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Intercalation of Gastropod Shell Derived Calcium Oxide in Clay and Application in Phosphate Removal from Aqua Medium

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S Supporting Information

ABSTRACT: The phosphate sorption potential of the layered framework of naturally occurring clay, which acts as a host in the sorption process, was boosted via intercalation of CaO derived from a Gastropod shell (GS). GS was used as precursor for the synthesis of the CaO in the perspective of waste recycling and cost minimization in environmental remediation. The phosphate sorption potential, PZC, and the surface area of raw clay sample were substantially enhanced by the intercalation process. The value of the Langmuir monolayer sorption capacity (q_m mg/g) increased from 49.02 to 71.43, PZC values increased from 4.70 to 7.20, and the surface area (m^2/g) value increased from 23 to 103 after the intercalation process. The modification caused no change in the clay surficial microstructure but increased the lattice spacing of the clay framework. Increase in phosphate solution pH triggered monotonical reduction in the magnitude of phosphate sorbed while increase in phosphate solution ionic strength and concentration of anionic interferences caused an increase in the amount of phosphate sorbed per gram of sorbent. Phosphate sorption caused no change in the surficial microstructure of either sorbents but the crystallinity of the sorbent was considerably impacted, especially in the raw sample

1. INTRODUCTION

An essential nutrient, which is the growth-limiting factor, of aquatic vegetation in water bodies is phosphorus (P), which occurs mainly as phosphate in aqua systems. Daniel et al.¹ reported that the critical level that accelerates the growth of aquatic plants is 0.01 mg/L for dissolved P and 0.02 mg/L for total P. The presence of trace amounts of phosphate (even <1.0 ppm) in the treated wastewater is often responsible for eutrophication, which leads to short- and long-term environmental and navigational problems in water bodies.^{2,3}

Phosphate is an issue in an assortment of biological and chemical processes in an aquatic system. Removing phosphorus via the conventional water or wastewater treatment route is taxing, hence the innovation of highly effective but uneconomical tertiary methods such as reverse osmosis or electrodialysis. Removal of phosphate in an economical fashion, without laying on the line the system efficiency, culminated in the development of array of physical,⁴ chemical,⁵ biological,⁶ crystallization,⁷ and flotation methods.⁸ Chemical precipitation/crystallization and biological processes are widely used for phosphate removal from industrial effluents;^{9,10} however, it is technically tedious and uneconomical for both techniques to meet the increasingly stringent regulations on phosphate discharge. Karageorgiou et al.,¹¹ also opined that the cost associated with the use of metal salts and management of the metal phosphate sludge, derived from chemical precipitation, could hinder the acceptance of this method as a convention in aqua phosphate management. Adsorption seems attractive for phosphate removal due to its operational simplicity and economics.¹² In order to improve the efficiency of adsorption process, the development of phosphate-specific adsorbents is vital.^{13,14}

The major components of materials for phosphate removal are Al, Fe, and Ca compounds. Phosphorus removal, via the use of these materials, occurs through both adsorption and precipitation, determined by redox potential and pH value.^{15–17} Metal oxides are important PO_4^{3-} adsorption sites due to their multiple charged cation, high positive surface charge densities at near-neutral pH, and a propensity to hydroxylate in aqueous systems.¹⁸ The reaction with calcium oxide, calcite, or gypsum particle surfaces involves the adsorption of small amounts of phosphate followed by the precipitation of calcium phosphate. Initial adsorption is thought to occur at sites where lateral interaction with phosphate ions produces surface clusters that then act as nuclei for subsequent crystal growth.¹⁹

Natural clay minerals are low-cost materials due to their abundance in most continents of the world and possess a layered structure which can act as host materials with high sorption properties. Although clays themselves possess the high adsorption capabilities, the modification of their structure can successfully improve their capabilities.²¹ The shell of African land snail (SS) is being proposed as the Gastropod shell to be used as a precursor for the derivation of the CaO to be used for the intercalation because of the chemical and mineralogical assemblage. Gastropods have worldwide distribution from the near arctic and Antarctic zones to the tropics and very striking in its extraordinary diversification of habitats. Large tonnages of Gastropod shells are discharged annually, as waste from food

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processing industries, which made it a low cost and abundant material that could be harnessed for CaO synthesis. SS has the same basic construction as other Molluscan shells and consists three layers whose basic building block is aragonite.^{20,22} In the present study, naturally occurring tropical clay was modified by intercalation of CaO derived from the shell of a Gastropod, African land snail (*Achatina achatina*), and characterized. The ability of the modified clay was tested against raw clay in phosphate removal from aqua system in a batch adsorption process. Sorption process data were obtained via equilibrium isotherm analysis and kinetic studies. Process variables were optimized by method of continuous variations and the effects of the sorbate uptake on the sorbent surface microstructure and crystallinity were investigated via SEM and XRD analysis of the spent and virgin sorbents

2. MATERIALS AND METHODS

2.1. Gastropod Shell Preparation and Characterization. The shell of the African land snail (*Achatina achatina*) was used as a source of the Gastropod shell. The snail shell (SS) was prepared as previously described in the literature.²⁰ The physicochemical characteristics of the SS have been determined and reported in our earlier treatise²⁰

2.2. Clay Modification and Characterization. The natural clay used was obtained from Ozanagogo town in Delta State, Nigeria. The clay was modified with CaO derived from SS following the protocol described by Eren et al.,²³ (Figure 1) thus: 20 g of clay, previously sieved with a standard

