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Kinetics and Equilibrium Studies of the Adsoption of Methylene Blue Dye from Aqueous Solution on Carbonized Groundnut Shell

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Abstract
This study investigated the adsorption of Methylene Blue dye present in aqueous solution onto the activated carbon produced from groundnut shell. The dried groundnut shell was carbonized at 300^{o}C using a crucible in a muffle furnace for 20 minutes which was characterized using Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) Spectrophotometry before and after adsorption. Batch adsorption was carried out to study the various parameters influencing the adsorption such as the contact time, the adsorbate concentration, adsorbent dosage, pH and the temperature. The highest percentage removal of methylene blue dye was achieved with an adsorbent dosage of 1.0 g, an adsorbate concentration of 15 mg/L methylene blue dye, pH of 7.0, the contact time of 90 minutes and temperature of 30 °C. Generally, the removal of methylene blue dye decreased as temperature increased from 30-50 °C except for an increase at temperatures of 40-45 °C. The variation of contact time showed an increase from 30-90 minutes, after which a decrease occurred from 90-120 minutes. As pH increased from 3-11, adsorption reached a maximum at pH of 6.68 and then there was a decrease. There was a progressive increase with a variation of adsorbent dosage from 0.2-1.0 g. A variation in adsorbate concentration from 1-15 mg/L also showed a progressive increase in adsorption. The three most common adsorption equations, Temkin, Freundlich and Langmuir adsorption isotherms were used in the study to verify the adsorption performance. From the interpretation of the equations, the Freundlich adsorption isotherm (R^2=0.802) was found to fit the experimental data better than the other two.

Keywords: Groundnut shell, methylene blue dye, adsorption, adsorbent, characterization

1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. Industries such as paper, Textile, Plastic, Detergents, Cosmetics, Leather, Pharmaceutical and Food industries continually discharge effluents containing

dyes and their breakdown products which are toxic to living organisms into the ecosystem (Nguyen, 2012; Patil and Shrimastava, 2010).
About 1–20 % of the total world production of dyes is lost during the

dyeing process and is released in the textile effluents (Mansour et al, 2012). The toxicity of some dyes even at very low concentrations may significantly affect aquatic life. Incidences of skin irritation, allergy, and cancer to humans may also result (Arami et al, 2005; Yang et al, 2003). Therefore, the decolorisation of dyes is an important aspect of wastewater treatment before discharge (Karitha and Senthamilserfi, 2012). In Nigeria, several treatment methods such as biological, chemical and physiochemical are used for the removal of dyes from wastewater, such include electrochemical oxidation (Nidheesh et al, 2018), ozonation (Wijannarong et al, 2013), electrocoagulation (Pirkarami and Olya, 2017), photo process Fenton (Sohrabi et al, 2017), nanofiltration, reverse osmosis (Wataraj et al, 2009), etc are used in order to remove these substances from wastewater, but most of these methods have serious restrictions such as formation of hazardous by-products, intensive energy requirement or high cost (Omotayo et al, 2014).

Although activated carbon is one of the most effective and efficient treatment techniques for the removal of dyes from wastewater, its cost and disposal problems (Malik, 2014) informed its preparation from agricultural by-products especially for applications concerning the treatment of wastewater. Researchers have studied the production of activated carbon from agricultural wastes such as groundnut shell (Alaa et al, 2016), rice husk (Hameed, 2008) pineapple peels (Nguyen, 2012), coconut, sawdust (Malik, 2014), yam fibre (Crini, 2006), maize cobs (Alaa et al, 2016), palm kernel shell (Omotayo et al,2014), banana peel, neem leaf (Nguyen, 2012), mango seed carnal (Hameed, 2008), vegetable waste (Malik, 2014). The advantage of using inexpensive natural resources as raw materials for manufacturing of activated carbon is that these raw materials are renewable and potentially less expensive. The idea of using groundnut shell (which ordinarily contributes to environmental pollution in some areas) to produce activated carbon rises in this context in the management of dyes. Thus, the utilization of these shells in the removal of dyes will be a great advancement in researches involving chemists. This is because, they will not only help in reducing the dangers man is exposed to by having direct contact with such dyes, but also provide the solution to littering problems which these shells invariably constitute in some areas. The present study was undertaken to evaluate the efficiency of activated carbon produced from groundnut shell in the removal of methylene blue dye.

