Equilibrium Studies and Optimization of Phosphate Adsorption from Synthetic Effluent Using Acid Modified Bio-Sorbent

1Babayemi, Akinpelu Kamoru and 2Onukwuli, Okechukwu Dominic

1Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, (formerly known as Anambra State University) Uli, Nigeria
2Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria

Abstract: Adsorption potential of periwinkle shell (PRW), an agricultural waste, for the removal of phosphate from aqueous solution was investigated through equilibrium studies at various experimental conditions. PRW was carbonized and chemically activated with 1M H2SO4 before it was subjected to characterization using Fourier Transform Infrared (FT-IR), Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM). Adsorption data were analyzed using various kinetic and isotherm models. Statistical modeling through Central Composite Design (CCD) was also employed. The results showed that, FT-IR spectrum of the activated PRW shows many absorption peaks and a variety of functional groups such as –OH, -NH, C = O, C-H, C-N, CH3 and CH2 which explains its improved adsorption behavior on the colloidal particles. SEM shows the morphological changes with respect to the shape and sizes of the adsorption sites. EDX indicates the higher percentage composition of carbon (11.66%), Oxygen (63.18%) as important constituent elements for adsorption. Equilibrium data were well fitted to pseudo second order kinetic model and were best described by Langmuir Isotherm model at the temperature of 303K. Removal efficiency of 95.90% was obtained. A statistical model equation was developed for the adsorption process which reveals contact time as the most significant main effect for performance of the adsorbent.

Keywords: Adsorption, Phosphorus, Periwinkle, Equilibrium, Isotherm, Kinetics

Introduction

Phosphorus is an essential element for both animals and plants on the earth. It is needed for the growth of algal and other biological organisms (Xiong et al., 2011; Yeddou and Bensmaili, 2009) Phosphorus in natural waters is dissolved and particulate form. They exist as polyphosphates, orthophosphates and organic phosphates in aqueous solution (Czelej et al., 2016). The principal phosphorus compounds in wastewater are generally orthophosphates (Grubb et al., 2000; Jiang et al., 2008) municipal wastewater may contain from 4 to 15mg/l phosphorus as PO43- (Akay et al., 1998)

However, inordinate quantity of phosphorus in water bodies results in extensive algae growth, exhaustion of dissolved oxygen, turbid, dirty, odorous and unhealthful surface waters and extinction of many aquatic animals (Bhargava and Sheldarkar, 1992). Against this background, it is vital that a solution be urgently found to stop further degradation of environmental quality and its associated inauspicious socio-economic effects on the large segment of the community. Several methods have been introduced to the removal of phosphorus from wastewater and the commonly used techniques include precipitation (Chen and Zhuang, 2003), biological treatment (Wang et al., 2009), use of synthetic organic and inorganic chemical and adsorption (Liu and Hesterberg, 2016; Babayemi and Onukwuli, 2016). Adsorption on activated carbons has been considered, among others, to be more dependable and effective due its simplicity and cost effectiveness (Xiaoli et al., 2015; Yin and Cui, 2006).
Table 1: Previous adsorption studies on phosphorus

| Adsorbent                              | Adsorption conditions                          | Maximum removal efficiency (%) | Reference                        |
|----------------------------------------|------------------------------------------------|-------------------------------|----------------------------------|
| Activated carbon produced from Tamarind Nutshell (TNSAC) | Effects of adsorbent dose and size on phosphate removal from wastewater | 57                            | (Nafa, 2002)                    |
| Slag and Fly ash                       | Phosphate removal efficiency of slag and fly ash at various operating conditions | 96.9                          | (Safaa, 2013)                   |
| Iron hydroxide-egg shell Waste Activated carbon from dolomite mineral | The feasibility of using iron hydroxide egg shell waste for phosphate removal | 73                            | (Yeddou and Bensmaili, 2009)    |
| Activated carbon from palm kernel shell | Adsorption of phosphate from aqueous solution on dolomite minerals at different experimental conditions | >95                           | (Xiaoli et al., 2015)           |
| Activated carbon from animal bone      | Adsorption potential of animal bone for the removal of phosphates from wastewater | 93.54                         | (Bhargava and Sheldarkar, 1992) |
|                                        |                                                | 97                            | (Xiong et al., 2011)            |

Activated carbons are mostly produced from carbonaceous materials such as palm nut (Joseph and Philomena, 2011), sawdust (Zeng et al., 2004), prawn shell (Nafa, 2002), animal bone, palm kernel shell and other raw materials. Their distinctive adsorption properties result from their high surface areas, adequate pore size distributions, broad range of surface functional groups and comparatively high mechanical strength. Activated carbons are largely used for the removal of unpleasant organic and inorganic impurities from domestic and industrial wastewater.

