

Adsorptive Potentials of Salt-Modified Biosorbent For Wastewater Treatment.

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ABSTRACT: Activated carbon were prepared from periwinkle shells through carbonization in muffle furnace and activation in sulphate salt $[Al_2(SO_4)_3]$. The prepared activated carbon (PWS) was used as adsorbent for the removal of phosphate from wastewater. Equilibrium studies on the adsorption process were carried out during which the effects of particle size, batch time and adsorption dosage on the adsorptive potentials of PWS were investigated. Adsorption isotherm models were also employed to describe the equilibrium data. The process was optimized and optimum process parameters obtained. The optimization results present PWS, a potential adsorbent with a performance of 95.38%. The results of the determined thermodynamic parameters reveal that, the adsorption process was endothermic ($\Delta H > 0$) and spontaneous ($\Delta G > 0$), except at a temperature of 313K when ($\Delta G < 0$). The increased randomness of the adsorbate molecules at the solid- solution interface was also confirmed by the positive value of the entropy ($\Delta S > 0$). The adsorption data were best described by Freundlich and Temkin isotherms with $R^2 > 0.9$.

Keywords: Wastewater, Optimization, Adsorption, , Isotherms, Phosphates, Equilibrium, Periwinkle.

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I. INTRODUCTION

Wastewater is referred to as polluted when it is contaminated naturally or through human activities, as such, it is neither fit for human use nor suitable to sustain aquatic life. This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. The damaging effects of these unwholesome activities are considered the global health risk, threatening not only humans but also several other plants and animals that rely on water to live. This calls for an urgent need to search for a technologically feasible, economically viable and socially acceptable method of treating the generated wastewater before discharging to the water bodies.

Many researchers have made use of agricultural wastes of different kinds in various forms for the treatment of wastewater. Chestnut shells were used to remove Cd^{2+} , Pb^{2+} , [1], Prawn shells and *euchhorniacrassipes* roots for Cr^{3+} removal [2,3], Cedar sawdust and *guvajava* leaves for Cu^{2+} and Zn^{2+} uptake [4,5]. Also, florides were removed by adsorption on activated carbon prepared from rice straw [6] while materials such as palm kernel shell [7], animal bone [8], slag and fly ash [9], *Afzella-Africana* [10], eggshell waste [11], Tamarind nutshell [12], *Gossypium* spp [13], *Mucunasloanei* seed [14] and local clay [15] have been tested for the removal of phosphates and dyes. However, much attention has not been given to the use of salt-activated periwinkle for phosphate removal from wastewater. This work focused on the treatment of phosphorus containing wastewater owing to its damaging effects on water bodies. Eutrophication, which is one of its negative impacts on the water bodies, is described as the excessive growth of algae that leads to the depletion of dissolved oxygen in water and consequently, death and reduction in aquatic animal population [16].

Various methods are available for wastewater treatment such as chemical precipitation [17], biological treatment [18], ion exchange and reverse osmosis, but the cost implication and the detrimental effects of the chemicals used in those methods have necessitated the search for alternative methods. In this research work, a batch adsorption method using activated carbons produced from periwinkle shell is adopted.

Activated carbons are used extensively for the removal of undesirable odour, colour, taste and other organic and inorganic impurities from domestic and industrial wastewater. Their unique adsorption properties

result from their constituent carbonaceous backbones[19], high surface area, adequate pore- size distribution, broad range of surface functional groups and relatively high mechanical strength [20]. More importantly, this activated carbon is prepared from agricultural waste, thereby making it cost-effective in addition to its availability, bio-degradability and eco-friendliness

II. THEORETICAL BACKGROUND

1.1 Adsorption Isotherms model development

1.1.1 Langmuir Adsorption Isotherm

The assumptions inherent in the Langmuir isotherm are:

- i. Adsorption occurs on vacant sites and adsorbed molecules are immobile
- ii. All adsorption sites are equivalent and each vacant active site can only accommodate one adsorbed specie.
- iii. The surface is energetically homogeneous and adsorbed molecules do not interact
- iv. At the maximum adsorption, only a monolayer is found, adsorption only occurs on localized sites on the surface not with other adsorbates.

