# Nutrients Recovery From Aquaculture Wastewater Using Thermally Treated Gastropod Shells

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## Abstract

Various technological options are currently being assessed towards phosphorus recovery from waste streams. Premised on the development of sustainable appropriate technology, gastropod shell was thermally modified in this study to enhance its sorption capacity as a substrate material for P recovery from aquaculture used water. It was revealed that the thermal treatment impacted enhanced defects in the surficial morphologies of the gastropod shell leading to an increased P recovery efficiency; this was contrary to the general view that high P recovery efficiency of calcined calcium – rich materials was as a result of conversion of $CaCO_3$ to CaO. Furthermore, about 60% P recovery was obtained and a substantial recovery of the total Nitrogen was also achieved. There was a significant improvement in the overall characteristics of the treated used water for safe disposal or reuse.

**Keywords:** Aquaculture wastewater; Calcination temperature; Gastropod shell; Resource recovery.

## 1. Introduction

The wastewater treatment plants (WWTP) and animal husbandry facilities are the two major sources of phosphorus (P) recovery. However, P concentration in animal husbandry is much higher than the WWTP [1-3]. The aquaculture industry places a high demand on water resources: about $200 - 600 \, m^3$ of water is used to produce 1 kg of fish [4] which invariably generates huge amount of used water. Constituents of aquaculture wastewater are characterised with high concentration of nitrates, particulates, dissolved organic matter and phosphates requiring treatment either for reuse or safe disposal [5]. Numerous benefits accrued for P recovery from waste streams: environmental sustainability, global food security and preservation of the non- renewable finite phosphorus ores.

Traditionally, aquaculture wastewater treatment involves discharge into sedimentation ponds for 72 h prior to release into river body. However, this method is only effective in reducing suspended particulates, but ineffective for nutrient recovery and/or removal [6]. Conventional wastewater treatment methods using physical, chemical and biological processes have been applied in aquaculture effluent treatment [7, 8]. However, have the disadvantages of huge capital investment, large volume of sludge production, high-energy demand and frequent maintenance requirements [9]. Constructed wetland systems are increasing in popularity being characterized by low energy consumption and maintenance requirements for pollutants removal/recovery from aquaculture wastewater [10-12]. Numerous aquatic wetland plants, with considerable potential for nutrients removal have been employed in the treatment of wastewater from different sources [13]. Wetland system operations is hampered with land requirements, imprecision in design and operation criteria, cost implications of gravels fills and site grading during construction.

Phosphorus recovery from waste streams via adsorption - based technologies is continuously being assessed above other methods (filtration, ion-exchange, coagulation, and crystallisation) due to its simplicity, cost effectiveness and availability of large array of cheap and eco-friendly adsorbents. Studies have shown that excellent and efficient P substrates have high metallic contents of aluminium, iron or calcium [14-16]. However, further use of the recovered phosphate sludges of Fe and Al as fertilizers is usually limited because recovered phosphate are either too tightly metal-bounded or toxic to living things [2, 6]. Calcium - rich materials are preferably used as sorbent for P recovery: the sludges produced could be readily assessed as slow release fertilizer (hydroxyapatite and whitlockite). Premised on a high P removal efficiency (.> 90%) from a synthetic P feed wastewater in a batch system and column reactor achieved in our laboratory using gastropod shell [17, 18], this studied is proposed at using calcined gastropod shell for P recovery from aquaculture wastewater. Gastropods live in every conceivable habitat on earth. Gastropod shells (GS) are composed of polymorphs $CaCO_3$ [2] as well as various organic macromolecules: mainly proteins and polysaccharides [19]. Several studies have reported a higher P sorption capacity of calcium – rich materials (e.g. opoka and oyster shell) after thermal treatment [20, 21]. This present work therefore aimed at studying the effect of thermal treatment on P recovery efficiency of gastropod shell from aquaculture wastewater (ACW) as well as investigating the effect of the recovery process on the quality of the treated water.

## 2. Materials and Methods

The gastropod shell (GS) used was that of the African land snail (*Achatina achatina*), prepared as described in our previous treatise [17], subjected to thermal treatment at different temperature ranges (100, 250, 500, 750, 1000∘C) in the furnace for 2 h and labeled accordingly ($GS_0$, $GS_{100}$, $GS_{250}$, $GS_{500}$, $GS_{750}$, $GS_{1000}$). The effects of the thermal treatment temperatures were elucidated via instrumental characterisation of the samples vis-a viz: XRD for mineralogical assemblage, XRF for elemental composition, surface architecture was determined by a scanning

electron microscope (SEM) while FTIR spectrophotometer (Thermo Scientific, USA) was used to determine the functional groups present on the surface of the materials.

