Characterization of Date Pits Activated Carbon Adsorbent Using Adsorption Isotherm

Adeola G. Olugbenga[1], Abubakar Mohammed[2*], Clement B. Arowosola[3]
[1]Department of Chemical Engineering, Federal University of Technology Minna, Nigeria
[2]School of Mechanical Engineering, University of Leeds, Leeds, United Kingdom
[3]Department of Chemical Engineering,Abubakar TafawaBalewa University, Bauchi, Nigeria

Abstract- **Date Pits Activated carbon has been characterized using adsorption Isotherms. Batch adsorption was carried out by transient adsorption of a solute from a dilute solution which was made to be of a constant volume, well-mixed batch system. The chromium VI particles initially were of uniform adsorbate concentration and later successful step change in concentration of the external fluid. The adsorption rate shows that the adsorbents are highly porous materials and adsorption takes place at specific sites inside the particle. The pores were generally very small, the internal surface area has orders of magnitude greater than the external area and it was $500m^2/g$ to $1000m^2/g$. it provides a useful conclusion that the separation that occurs because the difference in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. the adsorbing component or adsorbate was found to be held strongly enough to permit data collection for plotting isotherm curves for the chromium VI ions from the fluid with very little adsorption of other components permitting possible regeneration. The adsorption data was well described by Freundlich isotherm**.

Keywords-CAC, DPAC, Adsorption Isotherm,

I. INTRODUCTION

Adsorption occurs in many natural biological, physical, biochemical and allied chemical systems. It is used for water purification. Synthetic resins and activated carbon are used to carry out adsorption processes. Industrial wastewater purification uses adsorption processes [1]. Activated charcoal or activated carbon is a form of carbon that has been calcined to make it very porous and have a very large surface area available for adsorption or chemical reactions. The activated carbon can be made from carbonaceous material including coal (bituminous, sub-bituminous and lignite), peat, wood or nutshells (coconut) [2]. The reason that activated carbon is such an effective adsorbent material is due to its large number of cavernous pores. These provide a large surface area relative to the size of the actual carbon particle and its porous surface on the outside. An approximate ratio of 1 gram = $100m^2$ of surface area was achieved by Kvech[3].

In environmental engineering and specifically drinking water treatment application, the most commonly used isotherm is the Freundlich isotherm [3]. Activated carbons are complex products which are difficult to classify on the basis of their behaviour, as well as surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics such as powdered activated carbon, extruded activated carbon, impregnated carbon, polymer coated carbon and the granulated activated carbon which is the most effective in industrial effluent treatment. In Nigeria today, industrial growth is high and the emission of toxic metals into the environment through effluents is at an alarming rate. It is anticipated that isotherm provided in this work will contribute largely to abate the environmental pollution caused by the toxic Cr (VI) ions in industrial wastewater, since it is known to be carcinogenic. Chromium VI poses a serious threat to the human health and the ecosystem. Amazingly the solution to this threat is not far from the same community, in the Savannah region of Nigeria, palm dates are produced and commonly consumed in large quantity. The pits are disposed as load waste causing environmental nuisance. Adsorption reactions using these adsorbent is reported here to follow a Freundlich Isotherm. Isotherm has been used to provide the dose of carbon required for treatment whenever equilibrium is reached. In concurrently similar contacting processes, the capacity is set by the required effluent concentration whereas for counter-current processes, the capacity of the carbon is set by the untreated waste pollutant concentration. Thus, counter-current contacting was preferred [4].

