



Adsorption of Pesticides from Aqueous Solution using Kinkeliba (*Combretum micranthum* G.) Derived Activated Carbon

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Abstract

The utilization of kinkeliba (*Combretum micranthum* G.) leaves as precursor for producing activated carbon for adsorption of pesticides from aqueous solution was investigated in this study. The *Combretum micranthum* G. leaves were carbonized at a temperature of 500 °C for 1 h. After activation with H₃PO₄, the kinkeliba activated carbon (KAC) possessed bulk density of 78.6 g/dm³ and volatile component of 10%. The pH, percentage moisture and ash content of the KAC were 5.43 ± 0.36, 1.25 ± 0.04% and 5.01 ± 0.12% respectively. The adsorption of pesticides onto the prepared KAC adsorbent was optimized in terms of operating parameters (adsorbent dose, pH, contact time and initial adsorbate concentration). The results showed greater removal efficiency for the pesticides at pH 3 in 30 min. The results from isotherms studies showed that adsorption of pesticides onto KAC was best fitted to the Langmuir isotherm model ($R^2 > 0.99$), indicating monolayer adsorption. However, Freundlich isotherm model provided the best fit for the uptake of pendimethalin onto the KAC with q_e of 118.13 mg/g and R^2 of 0.935 suggesting multilayer adsorption.

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The present work showed that the kinkeliba activated carbon can be used as a potential low-cost adsorbent for the removal of pesticides from aqueous solutions.

Keywords: Adsorption; kinkeliba; activated carbon; pesticide; isotherm.

1. Introduction

Pesticides are toxic chemical substances or biological agents that are intentionally released into the environment in order to avert, deter, control and/or kill and destroy populations of insects, weeds, rodents, fungi or other harmful pests. Pesticides work by attracting, seducing and then destroying or mitigating the pests. Different kinds of pesticides including insecticides and herbicides have been used for crop protection. Pesticides benefit the crops; however, they also impose a serious negative impact on the environment. Excessive use of pesticides may lead to the destruction of biodiversity. Pesticides are a concern for sustainability of environment and ecosystems [1]. Insecticides and 95% of herbicides reach a destination other than their target species, because they are sprayed or spread across entire agricultural fields. [1] Runoff can carry pesticides into aquatic environments while wind can carry them to other fields, grazing areas, human settlements and undeveloped areas, potentially affecting other species. Other problems emerge from poor production, transport and storage practices. [2] Over time, repeated application increases pest resistance, while its effects on other species can facilitate the pest's resurgence [3]. Each pesticide or pesticide class comes with a specific set of environmental concerns. Such undesirable effects have led many pesticides to be banned, while regulations have limited and/or reduced the use of others. Though the pesticide industry in the developed world has made good progress in the field of development and production of low risk/low volume user and environment friendly pesticides formulation, pesticides in the developing countries still now are mainly available in conventional formulations such as dust, water soluble powder, emulsifiable concentrates and solutions etc. As pesticides are responsible for several adverse effects on human health other than acute intoxications [4-6]. There are four major routes through which pesticides reach the water: 1) it may drift outside of the intended area when sprayed, 2) it may percolate, or leach through the soil, 3) it may be carried to the water as runoff, or 4) be spilled, for example accidentally or through neglect [7]. They may also be carried into the water body by eroding soil [8]. Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop, and the method used to apply the chemicals [9]. In the US, maximum limits of allowable concentrations for individual pesticides in drinking water are set by the Environmental Protection Agency (EPA) for public water systems [9, 10]. Ambient water quality standards for pesticide concentrations in water bodies are principally developed by state environmental agencies, with EPA oversight [10-12]. The application of pesticides have proved to be a benefit for the farmers as well as people all around the world by increasing agricultural yield and by providing innumerable benefits to society indirectly. But the issue of hazards posed by the uncontrolled use of pesticides to human health, reduction of several terrestrial and aquatic animal and plant species and the environment has raised concerns about the safety from harmful effect of pesticides and need for proper mitigation [13]. The aim of this study is to investigate the potential of activated carbons prepared from *Combretum micranthum* G. in the removal of pesticides from aqueous solutions. The effect of adsorption parameters such as time, pH, adsorbent dosage, pesticide concentrations and isotherms were also investigated.

