

Gastropod Shell for Phosphate Removal and Recovery via Calcium Phosphate Minerals Crystallization

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Abstract — Waste biogenic Gastropod shell was used for the removal and recovery of phosphate via calcium phosphate mineral (CPM) crystallization. Removal efficiency values \square 99% was achieved when 2g of snail shell was used in water of phosphate concentrations that ranged between 25-1000mg/L. pH and ionic strength exhibited no influence on the removal efficiency. Concomitant removal of phosphate and organic matter revealed that phosphate removal efficiency was not impacted but the magnitude of the organics removed increased with increase in the organic load. Kinetic analysis showed that second order kinetic model gave a better description of the process. XRD analysis of the derived sludge showed the crystallinity and peaks synonymous with the presence of whitlockite, hydroxyapatite and calcium phosphate hydrate were detected. The FTIR of the sludge showed the disappearance of some naturally occurring functional groups and the appearance of phosphate peaks which confirmed the formation of CPM.

Key words - hydroxyapatite, gastropod, phosphate crystallization, eutrophication, snail shell.

I. INTRODUCTION

The eutrophication disposition of water bodies that are receptacles of chronic and episodic delivery of phosphate and the concomitant negative environmental impact has been chronicled. Phosphorus (P) is a limiting nutrient for eutrophication thus; its enhanced removal from waste streams before discharge into receiving waterways is of considerable significance [1]. Technologies for phosphate removal can be broadly classified as chemical precipitation, biological removal, and adsorption. Chemical precipitation and biological processes have been widely used but they are technically tedious and economically undesirable to be adopted as a convention in the management of phosphate bearing aqua streams. The sustainability of a wastewater treatment plants are assessed in terms of their performance in

removing contaminants, potential environmental impact of effluent discharged and their implementation of recovery and reuse of potential value added products. One of the most valuable products of a wastewater treatment plant is sludge since it contains high amounts of energy (biogas) and nutrients. Sustainable management of sludge urges the recovery of phosphorus not only from an environmental point of view but also based on the limited reserves of phosphorus rocks.

Chemical precipitation targeting the removal of P from wastewater is a well-established practice begun in the 1950s [2]. Precipitation (also called crystallization) requires sufficient phosphate concentration to yield thermodynamic supersaturation. While precipitation may occur spontaneously, it normally is initiated by the addition of a divalent or trivalent metal ion: e.g., magnesium (Mg^{2+}), calcium (Ca^{2+}), aluminum (Al^{3+}), or ferric iron (Fe^{3+}) [3]. The choice of the metal ion is important because recovered P that is too tightly metal-bound cannot readily be reused in industrial and agricultural applications [2]. Magnesium- and calcium-based precipitation products are most commonly recycled as fertilizer. Although P removal using aluminum- and iron-based precipitation is quite common in wastewater treatment [4,5], it is less appealing for recovery efforts since P recovery from these solids appears to be difficult, and aluminum is toxic to many plants and some soil organisms. The P in iron phosphates is generally considered to be unavailable to plants, although a fraction of the insoluble P may

eventually become bioavailable depending on hydration or aging [6]

Nutrient removal by struvite ($MgNH_4PO_4 \cdot 6H_2O$) or magnesium ammonium phosphate (MAP) precipitation is also an interesting alternative approach that is being touted to address phosphorus removal by water professionals [7]. MAP crystallization has been applied for several purposes, such as to prevent scaling problems [8] and to remove phosphate [9] or nitrogen [10]. Recent publications show an increasing interest in struvite precipitation as a technology for phosphorus recovery taking into account the economic impact of increasing energy costs and limited natural phosphorus resources [11, 12]. Consequently, integration of struvite formation as specific treatment of side stream wastewaters is becoming a common practice [13].

