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# Freundlich Adsorption Isotherms of Adsorbent from $H_3PO_4$ and $ZnCl_2$ Treated Irish Potato Peels.

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**ABSTRACT:** Activated carbon from irish potato peels, treated with $H_3PO_4$ and $ZnCl_2$ were prepared using the one and two stage processes. The study was designed to model the adsorption of a dye, methylene blue, using the Freundlich isotherm model. Both acid and salt catalyzed carbon presented favorable adsorption, with Freundlich constant values, n < 1. The adsorption capacities (k), intensities (1/ n) and correlation ($R^2$) values for the applicability of the model all compared favorably well with those of reference commercially available activated carbon.
**Keywords:** Freundlich, activated carbon, adsorption intensities, adsorption capacities, Irish potato.

## INTRODUCTION

The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherm. It is usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature and at equilibrium (Nur *et al*, 1998).Adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in the test medium at equilibrium (Chilton *et al.*, 2002).

Herbert Max Finley Freundlich,a German physical chemist, presented an empirical adsorption model for a non ideal system in 1906.The Freundlich isotherm is the earliest relationship describing the adsorption equation for a single solute system based on the distribution of adsorbate between the solid phase adsorbent and aqueous phase at equilibrium (Nur *et al* ,1998).The isotherm provides a panorama of the course taken by the system under study and indicates how efficiently the adsorbent will adsorb and allows an estimate of its economic feasibility (Chilton *et al*,2002). Freundlich isotherm is often described as;

$$X/m = k_f C^{1/n} \quad (i)$$

Where $x/m = q_e =$ the adsorption density (mg of the adsorbate per g of adsorbent, which is a measure of the amount of dye adsorbed). C is the concentration of adsorbate in solution ($mgl^{-1}$) (Malik *et al*, 2007).

It is also called the equilibrium liquid concentration of methylene blue or adsorbate. The $K_f$ and 1/n are empirical constants with 1/n>1. The n value < 1 is an indication of favourable adsorption (Ribeiro *et al*, 2001). It stands for the adsorption intensity which can also be expressed as 1/n. $K_f$ is the adsorption capacity (Malik *et al*, 2007). The Freundlich equation is conveniently used in a linear form by taking the logarithmic of both sides as

$$\text{Log } q_e = \log k_f + 1/n \log C \quad (ii)$$

A plot of log $q_e$ against log C yield a straight line that indicates the applicability of the Freundlich model if the regression correlation values ($R^2$) is close to unity. The constants are determined from the slope (1/n) and intercept (log k).

## MATERIALS AND METHODS

Irish potato peels were randomly obtained from waste baskets of the various restaurants around the main campus of the Usmanu Danfodiyo University, Sokoto. The samples were properly washed, sundried and later dried in an oven at 100°C overnight (Omomnhenle *et al*., 2006). The samples were pounded and pulverized, using <2mm and <0.5mm sieves. Methylene blue was used as adsorbate without further purification.

**Activation**

A one and two stage chemical activation procedures by Turoti *et al*, 2007 were modified. Dwell time activation of 5 and 10 minutes were separately carried out to investigate the effect of activation dwell time. After activation, the samples were cooled with ice cold water (Turoti *et al*, 2007). Washing methods by Malik *et al*, (2007) were adopted. The Samples were washed with 1:1 HCl followed by hot water to remove impregnated chemicals (ash, chlorides, and residual acids). The washed samples were finally rinsed with distilled water until a pH between 6 and 8 was reached (Malik *et al*, 2007). The samples were sun dried and later kept in a Gallenkamp size two oven at 110$^o$C overnight (Fan *et al*, 2003). Percentage yield was calculated as;

$$\% \text{ yield} = w_1/w_o \times 100 \quad \text{(iii)}$$

Where $W_o$ and $W_1$ are the weight of the samples (g) when raw and activated respectively (Yulu *et al*, 2001).