2. Materials and Methods

2.1 Collection of *Combretum micranthum* G. leaves

The leaves of *combretum micranthum* G. were collected from a bush in Kebbi State University of Science and Technology, Aleiro, Nigeria. The leaves were washed with distilled water and air dried for 3 days. The dried leaves were then pulverized using mortar and pestle.

2.2 Preparation of activated carbon

The preparation of the activated carbon from *C. micranthum* G. was carried out in two stages: carbonization and activation. The powdered sample was weighed into a clean crucible, placed in muffle furnace and carbonized at 500 °C for 3h. The carbonized sample was mixed with 75% H₃PO₄ in a beaker with the weight ratio of H₃PO₄ to carbonized material of 1:10. The slurry was dried at 60 °C for 24 h and washed to a neutral pH. The sample was then transferred into a beaker containing 250 ml of 0.1 M of HCl, stirred for 1 h and finally rinsed with distilled water until the pH of 6 to 7 was obtained. The residue was air dried and labelled as KAC (kinkeliba Activated Carbon) and kept in a tight container for characterization and application.

2.3 Characterization of KAC Adsorbent

2.3.1 Determination of pH

One gram (1 g) of the sample was boiled gently in a beaker containing 100ml of distilled water for 5 min, then diluted to 250 ml and cooled. The pH was taken with a digital pH meter (827 Metrohm).

2.3.2 Determination of Iodine value

Approximately 0.5 g of the sample was added to 250 ml of 5% of HCl solution and heated at 70°C for 1h. After cooling to room temperature, 100 ml of 0.1 M iodine solution was added. The content was shaking vigorously and filtered. About 25 ml of the filtrate was titrated with 0.1N sodium thiosulphate in the presence of starch as indicator [13]. The iodine number was calculated using Eq. 1.

$$\text{Iodine number} = \frac{12.69(B-A)}{W} \quad (1)$$

Where, B= Volume of blank, A= Volume of iodine solution, W= Weight of the sample

2.3.3 Ash content determination

The ash content was determined in accordance with [14]. An empty dry crucible was heated in a muffle furnace at 500 °C, cooled in a desiccator and weighed. Then 0.5g of the sample was transferred into it and re-weighed. The crucible containing the sample was placed in a furnace at 500 °C and heated for 2h, cooled in a desiccator and weighed again. The ash in percent was calculated as.

$$\text{Ash content}(\%) = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \quad (2)$$

Where,

W_1 = Weight of empty crucible; W_2 = Weight of crucible and sample before ashing; W_3 = weight of crucible and sample after ashing.

2.3.4 Determination of Moisture content

A weighed clean and dried empty crucible was taken and 1 g of the sample was added to it. The crucible was placed in the oven at a temperature of 105°C until a constant weight was obtained. The content was cooled in desiccator and reweighed [14] (<https://doi.org/10.1155/2017/8635615>)..

$$\text{Moisture contents}(\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (3)$$

Where

W_1 = Weight of empty dry crucible; W_2 = Weight of crucible and sample before drying

W_3 = Weight of crucible and remaining sample after drying.

2.3.5 Determination of Volatile Content

A dry crucible was weighed and 1g of the sample was added to it. The crucible was heated in a furnace at 500 °C for 10 min, cooled in desiccators and reweighed [14].

The % volatile content was calculated as follows:

$$\text{Volatile content}(\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (4)$$

Where

W_1 = Weight of empty dry crucible; W_2 = Weight of crucible and sample before heating

W_3 = Weight of crucible and remaining sample after heating

2.3.6 Determination of Bulk density

Bulk density of the activated sample was determined gravimetrically; an empty 10ml measuring cylinder was weighed and then filled with water to determine its exact volume. The bottle was empty, dried and then filled with the sample followed by tapping to ensure compactness and reweighed. The bulk density is given by the ratio of difference in masses to the volume of the bottle.

$$\text{Bulk density} = \frac{W_2 - W_1}{V} \quad (5)$$

W_1 = weight of an empty 10ml measuring cylinder; W_2 = weight of measuring cylinder filled with an adsorbent; V = exact volume of measuring cylinder.

