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Kinetics of Adsorption of Phosphorus from Phosphate Containing Synthetic Effluent Using Locally Prepared Bio-Sorbent.

Babayemi, A.K, Onukwuli, O.D

***Abstract*— Adsorption kinetics of phosphorus from phosphate containing synthetic effluent was studied using acid treated activated carbon (AAB) prepared from animal bone. The rate of phosphorus removal as a function of adsorbent dosage, particle size and residence time was carried out through batch adsorption experiment. It was discovered that, over 95% phosphorus was removed by AAB at 60 minutes residence time,50g/l dosage and 0.2mm particle size. Adsorption kinetic data were described using pseudo first order, second order, pseudo second order, Elovich equation, Bhattacharya Venkobachor model (BVM) and Intra particle diffusion models. The results indicate that, the data conform to second order, pseudo second order and Elovich kinetic models at temperature of 303k, 308k and 313k but pseudo second order best described the adsorption kinetic data.**

***Index Terms*— Phosphorus, activated carbon, kinetics, adsorbent, carbonization, adsorption**

I. INTRODUCTION

Phosphorus pollution is a major problem resulting from improper disposal of the generated wastes especially from chemical industries such as fertilizers, soap and detergent manufacturing companies [1]. These phosphorus containing wastes from run off eventually get into water bodies such as lakes, rivers, creeks resulting to eutrophication, which is the abundance of aquatic plants, growth of algae and depletion of dissolved oxygen. The result of this unwholesome act is coloured, murky, odourous surface waters, fish kills and loss of many other aquatic animals. Several treatment methods such as biological and chemical precipitations, crystallization and the use of anaerobic membrane bio-reactor have been used in the past for the removal of phosphorus from wastewater but the cost inefficiency and the detrimental effects of the chemicals used in these methods have necessitated the need to explore alternative methods. To this end, this work focuses on the use of activated carbon through batch adsorption process for the removal of phosphorus from wastewater.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, liquid forming a film of molecules or atoms [2,3,4,5]. 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. 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 [7]. The word activated in the name is sometimes substituted by active. Activated carbons are amorphous solid adsorbents that can be produced from almost all carbon-rich materials including wood, fruit stones, peat, lignite, anthracite, shells, animal bones and other materials [8].

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Babayemi, A.K, Department of Chemical Engineering, Anambra State university, Uli. Nigeria.

Onukwuli, O.D, Department of Chemical Engineering, Nnamdi Azikiwe University, Awka. Nigeria

II. MATERIALS AND METHODS

Animal bones were obtained from an abattoir at Ihiala, Anambra State. The bones were cleaned, dried and broken into smaller pieces before drying in an oven for 2hours at 110^0C. The dried bone was taken into the hot zone of the muffle furnace for carbonization at a temperature of 800^0C.for 2hours.The charred material was allowed to cool to room temperature, ground and sieved into various particle sizes (0.2, 0.4, 0.6, 0.8) mm. Each of the sieved particle size material was weighed and purified by washing with 0.5M HCl solution and then rinsed three times with distilled water to remove excess acid solution. The purified material, after drying, was subjected to activation with 1M H_2SO_4. The acid treated activated carbon(AAB) was packed in an air tight sample bag with labels. Proximate analysis was carried out on AAB to determine the weight loss, bulk density, % ash content, iodine number, %volatile matter, %moisture content and fixed carbon using Standard methods [9,10]. Surface area was estimated using Sear's method [11].

A. Batch Adsorption Experiment

The adsorption experiment was carried out by batch method. 0.10g each of various particle sizes of the AAB which were earlier prepared, were collected in five different bottles each containing 10ml of phosphate rock solution. The bottles were labelled and placed in a centrifuge for agitation at a constant speed of 100rpm for 30min. after which the content was filtered and final phosphate concentration of the filtrate was determined using UV spectrophotometer set at 650nm. The same procedure was repeated for 0.2g, 0.3g, 0.4g and 0.5g dosage of AAB respectively at 30min. intervals. The influence of temperature on adsorption behavior of phosphorus onto AAB was determined at 303k,308k and 313k.

B. Adsorption Kinetics

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, six kinetic models (pseudo first order, second order, pseudo second order, BVM, Elovich and Intra particle diffusion models) were used to evaluate the behavior of AAB in phosphorus removal.

