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ADSORPTION OF PARAQUAT DICHLORIDE FROM AQUEOUS SOLUTION BY *JATROPHACURCAS* SEED COAT ACTIVATED CARBON

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ABSTRACT

JatrophaCurcas seed coat activated carbon was used as adsorbent for the adsorption of paraquat dichloride (herbicide) from aqueous solution. Paraquat dichloride adsorption spectrum ranges from 0.029 to 3.145 and the maximum absorbance was recorded at 500 nm. The standard calibration curve obeys Beer-Lambert's Law as the absorbance increases with increase in concentration. The effects of initial concentration was studied and the percentage absorbed ranges from 42.85 % to 84.69 %, the effect of contact time shows that the amount adsorbed decreased as the contact time increases. The effect of pH shows absorbance ranges from 1.173 to 1.906 within a pH range of 2 to 10 and the effect of temperature shows Qe ranges from 0.0086 mg/g to 0.121 mg/g within a temperature range of 35 ^{0}C to 55 ^{0}C. Isotherm studies indicate an inhibitory effect, promoted by *JatrophaCurcas* seed coat activated carbon. Overall, the results from this study demonstrated that the *JatrophaCurcas* seed derived activated carbon can be used as a low-cost adsorbent for the removal of environmental cationic organic pollutants from the environment.

KEYWORDS: Adsorption, Aqueous Solution, Paraquat Dichloride, *JatrophaCurcas*, Activated Carbon, Pollutants.

INTRODUCTION

Herbicide poses great danger and threat to the environment thereby constituting serious problem to plants, animal and mankind. In modern agriculture, the use of herbicides is of good importance which improves longevity and survival of crops by eliminating weeds. However, pesticides are poisons and can be particularly dangerous when not properly usedor used with foul intentions [1]. Paraquat (1,1-dimethyl-4,4-dipyridinium dichloride), is a quaternary ammonium herbicide, which is highly soluble in water and its nonselective action within plant cells makes it widely accepted and used in agriculture [2] and recently it was recorded as one of the highest selling herbicide in the global herbicide market [3]. Despite its benefits, this compound is included in a priority list of herbicides of potential concern established for the Mediterranean countries by the European Union [4].

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This compound is extremely toxic and may pose potential environmental hazards to humans, often triggering cases of poisoning. When deliberately or accidentally ingested, its acute toxicity by oral route, it can also be absorbed through the skin or respiratory route without acute toxic damage [5]. Since there is no antidote to reverse the effects of this chemical in the human body, the current use of paraquat results in a health risk [6].

Paraquat is high solubility in water thus it can easily contaminate water. Moreover, contact with the skin or eyes have adverse effects on humans and animals. A convenient method of removal paraquat is adsorption because it is simple, efficient, and inexpensive [7].

Activated carbon is a popularly known adsorbent for it's widely applications in the treatment of gaseous effluents discharged from industry and remediation of polluted environment. Activated carbon can be prepared from various biomaterials thereby making it simple, cost effective, and efficient in removing organic and inorganic contaminants [8]. This study has the purpose of investigating aspects of paraquat dichloride adsorption using activated carbon from J*atrophacurcas* in aqueous medium.

MATERIALS AND METHODS

COLLECTION AND PREPARATION OF MATERIALS

Jatropha seed coats were collected from the Faculty of Agricultural science, University of Ilorin and paraquat dichloride (an herbicide) was purchased from an agrochemical dealer in Ilorin, Kwara state Nigeria. The jatropha seed coats were repeatedly washed under running water to remove dust and soluble impurities and were allowed to dry at sunlight in a shade for 48 hours.

PRODUCTION OF ACTIVATEDCARBON

The method of [9] was used for activation was chemical activation. The seed coats were activated with 0.1M H_3PO_4 acid, 20 g of the carbonized sample was weighed and soaked in the activating agent for 24 hours. The sample was heated in a 100 mL pyrex bottle to allow for uniform pore space. It was stirred alongside heated for 30 mins. The sample was washed with distilled water and adjusted to pH 7.

SPECTROPHOTOMETRIC ANALYSIS

Absorption spectrum of the adsorbate was obtained by measuring the corresponding absorbance at a range from 200 nm-700 nm using a DU 730 Life science UV/Vis spectrophotometer. The wavelength corresponding to maximum absorbance, the peak of the spectrum was noted and was used as the wavelength of subsequent measurement of absorbance[10].

