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Adsorption Isotherms, Thermodynamics And Statistical Modeling of Phosphate Removal From Aqueous Solution By Locally Prepared Bio-Sorbent.

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Abstract: *Animal bone was carbonized and activated with ammonium salt (NH_4Cl) for the removal of phosphorous from aqueous solution through batch adsorption process. The obtained activated carbon was subjected to physico-chemical characterization. The effect of pH and sorption time was investigated. The experimental equilibrium adsorption data were described using Freundlick, Langmuir and Temkin Isotherms. The mechanism of adsorption was determined through thermodynamic properties such as change in free energy ΔG ($KJmol^{-1}$) and change in entropy ΔS ($Jmol^{-1}K^{-1}$). Statistical modeling via Central Composite Design CCD for process optimization was carried out. The obtained results showed that at sorption time of 120 minutes and optimum pH 6, removal efficiency was higher than 97%. The adsorption data conformed to Freundlick Isotherm at the temperature of the experiment 303K, 308K and 313K. The positive values of ΔH ($KJmol^{-1}$) and ΔS ($Jmol^{-1}K^{-1}$) indicate the endothermic character of the reaction and increase randomness at the solid-solution interface respectively during the adsorption process. The most significant main effect for performance of the adsorbent is contact time ($P_{value} = 0.0007$) while pH ($P_{value} = 0.0224$) is the least significant.*
Keywords: *Adsorption, Isotherms, Phosphorus, adsorbent, thermodynamics.*

I. Introduction

Activities such as farming, laundry and industrial use of chemicals often lead to the release of chemicals or nutrients into water bodies. Phosphorus is one of such elements which, when in water bodies may give rise to algae growth (eutrophication) resulting to significant loss of water quality and as well endangering the lives of fishes and many other aquatic animals[1]. The removal of phosphorus from water and wastewater is thus very important.

Conventional methods of wastewater treatment with emphasis on phosphorus removal include biological, chemical, bio-chemical and tertiary treatments [1]. The cost inefficiency and the detrimental effects of the chemicals used in these methods have necessitated the need to explore alternative methods. This work focuses on the use of animal bone based activated carbon through batch adsorption process for the removal of phosphorus from wastewater. The term activated carbon defines a group of materials with highly developed internal surface area and porosity and hence a large capacity for adsorbing chemicals from gases or liquids [2].

Activated carbons are amorphorous solid adsorbents that can be produced from almost all carbon-rich materials including wood, fruit stones, peat, lignite, anthracite, shells, animal bones and other raw materials [3]. Activated carbon is one of the best tools which can be used to reduce risk to human health and provide an aesthetically pleasing product at reasonable cost [4].

Adsorption is a process that occurs when a gas or liquid solute accumulate on the surface of solid or liquid forming a film of molecules or atoms [2,5,6,7]. The substance attached to the surface is called adsorbate, and the substance to which it is attached is known as the adsorbent [6]. Adsorption is different from absorption in which a substance diffuses into a liquid or solid to form solution. Adsorption is a surface phenomenon while absorption is a bulk phenomenon.

II. Materials And Methods

Animal bone used as base material was obtained from an abattoir at Ihiala, Anambra State, Nigeria. The bones were cleaned, pre-dried and broken into smaller sizes before being subjected to further drying in an oven. The dried bone was then carbonized in a muffle furnace at a temperature of 800^0c for 3 hours. The charred material was allowed to cool to room temperature, ground and sieved using 0.2mm mesh.

The sieved 0.2mm particle size material was weighed and purified by washing with 0.5M HCl solution and rinsed three times with distilled water to remove excess acid solution. The purified material after drying, was subjected to activation with 1M NH_4Cl.The activated carbon was packed in an air tight sample bags with labels.

Proximate analysis was carried out on the activated carbon to determine the weight loss, bulk density, % ash content, iodine number, % volatile matter, % moisture content, fixed carbon using standard methods [8,9]. Surface area of the activated carbon was estimated using Sear's method [1, 8] by agitating 1.5g of the activated carbon samples in 100ml of diluted hydrochloric-acid at pH3. Then 30g of sodium chloride was added while stirring the suspension and then the volume was made up to 150ml with de-ionized water. The solution was titrated with 0.1N Na0H to raise the pH from 4 to 9 and the volume V recorded. The surface area according to this method was calculated by the following equation $S = 32V – 25$ - - [1]

Where S =surface area of the activated carbon

V = volume of sodium hydroxide required to raise the pH of the sample from 4 to 9.