2. Material and Methods

2.1 Preparation of Carbonized Groundnut Shell

Groundnut shells were obtained from Wadata market, Makurdi, Benue State. They were washed to get rid of sand and other impurities, and then sun-dried. The dried groundnut shells were subjected to further crushing, after which they were ground using a mortar and pestle into fine size particles. The ground groundnut shell was sieved through a 52μm sieve (Akinola and Umar, 2015). The sieved size groundnut shell was steeped in a saturated solution of Ammonium chloride (NH_4Cl) for 24hr, thereafter it was rinsed with

distilled water, filtered and the residue of the groundnut shell was dried at room temperature. The dried groundnut shell was carbonized at 300 ^{o}C using a crucible in a Ney M-252 Model muffle furnace for 20 minutes (Kannan and Sundaram, 2001). The carbonized groundnut shell was washed with distilled water to get rid of ash content, dried in the laboratory and stored in an airtight container for further use.

2.2 Preparation of Methylene Blue Dye Stock Solution

1000 mgL^{-1} stock solution of Methylene blue was prepared by dissolving l g of Methylene blue in distilled water and the volume made up to graduated mark in a 1000 mL volumetric flask that was shaken to obtain homogeneity and kept for serial dilution.

2.3 Experimental Procedure

1000 mgL^{-1} stock solution of Methylene blue was prepared by dissolving l g of Methylene blue in distilled water and the volume made up to graduated mark in a 1000 mL volumetric flask that was shaken to obtain homogeneity and kept for serial dilution. Batch adsorption studies were carried out to obtain the rate of adsorption and equilibrium data. This was performed at varying temperatures, concentrations, adsorbent dosage, contact time and pH. A calibration curve was obtained by Uv-visible spectrophotometer at concentrations from 1 mgL^{-1} to 15 mgL^{-1}. A mass of 1 g of the adsorbent was contacted with 50 mL of Methylene blue dye solution of concentration range 1.0-15.0 mgL^{-1}, in 100 mL beakers using Clifton Model thermostat water bath maintained at 25^{o}C. Samples of carbonized groundnut shell of mass range 0.2-1.0 g were added to 50 mL of Methylene blue (15 mgL^{-1}) in different 100 mL beakers. These were all stirred using Hy-2 model mechanical vibrator for one hour, after which they were filtered. The effect of contact time on the adsorption capacity was studied in the range of 30-150 minutes at room temperature. 50 mL (of 15 mgL^{-1}) of the adsorbate was added to 1 g of carbonized groundnut shell in a 100 mL beaker, then dipped in a Clifton model water bath. Adsorbents of 1 g were weighed and poured into five separate conical flasks. Then 50 mL of the standard solution of methylene blue dye was added to each conical flask and their pH was adjusted to 3.0, 5.0, 7.0, 9.0 and 11.0 respectively. They were all placed on a Hy-2 Model mechanical shaker at 25 ^{o}C for 1 hour**.** The effect of temperature on adsorption was carried out at varying temperatures of 30, 35, 40, 45 and 50 ^{o}C. l g of the adsorbent was contacted with 50 ml of 15 mgL^{-1} adsorbates for one hour each. After contacting, each of the solutions was filtered and the filtrate analyzed on the 7305 JENWAY Uv-visible spectrophotometer.