2.4 Adsorption Experiments

2.4.1 Preparation of pesticides solution

Stock solutions were prepared by dissolving appropriate amount of the pesticides (pretilachlor (PRE), mefenacet (MEF), butachlor (BUT), bentazone (BEN), fluroxypyr (FLU) and pendimethalin (PEN)) in the required amount of distilled water in 1000 ml volumetric flask. Solutions of different concentrations ranging from 25, 50, 100, 150, 200, 250 and 300 mg/l for each of the pesticides were prepared by dilution of appropriate amount of the stock solution

2.4.2 Effect of adsorption parameters

Batch adsorption method was used to investigate the effect of various adsorption parameters such as adsorbate concentration (25, 50, 100, 200 and 300 mg/l), adsorbent dosage (0.5, 1.0, 1.5, 2.0, and 2.5 g), pH (2 – 9) and contact time (10, 20, 30, 60, 90 and 120 min) on the adsorption efficiencies of the pesticides on KAC adsorbent. 25mL of pesticide solution was mixed with appropriate amount of the KAC adsorbent in a 100 ml conical flask at a given pH. The flasks were then placed on an orbital shaker at 30°C and agitated at 200rpm for 1h. The samples were then filtered using whatman filter paper and analysed for the remaining pesticides using UV-vis spectrophotometer (Shimadzu UV-12400, Japan) at the wavelengths (of 243, 246, 258, 265, 287, 306 and 325 nm) for PRE, MEF, BUT, BEN, FLU and PEN respectively.

The percentage pesticideS removal by KAC adsorbent was calculated as

$$\% \text{ pesticides removal} = \frac{C_f - C_i}{C_i} \times 100 \quad (6)$$

Where;

C_i = initial metal concentration (mg/L); C_f = final metal concentration (mg/l)

2.5 Adsorption Isotherm Models

The equilibrium isotherm modeling of pesticides (PRE, MEF, BUT, BEN, FLU and PEN) adsorbed onto the KAC adsorbent was carried out by the application of the Langmuir, Freundlich and Termkin models.

The Langmuir isotherm is represented in linear form as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (7)$$

When $\frac{C_e}{q_e}$ is plotted against C_e , the slope is $\frac{1}{Q_o}$ and the intercept is $\frac{1}{Q_o b}$. Where Q_o and b are the maximal adsorption capacity per weight of MFC and solute-surface interaction energy parameters.

The Freundlich isotherm in linear form is represented by Equation 8 as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (8)$$

Where K_F and n are the Freundlich model capacity factor and the linearity parameter respectively. The values of K_F and n may be calculated by plotting $\log(q_e)$ versus $\log(C_e)$. The slope is equal to $\frac{1}{n}$ and the intercept is equal to $\log K_F$ (Unuabonah and his colleagues 2008; Das and Mondal, 2011).

The linear form of the Temkin isotherm model is given by the following:

$$q_e = \frac{RT}{b_T} \ln k_t + \frac{RT}{b_T} \ln C_e \quad (9)$$

where K_T = Temkin isotherm equilibrium binding constant (L/g), b_T = Temkin isotherm constant, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K) and $RT/b = B$.

3. Results and Discussion

3.1 Characterization of KAC Adsorbent

The pH, bulk density, moisture content, ash content and volatile content of the KAC are presented in Table 3.1. The pH of KAC was measured as 5.43 ± 0.36 while the bulk density of the KAC was recorded as 76.8 g/dm^3 . The percentage moisture and ash contents of the adsorbent were calculated as $1.25 \pm 0.04\%$ and $5.01 \pm 0.12\%$ respectively. It was observed that the acidic pH of KAC has enhanced its adsorption capacity towards the pesticides uptake. High ash content will reduce the mechanical strength of the carbon and in turn affect the adsorptive capacity. Since the ash content of KAC is low, suggests that kinkeliba derived activated carbon possess the good adsorptive performance. The moisture content of KAC adsorbent is small, hence the adsorption of moisture is less and the uptake of pesticides (pretilachlor (PRE), mefenacet (MEF), butachlor (BUT), bentazone (BEN), fluroxypyr (FLU) and pendimethalin (PEN)) onto the KAC is enhanced [14].

