The Adsorption Equilibrium and Kinetic Studies for The Removal of Crystal Violet Dye (Methyl Violet 6b) from Aqueous Solution Using Avocado Pear Seed Activated Carbon

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Abstract: In this study, adsorption equilibrium and kinetic studies for the removal of crystal violet (CV) from an aqueous solution were investigated using a batch adsorption process. The activated carbon was prepared by carbonizing the avocado pear seed at a carbonization temperature of 500^OC for 1hr and was impregnated with a 30% concentration of aqueous HCl solution which was further activated in a muffle furnace at a temperature of 500^OC for 1hr. The avocado pear seed activated Carbon obtained was characterized using proximate analysis, Fourier Transform Infra-Red Spectrophotometer (FT-IR) analysis and Scanning Electron Microscope (SEM) analysis. The effect of various adsorption parameters such as contact time (15-150 min), initial dye concentration (25-150 mg/L), adsorbent dosage (1-9 g), particle size and pH of dye solution were investigated. The adsorption equilibrium data were fitted into different isotherm models and the Langmuir model exhibited the best fit which implied that the adsorption of CV dyes onto avocado pear seed activated carbon was monolayer and the adsorbent surface was homogeneous and also; adsorption energy was uniform for all sites and there was no transmigration of adsorbate in the plane of the surface. The kinetic studies revealed that the adsorption data fitted well to the pseudo-second-order model with a high correlation coefficient of 0.977 when compared to other models, thus; signifying that the adsorption's mechanism was chemisorption. APSAC shows a much better adsorption capacity for CV dye removal having a maximum adsorption capacity of 3.3254 mg/g and percentage removal of 99.995 %. Hence, APSAC can be used as an effective and low-cost adsorbent for the removal of CV dye from an aqueous solution.

Key Words: Adsorption studies, Isotherm models, Kinetic models, Activated carbon, Wastewater treatment, Chemical activation, Crystal violet dye.

I. Introduction

Globally, textile and dye intermediate industries are considered to be major sources of industrial waste water, resulting in critical environmental pollution problems (Rosenwinkel and Haun, 2008). Water pollution is one of the most undesirable environmental problems in the world; thus, requires urgent solutions. Textile industries produce a lot of waste water which contains several contaminants including acidic or caustic dissolved solids, toxic compounds and different dyes; many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species, and microorganisms (Konicki *et al*., 2013). Hence, their removal from aquatic waste water becomes environmentally important. Large quantities of dangerous dyes, pigments and metals originating from dye manufacturing; textile as well as pulp and paper industries are emitted into these waste waters. This makes the treatment of contaminated water difficult, because the colour tends to persist even after the conventional removal processes (Visa *et al*., 2010). The dye contaminations in water tend to prevent light penetration and therefore, affect photosynthesis considerably (Banerjee and Chattopadhyaya, 2017; Hajati *et al*., 2014; Hameed *et al*., 2017).

The increase in urbanization and industrialization has led to an exponential increase in the amount of sewage sludge generated which invariably affects the financial burden of Waste water treatment companies. Some of these waste water contaminants are non-biodegradable; thus, to minimize the risk to the environment and public health, there is a need for proper treatment processes for industrial wastewater effluents before they are discharged onto water bodies. Due to the wide application of dye compounds and their numerous hazardous and toxic derivatives, the treatment of waste water from colour dyestuff becomes very important from an environmental point of view (Ghaedi *et al*., 2013). There are several methods available for waste water treatment such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, reverse osmosis etc (Teng and Low, 2012). The adsorption technique, which is based on the transfer of pollutants from the solution to the solid phase, is known as one of the most efficient and general waste water treatments method (Ghaedi *et al*., 2012). The method is superior to other dye removal techniques in terms of initial cost, simplicity of design, ease of operation, and non-toxicity of the utilized adsorbents compared to other conventional waste water treatment methods (Kismir and Aroguz, 2011). Activated