The obtained results are presented in table 1.

The phosphate solution used as effluent in this study was prepared by first dissolving 500g of phosphate rock sample in 1000 cm^3 of distilled water. The solution thoroughly stirred and left for about 30 minutes to allow the particles enough time to dissolve. After that, the solution was again stirred and filtered off the silts, organic matters and insoluble phosphate rock particles. The homogenous solution was further diluted with 3000cm^3 distilled water before it was tested for pH level with digital pH meter and its phosphorous content concentration was measured in UV spectrophotometer set at a wavelength of 650nm. The initial pH was 2.8 and phosphorus concentration was 373mg/l.

Batch Adsorption Experiment

The adsorption experiment was carried out by batch method. The pH level of the effluent was measured with the aid of a digital pH meter. Five separate test-tubes were washed and rinsed with distilled water, after which they were filled each with 10ml of the effluent and labeled 2,4,6,8 and 10 respectively. The pH of the effluent in the labeled test-tubes was adjusted to 2,4,6,8 and 10 respectively using 0.5M HCl or 1M Na0H as the case may be. Thereafter, 0.5g of the prepared activated carbon was added to the effluent in each of the test-tubes and were then placed in a centrifuge. A constant rotational speed of 100rpm was maintained throughout the period of agitation of 30minutes. The test-tubes were then removed from the centrifuge and the contents filtered. The filtrate was tested for its residual concentration using UV-spectrophotometer set at 650nm. The same procedure was repeated for 5 hrs of agitation at 30 minutes intervals. Removal efficiency E% was calculated using equation (2).

$E\% = (C_0 – C_1) / C_0 \times 100$ - - - - (2)

Where C_0 and C_1 are respectively the initial and residual concentrations of phosphorus in the effluent (mg/l).

Adsorption Isotherms Studies

Isotherms studies provide information on the capacity of adsorbent which is an important parameter for adsorption system. Adsorption isotherms are characterized by certain constants and described the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium. In this work, Langmuir, Freundlick and Temkin Isotherm models have been considered to analyze adsorption data.

Thermodynamics studies

The mechanism of adsorption was determined through thermodynamic properties such as change in free energy ΔG and change in entropy ΔS. The thermodynamic equilibrium constant K_L for the sorption was determined from the intercept of the plots C_e/q_e versus C_e as presented in (Fig.1). ΔG, ΔH and ΔS are calculated from Van't Hoff equation [1,5,11]

$\Delta G = RT\, \mathrm{In}K_L$ - - - - - - (3)

$\mathrm{In}K_L = \Delta S/R - \Delta H/RT$ - - - - - - (4)

$\mathrm{In}K_{L1}/K_{L2} = - \Delta H/R\,(1/T_2 – 1/T_1)$ - - - - - - (5)

III. Results And Discussion

Effect of pH and contact time on phosphorus adsorption

Removal efficiency (E%) profile of animal bone activated with ammonium salt (BAS) as a function of time at varied pH levels is presented in Fig. 2. It can be seen from the figure that E% increases with time as well as with increasing pH. The effects of pH were not as significant as contact time on phosphorous adsorption. At pH6, the rate of phosphorous removal increased very fast as the contact time increased from 30 minutes to near equilibrium at 180 minutes but a decline in rate of E% was observed as the contact time was increased above 180 minutes.

E% = 93.48, 98.77 and 98.89 at 30 mins., 180 mins., and 300 mins respectively.

Freundlick Isotherm model

The Freundlick constants, 'n' giving an indication of how favourable the adsorption process is, and K_F which is the adsorption capacity of the adsorbent are calculated from the slope and intercept of the linear plots $Inq_e = InK_F + 1/n\ InC_e$.