Table 1: Physical characteristics of the KAC

| Parameter | Volatile Content (%) | Bulk density | pH | Ash content (%) | Moisture content (%) |
|-----------|----------------------|-----------------------|-----------------|-----------------|----------------------|
| KAC | 10 | 76.8 g/dm^3 | 5.43 ± 0.36 | 5.01 ± 0.12 | 1.25 ± 0.04 |

3.2 Effect of pH on pesticide adsorption

The results obtained for the effect of pH on the adsorption of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr and pendimethalin in the aqueous solution by KAC are presented in Figure 3.1. The pH of the solution affects the surface charge of the adsorbent, as well as the degree of the ionization and speciation of different pollutants. A change in pH affects the adsorptive process through the association/dissociation of functional groups on the adsorbent surface active sites and chemistry of the adsorbates in aqueous solution [14]. The results revealed that the maximum percentage uptake of mefenacet (90.75%) onto KAC adsorbent surface was observed at optimum pH 3, above which there was marginal increase in the percentage pesticide until alkaline pH 9. Percentage removal of other pesticides were PRE (89.64%), BUT (89.5%), BEN (76.02%), FLU (79.6%) and PEN (86.9%).

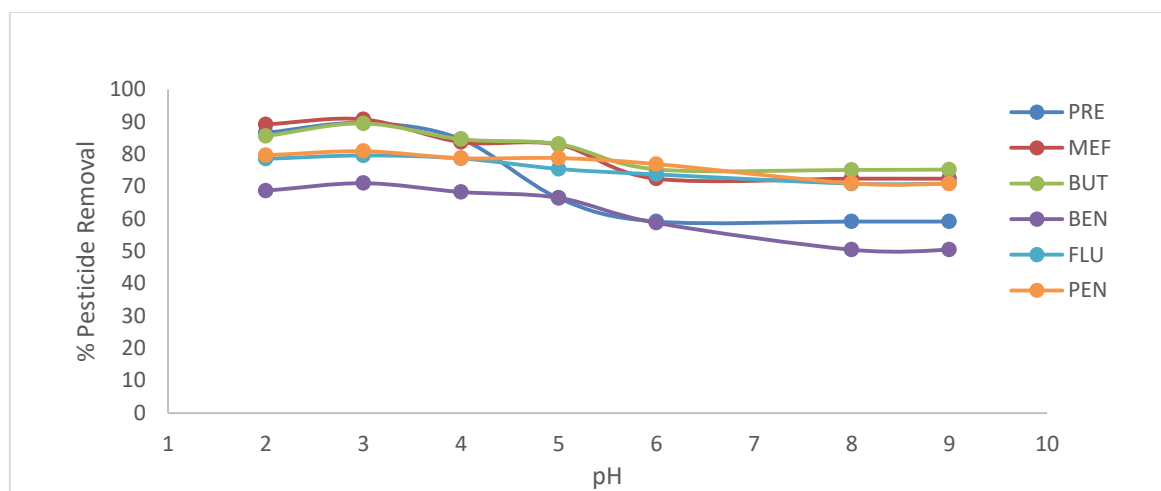


Figure 1: Effect of pH on adsorption pesticides onto KAC

3.3 Effect of Contact Time

The result obtained for the effect of contact time on the adsorption of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr and pendimethalin in the aqueous solution by KAC is presented in Figure 3.2.

The result indicated that the rate of adsorption increased significantly for the pesticides in the aqueous solution between 10-30 min of the contact time. However, the optimum time for maximum adsorption percentages of pesticides (PRE (94.64%), MEF (93.73%), BUT (89.6%), BEN (78.3%), FLU (78.67%) and PEN (80.75%) onto KAC was observed in 30 min. This was also seen to be due to the saturation of the adsorption sites after 30 min after which a decrease in percentage pesticide uptake was observed as contact time increased. This result was found to be important because equilibrium time was one of the important parameters required for any economical wastewater treatment system. This trend was found to be in conformity with the observation made by Nduka *and his colleagues* [14]. The rapid initial rate increase followed by a slow rate at a later period attributable to the availability of excess adsorption sites on the adsorbent. The initial high adsorption rate could also be due to ion exchange followed by a slow chemical reaction of the metal ions with active functional

groups on the KAC sample, in line with what was reported in the work [15, 16]. KAC was found to be efficient in the adsorption of the pesticides studied.