ABSORPTION-CONCENTRATION CALIBRATION

The absorbance of different concentrations of paraquat dichloride (standard solution of different concentration ranging from 5 mg/L -25 mg/L) was measured at the wavelength of maximum absorbance and was plotted against the various concentrations. A linear calibration graph shows that the compound obeys Beer Lambert's law. The concentration of the unknown solution can thus be determined from the calibration graph when the absorbance of the solution was measured [11].

BATCH STUDY

The batch adsorption was carried out in 250 mL conical flasks by mixing 2 g amount of adsorbent with 20 mL of aqueous herbicide solution of a particular concentration varying with the desired concentrations which have been prepared. The conical flasks were kept in a rotary shaker and agitated for a pre-determined time interval at a constant speed.

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EFFECT OF INITIAL CONCENTRATION

The actual concentration of each solution previously prepared was determined using a spectrophotometer. 20 mg/L of each concentration was measured into calibrated bottles and 2 g of the activated carbon was transferred into each bottle and agitated in a rotary shaker at room temperature at 75 rpm for 2h. The final concentration of the filtrates was determined using the formula:

$$Qe = \frac{(\mathrm{Co}-\mathrm{Ce})\mathrm{xV}}{m} \quad \textbf{Equation 1}$$

Where Qe = Amount of adsorbate adsorbed by adsorbent (mg/g)
Co = Initial concentrations of paraquat solution at time (mg/L)
Ce= Liquid-phase concentrations of paraquat solution at time (mg/L)
V= Volume of paraquat solution used (mL)
m = Mass of activated jatropha seed coats used (g)

EFFECT OF PH

From the calibration curve of Qe, the equilibrium constant or concentration was determined and the effect of pH on adsorption of paraquat dichloride was analysedusing pH range of 2-10. 20 mL of 15 mg/L herbicide solution was measured into different bottles and 1g of the activated carbon was added and agitated at 75 rpm for 1hour. The solution was filtered using a filter paper and the pH of the filtrate was measured [12].

EFFECT OF TEMPERATURE

20 mL of the adsorbate was pipetted into a conical flask and 2 g of the adsorbent was added. Three different solution of this was prepared by varying the temperature at 35^0C, 45^0C and 55^0C respectively. The mixture was filtered after shaking and the amount adsorbed was determined using a spectrophotometer.

EFFECT OF CONTACT TIME

The effect of contact time on removal of paraquat dichloride was studied for a period of 100 min. 2 g of the activated carbon was added to different conical flasks containing 20 mL of 15 mg/L solution, corked and agitated in a shaker at 75 rpm for different contact times (20, 40, 60, 80 and 100 min). After each agitated time, the mixture of each flask was then filtered after shaking and the amount adsorbed was determined using UV-visible spectrophotometer [13].

ADSORPTION ISOTHERMS

The study of isotherm data is important to find out the adsorption capacity of various adsorbents. In order to investigate the adsorption isotherm, three equilibrium isotherms were analyzed: Langmuir, Freundlich and Tempkin isotherms were used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption [14].

The Freundlich constant was determined from:

$$Log\ qe = Log\ Kf\ + 1/nLogCe \quad \textbf{Equation 2}$$

From the results obtained, the applicability ofFreundlich isotherm wasanalysed by plotting Log (qe) versus Log (C_e) which k and n were calculated

The Langmuir non-linear equation is commonly expressed as follows:

$$qe = \frac{Qm+KeCe}{1+KeCe} \quad \textbf{Equation 3}$$

Qm is a constant and reflect a complete monolayer, Ke is equilibrium constant that is related to the apparent energy of sorption.