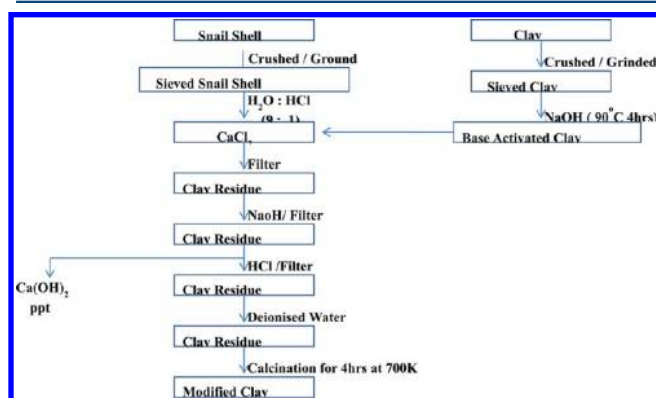


Figure 1. Flowchart for clay modification.

laboratory sieve of 425 μ , were immersed in sufficient 2.0 M sodium hydroxide and temperature of the reaction mixture was maintained at 90 °C for 4 h. CaCl_2 solution was derived from SS (4.0g) following the procedure described by Oladoja et al.^{22,24} The base activated clay was dispersed into 150 mL of CaCl_2 solution prepared from SS and 300 mL of 0.1 M sodium hydroxide aqueous solution was slowly added. The obtained powder was rinsed with 200 mL of 0.01 M HCl aqueous solution to remove the excess $\text{Ca}(\text{OH})_2$ precipitated on the outer surface of the clay and further washed with deionized water. Then, this sample was heated for 4 h in air at 900 °C to obtain the CaO modified clay.

The CaO modified (CIC) and unmodified natural (UNC) clay samples were characterized thus: specific surface area was determined using the method of Sear's,²⁵ the point zero charge (PZC) was determined by solid addition method,²⁶ the surface microstructure was determined by scanning electron micro-

scope and the crystallinity was determined by X-ray diffractogram.

2.3. Sorption Experiment. Owing to the reports^{27,28} that orthophosphate is the primary form of phosphorus responsible for eutrophication, potassium dihydrogen phosphate (KH_2PO_4) was used in as the source of orthophosphate. A stock orthophosphate solution of 2000 mg/L was prepared with distilled water and working solutions of different orthophosphate concentrations were prepared, as required, from the stock by serial dilution.

The effect of the CaO modification on the sorption capacity of the clay materials for phosphate was evaluated via equilibrium isotherm analysis. The sorption capacities of both the CIC and UNC were determined by contacting 50 mL solution of known phosphate concentration that ranged between 25 and 300 mg/L with 0.1 g of either adsorbent (i.e., CIC and UNC). The mixture was stirred at 200 rpm in thermostatic shaker for 2 h, samples were removed, centrifuged, and the supernatant was analyzed for residual phosphate (as phosphorus) by the molybdenum-blue ascorbic acid method with a UV-vis spectrophotometer.²⁹ The method is suitable in the 0.01 to 0.5 mg P/L range. The amount of phosphate sorbed per unit mass of the adsorbent (in mg/g) was calculated using the mass balance equation.

The sorption process variables were optimized thus: the effect of pH on the sorption process was investigated by varying the pH of the initial phosphate solution between pH 3 – 10; the effects of ionic strength was tested in NaCl solutions of the following concentrations (%): 0, 0.05, 0.1, 0.5, and 1; inorganic salts was simulated by the addition of different concentrations (0.5, 1, 2, 3, 5%) of the potassium salts of different anions viz: (NO_3^{2-} and SO_4^{2-}),

Phosphate sorption kinetic parameters, via initial phosphate concentration optimization, were evaluated by the addition of 2.0g of either adsorbent into a liter of phosphate solution of different concentrations. Solution samples were withdrawn at intervals between 0 and 4 h, of sorption, centrifuged and the supernatant phosphate concentration was determined.

3. RESULTS AND DISCUSSION

3.1. Sorbent Characterization. The kaolinitic clay sample used in the present studies is of the sedimentary type. Sedimentary kaolin deposits are known to occur in Nigeria mainly as beds, lenses or bands within the cretaceous and tertiary sedimentary sequences in Sokoto, Benue, Chad and particularly the Niger-Delta basins.³⁰ The deposits are located in southwestern Nigeria. In this area, the rainfall (1600 mm annually) and temperatures (22–27.5 °C) are moderate to high as is typical of a tropical region.³¹

The CaO modification of the clay framework produced a material (CIC) whose PZC value (7.20) was greater than that of the unmodified clay (UNC) (4.70) (Supporting Information SF1a and b). Values of PZC that ranged between 3.0 and 7.5 have been reported for kaolinite,^{32,33} and.³⁴ The estimated PZC values of 4.70 and 7.2 for both UNC and CIC are within the range of values reported in literature for kaolinite samples. The higher value of the PZC obtained for the CIC could be ascribed to the presence of the CaO, within the clay framework, which possibly modified the surface charge of the clay. Zou et al.³⁵ have also recorded an improved surface charge in sepiolite, when it was modified with Fe^{3+} .

The results of the specific surface area of the UNC and CIC showed that the CIC had higher specific surface area (103m²/

g) than that of the UNC (23m²/g). The higher specific surface area of the CIC could be ascribed to the CaO modification of the clay which opened up the silicate layers and the pores.