The optimum thermal treatment temperature for the GS was determined via batch sorption process viz.: 50 mL of synthetic P solution ($KH_2PO_4$ salt) of 40 mg/L and 0.1 g of adsorbent (calcined gastropod shell) was agitated on magnetic stirrer at 200 rpm for 2 h. Samples were withdrawn with a syringe, filtered using polypropylene membrane (0.45μm). The residual P concentration in the filtrate was determined by using the molybdenum-blue ascorbic acid method with a UV–VIS spectrophotometer at 801nm. The amount of P recovered was determined using the mass balance procedure. The calcined sample that gave the optimal P recovered was used for further studies.

Kinetic studies were assessed by contacting 0.5 g of the calcined material to 1.0 L of P solution of different concentrations (2.5- 30 mg/L) and agitated for 5 h. Equilibrium isotherm study was evaluated by contacting 100 mL solution of known P concentration (2.5 - 30 mg/L) with 0.05 g of the calcined material, agitated until equilibrium was attained. The residual P concentration in the filtrate was determined as previously described.

P recovery efficiency of the calcined sample from aquaculture used water (ACW) was determined in a batch reactor thus: Sample of the ACW was collected from an aquaculture farm that breeds catfish and characterized. 0.5 g of the calcined sample was contacted with 1.0 L of the wastewater, agitated on a magnetic shaker of 30 min before sample was withdrawn and filtered. The residual P concentration in the filtrate was determined as previously described. The effects of the recovery process on the physicochemical characteristics of the treated water were evaluated using standard methods [22].

# 3. Results and Discussion
## 3.1. Characterisation of Raw and Calcined Gastropod Shell
The analysis of the elemental contents of the virgin and the thermally treated gastropod shell by XRF showed the presence of high inorganic fractions and predominance of $Ca^{2+}$ (98%) amongst the selected metal ions determined (Table 1).

**Table-1.** XRF Analysis of Virgin and Calcined Gastropod Shell Samples

| Metal oxides | GS$_0$ | GS$_{100}$ | GS$_{250}$ | GS$_{500}$ | GS$_{750}$ | GS$_{1000}$ |
|---|---|---|---|---|---|---|
| $Al_2O_3$ | 0.37 | 0.29 | 0.39 | 0.53 | 0.56 | 0.41 |
| $SiO_2$ | 1.66 | 1.33 | 1.34 | 1.85 | 1.18 | 0.36 |
| $P_2O_5$ | 0.12 | 0.06 | 0.09 | 0.11 | 0.08 | 0.01 |
| $SO_3$ | 0.06 | 0.04 | 0.05 | 0.05 | 0.05 | 0.03 |
| Cl | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 |
| $K_2O$ | 0.19 | 0.16 | 0.19 | 0.20 | 0.16 | 0.05 |
| CaO | 96.38 | 96.58 | 96.73 | 96.92 | 98.19 | 98.62 |
| $Cr_2O_3$ | 0.11 | 0.94 | nd | nd | nd | nd |
| $Fe_2O_3$ | 0.23 | 0.23 | 0.29 | 0.24 | 0.36 | 0.30 |
| NiO | 0.20 | 0.02 | 0.16 | 0.01 | nd | nd |
| CuO | 0.06 | nd | nd | nd | nd | nd |
| ZnO | 0.20 | 0.09 | 0.01 | 0.01 | 0.03 | 0.07 |
| SrO | 0.69 | 0.69 | 0.68 | 0.68 | 0.66 | 0.52 |
| TnO | nd | nd | nd | 0.24 | nd | nd |

The diffract gram of the XRD analysis of the gastropod shell indicated a high crystallinity in sample which was retained over the entire thermal treatment temperature ranges that was adopted (Figure.1). The Mineralogical analysis revealed the presence of aragonite, calcite and vaterite (polymorphs of $CaCO_3$) in the gastropod shell. The spectral pattern of the surface functional groups from FTIR analysis and summary of the functional groups is presented Fig. 2 and Table 2, respectively.