**Batch Adsorption Test:**

The method developed by Omomnhenle *et al*. (2006) was modified for the batch adsorption studies as follows;

- 0.1g of the irish potato peels carbon (adsorbent) was interacted with 10 $cm^3$ of methylene blue solution. The concentration of adsorbent was 10g/$dm^3$
- The conical flask containing the mixture was capped and allowed to stand for 24 hours to attain equilibration
- Five (5) different concentrations of working solutions from the 1200 mg/$dm^3$ methylene blue stock were further prepared by further dilution to obtain ranges of concentrations (between 10 to 50 mg/$dm^3$).
- The separately interacted samples were filtered after 24 hours, using 540 mm Whatman filter paper and the absorbance was taken using the 610 Jenway model spectrophotometer
- Each experiment was done in triplicate under identical condition and the % $q_e$ was calculated as;

$$\% q_e = (C_o - C_e)\, V/W \times 100 \quad \text{(iv)}$$

Where $q_e$ = amount of dye adsorbed ($mgg^{-1}$), $C_o$ and $C_e$ ($mgl^{-1}$) are the initial and final liquid phase equilibrium respectively.**V** ($cm^3$) is the volume of dye solution (10 $cm^3$) and W (g) is the adsorbent dose (0.1g) (Hameed *et al*, 2007).

- Log $q_e$ against log $C_e$ were plotted.

**RESULTS AND DISCUSSIONS**

To establish the adsorption isotherm and evaluate the adsorption capacity, intensities and applicability of the model, values were tested and results presented in Tables 1-3 as the average of three sets of test.

Ioannidou and Zabaniou (1996) defined burn off as the weight difference between the raw sample (Wo) and activated sample, ($W_1$) divided by the weight of the raw sample. Table 1a and b presented higher values for the samples activated at longer dwell time with corresponding lower yield. The % burn off for the two stage method was based on the weight of char ($W_o$), hence, low values were reported (14.02-31.20 %) on table 1b. The expected low % yield with a corresponding high burn off is more feasible for the one stage process (Martinez *et al*, 2006). It was therefore evident that at longer dwell time, more volatiles are released from the char thereby resulting in a higher burn off with reduced yield (Ahmedna *et al*, 2000).

Table 2 revealed that the nature of the activating agent has no significant role on the amount of dye adsorbed. Both acid and salt-catalyzed adsorbent gave over 90 % $q_e$.This however is not true at low initial methylene blue concentrations, between 10 – 20 mg/l,where the $H_3PO_4$ catalyzed irish potato peel carbon gave higher % $q_e$ for both 5 and 10 minutes activation dwell time. At extremely high (50mg/l) methylene blue concentration, the $ZnCl_2$ catalyzed adsorbent presented higher values. i.e. 95.20% (95.80) % for IP/$H_3PO_4$/5 (IP/$ZnCl_2$/5) and 95.40% (97.00%) for IP/$H_3PO_4$/10 (IP/$ZnCl_2$/10).

The results of the methylene blue adsorption studies are presented as isotherms (Fig. 1 – 8) and the values for the slopes (1/n, given as n) and

intercept (log k) of the linear regression lines are reported in table 3. The n values (which were all less than unity) fall within the range reported for favourable adsorption. i.e. n<1(Turoti *et al*, 2007). The fact that the regression coefficients were very close to 1 also indicates good linearity and applicability of the model (Nur *et al*, 1998).

The log K values, an indication of adsorption capacities for < 0.5mm IP carbon (3.78 -5.25) is closer to that of commercial carbon (3.40) than it does by the <2mm IP carbon (4.57 -23.16).

The data on Table 3 is a summary of the linear equations obtained from the Freundlich isotherms and their correlation coefficients. The <2mm carbon presented higher adsorption intensities (1/n) than their corresponding <0.5mm carbon. This therefore implies that grain size plays a great role and is critical for this study. Generally, high adsorption capacity is expected for lower grain size carbon as obtained for the commercial carbon. Same trend was observed for IP/$H_3PO_4$/10.This implies that the <0.5mm grain size carbon experienced steric hindrances for the concentrations to a higher extent (Valix *et al*, 2004). The data obtained in this work is in close agreement with those obtained for cassava peels which revealed that activation time at such close range has no significant effect on adsorption properties (Sudaryanto *et al*, 2006).

**Table 1a:** Percentage burn off, % yield and bulk density of Irish potato carbon generated using the one stage scheme.

| Samples | Activation burn off (%) | Yield (%) | Bulk density ($glcm^3$) |
|---|---|---|---|
| IP /$H_3PO_4$/5 | 65.60 | 34.40 | 1.093 |
| IP /$H_3PO_4$/10 | 69.60 | 30.40 | 1.051 |
| IP /$ZnCl_2$/5 | 68.68 | 31.32 | 1.072 |
| IP /$ZnCl_2$/10 | 71.20 | 28.80 | 1.041 |

IP /$H_3PO_4$/5 – irish potato carbon modified with $H_3PO_4$ at 5 minutes activation time.

