

Effects of Activating Chemicals on the Adsorption Capacity of Activated Carbons Prepared from Palm Kernel Shells.

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Abstract: *This work studies the effects of H_2SO_4 , $Al_2(SO_4)_3$, NH_4Cl as activating chemicals on the adsorption capacity of activated Palm Kernel Shells (PKN). Proximate analysis was carried out on PKN. Batch mode experiments were employed to study the effects of adsorbent dosage and contact time on PKN for the removal of phosphorus from wastewater. Adsorption equilibrium data were described by Langmuir, Freundlich and Temkin Isotherms using non-linear regression analysis. Statistical modeling via Central Composite Design (CCD) for process optimization was carried out. From the obtained results, the activating chemicals can be arranged in order of increasing effectiveness thus: $NH_4 < Al_2(SO_4)_3 < H_2SO_4$. The optimization presents H_2SO_4 , among others, the best activating chemicals with a performance of 93.54%. The adsorption data were best described by Freundlich Isotherm model.*

Keywords: *activating chemicals, phosphorus, adsorption, adsorbent, activated carbon.*

I. Introduction

Environmental degradation caused by human activities has become a serious concern to many researchers worldwide. Such activities include industrial operations particularly in chemical, agricultural, textiles mining and petrochemical industries. In the course of these operations, a lot of hazardous wastes are generated and indiscriminately discharged into surface waters. These wastes contain heavy metals organic and inorganic substances such as Nickel, Chromium, Lead, Zinc, Arsenic, Cadmium, Phosphate, Chloride and Nitrate to mention but few [1,2,3]. The presence of these contaminants in the receiving waters might cause health hazards to a large segment of the population in addition to loss of many aquatic animals. Many researchers [4,5,6,7,8,9,10] have done a great work in removing heavy metals from wastewaters, however it is imperative to find an effective method to equally remove nutrients particularly phosphorus from wastewater because of its dangerous effects on the water bodies. One of the resulting effects is eutrophication. It is described as the excessive growth of algae, which leads to the depletion of dissolved oxygen in water and consequently death and reduction in aquatic fish and other animal population [11]. Against this background, an activated carbon prepared from palm kernel shells has been adopted for the removal of phosphorus from wastewater through the process of adsorption. In a further search for highly effective activated carbons, chemical activation was introduced using three different activating chemicals and a comparison was made among them to know which of them would enhance the performance of the adsorbents.

II. Materials And Methods

Palm Kernel Shells were obtained from Ihiala, Anambra State. The shells were washed of the accompanying dirt and thereafter, dried in an oven at $110^{\circ}C$ for 24 hrs. The dried sample was then carbonized in a muffle furnace at a temperature of $800^{\circ}C$ for 3 hrs. The carbonized material was allowed to cool to room temperature, ground and sieved using 0.2mm mesh. 20g of the sieved fractions was added into each of three separate beakers containing 200ml 1M H_2SO_4 , 1M $Al_2(SO_4)_3$ and 1M NH_4Cl respectively for 12 hrs. Impregnating the carbonized material in the activating chemicals was to open up and activate the pore surfaces of the carbon for effective adsorption. The impregnated sample was washed with de-ionized water until pH7, filtered and dried in an oven at $1110^{\circ}C$ for 24 hrs before being packed in an air tight sample bags for use. Proximate analysis was carried out on the activated PKN to determine the % weight loss, bulk density (g/cm^3), % moisture content, % volatile matter, % fixed carbon and iodine number using standard method [12,13]. Surface area of the PKN was determined using Sear's Method [3,14].

Batch Adsorption Experiment

The effluent used was synthesized using phosphate rock obtained from Federal Superphosphate Fertilizer Company, Kaduna, Nigeria. The initial pH of the effluent was measured with a digital pH meter and recorded. 1.0g of the PKN activated with H_2SO_4 was added into the beaker containing 100ml of the prepared effluent and placed on a magnetic stirrer. Stirring was done at 30 mins, 60 mins, 120 mins, 180 mins, 240 mins and 300 mins respectively. Upon the completion of each stirring period, the solution was filtered and the residual concentration of the filtrate was determined using UV-spectrophotometer set at a wavelength of 650nm [11]. The same procedure was repeated for 2.0g, 3.0g, 4.0g and 5.0g of the adsorbent.

III. Results And Discussion

The characterization results of PKN are presented in Table 1. It was evident from the obtained results that activating chemicals have effects on the surface area of the adsorbents. The same PKN exhibiting different surface area as a result of different activating chemicals used. The higher surface area provided by the acid treated PKN is due to the significant removal of organic by-products and minerals present in the activated carbon surface during activation [11,15].