3. Results and Discussion

3.1 Characterisation

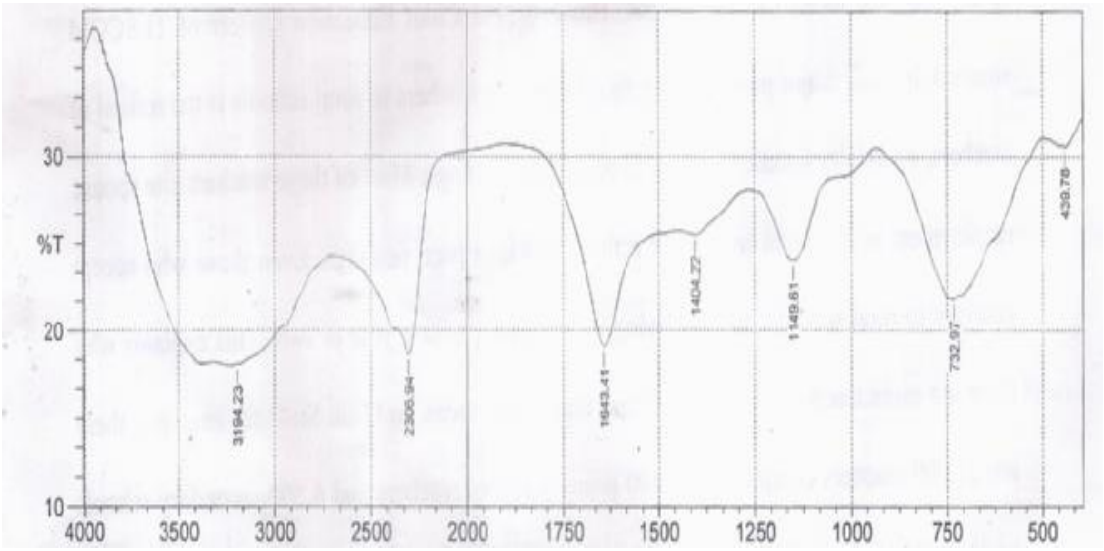


Figure 1a: FTIR Spectra of Uncontacted Groundnut Shell Adsorbent

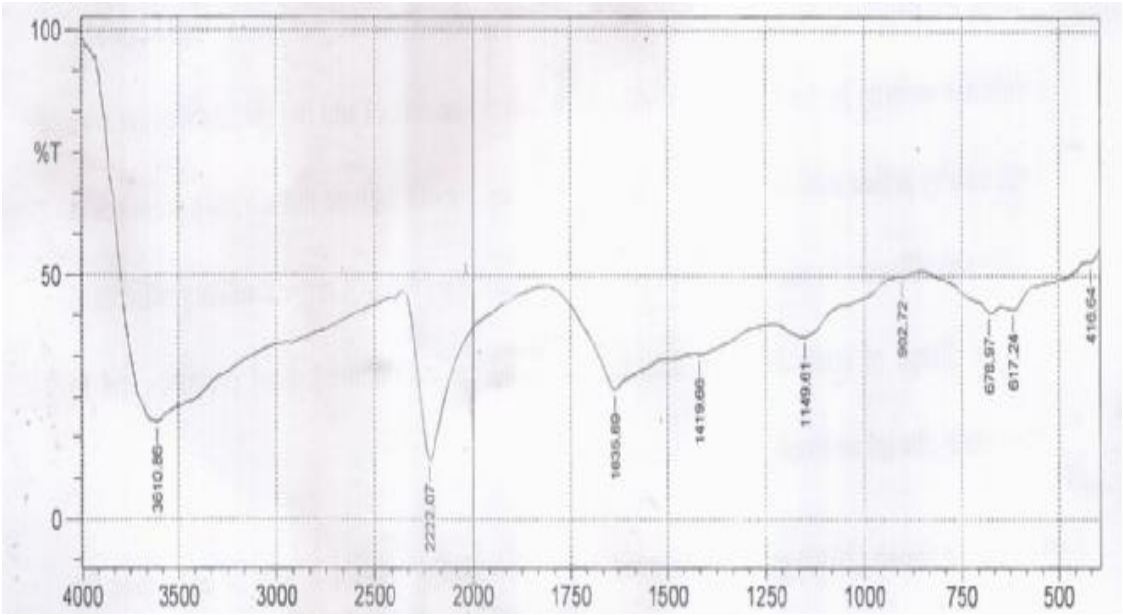


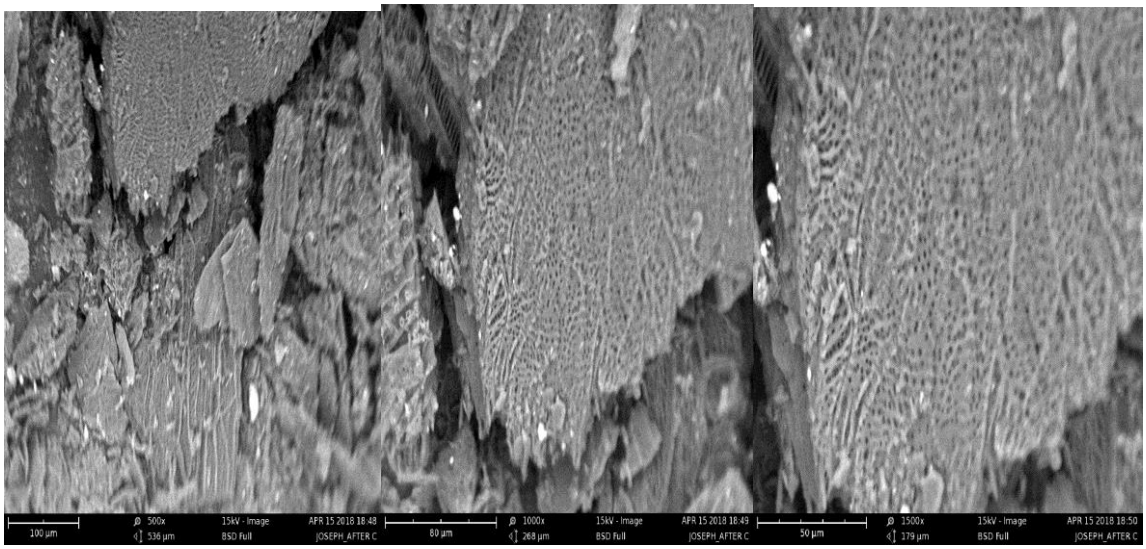
Figure 1b: FTIR spectra of contacted groundnut shell adsorbent

The FTIR spectra of contacted carbonized groundnut shell, showing a characteristic band at 3610.86 cm^{-1} corresponds to 0-H stretching vibrations, peak at 2222.07 cm^{-1} can be linked to the C≡C stretching vibration in alkyne groups. 1635.69 cm^{-1} represents C=C stretch. The peak 1419.66 is a characteristic CH_2 bending vibration in

an aromatic ring. The appearance of a band at 1149.61cm^{-1} can be attributed to C-O stretching vibrations in alcohol, phenols, and peak 902.72cm^{-1} are due to = C-H functional groups of the alkenes. Peak 678.97cm^{-1} is band caused by O-H out of plane bending of benzene derivatives. Peak 617.24CM^{-1} is due to C-Cl stretch Alkyl Halide functional group. Peak 416.64 is due to C-1 stretch alkyl halide functional group.

This corresponds closely with other research work (Ejikeme et al, 2014). This implies that the carbonized groundnut shell is also a good adsorbent, for the adsorption of methylene blue dye. More so, the observed increase in the intensity of the peaks suggests that there is an addition of the methylene blue dye to the adsorbent and since there was no complete shift in adsorption, this mechanism is suggestive of physical adsorption (Yoshiyuki and Tukata,2003).

3.2 Scanning Electron Microscope



(a) (b) (c)

Figure 2: SEM images of groundnut shell adsorbent (a) 500x magnification (b) 1000x magnification (c) 1500x magnification