Premised on the underlying mechanism of nutrient removal via the crystallization process, the operational ease and the nutrient removal efficiency, the removal of phosphate via calcium phosphate minerals (CPM) crystallization is being proposed in the present studies. A Gastropod shell, African Land Snail (*Achatina Achatina*), is being proposed as a biogenic source of calcium ion in the phosphate removal via CPM crystallization because of the inherent physicochemical and mineralogical assemblage [14, 15]. Mollusks make up the phylum Mollusca and Gastropoda (snails and slugs) is a class under the phylum Mollusca. The snail shell has got the same basic construction as other Mollusk shells and it contains, mainly, $CaCO_3$, as well as various organic compounds. It consists of three layers. The Hypostracum, is the innermost layer, followed by the Ostracum, as the basically shell-building layer and the Periostracum as the outermost layer. The Hypostracum is a form of Aragonite, a type of $CaCO_3$ while the Ostracum is built by several layers of prism-shaped $CaCO_3$ crystals with embedded proteid molecules. The Periostracum, the outermost shell layer, is not made of $CaCO_3$, but of an organic material called Conchin, a mixture of organic compounds, mostly of proteids. Conchin not only makes the outer shell layer, but also embedded between the $CaCO_3$ crystals of deeper layers [14, 15]. In the present studies, the abstraction and recovery of phosphate

from aqua system via crystallization process as CPM, using Gastropods shell as a precursor shall be assessed. The effect of process variables (initial concentration, pH, ionic strength and organic matter) on the process removal efficiency shall be assessed and the time concentration profile of the process shall be studied to obtain the kinetic parameters of the process. spelling and grammar. Use high resolution (300dpi or above) figures, plots, drawings and photos for best printing result.

II. MATERIALS AND METHODS

A. Gastropod shell Preparation and Characterization

The snail shell (SS) was prepared as described in [14, 15]. The physicochemical characteristics of the SS are presented in Table 1a. The textural characteristics of the SS were determined by nitrogen adsorption at 77.15K to determine the specific surface area and the pore diameter using an ASAP 2010 Micromeritics instrument and by Brunauer-Emmett-Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15 K). The Barrett-Joyner-Hanlenda (BJH) method was used to calculate the mesopore distribution. FTIR spectral of the SS and CPM were determined using an FTIR spectrometer (Thermo Scientific

TABLE 1a

Proximate Physicochemical characteristics of SS*

Physicochemical Characteristics	Values
pH _{solution}	8.01
Bulk density (g/cm ³)	1.33
PZC	7.9
Particle size Distribution: (µm) (%)	
>90	54.06
90-63	41.32
<63	4.61
Volatile matter (%)	4.14
Ash (%)	93.76
Moisture (%)	2.10
Ca (%)	99.74
Mg (%)	0.0002
Na (%)	0.0008
K (%)	0.0009
Cu (%)	0.00002
Pb (%)	0.0005

*(*Oladoja and Aliu, 2009, Oladoja et al., 2011a and 2011b*)

USA). A sample pellet was prepared by mixing 1 mg of the sample powder with 250 mg of KBr (IR grade) and pressing at 10,000 psi using a hydraulic press (Carver laboratory press, mode C, Ser. No. 33000-577, Fred S. Carver Inc.). The scan covered the range from 4000 to 400 cm⁻¹.

B. Preparation of synthetic wastewater

Owing to the different reports [16, 17] that orthophosphate is the primary form of phosphorus responsible for eutrophication, potassium dihydrogen phosphate (KH_2PO_4) was used as the source of orthophosphate for the preparation of the synthetic phosphate laden water. A stock orthophosphate solution of 2000mg/L was prepared

with reagent-grade water and stock solution of different orthophosphate concentrations were prepared, as required, from the stock by serial dilution.

C. The crystallization procedure

The ability of the proposed protocol to treat phosphate contaminated water was assessed thus: CaCl₂ solution was prepared from the SS via the procedure described in [18]. Phosphate solution of known concentration was added to the CaCl₂ solution and mixed thoroughly before the precipitant (1M NaOH) was added. The precipitating mixture was allowed to settle for 30minutes and the supernatant was withdrawn for the determination of residual phosphate.

