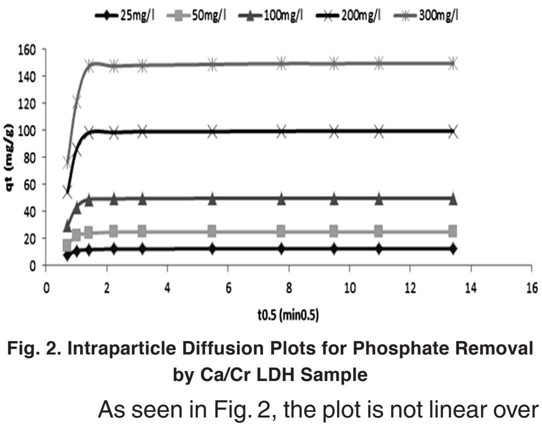

Fig. 2. Intraparticle Diffusion Plots for Phosphate Removal by Ca/Cr LDH Sample

As seen in Fig. 2, the plot is not linear over the entire time range of the sorption process; more than one linear portion is depicted, suggesting a multi-step process. The plots obtained in Fig. 2 indicated three steps, which is an indication that intraparticle/pore diffusion is not the singular rate limiting step in the process. The first part was attributed to boundary layer diffusion, the second part was attributed to the intraparticle diffusion (micropore or macropore diffusion) and the third step to the chemical reaction [Novillo *et al.,* 2014]. Furthermore, the low linearities of R_2 (0.241-0.289) in Table 2 of the plots also lend credence to the submission that intraparticle diffusion was not the singular rate limiting step in the process. The deviation of the straight lines from the origin may be due to the difference in the rate of mass transfer in the initial and final stages of the process. Details of the intraparticle diffusion parameters are presented in Table 2. From the results, it could be observed that as the initial phosphate concentration increased from 25 to 300 mg/l, the value of C also increased from 10.83 mg/g to 123.90 mg/g and the value of kid increased from 0.172 to 6.656 mg/g min0.5. Higher values of kid implies increase in the rate of adsorption.

Table 2: Intraparticle Diffusion Parameters of Phosphate Removal by Ca/Cr LDH

Initial conc (mg/l)	R^2	k_{id} (mg/g $min^{0.5}$)	C (mg/g)
25	0.289	0.172	10.83
50	0.253	0.345	21.62
100	0.251	0.710	43.04
200	0.241	1.533	84.82
300	0.266	2.656	123.90

Effect of Adsorbate Initial Solution pH

The pH of a solution has impact on the surface charge of the adsorbents and also on the degree of ionization and speciation of adsorbate in solution. Adsorption is affected by changes in pH, through dissociation of functional groups on the active sites on the surface of the adsorbent which brings about a shift in the reaction kinetics and equilibrium characteristics of the adsorption process [Koilraj *et al.,* 2013]. In order to prevent the dissolution of the Ca/Cr LDH constituents (Ca^{2+} and Cr^{3+}) in acidic pH region, the effects of initial solution pH on phosphate removal using CaCr LDH was assessed at different initial solution pH value that ranged between 7 and 10. A slight increase (Fig. 3) in the magnitude of phosphate uptake with increasing initial solution pH was observed. This implied that the magnitude of phosphate sorption by the LDH was almost steady (98.7- 99.1 %) in the pH range used.

The pH that corresponds to the point of zero charge (pHPZC) of the LDH was found to be 12.0

(Fig. 4). This implied that the predominant surface charge on Ca/Cr LDH was positive within the pH range studied favoring adsorption of phosphates. The surface of adsorbent interaction with cations is favoured at pH > pHPZC, while anion interaction is favored at pH < pHPZC. This implies that the surface of the CaCr LDH samples are dominated by positive charges at pHs less than 12 and as such favoured phosphate sorption from solution while at pHs greater than the pHPZC, the surface is dominated by negative charges, leading to repulsion of phosphate anions. The equilibrium solution pH (pH_f), determined at the end of the sorption process was found to be higher (7.96 - 10.43) than the initial solution pH. This trend is attributed to the strong buffering capacity of the Ca-based LDHs, as a result of Ca^{2+} being leached into solution. The leached Ca^{2+} could react with PO_4^{3-} via precipitation to form the possible Ca_2PO_4 precipitate, suggesting the possibility of precipitation as a contributing mechanism in the process [Hosni and Srasra, 2010; Novillo *et al.,* 2014]. This suggests that the adsorption is a combined process of both chemical and electrostatic interaction between the LDH surface and phosphate anion.