The Langmuir Isotherm can be linearized can be linearized into the following form:

$$\frac{1}{qe} = \frac{1/Ke}{Qm}\left({}^{1}/_{Ce}\right) + {}^{1}/_{Qm} \quad \textbf{Equation 4}$$

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The plot of 1/qe versus 1/Ce gives a linear relationship from which Qmax and Langmuir constant were calculated

The derivation of the Tempkin isotherm assumes that the fall in the heat of adsorption islinear rather than logarithmic, as implied in the Freundlich Isotherm. The Tempkin isotherm can be simplified to the following equation:

$$qe = \beta Ina + \beta InCe$$ **Equation 5**

RESULTS AND DISCUSSIONS

PARAQUAT DICHLORIDE'S ADSORPTION SPECTRUM

The adsorbate used in the experiment is paraquat dichloride. Spectrophotometric analysis was carried out on paraquat dichloride using a spectrophotometer. The wavelength ranges from 200 nm to 700 nm while absorbance ranges from 0.029 to 3.145. From the plot of spectrum of paraquat dichloride as shown in Figure 3.1, it was observed that the maximum wavelength is 500 nm.

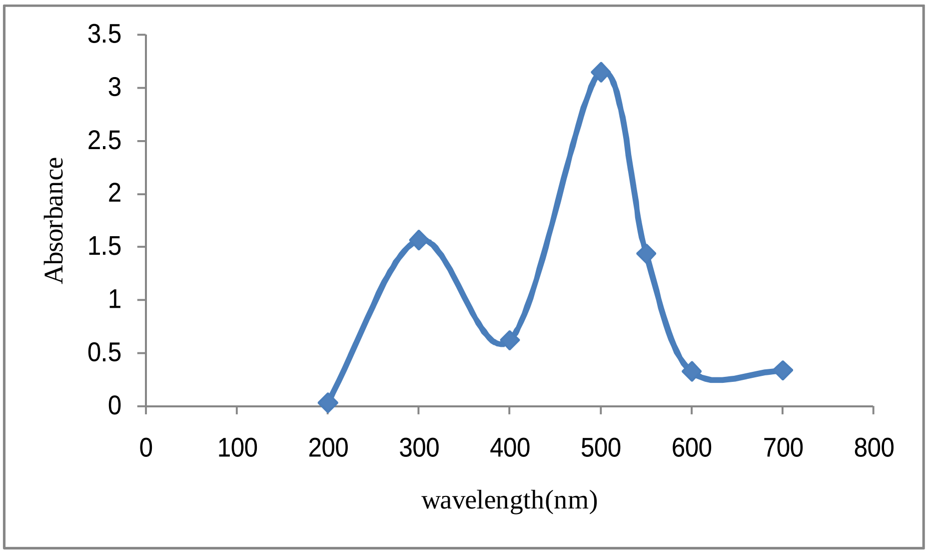

Figure 3.1.Paraquat Dichloride Spectrum

STANDARD CALIBRATION GRAPH FOR PARAQUAT DICHLORIDE

Absorption-concentration calibration which shows the concentration of amount of herbicide absorbed in the concentration range of 5-25 mg/L, the absorbance ranges from 0.784 to 3.145 and it was recorded that the absorbance increases with increase in concentration as shown in Figure 3.2 shows that it obeys Beer-Lambert's Law.

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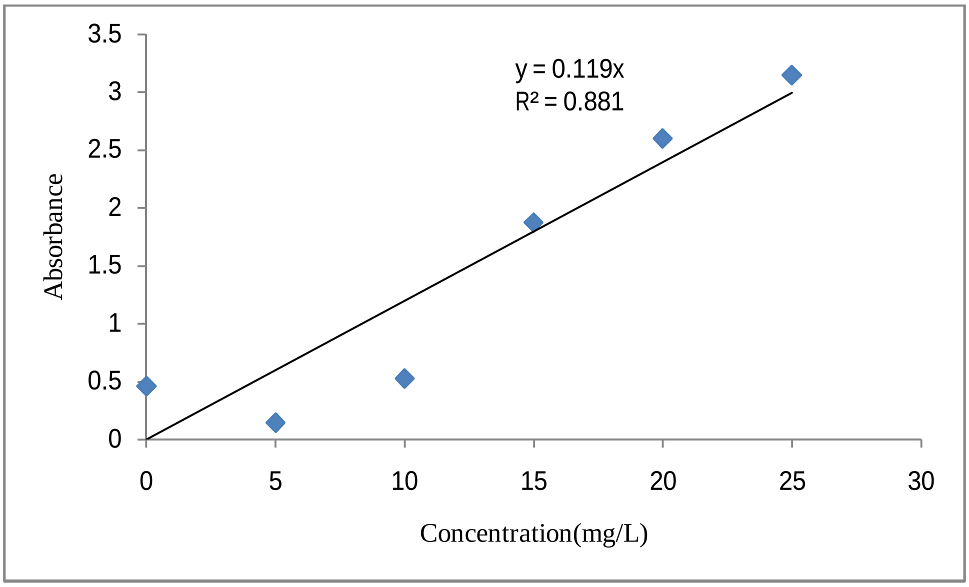