TABLE Ib SS Textural Characteristics

Textural Properties	values
Single point Surface Area	1.4514 m ² /g
S _{BET}	1.5312 m ² /g
S _{Langmuir}	2.2866 m ² /g
t-Plot Micropore Area	0.0957 m ² /g
t-Plot External Surface Area	1.4355 m ² /g
S _{BJH}	0.6864 m ² /g
V _{total}	0.003624 cm ³ /g
V _{micro}	0.000030 cm ³ /g
V _{BJH}	0.005939 cm ³ /g
V _{BET} average pore width	94.6641 Å
D _{BJH}	346.059 Å

V_{total} = total pore volume; V_{micro} = micropore volume; S_{BET} = BET Surface Area; $S_{Langmuir}$ = Surface Area; S_{BJH} = desorption cumulative surface area of pores; V_{BJH} = BJH desorption cumulative volume of pores; V_{BET} = BET average pore width; D_{BJH} = Desorption average pore diameter

The crystallization process variables optimized are initial phosphate concentration (mg/L) (25, 50, 100, 200, 300, 500, 700 and 1000); pH (4.0-12.0), by adding either 0.1 M HCl or NaOH solutions; ionic strength (tested in NaCl solutions (%): 0, 0.05, 0.1, 0.2, 0.5 and 1, equivalent to ionic strengths (mol/L) of 0, 0.0085, 0.017, 0.0342, 0.085 and 0.17); organic matter content (simulated by adding humic acid (HA) to the phosphate solution at 0 mg/L, 80 mg/L, 200 mg/L, 400 mg/L and 800 mg/L (equivalent to about 0 -1100 mg/L COD (Cr)).

D. The Crystallization kinetics

Kinetic studies related to phosphate crystallization were performed in duplicate at room temperature. Since the reaction was very fast, samples were withdrawn after the addition of the NaOH solution at 5, 10, 20 and 30s and immediately filtered to determine the concentration of phosphate in the supernatant. The residual phosphate concentration was used to follow the course of the reaction.

E. Characterization of the CPM

The sludge derived from the process was subjected to SEM, EDX, FTIR and XRD analysis to elucidate the surface microstructure, surficial elemental composition, surface functional properties, crystallinity, and mineralogical assemblage.

III. RESULTS AND DISCUSSION

A. SS characterization

Hydroxyapatite (HA) and other CPM are generally synthesized via wet chemical precipitation procedure involving calcium and phosphate bearing species. The use of SS as a calcium bearing specie is predicated on the findings of [14] concerning the mineralogical and physicochemical assemblage. The mineralogical assemblage of the SS, as reported by [14], (2009), showed aragonite as the sole mineral constituent. Aragonite is a stable form of calcium carbonate (CaCO₃) at high pressures. It may be distinguished from calcite, the commoner form of calcium carbonate, by its greater hardness and specific gravity. The physicochemical profile of the SS (Table 1) also revealed the very high inorganic fraction of the SS and the predominance of Ca²⁺ amongst the selected metal ions determined.

The determination of the functional group present in the SS via FTIR (Fig. 1) showed multitudes of peaks (cm⁻¹) between 1646-2814 and prominent peaks at 3595.75, 3574.14, 3291.32, 1471.32 and 1646.1. The multitude of peaks observed was not unexpected because of the biogenic nature of this material and the presence of conchin, a mixture of organic compounds, mostly of proteids in the SS. Conchin (sometimes referred to as Conchiolin) is a complex proteins which are secreted by mollusk outer epithelium (the mantle). These proteins are part of a matrix of organic macromolecules, mainly proteins and polysaccharides that assembled together form the microenvironment where crystals nucleate and grow. Thus, these range of peaks were ascribed to the presence of different organic functional groups viz: - C=C- stretch; N-H bend; C-H rock; C-N stretch; C-C stretch (in-ring) and C-O stretch. The prominent peaks at 3595.75, 3574.14 are characteristic peaks related to the H-bonding stretching vibration of the OH while the peak at 3291.32 was assigned to N-H stretch of primary, secondary amines or amides. The peaks at 1471.32 and 1646.1 were ascribed to the CO₃²⁻ band of CaCO₃ and N-H bend of primary amines respectively.