**Figure-1.** XRD pattern of raw and calcined GS Samples at designated temperature
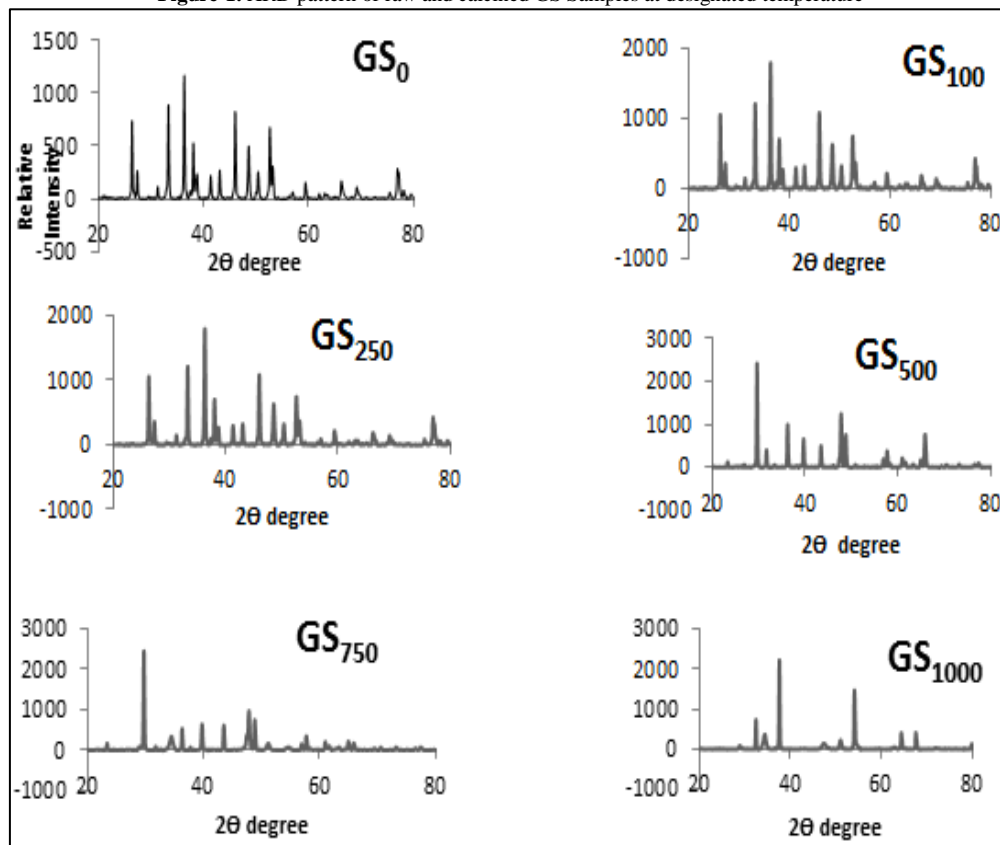