Consider the reaction below:



a simple reversible adsorption of a molecule A on a single site, R on a catalyst surface.

Rate of adsorption,

$$r_A = K_A C_A C_v \quad (1)$$

Rate of desorption,

$$r_{-A} = K_{-A} C_{AR} \quad (2)$$

Net rate of adsorption,

$$r_{net} = K_A C_A C_v - K_{-A} C_{AR} \quad (3)$$

K_A , K_{-A} are rate constants for forward and reverse reactions

C_A , C_v , C_{AR} are concentrations of specie A, vacant site and occupied sites respectively.

Summing up the vacant and occupied sites

$$C_t = C_v + aC_{AR} \quad (4)$$

Substitute for C_v in Eq.3

$$r_{net} = K_A C_A [C_t - C_{AR}] - K_{-A} C_{AR} \quad (5)$$

$r_{net} = 0$, at equilibrium

$$0 = K_A C_A [C_t - C_{AR}] - K_{-A} C_{AR}$$

After rearranging the above equation, and equating

$\frac{K_A}{K_{-A}} = K_{ads}$, we obtain

$$C_{AR} = \frac{K_{ads} C_A C_t}{1 + K_{ads} C_A} \quad (6)$$

Putting $\frac{C_{AR}}{C_t} = \theta$, Eq.6 becomes

$$\theta = \frac{K_{ads} C_A}{1 + K_{ads} C_A} \quad (7)$$

K_{ads} is the equilibrium constant

θ is the surface fractional coverage.

For liquid isotherm, the Langmuir isotherm is expressed as

$$q_e = \frac{(K_L q_{max} C_e)}{1 + K_L C_e} \quad (8)$$

q_e is the equilibrium value of adsorbate per unit mass of adsorbent (mg/g)

q_{max} is the maximum amount of adsorption corresponding to monolayer coverage (mg/g)

1.1.2 Freundlich Adsorption Isotherm

The Freundlich isotherm equation expresses the heterogeneity of adsorption sites for rough surfaces and is applicable only at low pressure or low solution concentration.

It is mathematically expressed as

$$\frac{x}{m} = K_F P^{1/n} \quad (9)$$

Taking logarithm both sides of the equation gives

$$\text{Log} \frac{x}{m} = \text{Log} K_F + \frac{1}{n} \text{Log} P \quad (10)$$

In term of solution concentration, Eq.10 becomes

$$\text{Log} \frac{x}{m} = \text{Log} K_F + \frac{1}{n} \text{Log} C \quad (11)$$

x, m are masses of adsorbate and adsorbent respectively.

K_F, n are Freundlich constants.

1.1.3 Temkin Adsorption Isotherm

Temkin adsorption isotherm considers indirect interactions between adsorbates. He discovered by experiments that, the heat of adsorption decreases more with increasing coverage. The linear form of the isotherm can be expressed as

$$q_e = \left[\frac{RT}{b_T} \right] \ln K_T + \left[\frac{(KT)}{b_T} \right] \ln C_e \quad (12)$$

K_T, b_T are Temkin constants

III. MATERIALS AND METHODS

1.2 Preparation Of Activated Carbon

Periwinkle shells were obtained, washed and dried in an oven at 110°C for 24h. The dried material was carbonized in the muffle furnace at a temperature of 800°C for 2h. The material was then ground and sieved into the desired particle sizes. Each of the various fractions was transferred into a beaker containing 1M $\text{Al}_2(\text{SO}_4)_3$ for impregnation. The volume of the salt solution in the beaker must be well above the material being impregnated. After 12h of impregnation, the activated carbon was washed with de-ionized water, dried and packed in an air tight sample bags for use [21].

1.3 Equilibrium Studies

An aqueous solution was prepared from the sample of superphosphate fertilizer obtained from a local market in Onitsha, Nigeria and its initial concentration was measured using UV- spectrophotometer. The adsorption experiment was conducted by batch method. 100mg of 0.2mm particle size of PWS was transferred into a beaker containing 10ml of the aqueous solution and stirred continuously for 30min. on a magnetic stirrer set at 30°C. A constant rotational speed of 200rpm was maintained throughout and at time intervals of 30min. After 30min of agitation, 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, particle sizes and time intervals.