The summary of the textural characteristics of the SS is presented in Table 2. The BET surface area of SS is 1.5312m²/g, while BJH adsorption/desorption surface area of pores is 0.6864 m²/g. The single point total pore volume of pores (d < 1098.594 Å) is found to be 0.003624 cm³/g, whereas cumulative adsorption/desorption pore volume of the pores (17A° <d<3000 A°) is 0.005939 cm³/g cm³/g, respectively. The average pore diameter by BET method is found to be 94.6641 Å, while the BJH adsorption/ desorption average pore diameter is 346.059 Å. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry [19], that is, micropores (diameter (d) <20 A°), meso-pores (20A° <d < 500 A°) and macropores (d > 500 A°). Micropores can be divided into ultra-micropores (d<7A°) and super-micropores (7A° <d<20 A°). Since the average pore diameter of the SS is greater than 20A° and less than 500 A° the material can be classified as a mesoporous material.

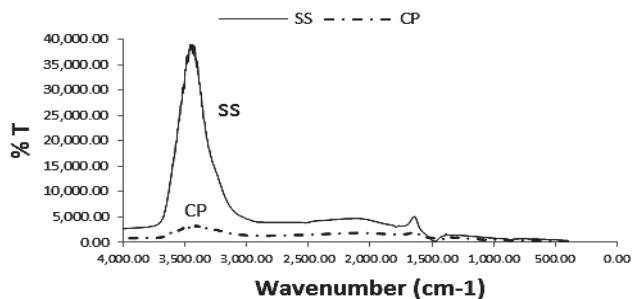


Fig. 1 FTIR spectra of the snail shell (SS) and calcium phosphate (CP) mineral

The surface microstructure of the SS, studied using SEM, is presented in Fig 2a. The different constituents of the SS appeared to have been homogeneously processed into closely knitted fibrous strands of varying lengths. The surficial elemental composition of the SS, determined via EDX analysis, which revealed the presence of calcium, carbon and oxygen, is presented in Fig 2b.

TABLE II
TYPE SIZE FOR PAPERS

Order	R ²	k (h ⁻¹)	Predicted C ₀ (mg/L)	Experimental C ₀ (mg/L)
1 st	0.835	230.4	10.33	1000
2 nd	0.9603	187.56	3.55	1000
3 rd	0.9478	266.04	0.803	1000

B. Phosphate removal from aqua system via crystallization

The removal of phosphate from the synthetic wastewater via the proposed protocol was studied at different initial phosphate concentrations and the results obtained showed that the removal efficiency was greater than 99% at all the initial phosphate concentrations studied (results not shown for brevity). The residual phosphate concentration (mg/L) was undetectable at initial phosphate concentration that ranged between 25mg/L and 500mg/L, hence the residual phosphate concentrations within this initial phosphate concentration range were assumed to be zero while residual concentrations (mg/L) of 0.3806 and 0.4341 were obtained at initial phosphate concentrations of 700mg/L and 1000mg/L. This was presumed as an indication that the appropriate phosphate-calcium molar ratio was not reached, for the CPM crystallization, within the initial phosphate concentration of 25-500mg/L and beyond this initial concentration (i.e. above 500mg/L) the molar ratio of phosphate to calcium has either been reached or being approached, which accounted for the presence of residual PO₄³⁻ in the treated aqua system.