Producing and making use of activated carbons from periwinkle shell, being an agricultural waste, for such purpose will not only reduce the health risk and environmental concerns associated with the use of synthetic organic and inorganic chemicals but also provides an alternative means of waste reduction and reuse. Previous works on the adsorption of phosphorus from aqueous solution are presented in Table 1.

Materials and Methods

Preparation of Activated Carbon from Periwinkle

Periwinkle shells were obtained from a local market in Port Harcourt, Rivers State, Nigeria. The shells were soaked in hot water for about 1h to remove the decayed flesh that was responsible for the bad odour oozing from the shells. Thereafter, the shells were carefully washed and dried in an oven at 110°C for 24h. The dried material was weighed and carbonized in the muffle furnace at a temperature of 800°C for 2h. After cooling to room temperature, the carbonized material was manually crushed using mortar and pestle before sieving to a desired particle size. The quantity needed for equilibrium studies was weighed and activated. The material was activated through impregnation in 1M H2SO4 in a beaker for 12h during which the surface pores of the carbon is activated. The activated carbon was then washed continuously with distilled water until pH7, after which it was filtered and the residue dried in an oven at 110°C for 24h and then packed in an air-tight sample bags for use.

Characterization of Activated Periwinkle Shell

Activated PRW was subjected to proximate analysis using standard method (Babayemi et al., 2015). Surface area was estimated using Sear’s methods (Alzaydien, 2009). The presence of their functional groups was determined through FT-IR, constituent elements and surface morphologies were analyzed via EDX and SEM respectively.

Equilibrium Studies

An aqueous solution was prepared from phosphate rock obtained from Federal Superphosphate Fertilizer Company, Kaduna, Nigeria. The batch adsorption experiment was performed. The solution pH was measured with a digital pH meter. About 100 mg of PRW was transferred into a beaker containing 10ml of the solution and placed on the magnetic stirrer at 30°C. A rotational speed of 200rpm was maintained throughout and at time intervals of 30 min. At the end of agitation of 30 min., the solution was filtered and the filtrate was tested for residual concentration of phosphate in a UV-spectrophotometer. The same procedure was repeated for the rest of the dosages, pH and temperature intervals.

The percent removal of phosphate was determined using Equation 1:

\[ E(\%) = \frac{C_0 - C_1}{C_0} \times 100 \]  

where, \( C_0 \) and \( C_1 \) are the initial and residual phosphate concentrations respectively.
Kinetic Studies

Lagergren first-order, pseudo second order and intra-particle diffusion kinetic equations were employed to represent the adsorption of phosphorus on activated PRW.

Lagergren first-order equation (Greenlee et al., 2010; Li et al., 2006; Otero et al., 2003).

The equation takes the form:

$$\frac{d}{dt} = K_1 (q_e - q_t)$$

(2)

After the definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q$ at $t = t$, Equation 2 becomes:

$$\ln (q_t - q_e) = \ln q_e - K_1 t$$

(3)

where:

$q_t$: Amount of adsorption at time $t$, (min)(mg/g)$^{-1}$

$q_e$: Amount of adsorption at equilibrium (mg/g)

$K_1$: The rate constant of the equation (1/min) and was determined experimentally from the slope and intercept of the plots

Pseudo Second Order Equation (Zhang and Land, 2003)

The equation is expressed as:

$$\frac{d}{dt} = K_2 (q_e - q_t)^2$$

(4)

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q$ at $t = t$, Equation 4 becomes:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e} + t / q_e$$

(5)

where, $K_2$ the rate constant of pseudo second order equation and can be determined from the slope and intercepts of the plots of $\frac{1}{q_t}$ versus $t$.