carbon, a widely used adsorbent in industrial processes, is composed of a microporous, homogeneous structure with a high surface area and shows radiation stability (Iqbal and Ashiq, 2007). Agro-waste materials that have been successfully used to manufacture activated carbon in the recent past include waste wood (Acharya *et al.*, 2009), bagasse (Tsai *et al.*, 2001), coir pith (Namasivayam and Kavitha, 2002), orange peel (Khaled *et al.*, 2009), coffee husk (Ahmad and Rahman, 2011), pine cone (Gecgel and Kolancilar, 2012), coconut tree (Senthilkumaar *et al.*, 2006), sunflower seed hull (Thinakaran *et al.*, 2008), pine-fruit shell (Royer *et al.*, 2009), hazelnut husks, rice hulls, oil palm shell (Tan *et al.*, 2008), and Coconut husk (Foo and Hameed, 2012). This research is limited to removing crystal violet dyes from an aqueous solution using avocado pear seed as activated carbon. The significance of this study shows that among the various types of chemical and physical methods developed for the treatment of waste water effluents, adsorption processes utilizing activated carbon are preferred because of their ease of application with good efficiency. However, commercial activated carbon is very expensive and non-renewable, which limits its practical utility, particularly for a large-scale setting.

II. Materials and Methods

2.1. Materials

Avocado pear fruits were sourced locally from Ukam market, Mkpat Enin L.G.A, Akwa Ibom State, Nigeria. Crystal violet, preferably methyl violet manufactured by (Sigma Aldrich, 98 %) and other chemical reagents was purchased from Mike-Ene Chemical Store in Akwa Ibom State, Nigeria and was of analytical grade and used without further purification.

2.2. Preparation of Adsorbent.

Avocado pear fruits were gotten from Ukam Market, Mkpat Enin L.G.A, Akwa Ibom State. The avocado pear fruits were selectively picked and the endosperm (copra) was separated from the shell. The seeds were soaked for about 1 h in water, well-scrubbed using a sponge and tap water

and then sun dried for 3 h. The dried seed was then placed on a clean hard surface and broken into smaller pieces with the use of a hammer. These smaller pieces were then dried in a laboratory Oven (N53C-Genlab) at 105 °C for about 3 h to constant (dry) weight. The crushed seed samples were carbonized in a muffle furnace (PECVD furnace) at a temperature of about 500 °C for 1 hr in the absence of oxygen. The sample was then impregnated by immersing it in a 30% concentration of Hydrochloric acid (HCl) solution using an impregnation ratio (I.R) of (1:2 w/w) for 24 h and thereafter was dried in a laboratory drying oven at a temperature of 105 °C for 12 h to remove moisture and was activated in a muffle furnace at a temperature of 500 °C. The avocado pear seed activated carbon (APSAC) produced was cooled to room temperature and washed with 0.1 M NaOH solution to remove residual ash content and with deionized water until the pH of the washing solution reached 7. The prepared APSAC was then oven dried at 105 °C for 2 h and was further crushed, sieved into 250 μm particle sizes and then stored in an air-tight sample container until needed for the adsorption experiment.

2.3. Preparation of Aqueous Solution

A stock solution containing 1000 mg/L of Methyl violet was prepared by dissolving 1.0g of the dye in 1000 mL of distilled water. The resulting solution was then transferred into a 1.0 L volumetric flask and then diluted to volume with distilled water. Other working solutions with concentrations of methyl violet ranging from 25 mg/L to 200 mg/L were prepared from the stock solution by serial dilution in 100 mL volumetric flasks. The pH and ionic strength of the working solutions were adjusted to the required pH and ionic strength by adding appropriate amounts of 1.0 mol/L HCl solution and 1.0 mol/L NaOH solution. All pH measurements were made using a pH meter (JENWAY 3505).

2.4. Batch Adsorption Studies

Batch adsorption experiments were carried out by measuring 100 mL of the aqueous solution containing varying initial concentrations into a 250 mL conical flask and 5.0g of the adsorbent was added to the solution. The mixture was agitated in an orbital shaker (Rotamax 120, Reidolph) at 150 rpm and a temperature of 25 °C for 1 h to attain equilibrium. The mixture was thereafter filtered using a Whatman No 14-filter paper and the resultant residual CV dye concentration was determined using UV-spectrophotometer (UV 2500) at a wavelength of 590 nm and the resultant amount of CV dye adsorbed was calculated. The experimental parameters such as initial concentration (25-150 mg/L), adsorbent dosage (1-9 g), contact time (15-120 mins), pH (3-11), particle size (100-300 μm) and temperature (20-60 °C) were checked to evaluate the optimum conditions for the maximum adsorption of crystal violet from 100mL aqueous solution over an applied adsorbent. For each batch experimental run, the amount of CV dye adsorbed per unit mass of activated carbon at equilibrium q_e, (mg/g), at time, t, q_t (mg/g) and the % removal of the CV dye was determined using Equation 2.1, Equation 2.2 and Equation 2.3 respectively.