The results of the SEM analysis of the UNC and CIC are presented in Figure 2a,b. Both samples are made up of discrete

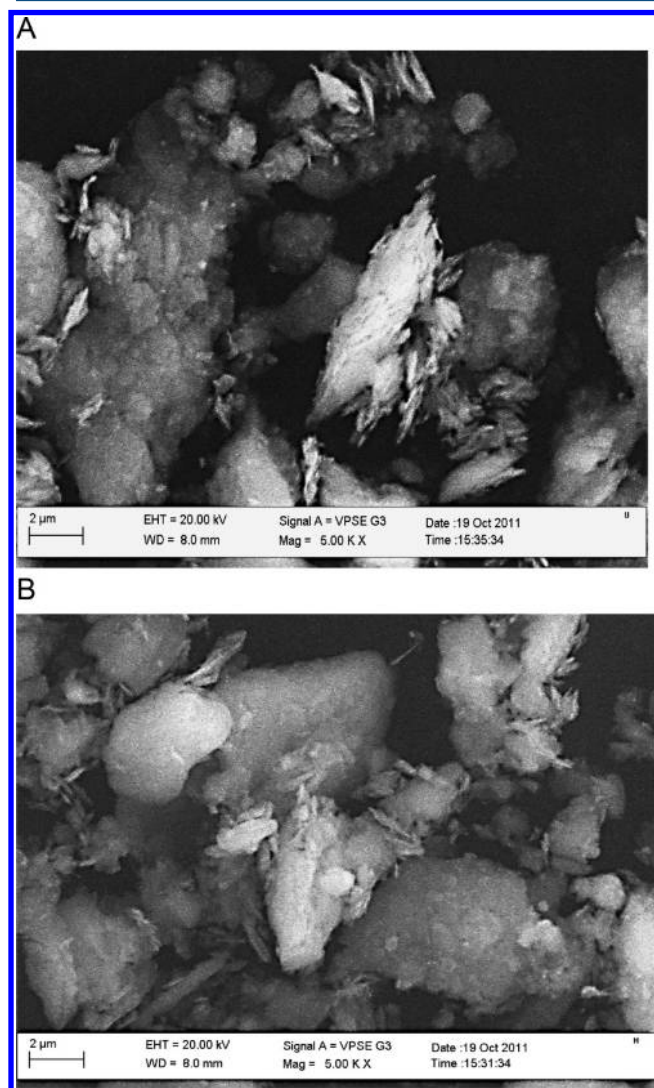


Figure 2. (a) SEM analysis of the UNC. (b) SEM analysis of the CIC.

particles of irregular size and shape and no distinct transformation in the surficial microstructure of the CIC could be deciphered. The XRD analysis of the UNC showed that the material is crystalline and some prominent peaks (degree) synonymous with kaolinite 12.46, 20.12, 24.99, 35.15, 36.03, 36.96, 37.85, 38.66, 40.99, 45.79, 54.62, and 55.12 were identified (Figure 3a,b). The CIC retained some of the prominent kaolin peaks but more peaks were introduced between the 2θ values of 20° and 30° and a slight increase in the basal spacing (>3 nm) of the lattice structure was observed. In the UNC, the d -spacing of the different 2θ values were mainly below 3 nm. The new found peaks and the broad increase in the d -spacing values were ascribed to the intercalation of the CaO in the CIC.

Borgnino et al.³⁶ postulated that changes in the basal spacing depend on the charge, size, and hydration behavior of the ion or molecule that is located in the interlayer and on interactions

between it and the phyllosilicate layers. The ionic radius of Ca²⁺ is 0.99 Å, whereas the single bond covalent radius of Ca²⁺ is 1.74 Å. Consequently, the hydrated form of the Ca–O bond length is 1.74 Å for the case of (Ca (OH)₂). The smaller size of Ca²⁺ can in principle explain the minimal increase in the basal spacing. Reduction in phyllosilicate basal spacing by addition of Fe³⁺ has been reported by Chen et al.,³⁷ who attributed this effect to strong attractive forces between iron and the silicate sheets of montmorillonite. Other authors, on the contrary, have observed a slight increase in basal probably due to the presence of polymeric species of iron within the interlayer.^{38,39}

3.2. Equilibrium Isotherm Analysis. The ability of both the CIC and the UNC to attenuate phosphate load in the aqua stream was assessed via equilibrium isotherm analysis at different initial phosphate concentrations. The isotherm parameters obtained, using the following linearized models of Langmuir, Freundlich, and Temkin-Pyzhev isotherm models are presented in Table 1.

$$\text{Langmuir: } C_e/q_e = 1/q_m C_e + 1/K_a q_m \quad (1)$$

$$\text{Freundlich: } \log q_e = \log K_f + 1/n \log C_e \quad (2)$$

$$\text{Temkin: } q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3)$$

The values of the monolayer sorption capacities, q_m (mg/g), obtained from Langmuir plot of sorption data for CIC (71.43) were higher than that of UNC (49.02). The magnitude of Langmuir constant, K_a , which is the sorption equilibrium constant (dm³/mg), was also higher (0.03743) in the CIC than in the UNC (0.00687). The higher the magnitude of the heat of sorption, the stronger the bond formed between the sorbate and the sorbent.

The values of the Freundlich constants, k_f and n , related to adsorption capacity and sorption intensity respectively, obtained from the plot of $\log q_e$ vs $\log C_e$, are presented in Table 1. K_f is the Freundlich affinity coefficient, and $1/n$ (unitless) is the Freundlich linearity index. As presented in Table 1, the value of K_f for CIC is higher in comparison with UNC which implied that the intercalation procedure produced more suitable conditions for phosphate sorption. The Temkin constants, K_T (Table 1), obtained from the plot of q_e vs $\ln C_e$. K_T is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption.

The fittings of the data obtained from the equilibrium isotherm studies to each of the equilibrium isotherm models were tested using the linear coefficient of determination, r^2 , and prediction of theoretical data from experimental data. The results from the fitting of the isotherm models to the data obtained from the present study revealed that highest correlation coefficient was obtained with the Freundlich equation than any of the other isotherm models (Table 1). Facts have emerged that the isotherms of phosphate sorption onto many adsorbents fit the Freundlich equation^{41,40} better.