Paying particular attention to the water pollution in Nigeria, adsorption contacting systems has been applied to industrial and municipal wastewater treatment from time immemorial without an understanding of the process and in the reports on processes of adsorption of the components of a fluid mixture in a packed bed of an adsorbent porous material reported by Babu et al[5], the adsorbent characterization has been neglected. This has prevented a proper understanding of its applicability and effectiveness of commercial and locally produced activated carbon. Also in Nigeria, some manufacturers cannot often provide adsorption isotherms for their products [2]. Some typical isothermal shapes are the arithmetic graph. Although their linear isotherm goes through the origin and the adsorption is proportional to the concentration of ions in the fluid. But

it is more desirable that isotherms should be convex upward because they are favourable as a relatively high solid loading will be achieved at low concentration in the fluid [6]. Thus, the aim of this research is to develop Date Pit Activated Carbon (DPAC) and define the adsorption isotherm so as to propose its maximum attainable sorption of chromium VI on the surface of PDAC to industries requiring its applications in Nigeria. A first attempt to understanding the effectiveness of the Nigeria Date Pits Activated Isotherm has to do with the adsorbent development. Olugbenga et al [7] recently studied the effect of contact time and metal ion concentration on the adsorption of Cr (VI) on palm date pits activated carbon (DPAC) and compared it with commercial activated carbon (CAC). They observed that the percentage removal increased with the increased contact time and reached its peak at 30 minutes and 75 minutes after which bleeding occurred for DPAC, while for CAC, the peak time was only at 30 minutes. Although a high adsorption density also occurred at 75 minutes, after which bleeding also occurred. They also observed that at low ion concentration, the adsorption density for DPAC is greater than thatof CAC. However, as the ion concentration increases above 22 mg/L, the adsorption density for CAC is greater than DPAC.

In this work the adsorption process has been clearly characterized by the isotherm defining the sorption of chromium VI present in the Kaduna wax textile industrial company effluent. The sorption processes involve the transfer of chromium VI from resulting equilibrium of one or more chromium ion between its fluid phase and Date Pit Activated Carbon. The adsorption process was successful because of the observed partitioning of the chromium VI in the fluid and sorbed phases towards multiple. It is Similar to surface tension exhibiting surface energy. The effluent contaminated with chromium VI and some solute contains ionic, covalent or metallic bonds of all the constituent atoms. Therefore atoms on the surface of the adsorbent are not entirely surrounded by other adsorbent atoms as such they can attract adsorbates. The true nature of the bonds relies on the specific species involved, the adsorption process is said to be physisorption because of weak Van der Waals forces. The binding to the surface is usually weak, therefore it's reversible. Just about anything including the fluid that dissolves or suspend the material of interest is bound, but compounds with colour and those that have taste or odour tend to bind strongly. Compounds that contain chromogenic groups (atomic arrangements that vibrate frequencies in the visible spectrum) very often are strongly adsorbed on activated carbon. Decolourization can be wonderfully efficient by adsorption and with negligible loss of other materials [8].

In batch adsorption, the solutions provided can approximate the response of a stirred vessel containing suspended adsorbent particles or that of a very short adsorption bed. Uniform spherical particles of radius r_p are assumed. These particles initially of uniform adsorbate concentration are assumed to be exposed to a step change in concentration of the external fluid [4, 6]. Industrial adsorbents fall into one of the three classes. Equilibriums

of adsorptions and their kinetics are important physiochemical aspects for the evaluation of adsorption process while the equilibrium studies give the capacity of the adsorbent its relationships between adsorbent and adsorbate are explained by adsorption isotherms [9]. The adsorption isotherm is the relationship of fluid phase and adsorbent particles concentrations at constant temperature [6].

Impregnated porous carbons containing several types of inorganic impregnate such as iodine, silver, cation (ie. Al, Mn, Zn, Fe, Li, Ca) have also been prepared for specific application in air pollution control especially in museums and galleries. For granular activated carbon (GAC), a relatively larger particle size compared to powdered activated carbon and consequently presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. Since carbons are preferred for all adsorption of particles in fluids because they are diffusion controlled.

II. THEORY
A. Adsorption Isotherms
The Freundlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption sites adsorbs molecules as in the Langmuir equation. The Freundlich isotherm equation is the most widely used.

$$\frac{x}{m} = KC^{\frac{1}{n}} \tag{1}$$

Where, x is the amount of solute adsorbed (g), m is the mass of adsorbent (g), C is concentration of solute remaining in solution after adsorption is completed at equilibrium (mg/L), K and n are constants that must be determined for each solute, carbon type and temperature.