Intra-Particle Diffusion Model

Role of diffusion in the adsorption process can be determined with intra-particle diffusion model (Babayemi, 2017; Venkata and Karthikeyan, 1997):

$$q_t = K_d t^{1/2} + C$$

(6)

$C$: A constant and represents the boundary layer thickness

$K_d$: (mg/min$^{1/2}$) = The intra-particle diffusion rate constant

According to Equation 6, the plot of $q_t$ versus $t^{1/2}$ should be linear passing through the origin if the adsorption process obeyed the intra-particle diffusion model.

Adsorption Isotherms

Langmuir Isotherm

$$q_t = (K_L q_{max} C_t) / (1 + K_L C_t)$$

(7)

$q_{max}$ is the maximum amount of adsorption corresponding to mono layer coverage $(mg/g) K_L$ is the Langmuir constant and is related to the measure of affinity of adsorbent for the adsorbed $(1/mg)$ (Nwabanne, 2010).

For correlation purpose, the equation is rearranged as follows:

$$\frac{1}{q_t} = \left[ \frac{1}{K_L q_{max}} \left( \frac{1}{C_t} + \frac{1}{q_{max}} \right) \right]$$

(8)

A linear plot of $\frac{1}{q_t}$ against $\frac{1}{C_t}$ has a slope and intercept corresponding to $\frac{1}{K_L q_{max}}$ and $\frac{1}{q_{max}}$ respectively.

The favourability of the adsorption process to Langmuir isotherm can be confirmed through the separation factor:

$$R_L = 1 / (1 + K_L C_t)$$

(9)

The value of $R_L$ indicates whether the isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$), (Babayemi, 2014).

Freundlich Isotherm

$$q_t = K_F n C_t^n$$

(10)

$1/n$ is a heterogeneity factor which is a measure of intensity of adsorbate on the adsorbent. For favourable adsorption ($0 < n < 1$), while $n > 1$ represents unfavourable adsorption and $n = 1$indicates linear adsorption, if $n = 0$, adsorption the process is irreversible (Ghosh and Bhattacharyya, 2002). $K_F$ is the Freundlich constant.

The linear form of Equation 10 is:

$$\ln q_t = \ln K_F + \frac{1}{n} \ln C_t$$

(11)
Temkin Isotherm

\[ q_e = \left( \frac{RT}{b_T} \right) \ln K_T + \left( \frac{RT}{b_T} \right) \ln C_e \]  

(12)

\( b_T \) represents the adsorption potential of the adsorbent \( K_T \) is the Temkin constant (Eletta et al., 2016). A plot of \( q_e \) versus \( \ln C_e \) gives a straight line graph from which the value of \( K_T \) and \( b_T \) can be obtained.

Results and Discussion

Characterization Results

Proximate Analysis

The proximate analysis of PRW samples is summarized and presented in Table 2.

SEM Results

The surface textures of PRW before and after adsorption are displayed in Plates 1a and b respectively. Some morphological changes were observed in the surface textures with respect to shapes and sizes, the surface also changed into a new shinning and large particles with whitish patches structures indicating the adsorption of phosphates on the surfaces of the activated PRW.

EDX Results

The characterization results of the EDX are presented in Table 3. It is evident from the table that, carbon and oxygen are the main constituents 11.66% and 63.18% respectively, indicating its suitability for adsorption.

FT-IR Results

FT-IR spectrum of the activated PRW shows many absorption peaks as presented in Fig. 1. Oxygen functional groups are said to be important characteristics of adsorbents because they determine their surface properties (Das et al., 2006). The broad stretching absorption peak at 3382.20 and 3975.42 cm\(^{-1}\) correspond to –NH and bounded –OH groups. The bands at 1602.9 and 1720 cm\(^{-1}\) represent C=O stretching vibration of carboxyl groups. Other significant band positions are noted at 1431.23 cm\(^{-1}\) indicative of scissoring and bending vibrations of CH\(_3\) and CH\(_2\) groups, 1144.79 cm\(^{-1}\) indicative of C-N stretching of C = O group, 884.39 cm\(^{-1}\) indicating bending vibration of C-H group and 596.99 cm\(^{-1}\) is assigned to alkane group.