**Figure-2.** FTIR Spectral of Raw and Calcined Snail Shell Samples
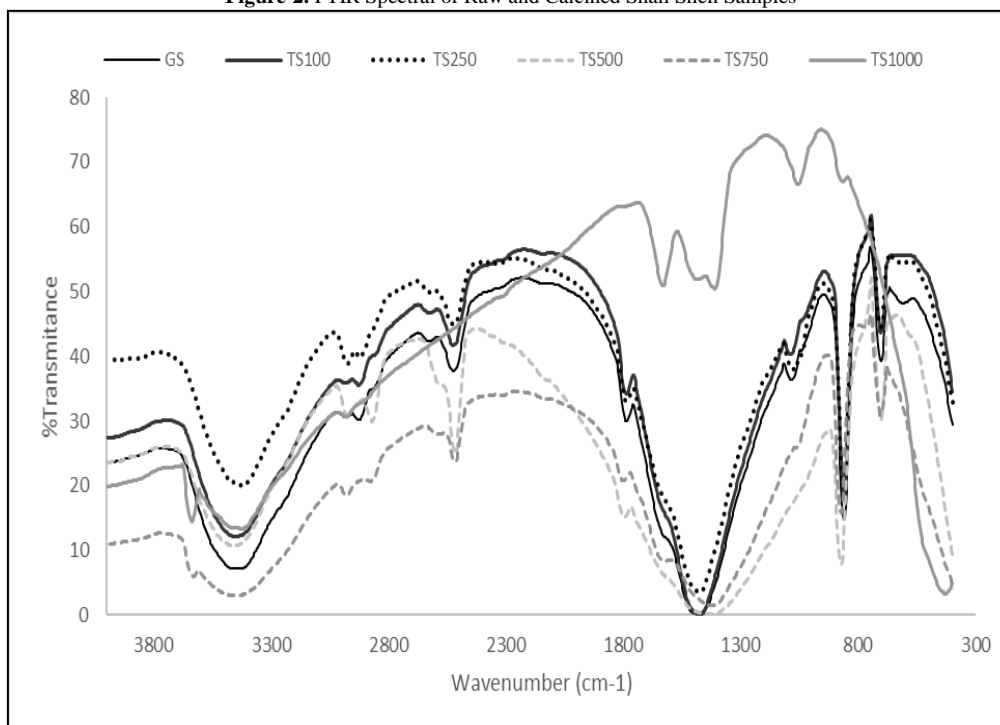


**Table-2.** Functional Groups and FTIR Peaks of Calcined SS

| Functional Group | SS$_{100}$ | SS$_{250}$ | SS$_{500}$ | SS$_{750}$ | SS$_{1000}$ |
|---|---|---|---|---|---|
| N-H (Primary Amine | 3456 | 3421 | 3460 | 3452 | 3460, 3425, |
| N-H (Ammonium) | 2981, 2924 | 2974, 2920 | 2970, 2870 | 2978, 2877 | 2981 |
| CO$_3^{2-}$ | 2627, 2522, 1786,1473, 869 | 2623, 2522, 2360, 1786 1477, 1068 860 | 2515, 2434, 1797, 1427, 871 | 2314, 2133, 1801,1624, 1419,871 | 1408,1056 |
| CaO | | | | 3630 | 3738, 3687, 3637, 864, 428 |

## 3.2. Evaluation of Optimum Calcination Temperature for GS

The results obtained from the screening of the calcined GS samples for optimum P recovery presented in Figure 3, showed that the maximum phosphorus recovery was achieved with GS samples calcined at $750^{\circ}$C. It could be observed that there was no apparent difference in the amount recovered by the GS samples treated below $500^{\circ}$C, however, when the calcination temperature was increased above $500^{\circ}$C, the amount of P recovered increased significantly and got to the maximum at $750^{\circ}$C. This higher P recovery capacity is attributed to the presence of CaO in the samples calcined at $750^{\circ}$C and $1000^{\circ}$C as a result of the transformation of $CaCO_3$ as attested to in the profiles of the surface functional groups in the calcined samples shown in Table 2 via FTIR analysis.

The marginal similarities in the P-recovery capacities of the two samples, $GS_{750}$ and $GS_{1000}$ as shown in Figure 3 despite the difference in the magnitude of their CaO contents (Table 2), revealed that the presence of CaO was not solely responsible for their relatively higher P recovery capacities as previously suggested. The surface morphological analysis of the virgin gastropod shell sample (Figure 4a), showed that the surface architecture of the gastropod shell was completely destroyed after the thermal treatment and transformed into a defective, corrugated surface with sharp and rough edges (Figure 4b).

The defects on the surface of the calcined sample made available atoms with incomplete valencies and a highly defective coordination environment, thus providing conducive active sites on the surface of the sample for P sorption from the solution [23].

Consequent upon the similarities observed in the recovery efficiencies of the two samples ($GS_{750}$ and $GS_{100}$) and lower energy consumption used for $GS_{750}$, the $GS_{750}$ sample was chosen for the further works.