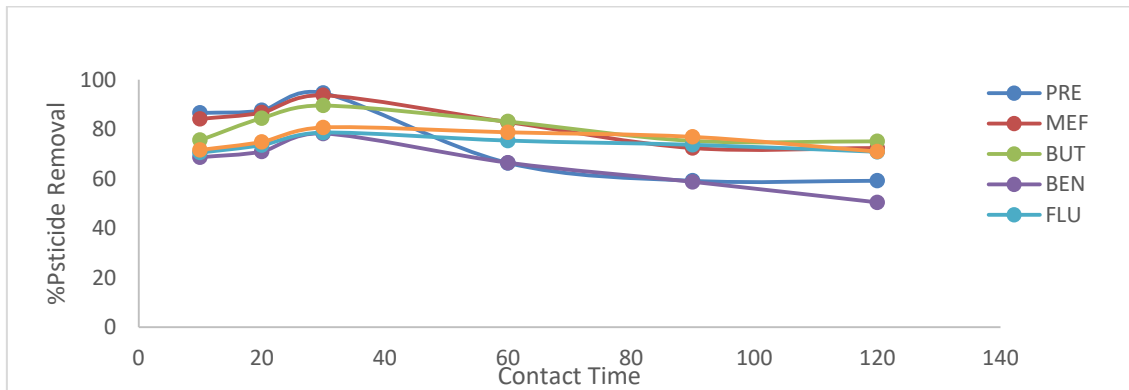


Figure 2: Effect of contact time on Adsorption pesticides onto KAC Adsorbent

3.4 Effect of adsorbent dosage

Figure 3.3 showed the effect of adsorbent dose on the percentage removal of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr and pendimethalin. The percentage of pesticides adsorbed by KAC decreases with an increase in the weight of adsorbent from 0.5 to 2.5 g of KAC. From the analysis of the experimental data obtained for metal the pesticides, it was observed that the adsorption efficiency remains relatively constant with an increase in adsorbent dose from 0.5 to 1.5 g, then increases reaching a maximum at adsorbent dosage of 2 g before it decreases again. An increase in activated carbon dosage generally increases the amount of pesticide uptake because of an increase in surface area of the KAC adsorbent, which consequently increases the number of available binding sites [16]. However, adsorption capacity (q_e) of pesticides increased continuously up to a particular dosage (1.5 g) above which efficiency increased slightly as the adsorbent was increased to 2g and later decreased again as the activated carbon dosage increases to 2.5g. The highest pesticide (mefenacet) uptake by KAC was 90.75%. Percentage removal of other pesticides were PRE (89.64%), BUT (89.5%), BEN (71.02%), FLU (79.6%) and PEN (84.9%) respectively.

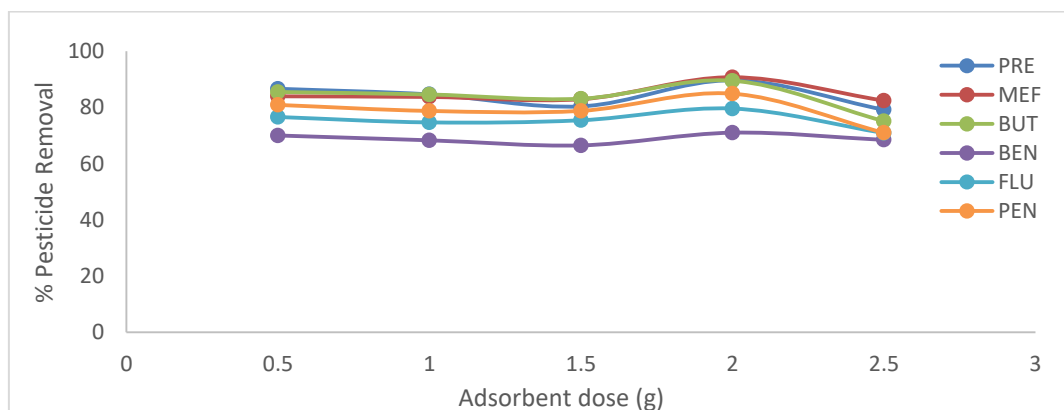


Figure 3: Adsorbent dosage on the adsorption of pesticides onto KAC adsorbent.

3.5 Effect of initial metal concentration on adsorption

Figure 3.4 showed the effect of pesticide concentration on the percentage removal of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr and pendimethalin. The percentage of pesticide adsorbed by KAC increased with an increase in the pesticides concentration. From the analysis of the experimental data obtained for pesticides, it was observed that the adsorption efficiency increased progressively with increase in initial metal concentration of pesticides. The optimum pesticide uptake by KAC adsorbent was achieved at 250 mg/l with maximum pesticides uptake of 95.17%. Similar observations were reported by Ofomaja and his colleagues and Ogbu and his colleagues [15, 16].