$$q_e = \frac{(C_o - C_e)V}{M} \qquad \text{Equation 2.1}$$

$$q_t = \frac{(C_o - C_t)V}{M} \qquad \text{Equation 2.2}$$

$$\% \text{ removal of CV Dye} = \frac{100(C_o - C_e)}{C_o} \qquad \text{Equation 2.3}$$

where C_o = initial concentration of solution (mg/L), C_e = equilibrium concentration (mg/L), C_t = concentration of solution at time, t, (mg/L), V = volume of the solution (mL) and M = mass of adsorbent used (g).

III. Result and Discussion

3.1 Characterization Avocado Pear Seed Activated Carbon (APSAC)

The physicochemical properties of Avocado pear seed activated carbon (APSAC) were determined using proximate analysis as shown in Table 3.1. Activated carbon is often produced free of moisture content, but if it contains moisture, it should not be more than 10% because moisture content reduces the adsorption capacity of activated carbon (Abiko *et al.*, 2010); thus, APSAC contained 0.67% moisture content.

Ash content negatively influences the overall activity of activated carbon and reduces reactivation efficiency. The typical range of values for commercial activated carbon (CAC) is 2-10% (Aznar *et al.*, 2011), and the ash content of APSAC was 2.25% which was well within the acceptable range. Activated carbon having a high value of fixed carbon implies that the adsorbent is having more efficiency and stability. The pH of APSAC was 6.99, determined using the method described by (Bansode *et al.,* 2004), and the acceptable pH for most commercial activated carbon is pH 6- 7.

Table 3.1: Physicochemical Analysis of Adsorbent (APSAC).

S/N	Property	Value
1	pH	8.23
2	Bulk Density (g/cm^3)	0.863
3	% Volatile matter Content	1.14
4	% Moisture Content	0.67
5	% Ash Content	2.25

3.2 FT-IR Analysis of the Adsorbent (APSAC).

The Fourier Transform-Infrared (FTIR) spectra analysis of APSAC before and after adsorption revealed the presence of several peaks indicating the presence of different functional groups within the wavelength of 1000-3500 cm^{-1} as shown in Figures 3.1 and 3.2. Figure 3.1 shows the FTIR spectra of the APSAC before adsorption, which revealed a broad and intense absorption peak between 2374.3 cm-1 and 2113.4 cm-1, representing the presence of –OH stretching of the alcohol group. While Figure 3.2 shows the FTIR spectra of adsorbed avocado pear seed activated carbon and the major bands. Its major functional groups are symmetrical stretching vibration of (OH) of phenol, C=C stretching of the carboxyl group, and OH stretch with wave numbers of 2370.6 cm^{-1} and 2117.1 cm^{-1} respectively. This significant change indicated that APSAC is a good precursor for the removal of crystal violet dye from an aqueous solution.
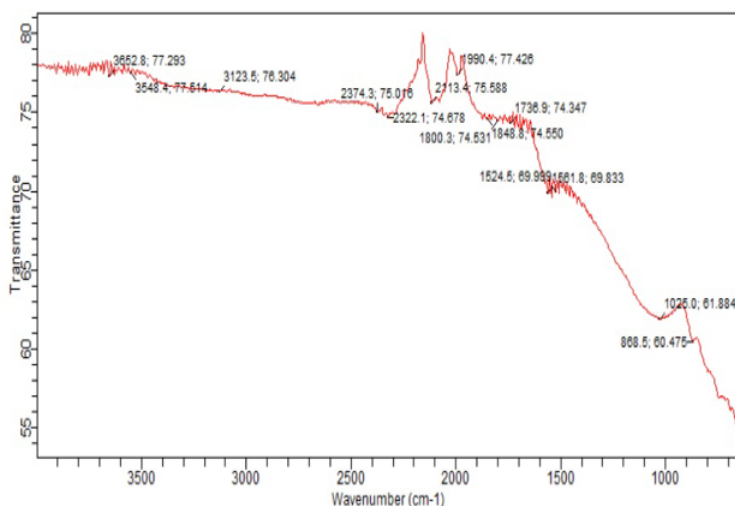
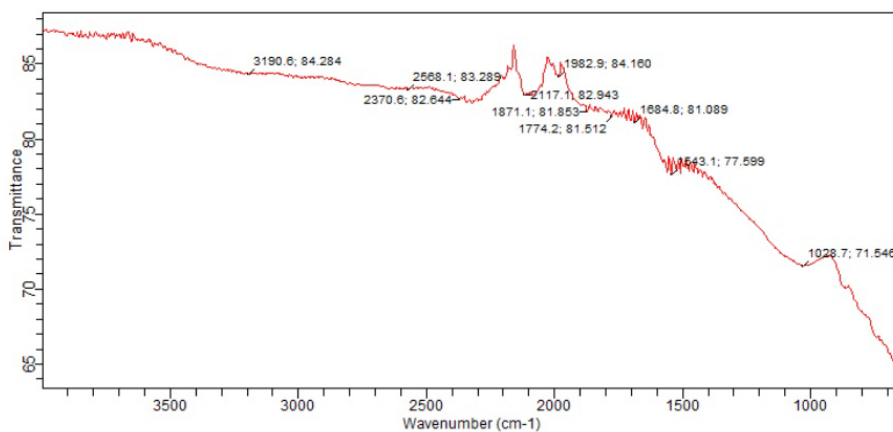Figure 3.1: FTIR spectra of the APSAC before adsorption