In order to further assess the different isotherms and their correlation with experimental results, the theoretical plots obtained from each isotherm analysis is shown with the experimental data in Figure 4a,b. The graph is plotted in the form of sorbate sorbed per unit mass of sorbent, q_e (mg/g), against the concentration of sorbate remaining in solution, C_e (mg/L). The Freundlich isotherm model showed the best description of the sorption process than the other isotherm models while Temkin isotherm model showed the poorest

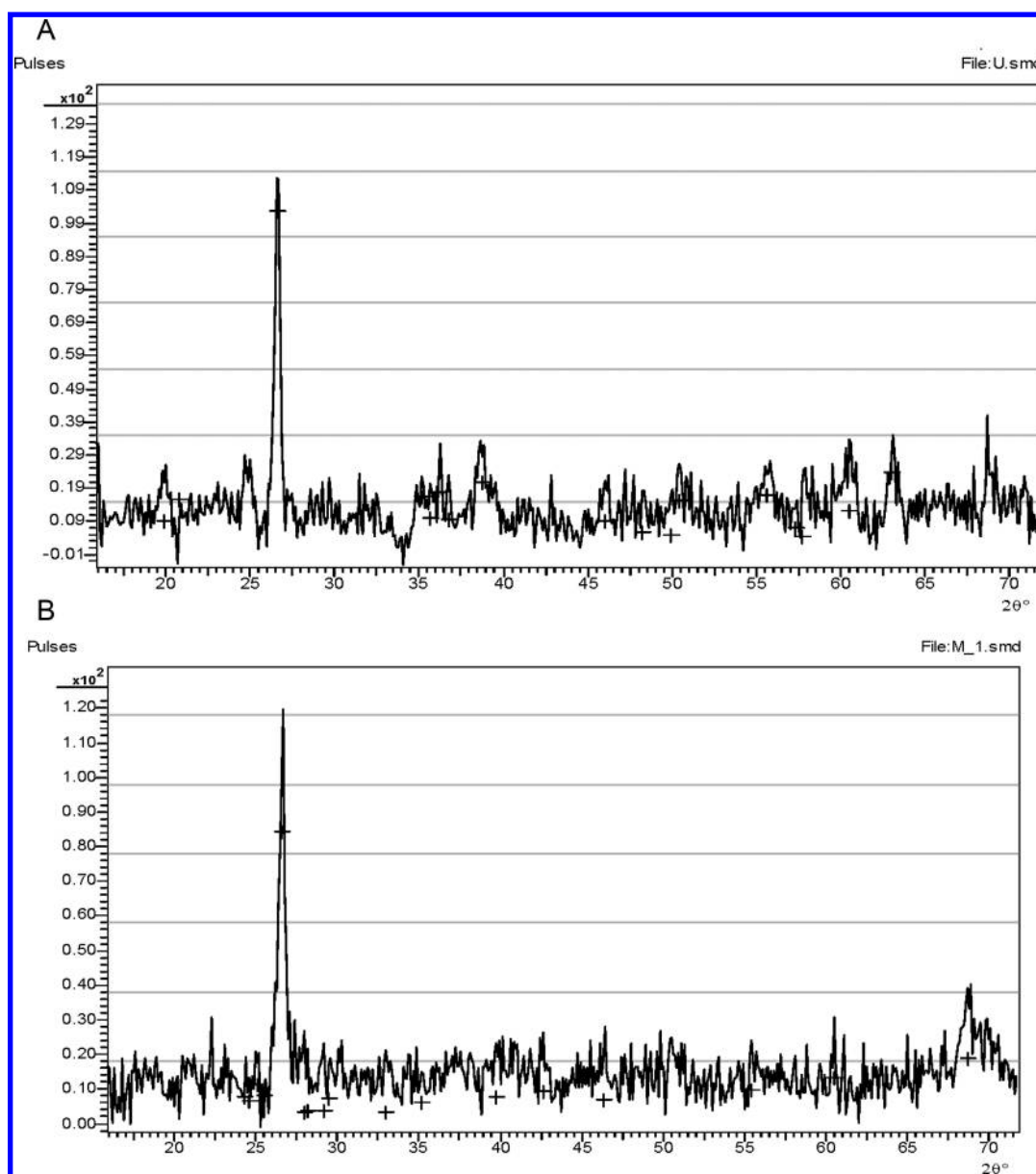


Figure 3. (a) XRD analysis of the UNC. (b) XRD analysis of the CIC.

Table 1. Results of the Isotherm Analysis

clay samples	Langmuir			Freundlich			Temkin-Pyzhev		
	q_m	K_a	r^2	k_f	$1/n$	r^2	B_1	k_T	r^2
CIC	71.43	0.03743	0.9086	9.12575	0.3806	0.9753	11.533	1.0475	0.8718
UNC	49.02	0.00687	0.8685	1.08904	0.6139	0.9943	9.0266	10.2394	0.8964

description, as it is clearly shown in the conformance of the predicted (i.e., theoretical, q_e) values to the experimental values (Figure 4a,b).