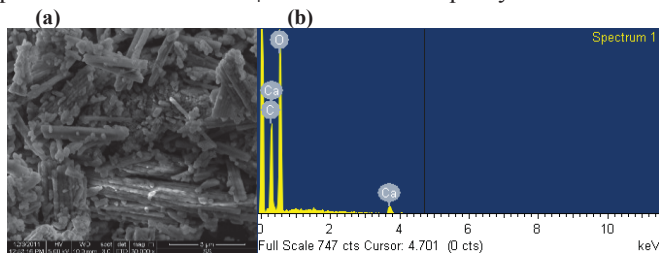
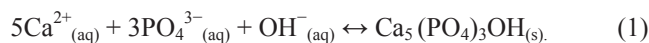
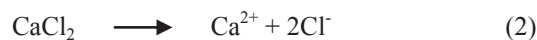


Fig. 2 (a) Results of the surface microstructural analysis of the SS via SEM and (b) surficial elemental composition of the SS via EDX analysis

Phosphate removal via the crystallization process occurred via an interaction between the phosphate, the Ca species and the hydroxyl group to form any species of the phosphate minerals viz: Ca₂HPO₄·2H₂O (dicalcium phosphate dihydrate, DCPD), Ca₈(HPO₄)₂(PO₄)₄·5H₂O (octacalcium phosphate, OCP), Ca₃(PO₄)₂ (tricalcium phosphate, TCP also known as whitlockite), CaHPO₄ (monenite), CaHPO₄·2H₂O (brushite) and Ca₅(PO₄)₃OH (hydroxyapatite, HAP). Hydroxyapatite (HAP) is thermodynamically the most stable one [20]. Ibrahim and Mostafa [21] surmised that high values of pH in solutions help to promote HAP nucleation. The reaction pathway for hydroxyapatite formation is represented by (1):



The Ca specie derived from the Gastropod shell is present as CaCl₂, via the dissolution of the SS using diluted HCl, and the form in which the calcium species is present in the aqua system is presented by (2):



The phosphate species derived from the KH₂PO₄, used as the phosphate source, occur in aqua system in various forms. The speciation of phosphates in aqua system, as described by Clifford [22], was adopted in this study and the various species is described by the following reactions with their respective pK at 25 °C:



The Clifford [22] speciation diagram showed that H₂PO₄⁻ and HPO₄²⁻ species are present in the pH region between 5 and 10. The concentration of H₂PO₄⁻ specie is higher for pH below 7 while HPO₄²⁻ specie prevail for pH between 7 and 10. For pH between 10 and 12, HPO₄²⁻ predominate over PO₄³⁻ specie, while for pH higher than 12.5, the concentration of PO₄³⁻ specie becomes significant and exceeds that of HPO₄²⁻.

Consequent upon the speciation pattern of phosphate moieties and the influence of solution pH on the species profile, the equilibrium solution pH of the CPM crystallization process was determined to give an insight into the possible phosphate species available for reaction with the Ca species. The results of the equilibrium pH at different initial concentration showed that the pH ranged between 10.65 and 11.43. Using the speciation diagram of Clifford [22] as a premise the phosphate species that predominated at the operating pH was HPO₄²⁻.

The preparation of CaCl₂ solution occurred in acidic medium and the phosphate solution was added to the CaCl₂ solution in this acidic medium. Thus, at the inception of the process (at pH ≈ 7.0), the phosphate species that dominated the system was H₂PO₄⁻ and possible interaction between this phosphate species and the Ca²⁺ ions could not be ruled out.

Albeit the possibility of interaction between these two ionic species is high, because of the contrast in the charge on each species, but the non-appearance of a precipitate implied that no such interaction occurred. The use of non-appearance of precipitate as a premise to judge the possible interaction between the two ionic species was predicated on the fact that all phosphate salts of Group IIA metals are insoluble. The addition of the precipitant (i.e. NaOH) produced a precipitate, which could be any of the insoluble calcium phosphate minerals. Since an insoluble product is obtained from the reactions of the different ionic species in solution the removal of phosphate via the crystallization process could be dubbed a metathesis or double replacement reactions.