Figure 3.2: FTIR spectra of the APSAC After adsorption

3.3 Surface Morphology Analysis of the Adsorbent.

Scanning Electron Microscopy (SEM) analysis of Avocado Pear Seed Activated Carbon before and after adsorption was observed based on the SEM images presented in Figures 3.3 and 3.4. Based on Figure 3.3, the Avocado pear seed activated carbon before adsorption was observed to have tiny hole-like pores with a proportional porosity and also rod-like structure with irregular sizes. The sharp edges on the structure indicate that the Avocado pear seed activated carbon has

good crystallinity and the presence of some luminous fragments which allows the site's interchanges thus making the adsorption mechanism possible. As seen in Figure 3.4, the surface morphology of Avocado pear seed activated carbon after adsorption was different as the treatment of the solute significantly altered the physicochemical properties and porosity of the adsorbent material. A decrease in the porosity and luminosity of the adsorbent material was noticed due to the adsorption of molecules onto its pores and surface respectively.
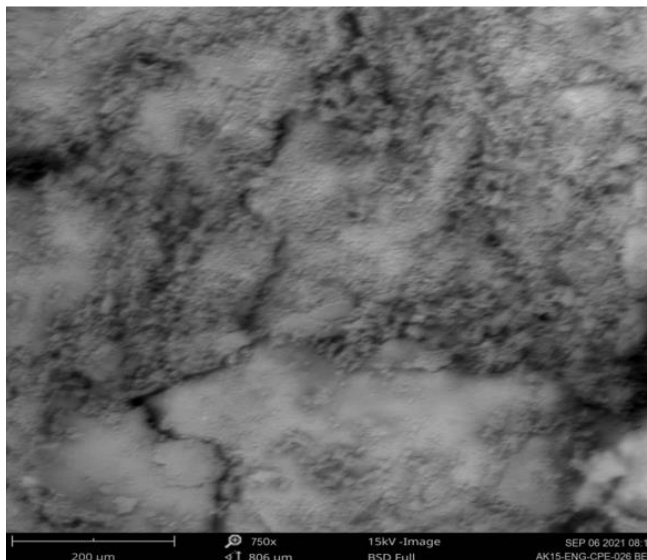
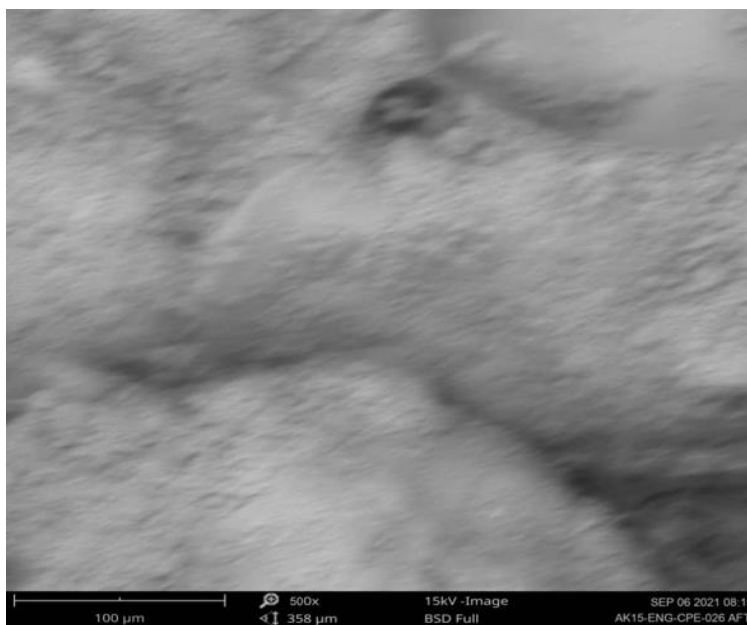Figure 3.3: SEM Analysis of the APSAC before adsorption