III. RESULTS AND DISCUSSION

A. *Effects of dosage on the adsorption process*

Fig.1 shows the removal efficiency of AAB as a function of time and adsorbent dosage. It also shows that the removal efficiency of AAB increases with dosage. It can be seen from the figure that at 60min. and 10g/l, 20g/l, 30g/l, 40g/l and 50g/l adsorbent dosages, the efficiencies are 94.49%, 95.15%, 95.65%, 95.99% and 96.32% respectively. At 300min.and the same dosages as stated above, the efficiencies are 97.49%, 98.08%, 98.47%, 98.99%and 99.26% respectively. The sharp increase in removal efficiency at the early stages of adsorption may be due to the availability of the active sites of AAB which were yet to be saturated by the adsorbates. It should also be noted that, as the percentage of adsorption increased with dosage, the amount adsorbed per unit mass of the adsorbent decreased. This is due to the adsorption sites remaining unsaturated during the adsorption reaction [12].

B. *Effects of particle size*

Four different particle sizes (0.2, 0.4, 0.6, 0.8) mm were used in this work and the results are graphically presented in Fig1. The figure shows that, the quantity of phosphorus removed decreased as the particle size of AAB increased. The relatively high adsorption with small particle size may be attributed to the tendency that a smaller particle produces shorter time to equilibrium [5]. The breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owning to the smaller particle size [13].

C. *Adsorption Kinetics*

a) *Pseudo first- order kinetic model*

The rate constants were determined from the slopes and intercept of the plots Ln(q_e-q_t) versus t in Fig.3 at different temperatures and the results are presented in Table2. The correlation coefficients ranged from 0.7943 to 0.8242 indicating that the data did not conform to pseudo first-order kinetic model.

b) *Second-order kinetic model*

The kinetic rate constants for second order kinetic model were evaluated from the plots of 1/(q_e-q_t) versus t. in Fig.4 and the values of the rate constants are presented in Table 2. The correlation coefficients showed that the data fitted well to the second order kinetic model.

c) *Pseudo second-order kinetic model*

From the slopes and intercepts of the plots of t/q_t versus t, in Fig.5, the rate constants of the pseudo second order kinetics were evaluated and presented inTable 2. The correlation coefficients which ranged from 0.9990 to 1.0000 obviously showed that the adsorption of phosphorus on the adsorbent AAB at temperature intervals of 303k,308k and 313k conformed to the model.

d) *Intra particle diffusion kinetic model*

Weber and Morris plot was used to describe the intra particle diffusion mechanism. The plots of adsorbate uptake q_t versus the square root of time $t^{1/2}$ are presented in Fig.6, and the calculated values of the intra particle diffusion constant K_d and δ are presented in Table 2. The deviation of straight lines from origin indicates that the intra particle transport is not the rate limiting step and that pore diffusion is the only controlling step and not film diffusion [14]. The results showed that the data did not fit well to the model.

e) *Elovich kinetic model*

The calculated coefficients from Elovich plots are presented in Table 2. The plots of q_t versus Lnt with a slope of 1/β and an intercept of 1/βLn(άβ), as presented in Fig.7 were linear with high value of correlation coefficient R^2 which ranged from 0.891.-0.9661.The values of R^2 indicated that the data fitted well to Elovich model.

f) *Bhattacharya Venkobachor Model (BVM)*

The plots of Ln[1-$U_{(t)}$] versus t are presented in Fig.8. The effective diffusion coefficient D_e was obtained at different temperatures and presented in Table 2. The high value of R^2 showed that the experimental data conformed to BVM at 313K.

IV. CONCLUSIONS.

The present study shows that acid treated activated carbon prepared from animal bone (AAB) is an effective adsorbent for the removal of phosphorus from aqueous solutions. The dependence of adsorption process on particle size, adsorbent dosage and residence time was studied and it was established that small particle size and high adsorbent dosage favoured phosphate removal by AAB. The kinetic data obtained conform to second order, pseudo second order, and Elovich kinetic model at temperatures of 303K,308K and 313K. The model fitted well to BVM at temperature of 313K only. The obtained results could be used for the design of wastewater treatment plants for the removal of phosphorus.

V. NOMENCLATURE

q_e and q_t amounts of phosphorus adsorbed at equilibrium and at time t(min.) respectively. mg/g
C_o initial concentration of phosphate, mg/l
C_t concentration of phosphate at time t, mg/l
K_1 first-order kinetic rate constant, min^{-1}
K_2 rate constant of pseudo second order adsorption, $gmg^{-1} min^{-1}$
K_B Bhattacharya Venkobachor's constant, min^{-1}
C_e concentration at equilibrium , mg/l
U_t fractional attainment of equilibrium
ά initial adsorption rate, mg/min
β Elovich constant related to sorption energy, g/mg
D_e effective diffusion coefficient, m^2/s
R^2 correlation coefficient,
δ Intra particle diffusion constant.