**Figure-3.** Evaluation of P-Recovery Capacity of Raw and Calcined GS



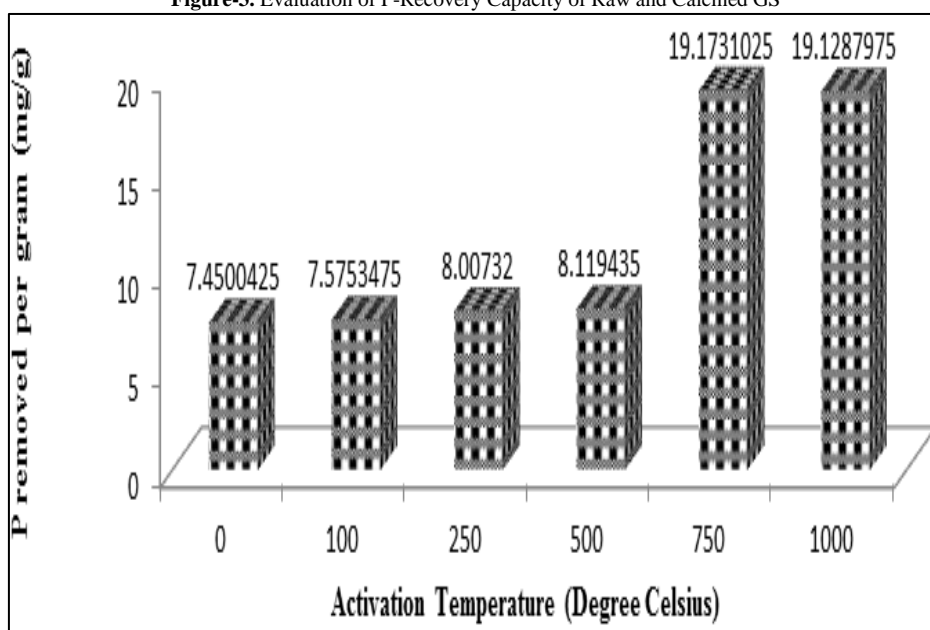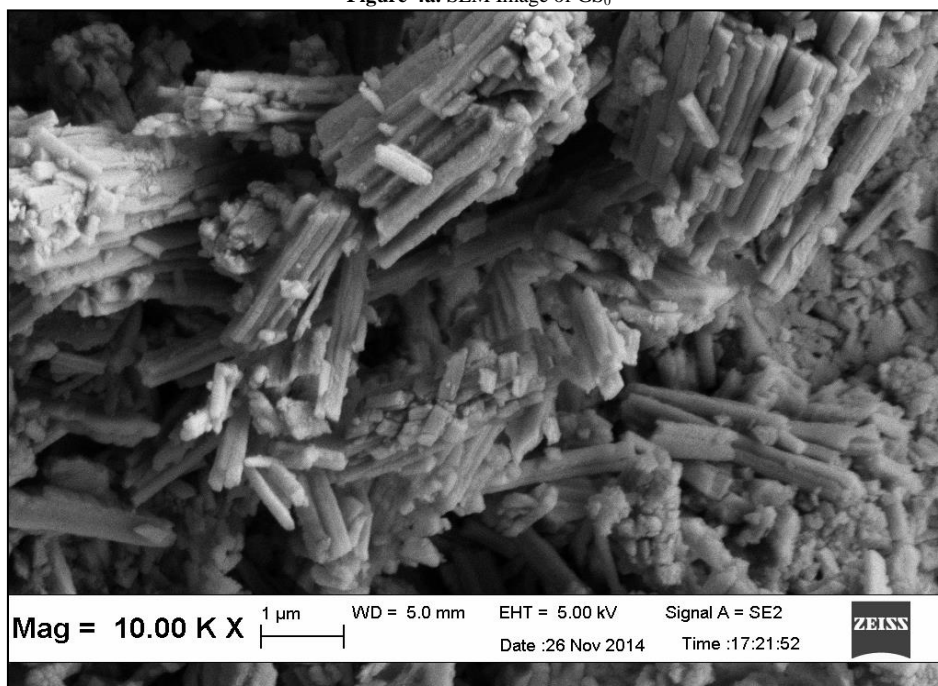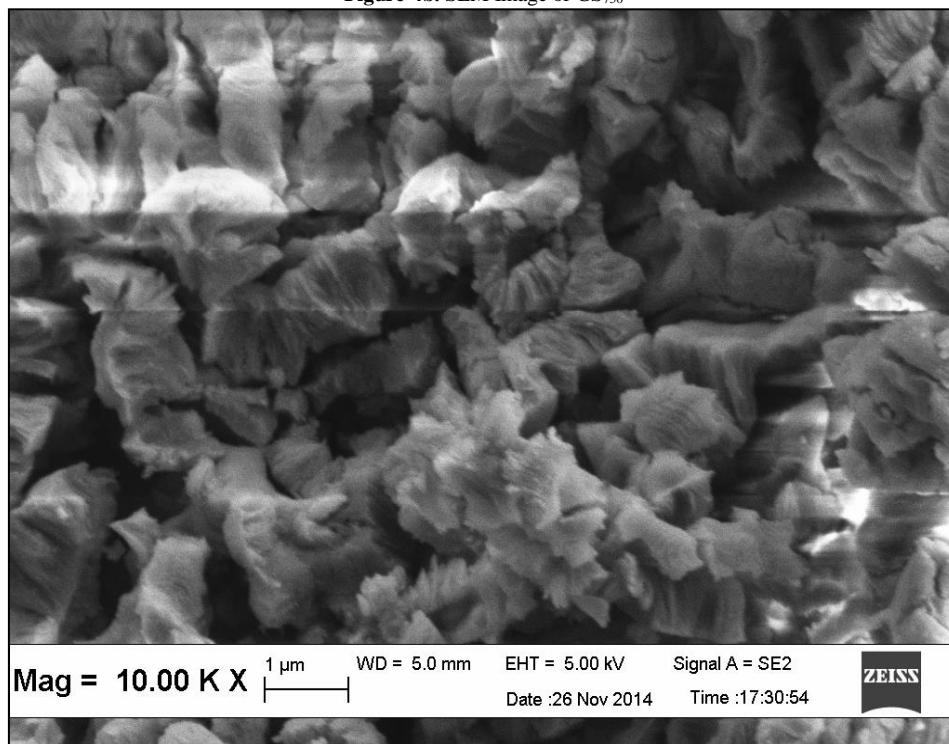**Figure-4a.** SEM Image of $GS_0$