The percent removal of phosphate was determined using Eq.13

$$E(\%) = \frac{C_0 - C_1}{C_0} \times 100 \quad (13)$$

C_0, C_1 are the initial and residual phosphate concentrations respectively.

IV. RESULTS AND DISCUSSION

1.4 Effects Of Adsorbent Dosage And Batch Time On Removal Efficiency

Figure 1 presents the removal efficiency of PWS as a function of time for various adsorbent dosages. The rate of phosphate removal increases very fast at the early stage of sorption owing to the available vacant sites on the surface of PWS. As the free sites get occupied in the course of the process, the unoccupied area of contact between the adsorbate and the adsorbent reduced, hence a decrease in the removal efficiency of the adsorbent. As fresh adsorbent dose was added, the rate of adsorption improved owing to fresh active sites made available for sorption. Maximum sorption of 98.89% was obtained at 50g/l and 300min.

1.5 Adsorption Isotherms

The adsorption equilibrium data was analyzed via Non-linear regression analysis. The obtained isotherm coefficients and graphical fit results for Freundlich, Langmuir and Temkin adsorption isotherms are presented in Table 1 and Fig. 2 respectively. It was clearly revealed from the graphical fit results presented in Fig. 2 and the coefficient of determination $R^2 > 0.9$ that, the adsorption data fit well to only Freundlich and Temkin isotherms but for the Langmuir isotherm $R^2 < 0.9$.

4.3 Thermodynamic Studies

The thermodynamic parameters: change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using Eqs. 14, 15, 16 and the results are presented in Table 2.

$$\Delta G = -RT \ln K_L \quad (14)$$

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} = -\frac{\Delta G}{RT} \quad (15)$$

$$\ln \frac{K_{L1}}{K_{L2}} = -\frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (16)$$

From the results obtained, the positive values of ΔH imply the endothermic nature of the adsorption and $\Delta S > 0$ shows the increased randomness of the adsorbate molecules at the solid-solution interface. The spontaneity of the adsorption process was confirmed by the negative value of ΔG at the temperatures of 303K and 308K, but at temperature of 313K $\Delta G > 0$, revealing that the adsorption of phosphorus on PWS was not spontaneous at that temperature.

4.4 Modeling And Optimization

The adsorption process was modeled using Response Surface Methodology, and the general equation for the model is given as

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 \quad (17)$$

x_1 , x_2 and x_3 are the coded values for dosage, particle size and batch time respectively.

The interactions x_1x_2 , x_2x_3 are not significant and are therefore deleted from the equations.

The model equation then obtained for the adsorption of phosphate on PWS is given as

$$Y = 95.4166 - 0.0494x_1 + 28.6451x_2 - 26.2835x_3 - 0.0016x_1x_3 + 0.000024x_1^2 + 10.7667x_2^2 + 3.2386x_3^2 \quad (18)$$

Of the three variables considered, batch time appears the main attribute to effective performance of PWS ($P_v=0.0000$, Reg. Coeff.=0.451). The interactions x_1x_3 ($P_v=0.0000$, Reg. Coeff.=0.5119) are so significant that any change in either x_1 (dosage) or x_3 (batch time) will have a significant effect on the removal efficiency. The quadratic profiles of the surface response of time-dosage, time-particle size and dosage-particle size are presented in Fig. 3, 4 and 5 respectively. The values of $R^2 > 0.9$ and the closeness of the actual experimental values to the predicted values confirm the validity of the model. The values of R^2 reveal that the model predicts the data to 98.53% accuracy. The graphical representation of the experimental and predicted values is presented in Fig.6.

V. CONCLUSION

This study has revealed that, a salt-modified adsorbent prepared from a low cost, periwinkle shell can be used as a substitute to conventional adsorbents to remove phosphate from wastewater. The optimization response surface model equation that was developed also established the optimum process parameters for the adsorption of phosphorus on PWS at the chosen experimental conditions. The minimum dosage (1000mg), particle size (0.2mm) were local, while the batch time (4.3h) is a global optimum. The effectiveness of the adsorbent can be improved upon by operating at lower particle size and higher dosage than that was used in this study but no improvement can be made by increasing batch time beyond the stipulated optimum. A performance of 95.38% was attained.