3.3. Process Variable Optimization. 3.3.1. Effects of pH.

The phosphate solution pH optimization (Figure 4) revealed a monotonic reduction in the magnitude of phosphate sorbed with increase in pH value and the amount of the sorbate sorbed became negligible at the highest pH studied. Lower pH values favored the removal of the phosphate moieties than higher pH values in both sorbents. The curve shows that phosphate adsorption on both clay samples could be likened to a simple anion/ OH^- exchange reaction on the clay surface. In the case of

a simple anion exchange, anion uptake decreases monotonically with pH, due to the increase of OH^- concentration and the change of surface charge to negative.¹⁴ The simple anion exchange reaction has been observed for oxomolybdenum ion adsorption on hydrous titanium oxide in seawater.⁴²

The trend in the observed results is not unexpected if the values of the PZC obtained for the two sorbents and the speciation of phosphate moieties at different pH is considered. The development of pH-dependent charges would affect the amount of phosphate ions adsorbed owing to electrostatic constraints. Interaction of cations with the surface of a material is favored at $\text{pH} > \text{pH}_{\text{PZC}}$, while the interaction of anions is

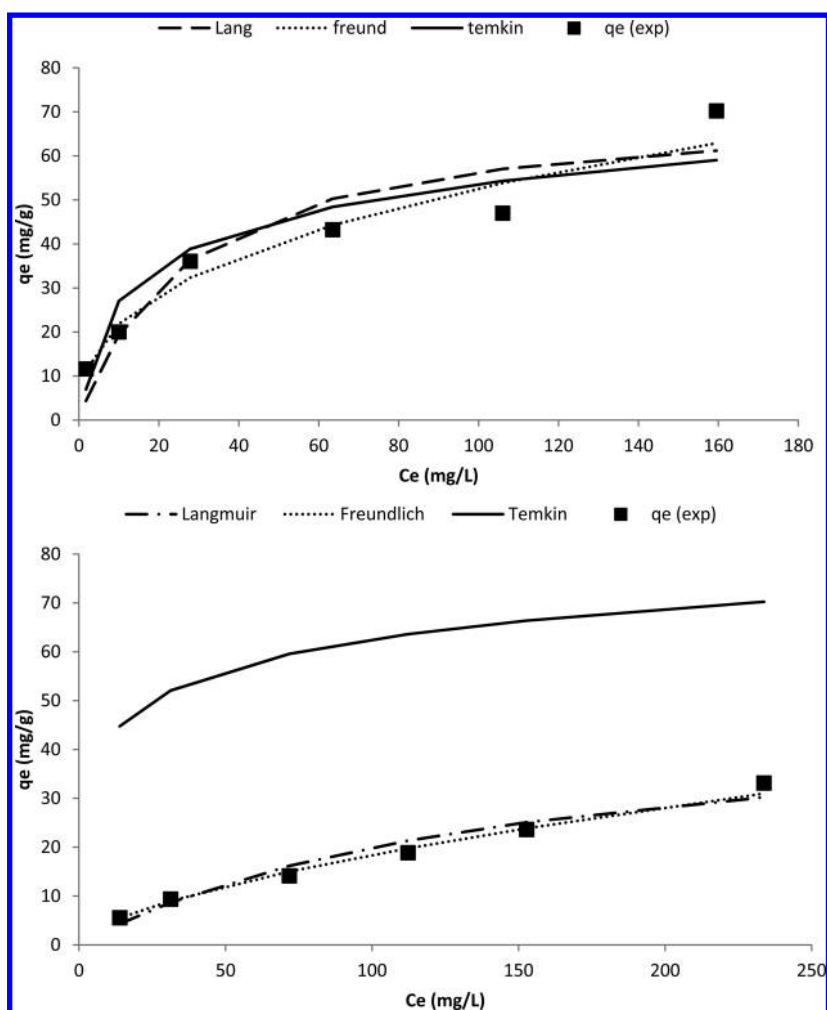
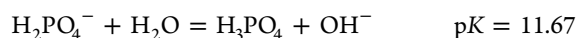
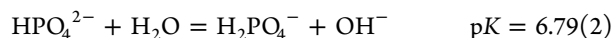
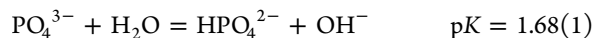


Figure 4. (a) Comparison of the experimental and predicted q_e (mg/g) values for the different isotherm models for the sorption of PO_4^{2-} onto CIC. (b) Comparison of the experimental and predicted q_e (mg/g) values for the different isotherm models for the sorption of PO_4^{2-} onto UNC.

favorable at $\text{pH} < \text{pH}_{\text{PZC}}$. Thus, at pHs less than the pH_{PZC} , the surface of the clay samples are preponderated by positive charges, while at pHs greater than the pH_{PZC} , the surface is preponderated by negative charges.

The phosphate speciation concept of Clifford⁴³ revealed that the phosphate species derived from the KH_2PO_4 , used as the phosphate source, shall occur in aqua system in various forms described by the following reactions with their respective pK at 25 °C:



The speciation diagram, as presented by Clifford⁴³ showed that H_2PO_4^- and HPO_4^{2-} species are present in the pH region between 5 and 10. The concentration of H_2PO_4^- species is higher for pH below 7, while HPO_4^{2-} species prevail for pH between 7 and 10. For pH between 10 and 12, HPO_4^{2-} predominate over PO_4^{3-} species while, for pH higher than 12.5, the concentration of PO_4^{3-} species becomes significant and exceeds that of HPO_4^{2-} .

This showed that the phosphate moieties are present in different forms and pattern at different time span and this

different species are influenced by the solution pH. Thus, the equilibrium solution pH was determined to give an insight into the possible phosphate species available for possible surface reactions with the sorbent surface at a particular pH. The results of the equilibrium pH at different initial solution pH (2–10) ranged between 2.49 and 9.00 for CIC and 2.25 and 8.50 for UNC (Figures 4 and 5). This showed that the sorbent addition had no significant effect on the initial solution pH.