A. Process Variable optimization

(i) Effect of pH

In optimization of the removal of phosphate, via the phosphate crystallization, all factors affecting the activity of ions should be considered, particularly pH being the most important factor. This is because all the species participating in the crystallization process are present in the aqua system in ionic form and the free concentrations of these ions, Ca^{2+} , OH^- , and PO_4^{3-} ions, fluctuates with pH change. The concentrations of free Ca^{2+} ions decrease with increase in pH as a result of formation of Ca^{2+} hydroxide. On the other hand, the concentration of free PO_4^{3-} and the OH^- ion is expected to increase as solution becomes more basic [23]. The effect of pH was studied between pH 4 and 12 and the results obtained are presented in Fig 2. The magnitude of phosphate removed from solution was comparable irrespective of the initial solution pH. Therefore initial solution pH could be assumed to have no visible effect on the phosphate removal efficiency via this process. This trend could be ascribed to the shift in the concentration gradient of both the H^+ and OH^- ions of the $\text{CaCl}_2/\text{PO}_4^{3-}$ system with the addition of the precipitant (i.e. NaOH). A diminution in the H^+ concentration and an accretion in the OH^- concentrations, with the addition of the precipitant occurred. Thus, the phosphate crystallization process occurred under akin pH condition, immediately the strongly alkaline precipitant was added, notwithstanding the initial solution pH. The results of the effect of the effect of precipitant addition on the equilibrium pH of phosphate crystallization are plotted as final solution pH versus initial solution pH in Fig 3.

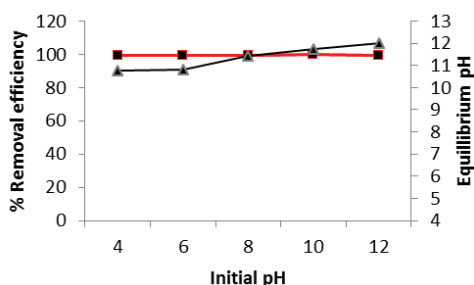


Fig. 3 Effect of initial pH on the phosphate removal efficiency and equilibrium solution pH

(ii) Effect of Ionic strength

Ionic strength is one of the factors that affects the activities of ions and the equilibrium constants [23], thus the effect of ionic strength was studied between 0-0.17mol/L NaCl solutions. The phosphate percentage removal efficiency is presented in Fig. 4a. The phosphate percentage removal efficiency was not affected by variation in the ionic strength of the medium. The only observable effect was in the sludge settling rate that increased as the ionic strength was increased. This same trend has been reported by [18] and was ascribed to the fact that particle surface charges are strongly impacted by ionic strength and conductivity of the suspension solution. The higher the ionic strength of a particle suspension, the lower its surface charge, thus its zeta potential. Owing to the weaker repulsive forces between particles, the stability of the suspension tends to decrease and the particles tendency to agglomerates and sediments accretes.

(iii) Effect of organic load

Owing to the complexity of the composition of wastewater and inability to exact a strict control over the composition, the presence of organic matter in the phosphate laden synthetic wastewater was simulated by the addition of humic acid (HA) at 0 mg/L, 80 mg/L, 200 mg/L, 400 mg/L and 800 mg/L. The humic acid added to the synthetic phosphate wastewater created a solution with the COD value equivalent to a range of 0-1100 mg/L COD (Cr). The results obtained (Fig. 4a) showed the high performance removal efficiency (>99%) of this process for phosphate, within the organic load concentrations studied. This is an indication of the inability of the presence of organic load to impact negatively on the phosphate removal efficiency from solution.