Effects of dosage and contact time

The profiles of removal efficiency (E%) as a function of time at varied dosage of PKN activated with H₂SO₄, Al₂(SO₄)₃ and NH₄Cl respectively are presented in Fig.1-3. E% for the three activating chemicals increased with time as well as with increasing dosages. However, it is worth noting that at the same contact time, the adsorption capacities of the various activated PKN differ. The contact time of 120 mins, dosage of 50g/l, E% = 96.99 for H₂SO₄ as presented in Fig. 1. Also, at the same contact time and dosage, E% for Al₂(SO₄)₃ and NH₄Cl are 96.41 and 95.82 respectively. This is an indication that, types of activating chemicals used for modification of adsorbent's surface play very important roles in enhancing their adsorption capacities.

Non-Linear Isotherm Model

The equilibrium concentration data and the amount of adsorption were fitted to Freundlich, Langmuir and Temkin Isotherms using the non-linear regression analysis of the curve fitting tool box of MATLAB 7.0. The numerical fit results are graphically presented in Fig. 4-6. It was evident from the results of the analysis that, the equilibrium data were best described by Freundlich Isotherm model.

Statistical Modeling and Optimization

The model fit for the adsorption process after deleting the insignificant interacting factors, is given as:

$$Y_{H_2SO_4} = 105.6181 - 0.0502x_1 - 28.3824x_2 - 0.0002x_1x_2 + 0.00024x_1^2 + 3.4835x_2^2$$

$$Y_{Al_2(SO_4)_3} = 107.9945 - 0.0587x_1 - 26.7049x_2 - 0.0019x_1x_2 + 0.000033x_1^2 + 3.3631x_2^2$$

$$Y_{NH_4Cl} = 111.5956 - 0.0687x_1 - 25.8122x_2 - 0.0031x_1x_2 + 0.000043x_1^2 + 3.3870x_2^2$$

Where $Y_{H_2SO_4}$, $Y_{Al_2(SO_4)_3}$, Y_{NH_4Cl} are the dependent variables representing the amount of phosphorus adsorbed per gram of PKN activated with H₂SO₄, Al₂(SO₄)₃ and NH₄Cl respectively. x_1 , x_2 are the independent variables representing dosage and contact time respectively.

In all cases of the activated PKN, the model accuracy is validated by the values of $R^2 > 0.9$ and Adj. $R^2 > 0.9$ and the closeness of the predicted values to the actual experimental values as presented in Fig. 7 – 9.

The main attribute to effective performance of PKN as adsorbent is its residence time. This agrees with the surface plots that show a quadratic profile with time as presented in Fig. 10 – 12. The optimization of surface response model reveals that PKN (H₂SO₄) reduced the phosphorus concentration in the effluent from 373mg/l to 24.1038mg/l, a performance of 93.54%, PKN (Al₂(SO₄)₃) reduced the phosphorus contaminants from 373 mg/l to 29.1313 mg/l giving a performance of 92.19% while PKN (NH₄Cl), has the least performance of 90.47%. Activating chemicals used in this research work can thus, be arranged in the order of decreasing effectiveness: H₂SO₄ > Al₂(SO₄)₃ > NH₄Cl

IV. Conclusion

Among the three activating chemicals considered in this study, H₂SO₄ was found the most effective. PKN activated with H₂SO has a performance of 93.54% while NH₄Cl was the least effective. The adsorption data were best described by Freundlich Isotherm Model.

Above all, this work has revealed that Palm Kernel Shell being an agricultural waste could be converted to useful and efficient adsorbent through the use of activating chemicals, particularly H₂SO₄.

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Table 1: Characterization Results of PKN

| Parameter | Activating chemicals | | |
|-----------------------------------|--------------------------------|---|--------------------|
| | H ₂ SO ₄ | Al ₂ (SO ₄) ₃ | NH ₄ Cl |
| % weight loss | 35.38 | 38.07 | 44.79 |
| Bulk density (g/cm ³) | 0.48 | 0.55 | 0.58 |
| % Ash content | 6.33 | 5.38 | 5.00 |
| Iodine number (mg/g) | 558.06 | 474.35 | 440.86 |
| Volatile matter (%) | 17.74 | 18.37 | 18.94 |
| Moisture content (%) | 5.81 | 5.98 | 6.01 |
| Fixed carbon | 75.28 | 63.99 | 59.47 |
| Surface area | 635.73 | 569.37 | 529.25 |

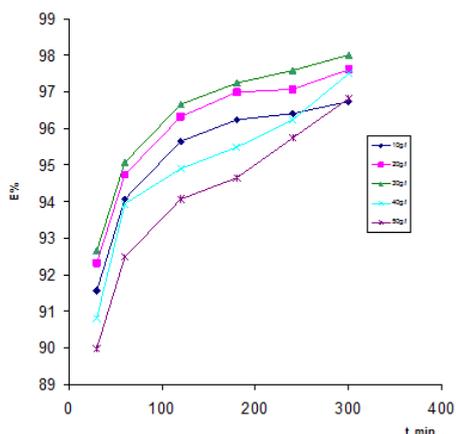


Fig. 1: Removal efficiency of PKN activated with H₂SO₄ at different adsorbent concentration