**Table 1 b:** Percentage burn off, % yield and Bulk density of Irish potato carbon, generated, using two stage scheme.

| Sample | Activation burn off (%) | Yield (%) | Bulk density ($glcm^3$) |
|---|---|---|---|
| IP /$H_3PO_4$/5 | 21.04 | 78.96 | 1.080 |
| IP /$H_3PO_4$/10 | 18.67 | 81.33 | 1.066 |
| IP /$ZnCl_2$/5 | 14.02 | 85.98 | 1.074 |
| IP /$ZnCl_2$/10 | 31.20 | 68.80 | 1.062 |

**Table 2:** Amount of dye adsorbed (%qe) by $H_3PO_4$ and $ZnCl_2$ catalyzed <2mm mesh size Irish potato carbon, using one stage process

| **Mass of MB per dose (mg/g)** | **% qe IP/$H_3PO_4$/5** | **% qe IP/$H_3PO_4$/10** | % qe **IP/$ZnCl_2$/5** | **% qe IP/$ZnCl_2$/10** |
|---|---|---|---|---|
| 1.0 | 96.00 | 95.00 | 93.00 | 93.00 |
| 1.5 | 98.66 | 98.00 | 95.00 | 95.00 |
| 2.0 | 99.00 | 98.00 | 98.00 | 98.5 |
| 2.5 | 98.00 | 97.20 | 98.00 | 97.60 |
| 5.0 | 95.20 | 95.40 | 95.80 | 97.00 |

MB – methylene blue

**Table 3:** Freundlich constants of methylene blue adsorption onto chemically treated <2mm and (<0.5mm) irish potato peels carbon.

| Contents | Samples | | | | |
|---|---|---|---|---|---|
| | **Com** | **IP/$H_3PO_4$/5** | **IP/$H_3PO_4$/10** | **IP/$ZnCl_2$/5** | **IP/$ZnCl_2$/10** |
| **1/n** | 5.73(3.21) | 17.20 (5.24) | 6.35 (5.11) | 2316 (2.41) | 4.57 (4.26) |
| **Log k** | 1.83(3.40) | 11.87 (4.92) | 4.68 (4.82) | 10.97 ( 5.25) | 5.53 (3.78) |
| **$R^2$** | 0.99(0.90) | 0.88 (0.91) | 0.91 (0.95) | 0.91 (0.92) | 0.94) (0.91) |
| **n** | 0.17(0.31) | 0.06(0.91) | 0.16(0.20) | 0.04(0.20) | 0.22(0.23) |

NB: values for <0.5mm mesh size are enclosed in brackets.