**Figure-4b.** SEM Image of GS$_{750}$



## 3.3. © P Recovery from Synthetic Phosphate Contaminated Water by Calcined GS

The sorption kinetic studies was carried out to predict the rate of phosphorus recovery by the calcined GS$_{750}$ from aqua system and to provide data that would enable the understanding of the mechanism of the process. The time-concentration profile of the P recovery process at different initial P concentrations is presented in Figure 5. The results obtained indicated that the process was both time and initial P - concentration dependent. Phosphorus recovery was very fast within the first 5 min and slowly attained equilibrium within 30 min of the process for all the initial P concentrations. The equilibrium adsorption time of 30 min could be considered economically favourable for the recovery of phosphorus by the GS$_{750}$. About 99% of the total phosphorus recovered was achieved within the first 2 min of contact between the adsorbate and the adsorbent for all the initial P concentrations studied. The rapid uptake of phosphorus by the calcined GS was attributed to the very high affinity of the adsorbate for the adsorbent.

**Fig-5.** The Time-Concentration Profiles of P Recovery Process by GS$_{750}$
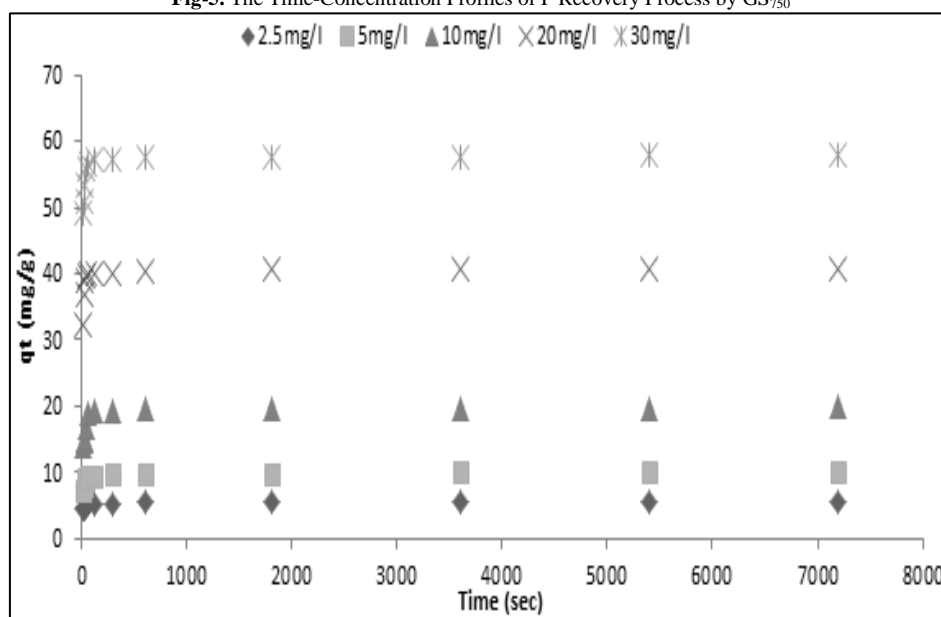


To understand the mechanism of the process and the potential rate determining steps, the time-concentration profile were analyzed using different kinetic equations viz: Lagergren [24] pseudo-first order (1898), pseudo-second order [25] and intraparticle diffusion equation [26]. The linearized equation of the equation is given as:

Lagergren pseudo − first order:     $\log(q_e - q_t) = \log q_e - \frac{k1_t}{2.303}$          (1)

Pseudo − second order:     $\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{t}{q_e}$          (2)

Where $q_e$ and $q_t$ are the sorption capacity at equilibrium and time $t$, respectively (mg/g). $k_1$ is the rate constant of pseudo – first order adsorption (min$^{-1}$) and $k_2$ is the overall rate constants of pseudo-second order sorption ((g/mg)/min). The results revealed that the pseudo-second-order kinetic equation gave a better fit ($r^2 > 0.99$) to the experimental data than the pseudo first order kinetic equation (Table 3). In furtherance to confirm the kinetic equation that gave better description of the time–concentration profiles, the non-linear chi-square ($\chi^2$) error analysis was performed. The results indicated and confirmed that pseudo second order kinetic equation gave the better prediction of the experimental $qe$ (mg/g) values (Table 3), a pointer to chemisorption as the underlying mechanism of interaction.