Table 2: Proximate analysis results of activated PRW

| Parameter      | Quantity |
|----------------|----------|
| Weight loss (%)| 47.31    |
| Ash content (%)| 5.98     |
| Volatile matter (%) | 23.51 |
| Moisture content (%) | 2.50 |
| Fixed carbon (%) | 72.55 |
| Bulk density (g/cm\(^3\)) | 0.53 |
| Surface area (m\(^2\)/g) | 620.81 |
| Iodine number (mg/g) | 553.06 |

Table 3: Characterization results of PRW using EDX

| Element | Atomic (%) | App.conc. | Intensity | Wt.% | Atomic (%) |
|---------|------------|-----------|-----------|------|------------|
| C       | 3.78       | 0.2842    | 7.12      | 11.66|
| O       | 57.74      | 0.6006    | 51.43     | 63.18|
| Al      | 19.48      | 0.8479    | 12.30     | 8.96 |
| P       | 13.41      | 1.2137    | 5.91      | 3.75 |
| S       | 16.53      | 0.8679    | 10.19     | 6.25 |
| Ca      | 22.35      | 0.9604    | 12.45     | 6.11 |
| Sn      | 0.84       | 0.7501    | 0.60      | 0.10 |
Plate 1: SEM images of PRW before and after adsorption

Fig. 1: FT-IR spectrum of the activated PRW
Experimental Results

Effects of Contact Time on Phosphorus Adsorption

The removal efficiency of the activated PRW as a function of time is presented in Fig. 2. The rate of phosphate removal increases very fast within the first 60 min. However, a gradual decrease in the removal efficiency with time was observed as the system approaches equilibrium between 180 min and 240 min. Availability of the fresh active sites of PRW surfaces might be responsible for the fast rise in removal efficiency at the early stage of adsorption, but as the available sites are getting saturated by the adsorbates, there was less contact between the surface area of the adsorbent and the solute ion which in turn led to the observed decrease in the rate of phosphate removal.

Effect of Dosage on Phosphate Removal

Adsorbent dosage plays a vital role in the removal of phosphate as presented in Fig. 3. As the adsorbent dosage was increased, more fresh active sites were made available for sorption, hence an increase in the removal efficiency. About 98.8% efficiency was obtained for a dosage of 50 g/l at 300 min.

Effects of pH on Phosphate Adsorption

Normally, pH is viewed as one of the important parameters that control the adsorption at water-adsorbent interfaces (Das et al., 2006). The plot of percent removal of phosphate at various pH at different time intervals in minutes (E30, E60, E120, E180, E240, E300) is presented in Fig. 4. It was observed that, as pH increased from pH2 to pH6 the amount of phosphate removed increased but further increase of pH brought about a steady decrease in removal. This may be as a result of the rising competition between OH$^-$ groups and phosphate species PO$_4^{3-}$ for the adsorption sites (Eletta et al., 2016).

Kinetic Studies

The kinetics parameters were evaluated and presented in Table 4. The adsorption data were well fitted to the pseudo second order kinetic model with the values of $R^2 = 1.0000$ at the chosen experimental temperatures. The deviation of straight lines from origin as presented in Fig. 5 implies that, the intra-particle transport is not the rate limiting steps and that pore diffusion is the only controlling step not film diffusion (Babayemi, 2014).
Fig. 4: Effects of pH on phosphate adsorption

Fig. 5: Intra-particle diffusion plot for phosphate adsorption on PRW

Table 4: Evaluated kinetic parameters at different temperatures

| Kinetic model equations | Parameters | 303K   | 308K   | 313K   |
|-------------------------|------------|--------|--------|--------|
| Lagergren first order   |            |        |        |        |
| \( \frac{dq}{dt} = K_1(q_e - q_t) \) |            | 0.0270 | 0.0135 | 0.0088 |
| \( \ln(q_e - q_t) = \ln q_e - K_1t \) |            | 5.8835 | 2.9418 | 1.8748 |
|                         |            | 0.8144 | 0.8144 | 0.7929 |
| Pseudo second order     |            |        |        |        |
| \( \frac{dq}{dt} = K_2(q_e - q_t)^2 \) |            | 0.0034 | 0.0034 | 0.0037 |
| \( \frac{1}{q_t} = \frac{1}{K_2q_e} + \frac{t}{q_e} \) |            | 34.7222| 35.2112| 35.9712|
|                         |            | 1.0000 | 1.0000 | 1.0000 |
| Intra-particle diffusion |            |        |        |        |
| \( q_t = K_d t^{1/2} + C \) |            | 0.5166 | 0.5166 | 0.4795 |
|                         |            | 25.6730| 26.1730| 27.5580|
|                         |            | 0.8787 | 0.8787 | 0.8675 |
Isotherm Models