Figure 3.2.Absorption-Concentration Calibration

EFFECT OF INITIAL CONCENTRATION

The effect of initial concentration of paraquat dichloride at the concentration range of 5-10 mg/L,was studied and the percentage absorbed ranges from 42.85 % to 84.69 %. It can be deduced from the graph below that the quantity adsorbed decreased as the initial concentration of paraquat dichloride increase. Similar results were observed by [5] for the adsorption system of paraquat onto the activated carbon derived from used tire.

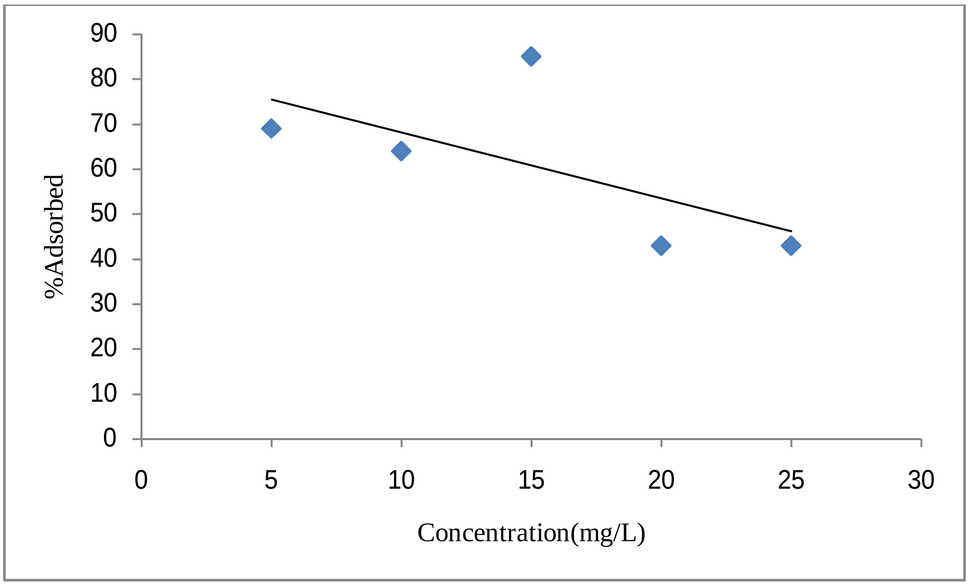

Figure 3.3.Percentage Adsorbed against (%) Concentration (mg/L)

EFFECT OF CONTACT TIME ON PARAQUAT DICHLORIDE ADSORPTION

The effect of contact time on the adsorption of paraquat dichloride was shown in Figure 3.4. It was recorded that the amount adsorbed decreased as the agitation time increases. The quantity adsorbed is expected to reduce with increases in time until equilibrium will be reached and no change in the quantity adsorbed could be seen beyond this point [15].

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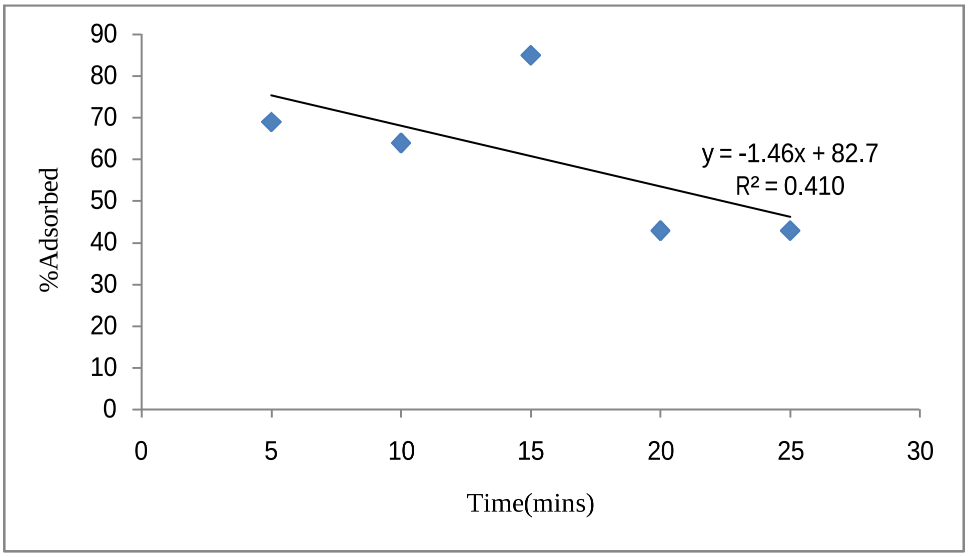