**Table-3.** Kinetic Parameters of Phosphorus Recovery by GS$_{750}$

| Initial Conc (mg/l) | qe(exp) | Pseudo 1$^{st}$ order | | | | Pseudo 2$^{nd}$ order | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $q_{e1}$ | $k_1$ | $R^2$ | $\chi^2$ | $q_{e2}$ | $k_2$ | h | $R^2$ | $\chi^2$ |
| 2.5 | 0.2209 | 0.039 | 0.0046 | 0.916 | 16.20 | 0.1615 | 0.127 | 0.0033 | 0.997 | 0.01 |
| 5.0 | 0.4629 | 0.088 | 0.0092 | 0.854 | 1.33 | 0.4260 | 0.220 | 0.0400 | 0.997 | 0.02 |
| 10 | 1.0528 | 0.609 | 0.0115 | 0.939 | 0.38 | 1.0930 | 0.126 | 0.1377 | 0.996 | 0.04 |
| 20 | 3.0015 | 0.936 | 0.0069 | 0.931 | 1.33 | 2.0080 | 0.077 | 3.1040 | 0.990 | 0.01 |
| 30 | 4.9131 | 1.631 | 0.0116 | 0.932 | 3.71 | 4.7620 | 0.211 | 4.7847 | 0.998 | 0.03 |

Insight into the rate determining step of the recovery process was investigated using the intraparticle diffusion equation. For a batch system, pore particle diffusion is often the rate determining step, and film diffusion is usually the limiting step for a continuous flow system, respectively. Even though the possibility for the pore particle diffusion to be the rate- limiting step is very high in a batch process, for most of the contact time in adsorption studies the intraparticle diffusion controls the batch process [27]. This possibility was explored by using the intra-particle diffusion model. The linear expression of the intraparticle diffusion equation for a sorption system was given by Weber and Morris [26] as follows:

$$q_t = C + k_{id}t^{0.5} \qquad (3)$$

Where, $k_{id}$ is the intra- particle diffusion rate constant (mg/gmin$^{0.5}$) and $C$ 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. According to the Weber and Morris model, if a plot of $q_t$ 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. 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. The plots of the intraparticle diffusion study of the P recovered by GS$_{750}$ are presented in Figure 6. The plots indicated two steps, suggesting that intraparticle/pore diffusion was not the singular rate limiting step in the recovery process.

**Figure-6.** Intra-particle Diffusion Plots of P-recovery by GS$_{750}$
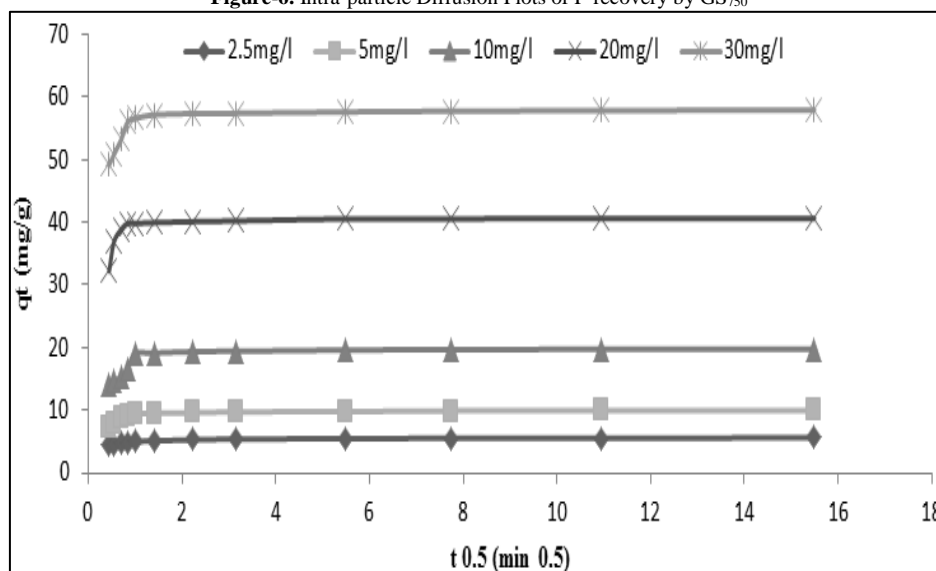


Insights into the surface properties and affinity of GS$_{750}$ for P in the liquid phase were evaluated via isotherm studies. In adsorption process, equilibrium is established when the concentration of the adsorbate in the bulk solution is in dynamic balance with that at the interface of the adsorbent. In order to understand the features of the process of sorption, the experimental data were fitted to different isotherm equations: Langmuir, Freundlich and Temkin isotherm linear equations:

Langmuir : $\dfrac{1}{q_e} = \dfrac{1}{q_m} + \dfrac{1}{bq_m c_e}$ $\qquad (4)$

$$Freundlich: \quad logq_e = \frac{1}{n} logc_e + logk_f \tag{5}$$

$$Temkin: \quad q_e = B_T lnA + B_T lnC_e \tag{6}$$

Where, $c_e$ is the concentration of P at equilibrium (mg/l), $q_e$ is the amount of P sorbed at equilibrium per unit mass of $GS_{750}$ (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 relative adsorption capacity of the adsorbent and $n$ is the sorption intensity. $B_T$ (J/mol) corresponds to the heat of adsorption and and $A$ (l/g) is the equilibrium binding constant, corresponding to the maximum binding energy. The results obtained from the equilibrium isotherm analysis indicated a monolayer sorption capacity of 84.75 mg/g, which competes very well with other adsorbents used for P recovery in literatures: palygorskite, akaganeite, calcite, date palm fibers [28-31], a favourable interaction between the $GS_{750}$ samples and P species in solution and heterogeneous sites on the surface of the $GS_{750}$ as indicated by highest correlation coefficient ($r^2$= 0.937) value by Freundlich amongst the isotherms models studied (Table 4)

**Table-4.** Equilibrium Isotherm parameters of the Recovery Process

| Langmuir Equation | Freundlich Equation | Temkin Equation |
|---|---|---|
| qm(mg/g) = 84.75 | $k_f$ (L/g) = 39.98 | $B_T$ = 10.73 |
| b (L/mg) = 1.192 | 1/n = 1.192 | A (L/mg) = 46.386 |
| $R^2$ = 0.637 | $R^2$ = 0.937 | $R^2$ = 0.744 |

The equilibrium adsorption curves, relating the $GS_{750}$ and aqua phase concentration of P, at equilibrium for each of the equilibrium isotherm equations are presented below:

$$Langmuir \quad q_e = \frac{101.02\, c_e}{1+1.192c_e} \tag{7}$$

$$Freundlich: \quad q_e = 39.98 C_e^{0.551} \tag{8}$$

$$Temkin: \quad q_e = 10.73 ln46.386 C_e \tag{9}$$

## 3.4. P Recovery from Aquaculture Used Water by Calcined $GS_{750}$

Phosphorus recovery efficiency of the calcined gastropod shell sample ($GS_{750}$) from aquaculture wastewater (ACW) was tested in a batch reactor. The physicochemical qualities of the used water and the treated water (TW) are presented in Table 5. About 0.09 mg/l of P was recovered, which is 60% of the original P content in the ACW. The quality characteristics of the TW showed that the P recovery process appreciably improved the quality characteristics of the ACW which was considered as a positive step towards the safe disposal of the TW (e.g. 74 % reduction in COD). The magnitude of the solids (TS, DS and SS) in the ACW substantially reduced after the P recovery process. The reduction in the solids was attributed to occurrence of precipitation reaction, ascribed to a phenomenon known as sweep coagulation, in coagulation–flocculation process. Moreover, notably, 47.4% removal of the Total Nitrate (TN) content of the ACW was achieved. The synchronous removal of both P and N in the aqua matrix is an indication that the sludge from the recovery process can be applied in agricultural practices as good source of these two nutrients. The sodium and potassium content of the TW was not influenced by the process but substantial amount of calcium was added into the TW after the process. The increase in the calcium content in the treated water was assumed to be responsible for the elevation of the pH and conductivity.

**Table-5.** Quality Characteristics of Raw and Treated Aquaculture Wastewater

| Characteristics | Raw Aquaculture Effluent | Treated Aquaculture Effluent |
|---|---|---|
| Phosphorus (mg/l) | 0.15 | 0.06 |
| Turbidity (NTU) | 20.2 | 8.70 |
| Conductivity (us/cm) | 92.5 | 192.5 |
| pH | 6.61 | 10.11 |
| TS (mg/l) | 643 | 261 |
| DS (mg/l) | 460 | 191 |
| SS (mg/l) | 183 | 70 |
| COD (mg/l) | 135 | 54 |
| TN (mg/l) | 19.76 | 10.40 |
| K (mg/l) | 6.01 | 6.88 |
| Ca (mg/l) | 5.43 | 23.10 |
| Na (mg/l) | 3.64 | 3.86 |

## 4. Conclusion

The efficiency of gastropod shell to recover phosphorus in aqua matrix can be improved significantly by its thermal treatment and the optimum thermal treatment temperature can be achieved at 750∘C. Increase in the P recovery efficiency of the calcined GS is due to defects in its surface morphology as a result of the calcination. The recovery of P from the aquaculture used water by the calcined sample led to an improvement in the quality of the treated water suitable for reuse or safe disposal.

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