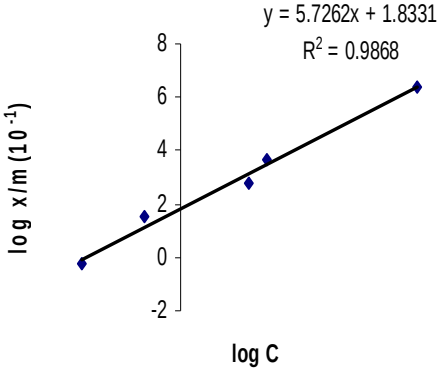


**Fig. 1:** Freundlich adsorption isotherm of < 2 mm commercial AC

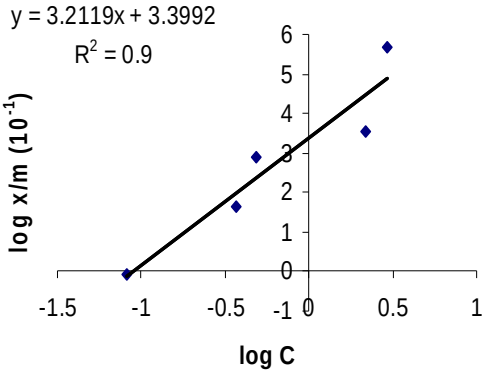


**Fig. 2:** Freundlich adsorption isotherm of < 0.5 mm commercial AC on MB

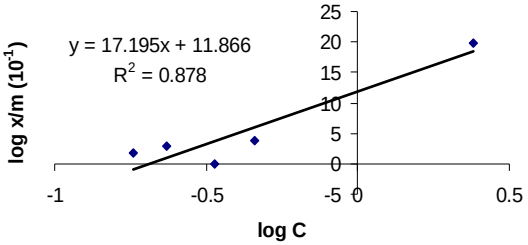


**Fig. 3:** Freundlich adsorption isotherm of < 2 mm commercial IP/$H_3PO_4$/5 on MB

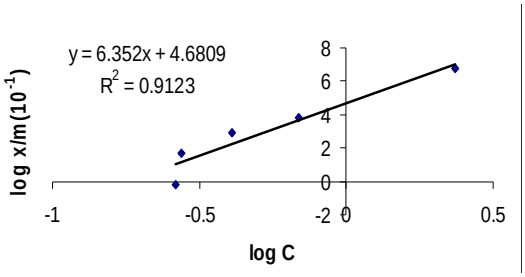


**Fig. 4:** Freundlich adsorption isotherm of < 2 mm commercial IP/$H_3PO_4$/10 on MB

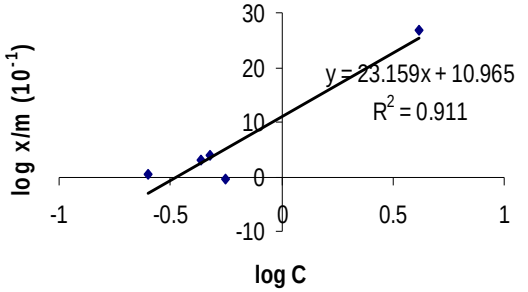


**Fig. 5:** Freundlich adsorption isotherm of < 2 mm IP/$ZnCl_2$/5 on MB

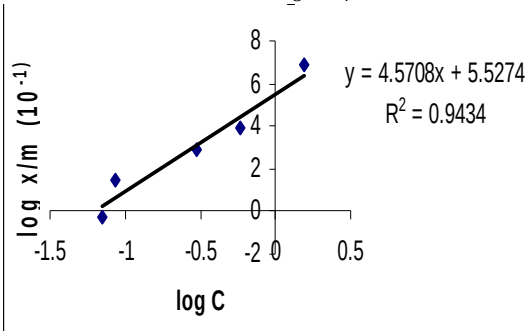


**Fig. 6:** Freundlich adsorption isotherm of < 2 mm IP/$ZnCl_2$/10 on MB

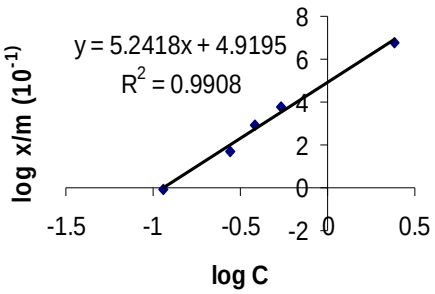


**Fig. 7:** Freundlich adsorption isotherm of < 0.5 mm IP/$H_3PO_4$/5 on MB

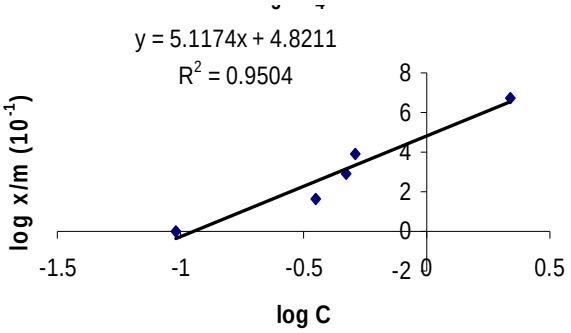


**Fig. 10:** Freundlich adsorption isotherm of < 0.5 mm IP/$H_3PO_4$/10 on MB

MB = Methylene blue AC = Activated carbon

## CONCLUSION

This research work was build on earlier work by Sudaryanto *et al*. (2006) which has shown that peels of tuber crops are critical for use as adsorbent. The data generated fitted well into the Freundlich model, indicating favourable adsorption (n<1). The adsorption intensities, capacities and regression correlation coefficients compete well with those of the commercial reference with a more pronounced role of grain sizes. The significance of grain size was reportedly more pronounced on the adsorption intensities (1/n) than its capacities. Both activating agents were complementarily good with the batch method at 24 hours contact time. The pour through Interaction process where the activated carbon serves as both adsorbent and as molecular sieves, using columns is therefore recommended.

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