Figure 3.4: SEM Analysis of the APSAC after adsorption

3.4 Effect of Contact Time

The effect of contact time on the adsorption process was studied by adding 5.0 g of the adsorbent to 100 mL of the solution having an initial concentration of 100 mg/L, pH of 7 into different 250 mL conical flasks of pH of 7 and was then agitated for a predetermined time interval of 15-150mins until equilibrium to attained. As illustrated in Figure 3.5, it may be seen that the extent of adsorption was rapid at the initial stages and became slow in later stages till saturation is attained. The fast adsorption at the initial stage (contact time of 15-30mins) may be because a large number of active surface sites are available for adsorption. At higher contact time, both the % removal of CV dye and adsorption capacity gradually decreased leading to an equilibrium where saturation was attained. This decline was due to a decrease in total adsorbent surface area and fewer available binding sites. Similar results have been reported by Chakraborty *et al*. (2011).
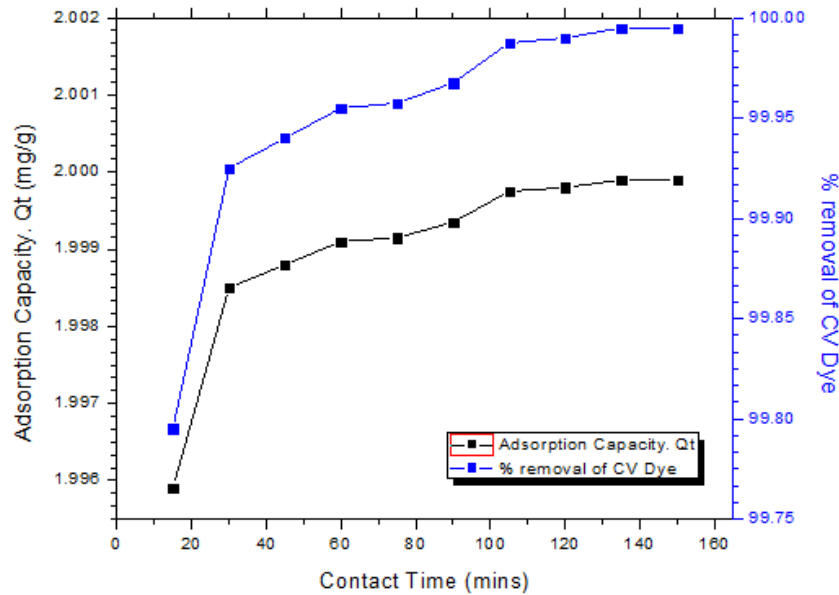
Figure 3.5 The effect of contact time on the adsorption capacity and % removal of Crystal Violet (CV) Dye.