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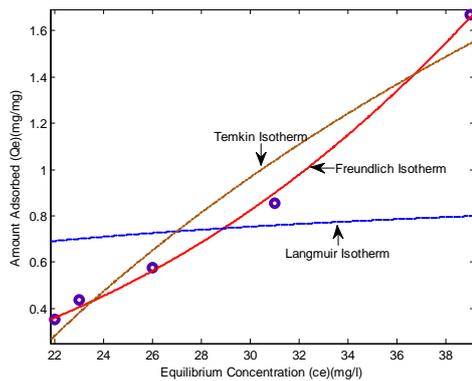


Fig.2, Isotherm plot for fit to PWS

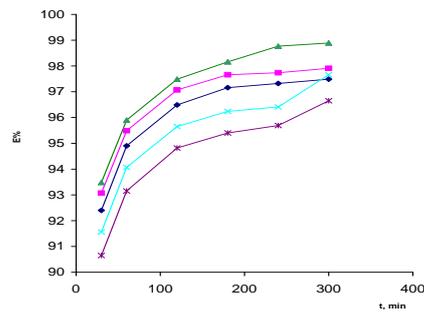


Fig.1, Removal efficiency of PWS at different dosages

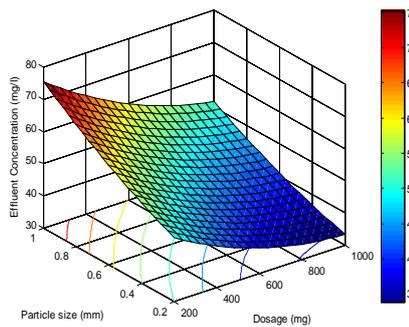


Fig.3 3D plot for PWS (particle size-dosage)

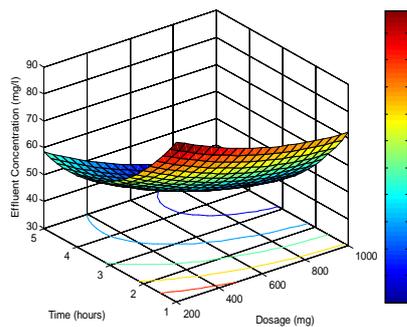


Fig.4. 3D plot for PWS (time-dosage)

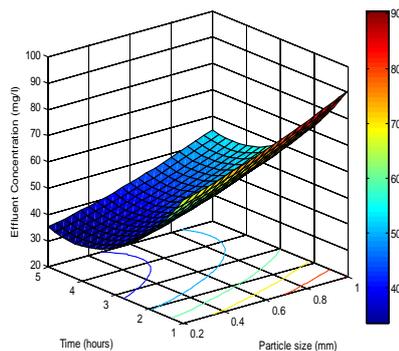


Fig.5. 3D plot for PWS (time-particle size)

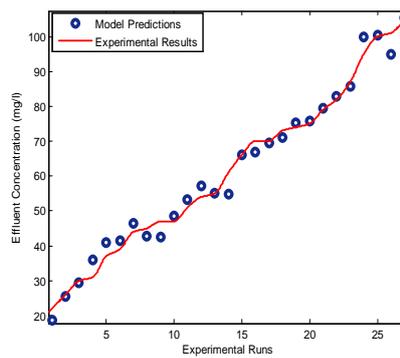


Fig.6. Experimental/predictions for PWS

TABLE1. Numerical fit results for adsorption isotherms.

Isotherm	K	b_T	K_T	R^2	Adj. R^2
Freundlich	9.38×10^{-5}	-	-	0.9970	0.9960
Temkin	-	2.206	0.0516	0.9451	0.9268
Langmuir	0.102	-	-	0.1446	0.1446

TABLE2. Thermodynamic parameters for the adsorption of phosphorus on PWS

Adsorbent	K_L	T(K)	$\Delta G(\text{KJmol}^{-1})$	$\Delta S(\text{Jmol}^{-1}\text{K}^{-1})$	$\Delta H(\text{KJmol}^{-1})$
PWS	1.703	303	-1.341	-	-
	1.128	308	-0.308	6 24.90	202.39
	0.9221	313	+0.211	-	-

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