After the quantification of the residual phosphate in the supernatant, another portion of the supernatant was filtrated through a 0.45 μm filtration membrane to measure the UV_{254} absorbance at a 254nm wavelength with a UV/VIS spectrophotometer. The estimation of UV_{254} absorbance in the treated water was used to evaluate the simultaneous organic matter removal efficiency of the crystallization procedure. The relationship between UV_{254} absorbance and HA concentration was determined and found to be linear as shown in Fig. S1, thereby constituting a basis of conversion of UV_{254} absorbance data to an equivalent HA concentration [24]. The HA removal efficiency increased (63.29%, 82.67%, 91.06% and 91.35%) with increase in the initial HA concentration (80mg/L, 200mg/L, 400mg/L and 800mg/L) (Fig 5).

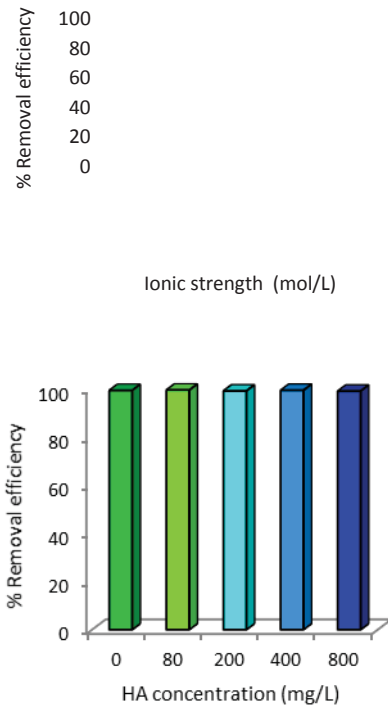


Fig. 4 Effect of (a) ionic strength and (b) organic load on the phosphate percentage removal efficiency

(iii) Reaction Kinetics

The kinetics of homogeneous chemical reactions can be written with respect to one species as [25]:

$$-\frac{d[C]}{dt} = k[C]^n \quad (6)$$

Where C is the concentration of reactant, k is the rate constant and, n, is the order of reaction. If the equation is integrated for the first, second, and third order, it yields the following integrated equations respectively:

$$\ln[C] = \ln[C]_0 - kt \quad (\text{First order kinetic equation}) \quad (7)$$

$$\frac{1}{[C]} = \frac{1}{[C]_0} + kt \quad (\text{Second order kinetic equation}) \quad (8)$$

$$\frac{1}{2[C]^2} = \frac{1}{2[C]_0^2} + kt \quad (\text{Third order kinetic equation}) \quad (9)$$

A plot of the left hand side of (7) to (9) against time, t, gives a straight line graph from which the phosphate removal kinetics were extrapolated (Fig. S2a-c) (SI). The determination of the correlation coefficient, R² of the plots of the experimental data using the different kinetic order showed that second order kinetic model fitted the experimental data better than other kinetic equations (Table 3). Other authors have also reported the best fitting of experimental data to the second-order kinetics when removing pollutants, such as fluoride [26], arsenic (V) [27], phosphates [28] and turbidity [29] from water. The initial phosphate concentration was predicted from the results of the analysis of the crystallization data and the predicted value was compared with the

experimental data. The prediction of the initial phosphate concentration was very poor by the three kinetic models.

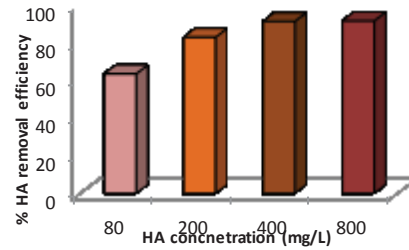


Fig. 5 Percentage simultaneous HA removal efficiency

(iv) Characterization of the sludge derived from the process

The SEM and EDX analysis of the sludge derived from the process is presented in Fig 6a and 6b. The SEM image of the CPM (Fig 7a) is a complete departure from the SS morphology presented in (Fig 2a). The EDX (Fig 6b) also showed the presence of more surface elements in the CPM than in the SS. The presence of phosphate and other residual elements from the reaction mixtures (Na and Cl) were confirmed.