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Table 1: Characterization results of AAB

Parameter	AAB
Weight loss	50.18
Bulk density (g/cm^3)	0.43
% Ash content	8.18
Iodine number (mg/g)	490.73
Volatile matter (%)	21.95
Moisture content (%)	9.66
Fixed carbon	74.33
Surface area (m^2/g)	666.4

Table.2: Calculated kinetic parameters for the adsorption of phosphorus on AAB

Kinetic Model	Parameter	303K	308K	313K	Remarks
Pseudo-first **order**	K_1(min^{-1}) q_e(mg/g) R^2	0.0272 6.0091 0.8242	0.0130 2.9116 0.7943	0.0085 1.8730 0.7936	Data do not conform to pseudo-first order at any of the three temperatures .
Second order	K_2(g/mg.min) q_e(mg/g) R^2	0.0202 1.1446 0.7985	0.0181 2.1281 0.9781	0.0348 0.8736 0.9624	Data fitted well to second order at 308K, 313K
Pseudo-second order	K_2(g/mg.min) q_e(mg/g) R^2	0.0032 35.0877 1.0000	0.0032 35.0877 1.0000	0.0043 35.9712 0.9999	Data fitted well at the three temperatures
Intra-particle diffusion	K_1 δ R^2	0.5240 25.830 0.8898	0..5077 26.627 0.8756	0.4795 27.558 0.8675	Data do not conform to the model at any of the three temperatures
Elovich	α (mg/g.min) β (g/mg) R^2	1.95x10^3 0.3541 0.9661	3.29x10^3 0.3642 0.9571	6.93x10^3 0.3746 0.891	Data fitted well at 308K, 313K
Bhatacharya -Venkobachor	K_B D_2 (m^2/s) R_2	0.0066 6.68X10^{-12} 0.8901	0.0081 8.20x10^{-12} 0.8764	0.0420 4.25x10^{-11} 0.9930	Data fitted well at 313K only

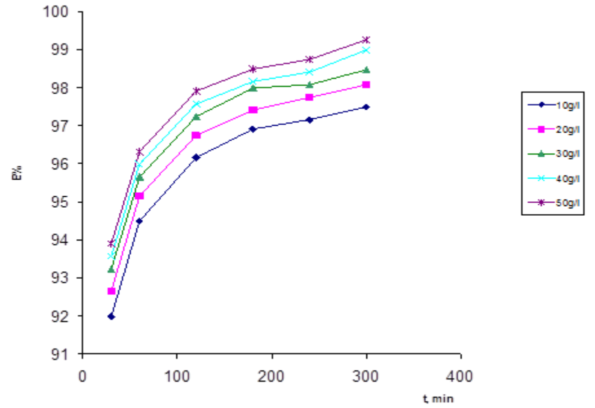

Fig.1 Removal efficiency of AAB_4 at different adsorbent concentration

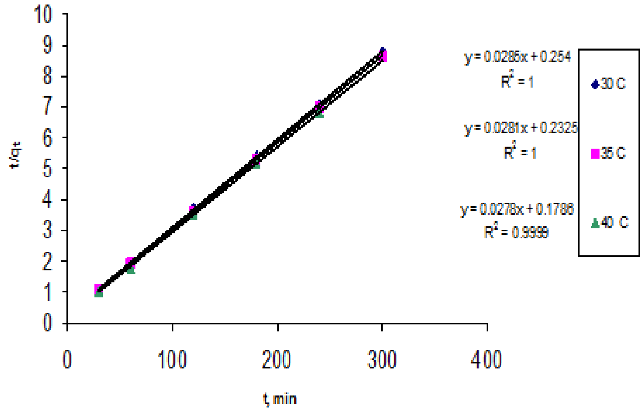

Fig.5. Pseudo second –order plot for the adsorption of phosphorus on AAB

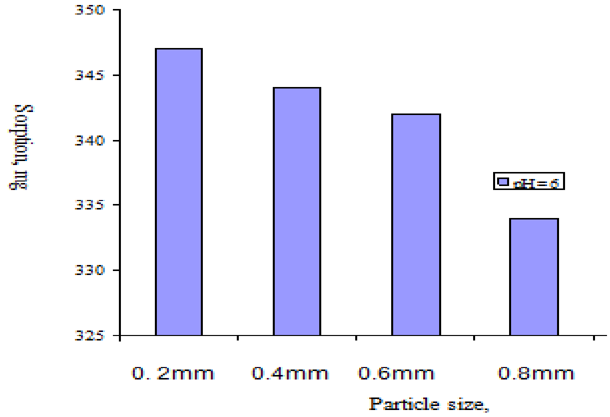

Fig.2. Removal efficiency of AAB at varying particle sizes, at 60min.and 50mg/l dosage.