Figure 3.4.Effect of Contact Time for Adsorption of Paraquat Dichloride

EFFECT OF PH

The Absorbance ranges from 1.173 to 1.906 within a pH range of 2 to 10. It was observed from the obtained result that the amount of paraquat dichloride absorbed increased with increasing pH. This trend was also recorded by [16] where he prepared activated carbon from *Jatrophacurcas*and *Terminaliacatappa*seed coats for adsorption of methylene blue from aqueous solution. The lower amount adsorbed at the lower pH indicated a competition between proton and paraquat to the adsorption sites. A similar effect was reported on adsorption of paraquat on silica by [17].

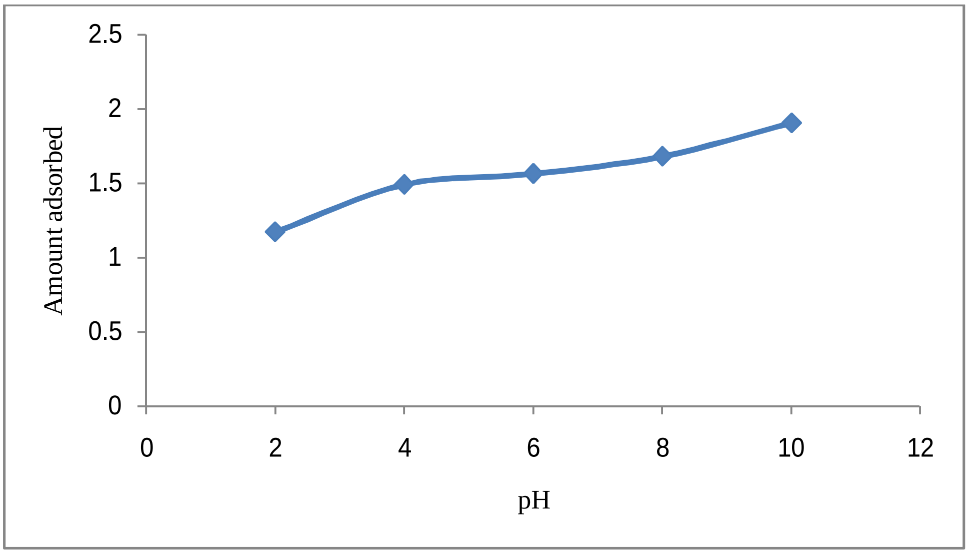

Figure 3.5.Effect of pH

EFFECT OF TEMPERATURE

The Qe ranges from 0.0086 mg/g to 0.121 mg/g within a temperature range of 35 ^{0}C to 55 ^{0}C. It was observed from the obtained result that the amount of paraquat dichloride adsorbed increased as the temperature increased from 35-45 ^{0}C after which a decrease was noticed in the amount of paraquat dichloride adsorbed from 45-55 ^{0}C. A similar observation was earlier recorded by [18]. This observation suggests that the force which binds the herbicides molecule to the activated carbon surface becomes weaker as the temperature of the medium is raised [19].