Langmuir isotherm
Irving Langmuir, an American chemist who was awarded the Nobel Prize for chemistry in 1932 for his discoveries and researches in the realm of surface chemistry developed a relationship between the amount of gas adsorbed on surface and the pressure of that gas. Such equations are now referred to as Langmuir adsorption isotherms, a theoretical adsorption isotherm in the ideal case. The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. It is perhaps the best known of all isotherms describing adsorption and is often expressed as [2];

$$Q_c = \frac{X_m K C_e}{(1 + K C_e)} \tag{2}$$

Where, Q_e is the adsorption density at the equilibrium solute concentration, C_e is the concentration of adsorbate in solution (mg/L), X_m is the maximum adsorption capacity corresponding to complete monolayer coverage, K is the Langmuir constant related to energy of adsorption.

The above equation 2 can be rearranged to the following linear form:

$$C_e/Q_e = 1/X_m K + C_e/X_m \qquad (3)$$

The linear form can be used for linearization of experimental data by plotting C_e/Q_e against C_e. The Langmuir constants X_m and K can be evaluated from the slope and intercept of the linear equation.

Freundlich isotherm
Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and it is often expressed as;

$$Q_e = K_f C_e^{1/n} \qquad (4)$$

Where, Q_e is the adsorption density, C_e is the concentration of adsorbate in solution (mg/L), K_f and n are the empirical constants dependent on several environmentalfactors and n is greater than one.

Equation (4) is conveniently used in the linear form by taking the logarithm of both sides as;

$$ln Q_e = ln K_f + 1/n \, ln C_e \qquad (5)$$

A plot of $ln C_e$ against $ln Q_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept [9].

III. METHODOLOGY

A. Materials and Methods
The commercial activated carbon (CAC) is obtained from the market. Chromium rich effluent was obtained from Challawa industrial area effluent Kano State the solution rich of chromium (VI) concentrated in the laboratory by futher addition chromium VI ions prepared in the laboratory by dissolution of $K_2Cr_2O_7$ with distilled water was collected from the Gubi dam water works, Bauchi state, Nigeria. The stock solution (1000mg/L) of Cr (VI) was prepared by dissolving 2.8g of $K_2Cr_2O_7$ into 1 litre of distilled water. 100mg/L stock solution is thus prepared from the 1000mg/L as the preferred stock solution in 100ml of distilled water. A series of flasks containing the respective solutions of varying concentrations from 5–25 mg/L was prepared from the stock solution. Adjustment of pH is carried out using NaOH. Agitation of the system under investigation is carried out using a magnetic stirrer at 300rpm [10].

The palm dates fruits were obtained from the market and the pits were removed from it. The production of activated carbon is one of the most important aspects of this study and the following procedure. The palm date pits were washed with distilled water in other to remove all dirt and impurities. The pits were left under the sun for about 3 days (72 hours) to allow for partial dryness. The partially dried date pits were then dried in an oven at about $100^{o}C$ for 24 hours to allow for easy crushing and to reduce moisture content. The palm-date pits were crushed, dried and sieved to different mesh sizes and 200g of each mesh sizes were treated with H_3PO_4 acid (85%) having 70% acid containing 30% distilled water for 2 days, pyrolysis proceeded immediately at $900^{o}C$ for 3hrs. and $600^{o}C$ of furnace setting [10]. Residual acid was removed with sodium carbonate, until a pH of 7 was reached.

B. Batch Equilibrium Experiments
Palm Date Pits Activated Carbon (DPAC) and a Commercial Activated Carbon (CAC) were separately used to attain equilibrium by carrying out a batchexperiments. 1000mg of $K_2Cr_2O_7$ was dissolved into 1000ml. The optimum pH, agitation speed and contact time and an adsortion isoterm experimet were made to proceed with 1g of $K_2Cr_2O_7$ in 1000ml. 100ml of 5-25 mg per liter of various solution the effluent was concentrated to match the five concentration prepared. The adsorption efficiency was calculated using equation

$$E = \left[\frac{C_0 - C_1}{C_0} \right] x 100 \qquad (6)$$

E (%) = [(C_0-C_1) / C_0] x 100

Where, C_0 and C_1 are the initial and equilibrium concentrations of the solutions respectively [9].