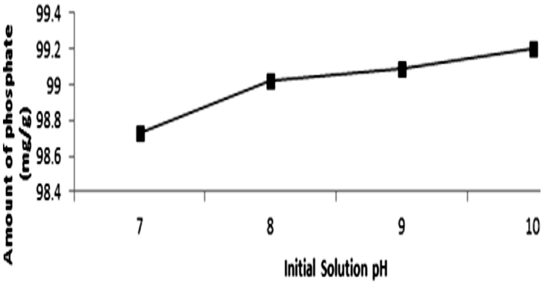

Fig. 3. Effect of Initial solution pH on phosphate uptake by Ca/Cr LDH Sample

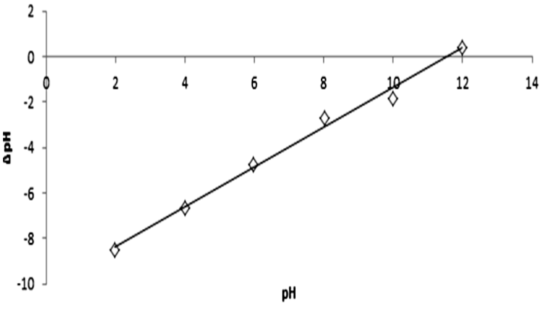

Fig. 4. Point Zero Charge of Ca/Cr LDH Sample

Effect of Ionic Strength

Varying the ionic strength of the phosphate solutions led to changes in the magnitude of phosphate uptake by the LDH (Fig. 5). The amount of phosphate removed reduced with increase in the solution ionic strength. There was a marginal decrease in the amount of phosphate sorbed from 99.15 mg/g to 96.07 mg/g when the ionic strength of the phosphate solution was increased from 0.0214 mg/l to 0.4275 mg/l. Similar results have been reported by Bowden *et al.,* (2009), Chouyyok *et al.,* (2010) and Yin *et al.,* (2011) who performed phosphate sorption studies using slag, Fe-rich material, and calcium rich sepiolite, respectively, as adsorbents. Some authors opined that electrolytes can form outer-sphere complexes through electrostatic forces or inner-sphere complexation [Hsia *et al.,* 1994; Oladoja *et al.,* 2014].

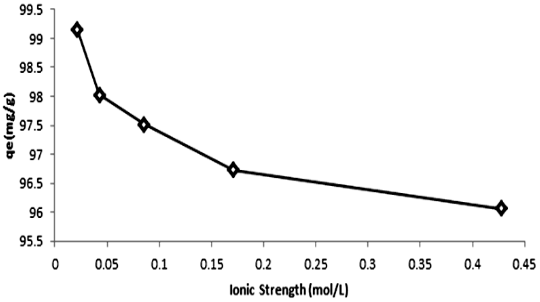

Fig. 5. Effect of Ionic Strength on Phosphate Sorption by Ca/Cr LDH Sample

Oladoja *et al.,* (2014) opined that anions that are adsorbed by outer-sphere complexation are strongly sensitive to ionic strength. The magnitude of such anions removal decreases with an increase in ionic strength. However, anions that are adsorbed by the inner sphere complexation are either minimally affected or respond with greater adsorption to changes in ionic strength. In the present study, the amount of phosphate removed was affected by the ionic strength of the adsorbate with reduction in the amount removed. This suggests the possibility of phosphate removal occurred via the formation of outer-sphere surface complexes.

Effect of Organic Load Contamination

The presence of organic matter in natural waters and wastewater, simulated by the addition of humic acid (HA) at varying concentrations to a fixed phosphate concentration indicated that the amounts (mg/l) of residual phosphate in the treated water were in the same range (98.46 –99.2 mg/g) for varying concentrations of the organics contamination in the phosphate contaminated water (Fig. 6). This implies that the presence of organic matter contamination has no significant impact on phosphate removal by the LDHs. Simultaneous evaluation of organic matter removal efficiency of the process in the treated water revealed that as the concentration of HA was increased, the amount of HA removed increased substantially (Table 3). This indicated that as phosphate was being removed by the LDHs, some amount of HA were simultaneously being removed, suggesting that the LDH could be used to treat organic matter in aqueous system. Carboxylic and phenolic group on the HA are deprotonated in weakly acidic to basic media thereby conferring negative charge on the HA molecule [Anirudhan *et al.,* 2008].

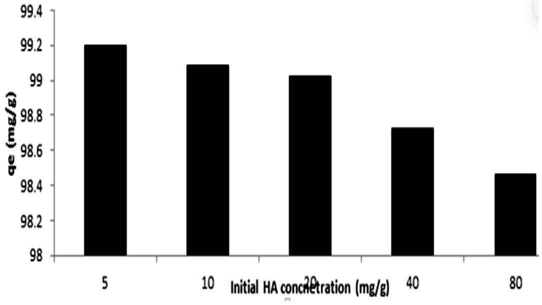

Fig. 6. Effects of Organic Load on Phosphate Removal by Ca/Cr LDH Samples

Table 3: Residual HA concentration after Phosphate Removal by Ca/Cr LDH Sample

Initial HA Concentration (mg/l)	Final HA Concentration (mg/l)
5	3.72
10	7.32
20	15.83
40	29.44
80	53.31

CONCLUSION

Kinetics adsorption experiments showed that phosphate sorption in aqueous system by CaCr LDH was very fast and initial concentration dependent. The kinetic modeling studies revealed that chemisorption and diffusion played important roles in the sorption process. Furthermore, the study revealed that solution chemistry was significant in the sorption kinetics.

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