The values of the Freundlick constants at 303K, 308K and 313 are presented in table 2. The value of 'n' is less than one (n<1) indicating favourable adsorption [1,12]. The correlation coefficient (R^2>0.9) showed that phosphorous adsorption on BAS followed Freundlick Isotherm at 303K, 308 and 313K.

Langmuir Isotherm model

The Langmuir constants, q_{max} and K_L were evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e. Favourability of an adsorption process to Langmuir Isotherm can be determined through the separation factor or equation parameter R_L which is expressed as $R_L = 1/(1 + K_L\ C_0)$ where C_0 is the initial adsorbate concentration [1,12].

The value of R_L, which is less than one (R_L<1) as presented in table 2., indicates favourable adsorption under the chosen experimental conditions.

Temkin Isotherm

The Temkin Isotherm constants K_F and b were evaluated from the plots of q_e versus InC_e and their values are presented in table 2. The correlation coefficient R^2<0.9 showed that, the data did not fit Temkin Isotherm.

Non linear Isotherm model

The equilibrium concentration data and the amount of adsorption were fitted to Freundlick, Langmuir and Temkin Isotherms using the non linear regression analysis of the curve fitting toolbox of MATLAB 7.0. The numerical fit results are graphically presented in Fig.3

Thermodynamics studies

The calculated thermodynamic parameters are presented in table 3. It was observed that, for the adsorption of phosphorus on BAS adsorbent, ΔH gave positive values indicating the endothermic character of the reaction. The positive values of ΔS showed the increased randomness at the solid- solution interface during the adsorption process. Also, the values of ΔG are positive and K_L<1 showing that the adsorption of phosphorous on BAS under the chosen experimental conditions was not spontaneous [1,5,12].

Statistical modeling and optimization

The model fits for adsorption using BAS after deleting the insignificant factors is given as $Y = 84.7476 + 0.8416x_1 - 21.5589x_2 - 0.0327x^2_1 + 2.7434x^2_2$

Where Y is the dependent variable in the model equation while the independent variables x_1, x_2 are the coded values for pH and contact time respectively. The main attribute to effective performance of BAS as an adsorbent is its contact time (P_{value} = 0.0007, Reg.Coeff. = 03272) while pH (P_{value} = 0.0224, Reg. Coeff = 0.1988) is not that effective. Changes in contact time have a major impact on the effectiveness of the adsorbent while pH has the least effect. The surface response plot revealed a higher quadratic profile for contact time and least for pH as presented in Fig.4. The model accuracy is validated by the values of R^2 (0.9813) and adjusted R^2 (0.9594) and the closeness of the predicted values to the actual experimental values as presented in Fig.5.

IV. Conclusion

This research work shows that animal bone treated with ammonium salt (BAS) is very effective as an adsorbent for the treatment of phosphorus contaminated wastewater. It was also established that BAS was highly efficient at the optimum pH6. The adsorption data was best described by Freundlick Isotherm. Adsorption of phosphorous on BAS through thermodynamic studies was also established to be endothermic. The statistical modeling of the process also indicated that, the most significant main effect for performance of BAS is its contact time. The high removal efficiency of BAS at the chosen experimental conditions, its availability, biodegradability and non-toxic nature present BAS as a good adsorbent for the removal of phosphorous from wastewater.

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Table 1: Characterization results of BAS

Parameters	BAS
Weight loss, %	39.64
Bulk density, g/cm^3	0.52
Ash content, %	6.46
Iodine number, mg/g	387.67
Volatile matter, %	17.34
Moisture content, %	7.82
Fixed carbon, %	58.72
Surface area, m^2/g	566.54

Table 2: Isotherm parameters for the adsorption of phosphorous on BAS

Isotherm	Parameters	Temperature, K			Remarks
		303	308	313	
Langmuir	q_{max} (mg/g) K_L (1/mg) R_L R^2 n	10.638 0.0208 0.1142 08919 0.3897	8.2781 0.02245 0.1066 0.9494 0.3626	7.5301 0.0196 0.1203 0.9369 0.3526	0< R_L<1 shows favourable adsorption of phosphorous on the adsorbent. Data conformed to Langmuir isotherm.
Freundlick	K_F (1/g) R^2	$4.178x10^{-3}$ 0.9513	1.579×10^{-3} 0.9495	$0.7538 x10^{-3}$ 0.9116	n<1 shows favourable adsorption. Data fitted well to Freundlick Isotherm.
Temkin	b ((J/mg) K_t (1/mg) R^2	58.71 0.0621 0.853	56.64 0.0534 0.8313	58.04 0.0451 0.7619	R^2 values showed that data did not fit Temkin Isotherm.