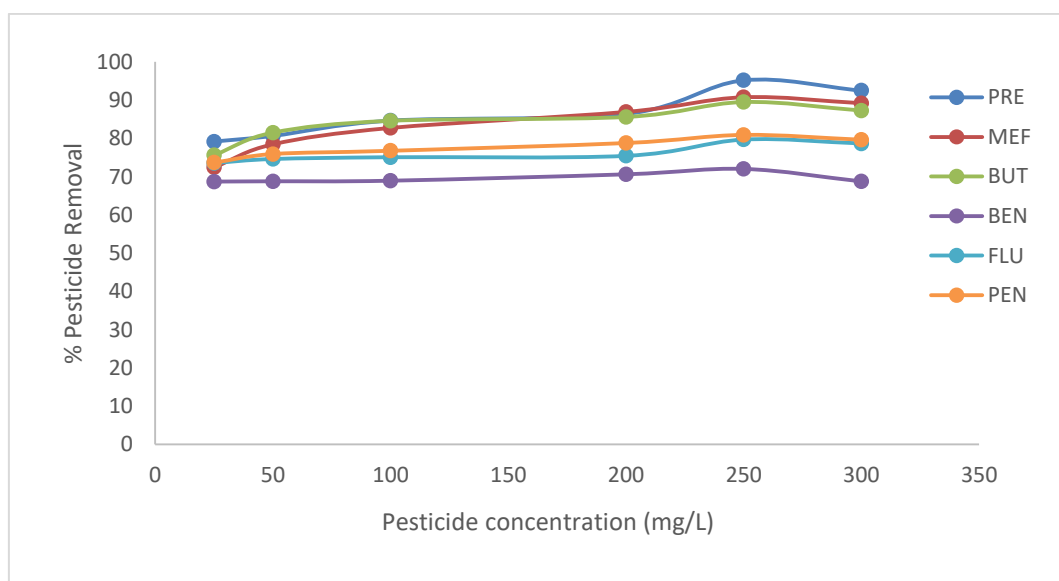


Figure 4: Effect of initial pesticide concentration on the adsorption of pesticides onto KAC adsorbent

3.6 Adsorption Isotherm Studies

The equilibrium data obtained from the adsorption of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr and pendimethalin onto KAC were fitted to Langmuir, Freundlich and Termkin isotherm models. The Langmuir isotherm parameters, constants and regression coefficients were calculated from the linear equations of the isotherm model plots and presented in Figures 3.5 a-f. The maximum Langmuir monolayer adsorption capacity, Q_o (mg/g), was 99.98mg/g for pretilachlor uptake by KAC. The Q_o values for the pesticides was higher than the values reported by Ogbu and his colleagues and Olu-Owolabi and his colleagues [16, 17]. As shown in Figures 3.5a-e, the Langmuir isotherm model was best fitted to the adsorption of pretilachlor, mefenacet, butachlor, bentazone, fluroxypyr onto KAC adsorbent with R^2 greater than 0.99. This suggests that the adsorption process might be attributed to monolayer adsorption onto a homogenous surface of the adsorbent. However, Freundlich isotherm model best fitted the uptake of pendimethalin onto the KAC with q_e of 118.13 mg/g and R^2 of 0.935 suggesting multilayer adsorption (Figure 3.5f). The results and observations were in agreement with that reported in the other previous works [18, 19 and 20].