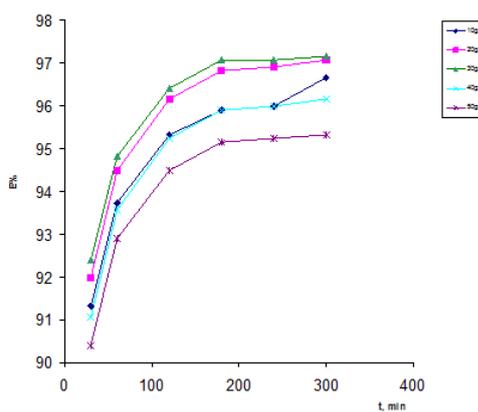


Fig. 2: Removal efficiency of PKN activated with Al₂(SO₄)₃ at different adsorbent concentration

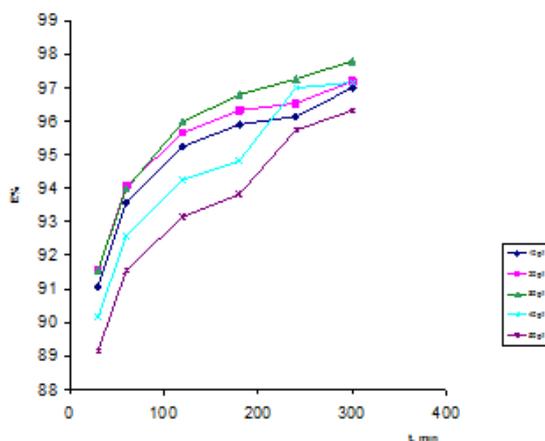


Fig. 3: Removal efficiency of PKN activated with NH₄Cl H₂SO₄

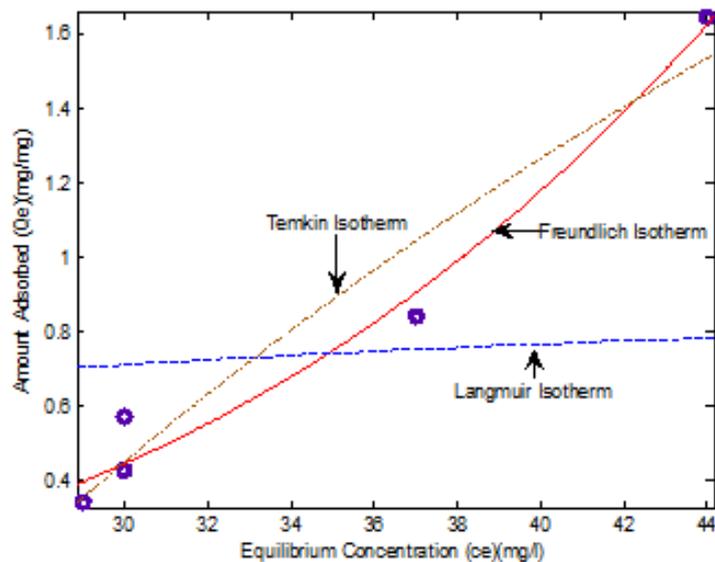


Fig. 4: Isotherm plot for fit to PKN activated with at different adsorbent concentration