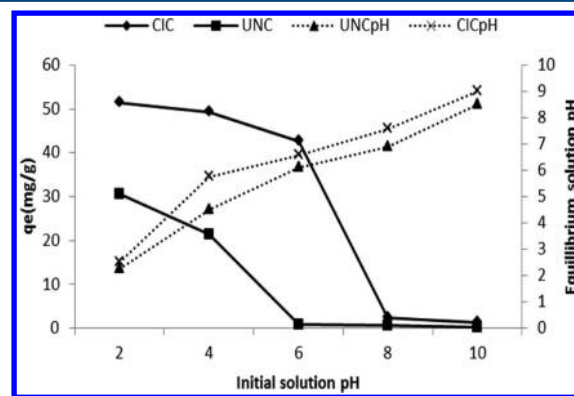


Figure 5. Effect of pH initial and equilibrium pH on the sorption of phosphate onto CIC and UNC.

Premised on the Clifford⁴³ speciation diagram, the phosphate species that predominated at the operating pHs (i.e., pH 2–10) were all negatively charged. Therefore, interaction between these species and the surface of the each of the sorbent is reduced above the pH_{PZC} because of the shift in the dominance of the surface charge which favored the uptake of positively charged species and the abundance of the OH group at alkaline pH. The shift in the dominant surface charge would take place at lower pH in UNC than in CIC, because of the lower pH_{PZC} , and caused a reduction in the magnitude of phosphate uptake by the UNC. The higher value of the pH_{PZC} of the CIC provided a wider pH range for phosphate.

3.3.2. Effect of Ionic Strength and Coexisting Anions. The results of the effect of ionic strength and anionic interference are presented in Table 2a and 2b. The amount of phosphate sorbed per gram of the sorbent increased with increase in ionic strength and the different coexisting ion for both sorbents.

Table 2a. Effect of Ionic Strength

ionic strength (% NaCl)	amount of phosphate sorbed (mg/g)	
	UNC	CIC
0.00	23.625	47.00
0.05	24.87	49.21
0.10	28.44	51.92
0.50	31.62	54.01
1.00	33.16	55.67

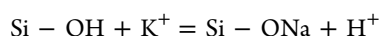
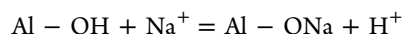
Table 2b. Effects of Anionic Interference

initial conc. of salts (%)	amount of phosphate sorbed (mg/g)			
	SO_4^{2-}		NO_3^-	
	UNC	CIC	UNC	CIC
0.5	24.12	45.98	23.11	46.91
1.0	26.82	48.22	26.18	48.71
2.0	29.42	51.62	30.31	50.64
3.0	31.11	54.19	32.21	55.91
5.0	33.91	57.22	33.01	56.47

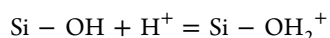
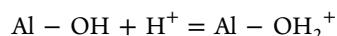
Electrolytes can form outer-sphere complexes through electrostatic forces.⁴⁴ Anions that are adsorbed through outer-sphere association are strongly sensitive to ionic strength; the adsorption is suppressed by competition with weakly adsorbing anions since electrolytes also form outer-sphere complexes through electrostatic forces. Conversely, anions that are adsorbed by the inner sphere association either show little sensitivity to ionic strength or respond to higher ionic strength with greater adsorption.⁴⁵ So, if the immobilization of phosphate ions on either the CIC or UNIC occurred through the formation of outer-sphere surface complexes, then the removal ratio will decrease with an increase of ionic strength. In the present study, the amount of phosphate removed did not

decrease with the increase in ionic strength, which implied that the immobilization of phosphate ions probably occurred via the formation of inner-sphere surface complexes.

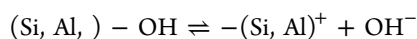
The trend in the uptake of phosphate, when the solution ionic strength was optimized (Tables 2a and 2b), is in tandem with the report of Pardo et al.,⁴⁶ and Giesler et al.,⁴⁷ on the sorption of phosphate by different soil materials and Liu et al.,⁴⁸ on the use of mesoporous ZrO_2 for phosphate attenuation in aqua system. Two consequences of the increase of ionic strength can account for this enhancement.⁴⁸ First, the H^+ in the hydroxyl on the adsorbent surface can be replaced with Na^+ from the electrolyte solution NaCl, thus:



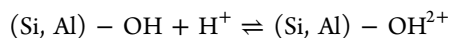
Some of the equivalent H^+ released can then be adsorbed to the other Al–OH or the Si–OH hydroxyl on the adsorbent surface thus



In addition, clay minerals possess OH^- groups, which are exposed to external reacting species. They are attached to silicon and aluminum, and are liable to either dissociate as:



or accept a proton as follows:



giving rise to positively charged clays, which take part in anion exchange.

The protonated Al–OH or the Si–OH surface will inevitably promote the phosphate adsorption capability.

The increase in the magnitude of phosphate sorbed with increase in the dosage of the coexisting anion could also be attributed to the ionic strength effect because the salts used to generate the different anions are also electrolytes (K_2NO_3 , KCl, and K_2SO_4) which ultimately increased the phosphate solution ionic strength.