3.4 Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied by adding various amounts of the adsorbents (1.0, 3.0, 5.0, 7.0, and 9.0 g) to 100 mL of the stock solution in different 250 mL conical flasks and agitating for 120mins. As shown in Figure 3.6, an increase in the adsorbent dosage led to a corresponding increase in the % removal of CV dye but decreased the adsorption capacity. The increase in the % removal of CV dye could be attributed to an increase in the adsorbent surface area which increased the number of active sites available for adsorption. Conversely, the decrease in adsorption capacity with increasing adsorbent dosage may be attributed to the unsaturation of the adsorption sites of the adsorbent during the adsorption process. These observations agree with those previously reported by other researchers for the adsorption of dyes using different precursor adsorbent materials (Aksakal and Ucun, 2010; Chakraborty et al., 2011).
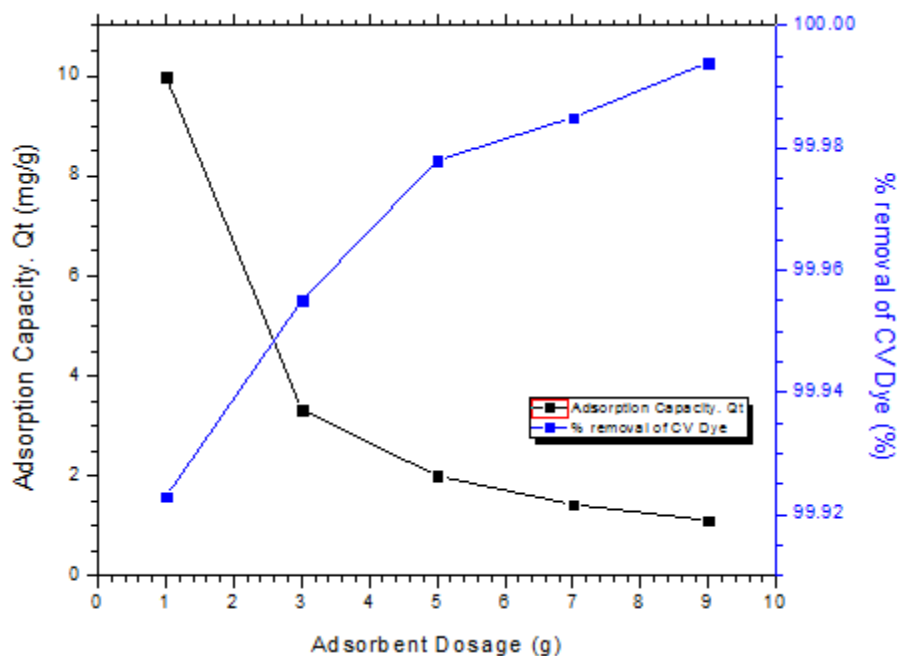

Figure 3.6: The effect of adsorbent dosage on the adsorption capacity and % removal of Crystal Violet (CV) Dye.

3.5 Effect of Initial Concentration

The effect of the initial concentration of CV on the adsorption efficiency by APSAC has been systematically investigated by varying the initial concentration of CV between 25-150mg/L. The experiments were conducted at the constant pH of 7, adsorbent dose of 5.0g/100mL and contact time of 150mins. Figure 3.7 shows that in CV adsorption by KPAC, the adsorption rate increased with an increase in CV concentration. This may be a result of an increase in the driving force of the concentration gradient.
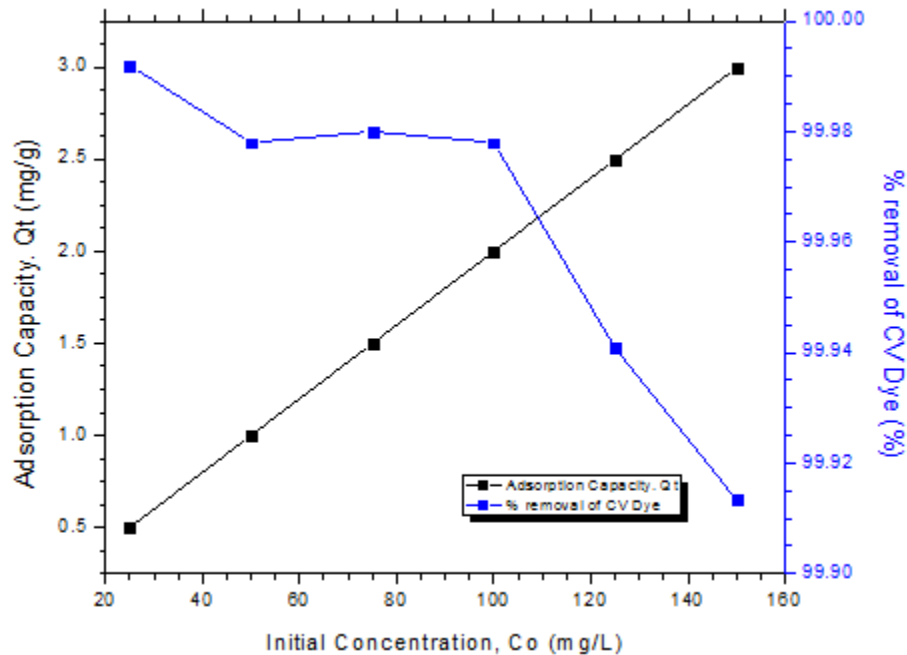

Figure 3.7: The Effect of initial concentration on the adsorption capacity and % removal of Crystal Violet (CV) Dye.