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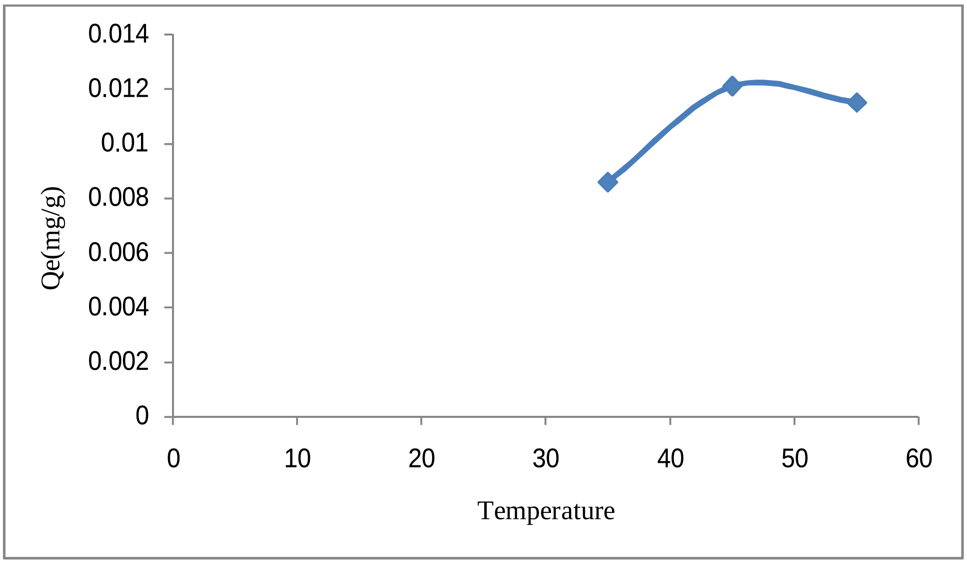

Figure 3.6.Effect of Temperature on Paraquat Dichloride Adsorption

ADSORPTION ISOTHERMS

The study of the Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective adsorption. The plot of 1/qe versus 1/Ce gives a linear relationship from which Qmax and B Langmuir constants were calculated. The data fitted to Langmuir model equations which was graphically represented in Figure 3.7 shows that the K_L= -0.0904 and Qo= -0.0904.

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems. The plot of Log x/m versus Log Ce(Freundlich Isotherm) gave a linear relationship from which k and n are calculated and the results obtained are graphically represented in Figure 3.8.

Tempkin Isotherm readings and the results obtained were represented graphically in Figure 3.9. The graph of Qe(mg/g) versus In Ce (mg/L) gives a linear relationship from which AT and Tempkin constant are calculated.

For Freundlich isotherm, the correlation coefficient R^2 value for paraquat dichloride is 0.86. Also, for the Langmuir isotherm, R^2 value is 0.87 while the R^2 value for Tempkin isotherm is 0.83.