IV. RESULTS AND DISCUSSIONS
A. Effect of Adsorbent
Figure 1 shows the comparison between the Commercial Activated Carbon (CAC) and the Palm Date Pits Activated Carbon (DPAC) on the effect of adsorbent dosage on the removal of Cr (VI). The conditions are 22mg/L chromium concentration, 300rpm and 30minutes. At low adsorbent dose (1g and 2g), the percentage uptake for CAC and DPAC arethe same at 9% and 32% respectively. As the adsorbent dosage increases from 2g to 5g, the percentageuptake for DPAC is higher than that of CAC. At maximum dosage, 79.55% was recorded for DPAC and 47.73% for CAC. This however signifies that the percentage uptake of CAC is less than that of DPAC. This indicated that DPAC adsorbed Cr (VI) in industrial waste water better than CAC due to either the high surface area or the binding attractive forces. The binding attractive forces and available surface for adsorption are largely dependent on the pH of the activated carbon surface and particle size.
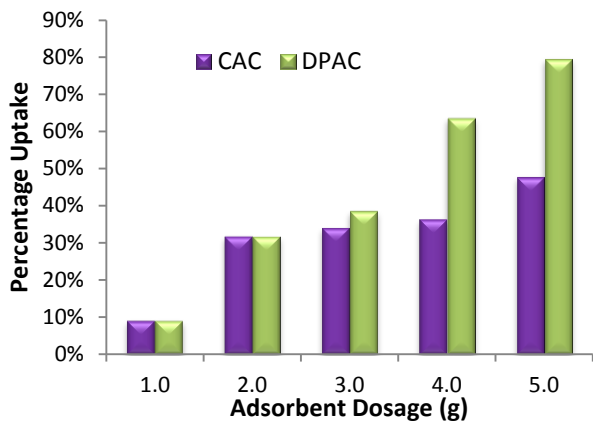
Figure 1. Comparison on the effect of adsorbent dosage on the removal of chromium (VI) byCAC and DPAC

B. Adsorption Isotherms

The adsorption isotherm describes how adsorbates behave towards the adsorbents used. This is critical in optimizing the use of the various adsorbents. Two models(Langmuir and Freundlich) were used to study the behavior of chromate ions adsorption on commercial activated carbon (CAC) and the date palm pits activated carbon (DPAC). The Langmuir and Freundlichisothermsare defined in equations (3) and (5) respectively.

$$ln Q_e = ln K_f + 1/n \, ln C_e \qquad (5)$$

With reference to the Freundlich isotherms equation above, Q_e is the amount of Cr (VI) adsorbed per carbon dosage, C_e is the equilibrium concentration of Cr (VI) in the solution, k and 1/n are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of $ln Q_e$ against $ln C_e$. Freundlich constants (k and 1/n) and correlation coefficients for Cr (VI) by the activated carbons are given in Table 1.

Table 1:Freundlich isotherm constants for chromium adsorption

Activated Carbon	k	1/n	Correlation factor
CAC	1.896	1.728	0.892
DPAC	54.217	0.767	0.456

The Langmuir adsorption isotherm is shown in Figure 2. The Langmuir isotherm did not accurately define the equilibrium condition of another allied sorption process, because the isotherm curve shown in Figure 2 gave a multiple correlation values of 0.025 and 0.537 for DPAC and CAC respectively. This indicatesclearly how the adsorption density measure can be used to replicate the isotherm within the 5–25 mg/L of chromium VI adsorption on 200g of adsorbent,which is an indicator of the effectiveness of the fitted regression. The value is as low as 2.5% for DPAC, meaning that a negligible percentage of the variation in surface area of DPAC can be accounted for by the adsorbed chromium VI ions. The rest of the variations are said to be unaccounted for.Therefore, this predictive power is not good for prediction of adsorption of DPAC. This may be as a result of the assumptions used to