Table 3: Thermodynamic parameters for the adsorption of phosphorus on BAS

Parameters	Temperature, K		
	303	308	313
K_L	0.0208	0.0225	0.0196
ΔG (KJ mol^{-1})	9.75	9.72	10.23
ΔS(Jmol^{-1}K^{-1})	-	487.92	-
ΔH (KJ mol^{-1})	-	160.56	-

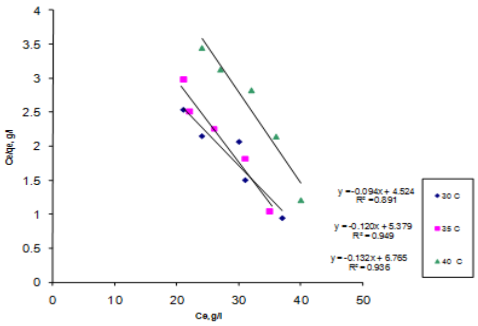

Fig. 1: Langmuir isotherm for the adsorption of phosphorus on BAS

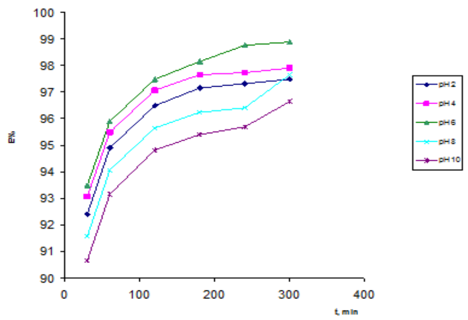

Fig.2: Removal efficiency ofBAS at different pH levels and adsorbent conc. =50g/l

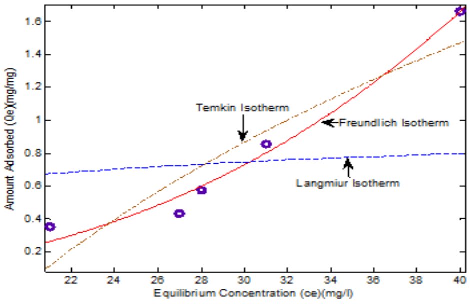

Fig. 3.: Isotherm plot for fit to BAS

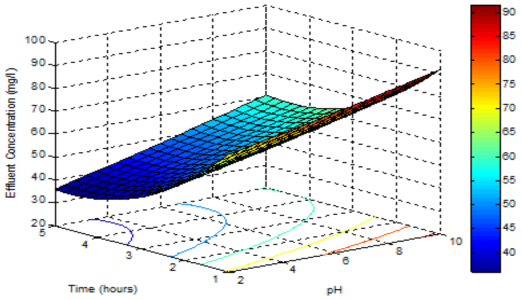

Fig. 4: 3-D Surface Plot for BAS

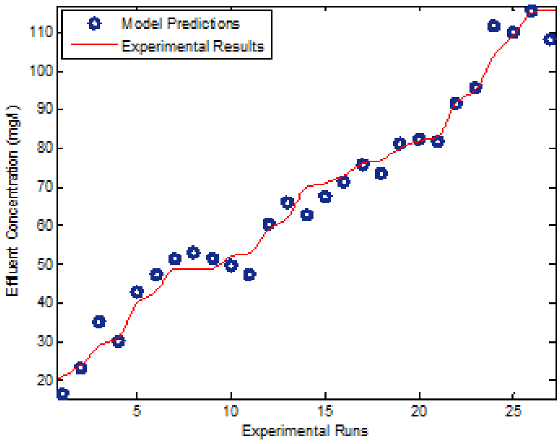

Fig. 5: Experimental vs. Model Predictions for BAS