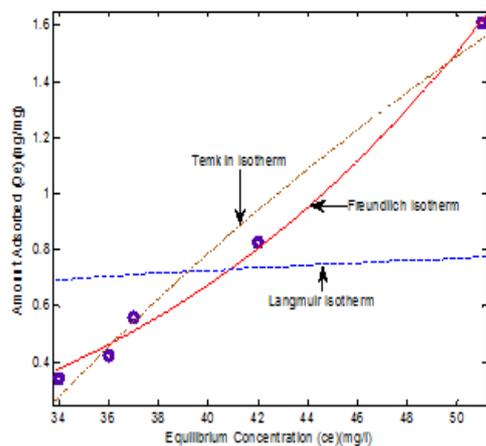


Fig.5: Isotherm plot for fit to PKN activated with $Al_2(SO_4)_3$

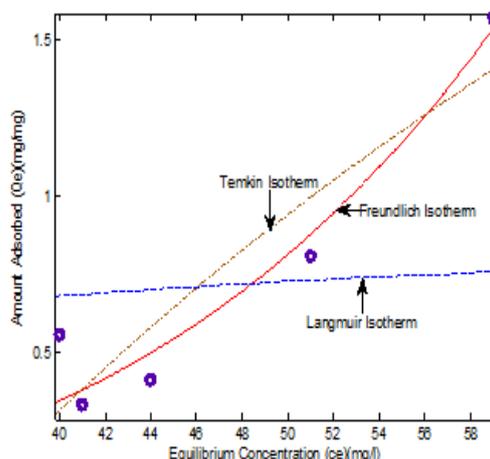


Fig.6: Isotherm plot for fit to PKN activated with NH_4Cl

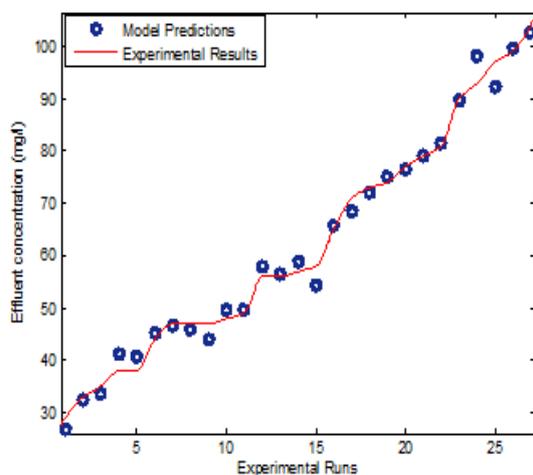


Fig.7: Experimental vs. Model Predictions for PKN activated with H_2SO_4

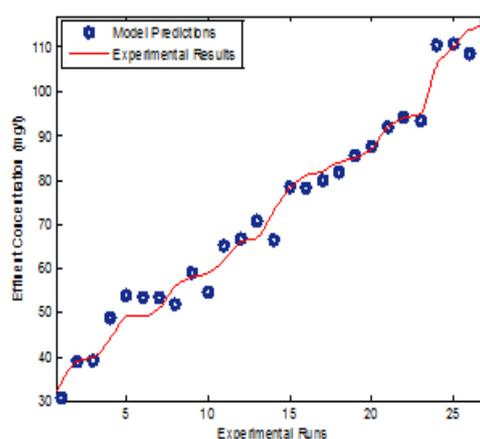


Fig.8: Experimental vs. Model Predictions for PKN activated with $Al_2(SO_4)_3$

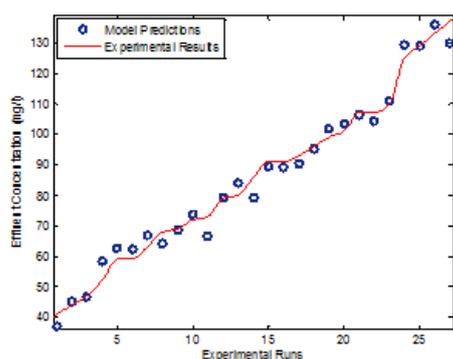


Fig. 9: Experimental vs. Model Predictions for PKN activated with NH_4Cl

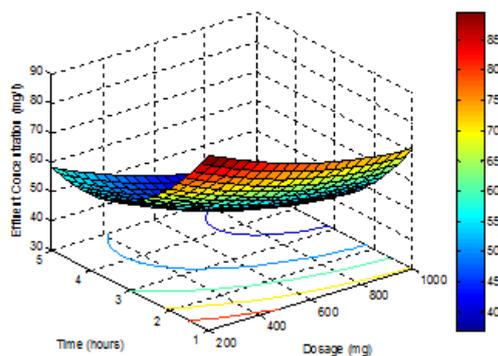


Fig. 10: 3-D Surface response Plot for PKN activated with H_2SO_4

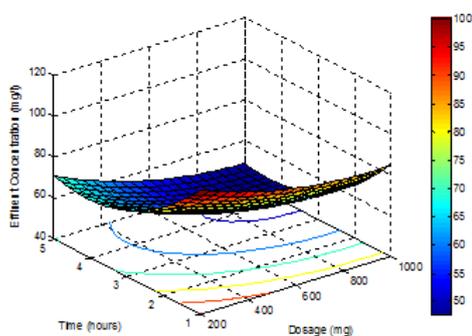


Fig. 11: 3-D Surface response Plot for PKN activated with $\text{Al}_2(\text{SO}_4)_3$

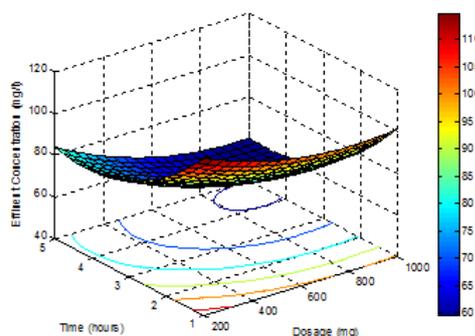


Fig. 12: 3-D Surface response Plot for PKN activated with NH_4Cl