The results of the mineralogical assemblage of the sludge via XRD (Fig. 7) analysis showed that the crystallization product is crystalline in nature and it is made up of different calcium phosphate minerals (Fig S3-S5). The fitting of the diffractogram to the data in the XRD catalogue showed that some of the peaks only fitted to the prominent apatite peaks at 2θ values of 32°, 34°, 40° and 47°. The presence of whitlockite (Ca₃(PO₄)₂) was confirmed by the fitting of the peaks at 2θ values of 10°, 12.5°, 18.5°, 22°, 29.8°, 32.5°, 34.5° and 47° while the presence of calcium phosphate hydrate (Ca₂P₂O₇·2H₂O) was confirmed by matching peaks at 2θ values of 11°, 21.5°, 29.5°, 30° and 32°.

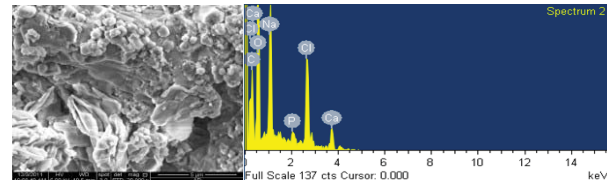


Fig. 6a: Results of (a) surface microstructural analysis of the CPM via SEM and (b) surficial elemental composition of the CPM via EDX analysis.

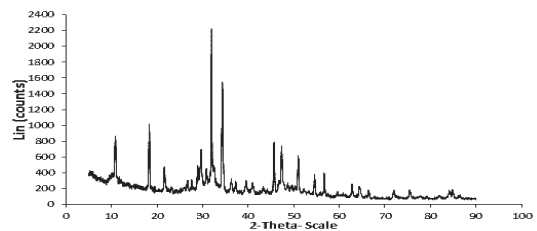


Fig. 7 Results of the XRD analysis of CP mineral

The FTIR analysis of the CPM (Fig. 1) showed the disappearance of most of the bands corresponding to multitudes of organic groups naturally present in the SS, while the representative bands of phosphate groups became appeared. A set of characteristic bands representing apatitic

PO₄³⁻ groups were observed in 700–1300 cm⁻¹ region. The bands at 699 cm⁻¹ and 712 cm⁻¹, 865 cm⁻¹ and 1038 cm⁻¹ were attributed to the ν₂ and ν₃ of P–O mode respectively [30,31]. The additional bands around 900 cm⁻¹ and 1213 cm⁻¹ were assigned to the HPO₄²⁻ group [32]. Bands between 1416 cm⁻¹ and 1539 cm⁻¹ were assigned to the presence of residual organic functional group of the precursor (i.e. the SS). Peak at 1416cm⁻¹ was ascribed to C (CH₃)₂ stretching vibrations), 1456cm⁻¹ (from various CH₂ or CH₃ bending vibrations), 1539cm⁻¹ (N–H and C–N vibrations of the peptide bond), and 1654 cm⁻¹ (from C=O stretching vibrations cm⁻¹ in proteins). The peaks between 1716cm⁻¹ and 1867cm⁻¹ were also assigned to the residual organic fractions. The broad peak around 3500 cm⁻¹ resulted from the overlapping of –OH and –NH groups.

IV. CONCLUSIONS

Gastropod shell can be used as a precursor for the removal and recovery of phosphate and concomitant removal of organic species from aqua system. pH, ionic strength and organic load had no impact on the phosphate removal efficiency and the process is described by second order kinetic equation. The FTIR of the sludge confirmed the formation of CPM and the XRD analysis showed that the CPM is crystalline and peaks synonymous with the presence of whitlockite [Ca₃PO₄]₂, hydroxyapatite [Ca₅(PO₄)₃OH] and calcium phosphate hydrate (Ca₂P₂O₇·2H₂O) were detected.

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