3.6 Adsorption Kinetic Studies

To investigate the mechanism of adsorption and potential rate-controlling steps such as mass transport and chemical reaction processes involved in the CV adsorption from the aqueous solution, several kinetic models such as the pseudo-first order, pseudo-second order, intraparticle

diffusion and Boyd models were used for the analysis. Table 3.1 showed that the correlation coefficients for the pseudo-second-order kinetic model for APSAC ($R^2 = 0.977$) were much higher and closer to unity than that of the pseudo-first-order kinetic model and intra-particle diffusion, thus; concluding that the adsorption behaviour of CV dye on APSAC predominantly followed the pseudo-second-order kinetic model. This also elucidated the fact that the overall rate of the adsorption process was controlled by chemisorption which involved co-valent forces through the sharing or exchange of electrons between the adsorbents CV dye and also that the rates of surface reaction, a chemical reaction (chemisorption) and transport of CV dye from liquid to adsorbent phase was faster due to the high hydrophobic nature of the modified adsorbents (Chakraborty *et al.*, 2011; Ukpong *et al.*, 2020). This kinetics result was similar to that obtained by Ahmad, (2009) and Depci *et al.* (2012) in the adsorption of crystal violet using coniferous pinus bark powder (CPBP) and activated carbon obtained from Golbasi lignite, in which pseudo-second-order kinetic model best described the adsorption kinetics as the most effective. Comparing the results of the kinetics models reveals that the pseudo-second-order model has the best agreement with the experimental data.

Table 3.1: Adsorption kinetic model constants for the removal of Crystal Violet (CV) Dye.

Adsorbents	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order			Intra-particle Diffusion			
		K_f (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2	K_s (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2	K_{ip} (mg/g.min$^{1/2}$)	C (mg/g)	$q_{e,cal}$ (mg/g)	R^2
APSAC	1.9999	0.423825	1.9994	0.861	15.607	2.000	0.977	0.000383	1.9957	2.00013	0.8135

3.7 Adsorption Isotherm Studies

The adsorption isotherm study was analysed using a plot of the adsorption capacity of CV dye at

equilibrium, q_e versus the equilibrium concentration of CV dye, C_e as illustrated in Figure 3.8 for CV dye adsorption onto APSAC. Six isotherm models namely; Langmuir, Freundlich, Temkin, Toth, Sip and Redlich-Peterson models were used and the applicability of these isotherm equations used to describe the adsorption process was determined using the correlation coefficients, R^2 values and other error functions. Table 3.2 showed that the Langmuir isotherm model had the best fit to the experimental data with a correlation coefficient, the R^2 value of 0.965, thus suggesting the formation of multilayer coverage of CV onto the heterogeneous distribution of active sites on the surface of APSAC.

Table 3.2: Adsorption Isotherm constant for the removal of Crystal Violet (CV) Dye.

Adsorbent	Adsorption Isotherm Models											
	Langmuir		**Freundlich**		**Temkin**		**Toth**		**Sip**		**Redlich-Peterson**	
APSAC	q_m (mg/g)	3.325	K_f (mg/g)	6.427	A (L/g)	849.31	q_m (mg/g)	3.9158	q_{ms} (mg/g)	3.6752	A	221.327
	K_L (L/mg)	53.524	N	2.772	B	0.61439	K_T (L/mg)	18.847	a_s (L/g)	21.7069	B	55.4098
							T	0.6888	B_s	0.828	β	0.9042
	R^2	0.965	R^2	0.9439	R^2	0.9505	R^2	0.966	R^2	0.9667	R^2	0.966