The Langmuir, Freundlich and Temkin isotherm parameters were evaluated and presented in Table 5. The values of $R_L$ indicate favourable adsorption of phosphorus on the activated PRW at all the chosen experimental conditions. The Freundlich constant 'n' being less than one (n<1) at all chosen temperatures also indicates favourable adsorption. The correlation coefficients $R^2$>0.9 confirms that the adsorption data fitted well to Langmuir and Freundlich isotherms but did not fit well to Temkin Isotherm $R^2$<0.9. The numerical fit results of non-linear regression analysis of the isotherm data are graphically presented in Fig. 6.

Statistical Modeling and Optimization

Statistical modeling Central Composite Design with a $2^3$ full factorial design was employed. The adsorption process was modeled using the general equation:

$$Y = b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1^2 + b_8x_2^2 + b_9x_3^2$$

$x_1$, $x_2$ and $x_3$ are the coded values for pH, dosage and contact time respectively.

Table 5: Isotherm parameters for the adsorption of phosphorus on PRW

| Isotherm model     | Parameter | 303K       | 308K       | 313K       |
|-------------------|-----------|------------|------------|------------|
| Langmuir isotherm | $q_e = (K_eq_{min}C_e)/(1+K_eC_e)$ | $K_L$      | 0.0221     | 0.0208     | 0.0178     |
|                   |           | $R_L$      | 0.1082     | 0.1142     | 0.1309     |
|                   |           | $R^2$      | 0.9466     | 0.9207     | 0.9151     |
| Freundlich isotherm | $q_e = x_{Fe}^n$ | $K_F$      | 0.0023     | 0.0006     | 0.0004     |
|                   |           | $R^2$      | 0.9466     | 0.9271     | 0.8964     |
| Temkin isotherm   | $b_T$     | 53.1000    | 55.8700    | 60.6700    |
|                   | $K_T$     | 0.0467     | 0.0402     | 0.0549     |
|                   | $R^2$     | 0.7972     | 0.7423     | 0.8085     |

Fig. 6: Isotherm plot for fit to PRW
The obtained model fits for adsorption of phosphates on activated PRW after deleting the insignificant factors is given as:

\[ Y = 94.2120 - 0.4247x_1 - 0.0465x_2 - 28.4349x_3 - 0.0002x_1x_2 \\
+ 0.1696x_1^2 + 0.000023x_2^2 + 3.4740x_3^2 \]

The main attribute to effective performance of activated PRW is its contact time \((P_{\text{value}} = 0.0000, \text{Reg.coeff.} = 0.4580)\). pH \((P_{\text{value}} = 0.0777, \text{Reg.coeff.} = 0.1394)\) is also significant but not very effective. The interactions between adsorbent dosage and contact time \(x_2x_3\) \((P_{\text{value}} = 0.0000, \text{Reg.coeff.} = 0.5195)\) are also significant and very effective. Changes in either adsorbent dosage or contact time will have a major effect on the adsorption process. The surface response plot as presented in Fig. 7, 8 and 9. revealed a higher quadratic profile for contact time than for either dosage or pH. The model accuracy. The model accuracy is validated by the values of \(R^2(0.9902)\) and adjusted \(R^2(0.9787)\) and the closeness of the predicted values to the experimental values as presented in Fig. 10.
Conclusion

This work has established acid modified periwinkle shell as a good potential, adsorbent for phosphate removal from aqueous solution being cost effective and non-toxic to the environment. The adsorptive performance of PRW was 95.90%. The adsorption data fitted well to pseudo second order kinetic model and were well described by Langmuir and Freundlich isotherms. A statistical model equation was developed for the adsorption process and the optimization response surface model established the minimum pH2, dosage (1000 mg) to be local while the contact time (4.1h) a global optimum for the process.
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Author’s Contributions

Babayemi, Akinpelu Kamoru: Participated in all experiments, coordinated the data analysis and contributed to the writing of the manuscript.

Onukwuli, Okechukwu Dominic: Designed the research plan and organized the study.

Ethics

The authors declare there are no ethical issues that may arise after the publication of this manuscript.

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