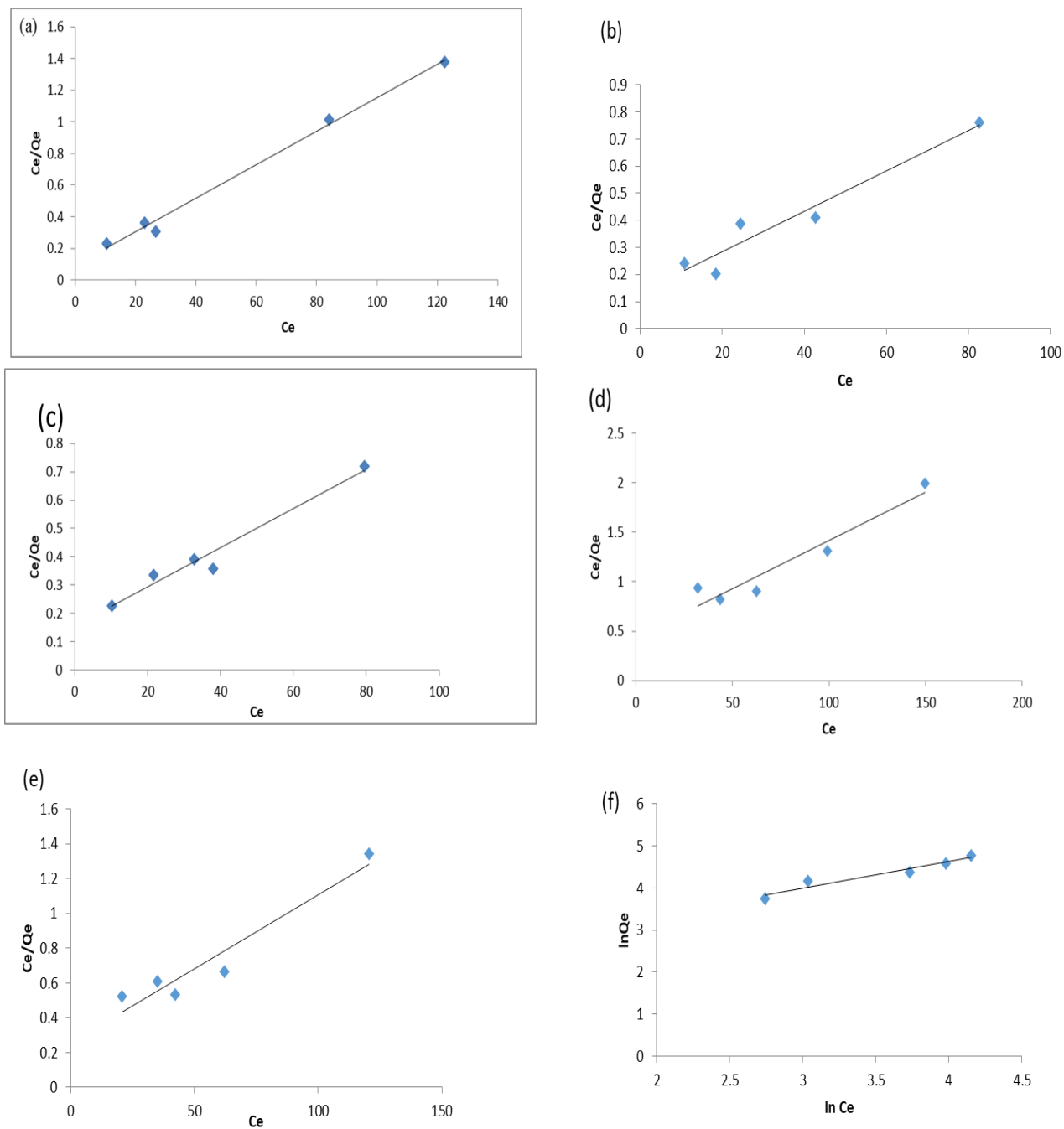


Figure 5: Langmuir isotherm plots of adsorption of (a) pretilachlor (b) Mefenacet (c)butachlor (d)bentazone and (e) Fluroxypyr on KAC adsorbent. (f) Freundlich isotherm plot of adsorption of Pendimethalin on KAC adsorbent

4. Conclusion

This study showed that kinkeliba (*Combretum micranthum* G.) leaves can successfully be used as a carbon source to prepare activated carbon for the removal of pesticides from aqueous solution. The prepared activated carbon had low values of ash and moisture which contributed to its high adsorption capacity. Factors such as pH, adsorbent dosage, contact time and adsorbent concentration were found to have significant effect on the

adsorption efficiency of the various pesticides studied on kinkeliba derived activated carbon. The Langmuir isotherm model provided the best fit to the experimental equilibrium sorption data of pretilachlor, mefenacet, butachlor, bentazone and fluroxypyr, which suggest chemical interaction between the pesticides molecules and the activated carbon adsorbent. However, for pendimethalin, the experimental equilibrium data best fitted the Freundlich adsorption isotherm model, suggesting multilayer adsorption on the KAC adsorbent with interactions between the pesticide molecules. The high adsorption capacity of the kinkeliba derived activated carbon for the studied pesticides demonstrated the potential of the KAC as an alternative low cost adsorbent for pesticides removal in water.

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