Figure 3.8 showed that the Langmuir isotherm model yielded the highest adsorption capacity of 3.325 mg/g for APSAC followed by the Freundlich, Sip, Toth, and Redlich-Peterson models.
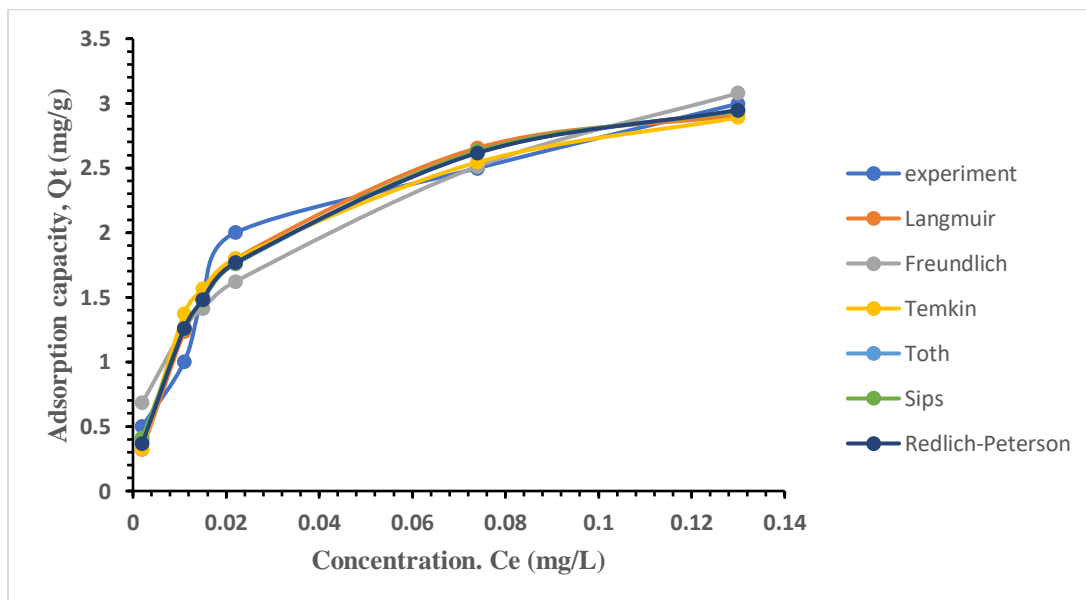

Figure 3.8: The Isotherm model plots for the removal of Crystal Violet (CV) Dye onto APSAC

3.8 Comparison of APSAC with other Adsorbent

Table 3.3 summarises the comparison of the maximum CV adsorption capacities of various sorbents including APSAC. The comparison shows that APSAC had higher adsorption capacity and % removal of CV dye than many of the other reported adsorbents. In addition, the precursor material (avocado pear seed) used to produce the activated carbon is a cheap and readily available material. The CV dye-loaded APSAC can be dried and used as fuel in boilers/incinerators or to produce fire briquettes (Chowdhury *et al.*, 2011). The ash may be used to make fire bricks, thus disposing of CV through chemical fixation (Chowdhury *et al.*, 2011). This approach of adsorbent disposal entails energy recovery from the adsorbent and the safe disposal of the adsorbed

CV. Thus, the use of APSAC as an adsorbent is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for waste water treatment processes.

Table 3.3 Comparison of CV adsorption capacity of APSAC with other reported low-cost adsorbents and their researchers.

Adsorbents	q_{max} (mg/g)	References
Sugarcane fibre	10.44	Parab *et al.* (2009)
Orange peel	14.3	Annadurai, Juang, and Lee (2004)
Sugarcane dust	3.8	Khattri and Singh (1999)
Coir pith	2.56	Namasivayam, Radhika, and Suba (2001)
Calotropis procera leaf	4.14	Ali and Muhammad (2008)
Avocado pear seed	3.3254	This study

IV. Conclusion

The present study focused on the adsorption of CV dye from an aqueous solution using APSAC as a low-cost adsorbent. The conclusions drawn from the study are as follows:

(i) Avocado pear seed which can constitute a waste material if not properly managed and controlled has been found to be a good precursor for producing activated carbon for the treatment of industrial effluents (textile dye) to achieve a cleaner environment.

(ii) The kinetic data fitted well into the pseudo-second-order model equation.

(iii) The experimental data were analysed using Langmuir, Freundlich, Temkin, Soth, Sip and Redlich-Peterson isotherm models and the Langmuir model provided the best correlation of the experimental equilibrium data.

(iv) The energy of adsorption of CV using the APSAC indicates that it is a physisorption.

(v) The pre-treatment of APSAC with a diluted concentration of HCL acid effectively enhanced its surface hydrophobicity, thus increasing the adsorption capacity and % removal of CV dye.

Thus, it is recommended that before final discharge, the secondary wastewater treatment should be carried out to further treatment for chemical oxygen demand (COD), Biochemical oxygen demand (BOD) and heavy metals. It is also recommended that the disposal of industrial waste water without proper treatment should be discouraged.

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