3.4. Sorption Kinetics. Kinetic modeling not only allows estimation of adsorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, several kinetic models including the pseudofirst-order equation (eq 4),⁴⁹ pseudosecond-order equation (eq 5),⁵⁰ Power function (eq 6),⁵¹ and simple Elovich equations (eq 7)⁵² were tested with the data obtained from the kinetic studies, thus:

$$\log[q_e - q_t] = \log[q_e] - [k_1/2.303]t \quad (4)$$

Table 3a. Kinetic Parameters of Phosphate Sorption on UNC

initial conc. mg/L	pseudo first order			pseudo second order			power function			simple Elovich		
	q_{e1}	$K_1 \times 10^{-2}$	r^2	q_{e2}	K_2	r^2	b	a	r^2	A	B	r^2
25	4.40	0.959	0.997	5.714	0.252	0.999	0.2782	1.448	0.8096	0.7266	0.977	0.8876
50	5.11	1.255	0.9494	9.662	0.056	0.9981	0.2534	2.891	0.6347	2.4349	1.480	0.7179
100	8.00	1.086	0.9972	15.015	0.025	0.9985	0.2516	4.496	0.6634	3.6217	2.314	0.7434
200	18.77	1.007	0.9701	26.882	0.018	0.9944	0.2951	5.974	0.8352	2.1121	4.614	0.9042
300	28.42	0.903	0.9611	35.09	0.008	0.9985	0.3142	7.377	0.8371	1.735	6.465	0.9007

Table 3b. Kinetic Parameters of Phosphate Sorption on CIC

initial conc.	pseudo first order			pseudo second order			power function			simple Elovich		
mg/L	q_{e1}	$K_1 \times 10^{-2}$	r^2	q_{e2}	K_2	r^2	b	a	r^2	A	B	r^2
25	9.38	0.695	0.9309	12.36	0.094	0.9963	0.3863	1.798	0.8298	0.6816	2.477	0.9098
50	17.70	0.838	0.9777	21.74	0.030	0.996	0.3899	3.128	0.8136	1.0889	4.35	0.895
100	38.57	0.764	0.9903	40.82	0.02	0.994	0.4329	4.513	0.8745	5.7244	8.541	0.9477
200	64.45	1.086	0.9438	52.36	0.006	0.9962	0.4072	6.725	0.8635	5.3296	10.787	0.9374
300	92.90	0.960	0.9937	78.74	0.0002	0.9946	0.4413	8.321	0.8852	12.259	16.678	0.9415

$$t/q_t = 1/kq_e + 1/q_e t \quad (5)$$

$$\log q = \log a + b \log t \quad (6)$$

$$q = A + 2.303B \log t \quad (7)$$

The results from the analysis of the data obtained from the sorption process are presented in Tables 3a and 3b (Supporting Information Figures 2–5). The experimental data showed better fitting to both the pseudo first order and pseudo second order kinetic equations ($r^2 > 0.9$) but the fitting of the pseudo second order was the best ($r^2 > 0.99$) (Supporting Information Figures 2–5). This is a pointer to the fact that the sorption of the phosphate moieties on either sorbent occurred via chemisorption. According to Ho and McKay,⁵² if the sorbate uptake is chemically rate controlled, then the pseudo second-order constants will be independent of particle diameter and flow rate and will depend on concentration of the ions in solution. A review of the results, presented in Tables 3a and 3b, showed that the pseudo second order parameters obtained from the uptake of phosphate onto each of the adsorbents (q_e and k_2 values) varied with the initial phosphate concentration.

3.5. SEM and XRD Analysis of Spent Sorbents.

Comparison of the SEM image of both the virgin and spent sorbent (Figure 6a,b) showed that the uptake of phosphate by both sorbents caused no change in the surficial microstructure. The XRD patterns of the phosphate laden (i.e., UNC and CIC) sorbent after phosphate uptake are compared in Figure 7a,b. The difference in crystallinity between the virgin and phosphate-laden sorbent is pronounced. While the virgin sorbents exhibited fine and intense peaks characteristic of a crystallized material, the phosphate laden samples displayed poorly crystalline state with ill-defined peaks, especially in the UNC. The appreciable reduction in the crystallinity of phosphate laden sorbents could be ascribed to the surface complexation of phosphate moieties on the sorbents which caused rearrangements of the layered framework. This attests for the general fact that impregnation process may reduce crystallinity⁵³ and the structures of the phosphate laden sorbents are more amorphous as compared with that of virgin sorbent. Some authors attributed the poorly crystalline state of anion exchanged Layered Double Hydroxides to a disturbance in the stacking sequence of the layers caused essentially by anions adsorbed on the surface.^{54–55} Reduction in the crystallinity of coir pith when the surface was impregnated with iron has also been reported⁵⁴

CONCLUSIONS

The intercalation of CaO in the clay framework enhanced the phosphate sorption potential, PZC, and surface area of the raw clay mineral. No appreciable transformation in the surficial microstructure of the sorbents was observed after the modification, but a minimal increase in the lattice spacing