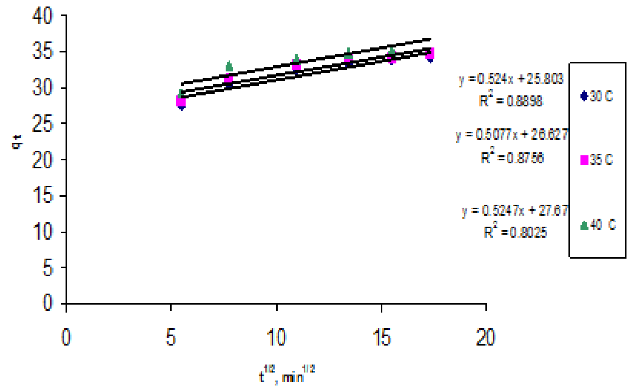

Fig.6. Intra particle diffusion plot for the adsorption of phosphorus on AAB

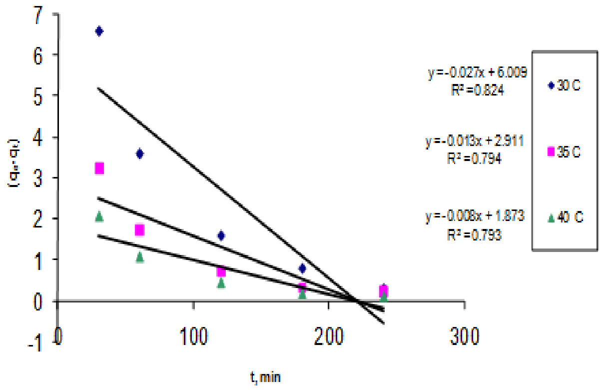

Fig. 3. Pseudo-first order plot for the adsorption of phosphorus on AAB

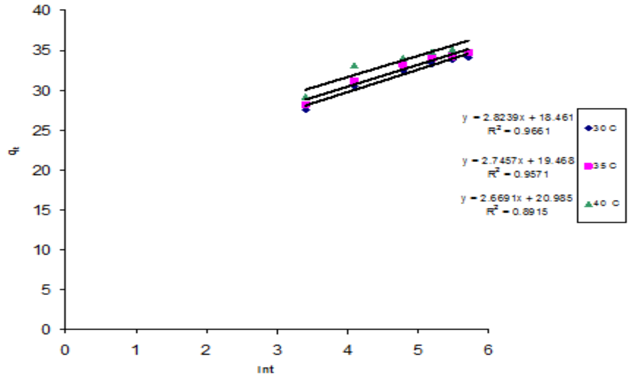

Fig.7. Elovich plot for the adsorption of phosphorus on AAB

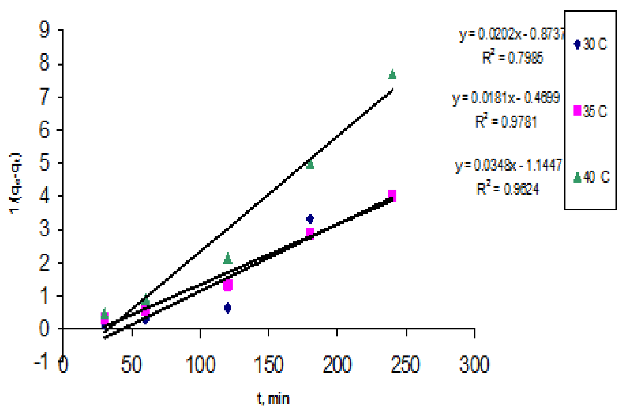

Fig.4 second-order plot for the adsorption of phosphorus on AAB

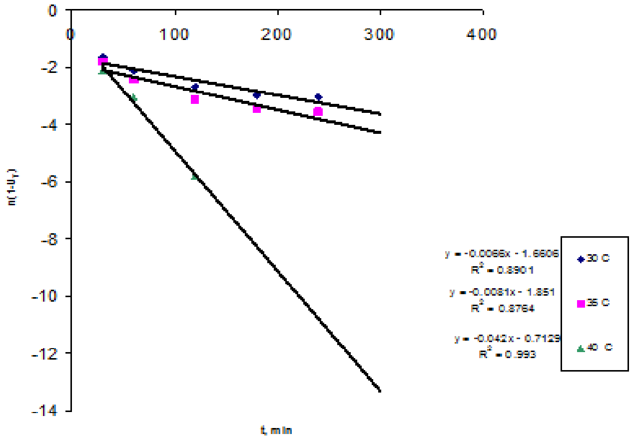

Fig.8. Bhattacharya-Venkobachor plot for the adsorption of phosphorus on AAB