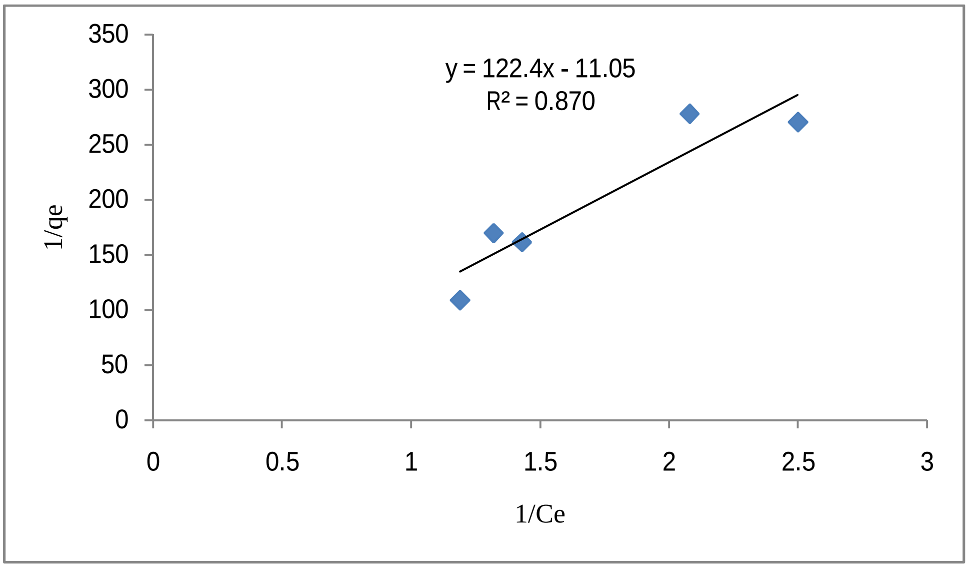

Figure 3.7.Langmuir Isotherm Plot

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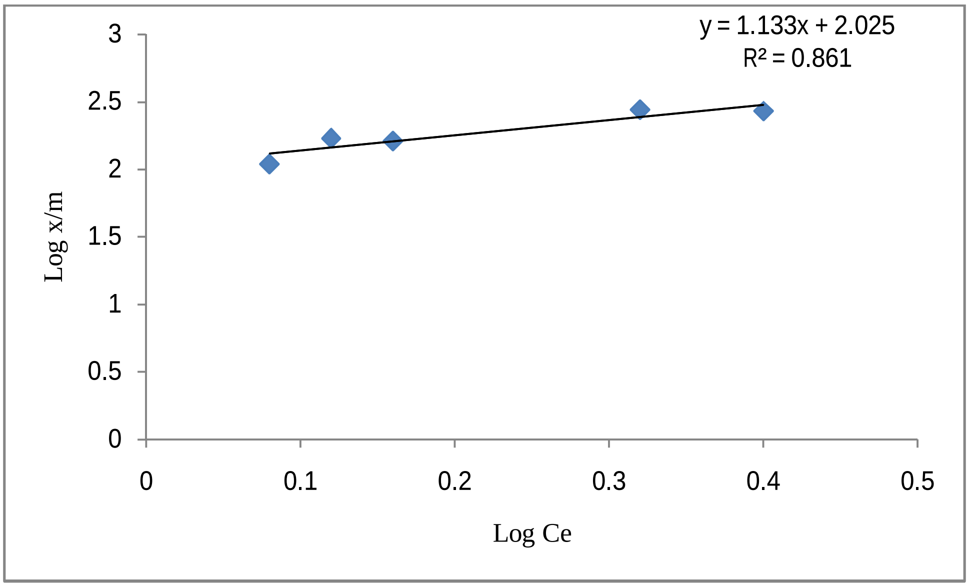

Figure 3.8.Freundlich Isotherm Plot of Adsorption of Paraquat Dichloride

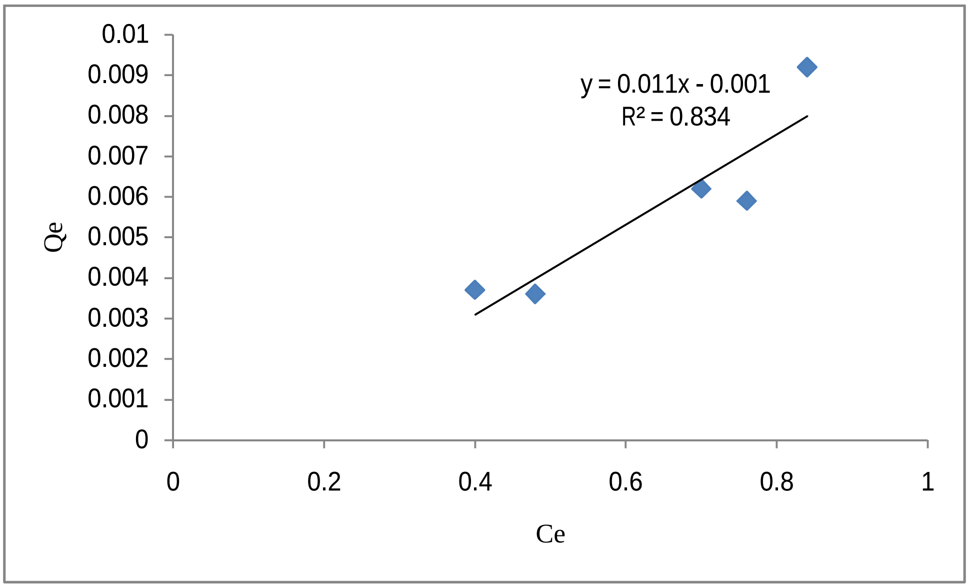

Figure 3.9.Tempkin Isotherm

CONCLUSION

The removal of herbicides from aqueous solutions using activated carbon prepared from activated jatropha seed coats was achieved by studying the effect of time, initial concentration, temperature and pH. It was obtained from the result that the percentage adsorbed decreased as the initial concentration increased as well as for contact time. The results however showed that the amount adsorbed increased as the pH increased and same occurred in the effect of temperature.

Although the adsorption of the herbicide is low, this may be due to the nature of the activated carbon, or the organic nature of the herbicide which may be of lower probability in adsorption on the activated carbon.

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