develop the Langmuir model requiring uniform surface with equivalent adsorption site, which was not so for the DPAC grains used. Another factor that may be responsible for the low regression fit is that, while Langmuir isotherm assumes that maximum adsorption must occur only on the monolayer, the result below indicates that chromium VI deposited on another ion already adsorbed on the free surface of the DPAC and penetrated beyond the monolayer causing adsorbed molecule interactions.
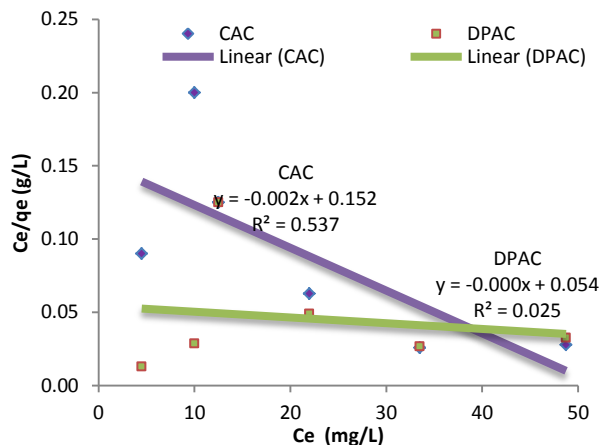

Figure2: Langmuir adsorption isotherm for chromium (VI) by CAC and DPAC

Figure 3 shows the fitted equilibrium data in Freundlich isotherm expression. It is observed that the equilibrium data fitted well in Freundlich expression with high correlation coefficients value of 0.892 and 0.456 for both CAC and DPAC respectively. The high correlation coefficient confirms the applicability of the isotherm.A larger value of k indicates good adsorption efficiency for the particular activated carbon, while a larger value of 1/n indicates a larger change in effectiveness over different equilibrium concentrations. Table 1 indicates that in these studies, DPAC had the highest k value 54.217 at a constant contact time of 30minutes. This confirms the adsorption effectiveness of DPAC over CAC. The higher values of correlation coefficients recorded for the DPAC may be an indication that the Freundlich adsorption isotherm applied is valid for the carbon dosage used as exemplified by the linear graph shown in Figure 3. However, CAC had the highest values of 1/n (1.728), indicating that it has the highest rate of adsorption of Cr (VI) in the solution followed by DPAC with 1/n value of 0.767. This implies that, although the rate at which CAC adsorbed Cr (VI) in the solution is high, its adsorption capacity for the Chromium solution is minimal.
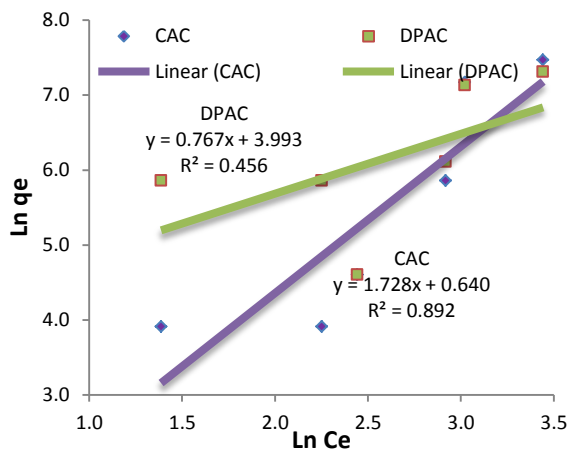
Figure3: Freudlich adsorption isotherm for chromium (VI) by CAC and DPAC

V. CONCLUSION

The Cr (VI) adsorption was characterized by the initial metal ion concentration and dosage of adsorbent. The removal of Cr (VI) increased with increasing initial metal ion concentration and adsorbent dosage used. The adsorption data was well described by Freundlich isotherm. The study indicates that the activated carbons are effective in removing heavy metals and that there are many factors of the adsorbent and the adsorbate which can affect the extent and rate of the adsorption process. An efficiency of 79.55% was obtained for DPAC and 47.73% for CAC.

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