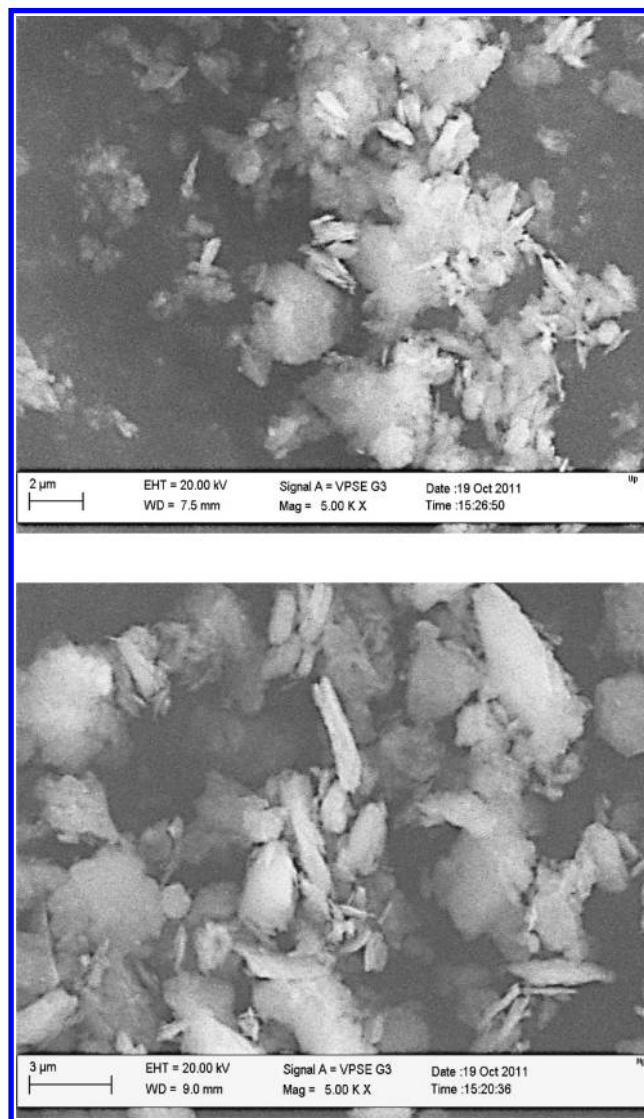


Figure 6. (a) SEM analysis of the phosphate laden UNC. (b) SEM analysis of the phosphate laden CIC.

was confirmed via XRD analysis. The phosphate sorption capacity of the sorbents reduced with increase in phosphate solution pH, while an increase in sorption capacity was recorded when the phosphate solution ionic strength and concentration of the anionic interference were increased. The sorption of phosphate moieties caused no change in the surficial microstructure but impacted on the crystallinity of the sorbent.

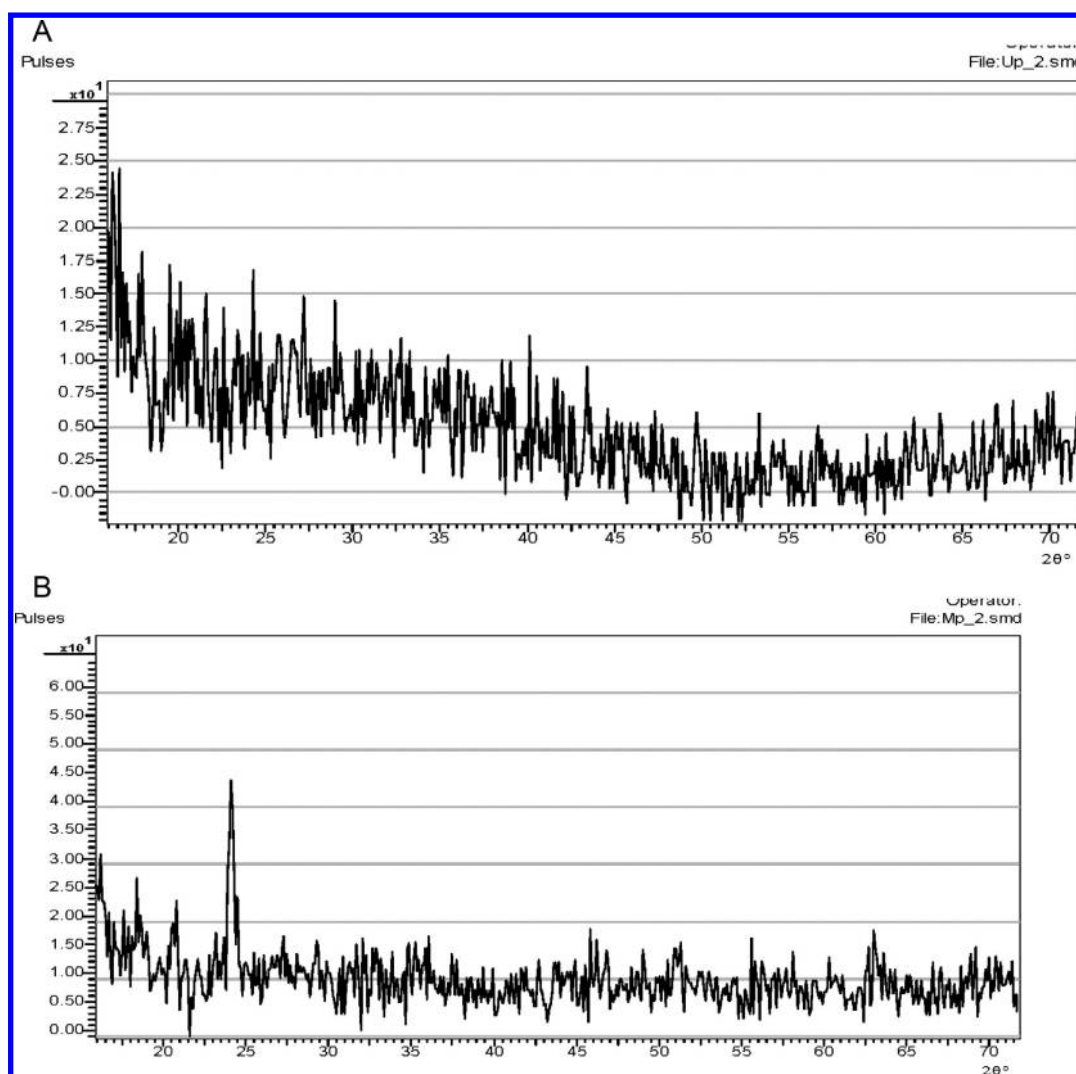


Figure 7. (a) XRD analysis of the phosphate laden UNC. (b) XRD analysis of the phosphate laden CIC.

■ ASSOCIATED CONTENT

■ Supporting Information

This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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