The scanning electron microscope (SEM) Microstructure revealed the physical morphology of the activated carbon derived from groundnut shell. The images of the pore on the surface of the carbonized groundnut shell were analyzed. This is necessary because Adsorption occurs at the surface via the pore.

Comparisons of analysis result were made of groundnut shell pore before and after contact with the adsorbates. SEM microgram of activated carbon shows the presence of wide pores which result due to chemical activation with the acid (Alaa et al, 2016).

3.3 Effects of Adsorbate Concentration

The result of the effect of concentration as represented in figure 1 shows that the adsorption increases with increase in concentration from 1- 4.5 mg/L, with methylene blue dye adsorption capacity decreasing as adsorbate concentration increases from 4.5-15 mg/L. This can be attributed to the fact that as the concentration increases, more molecules are available for the adsorption process. This reveals that more active sites are utilized at lower adsorbent concentration, producing a higher adsorption capacity, while only part of active sites is occupied at higher adsorbate concentration, leading to a lower adsorption capacity (Li et al, 2010). Adsorption of Methylene blue dye on carbonized groundnut shell beyond 15 mgL^{-1} results in no significant removal of methylene blue since internal saturation of pores occurs (Vanderwiel,1999). Generally, these results show that carbonized groundnut shell is good for the adsorption of methylene blue (dyes) from aqueous solution. This agrees with the result of another researcher (Nuhu et al, 2018), where the initial metal concentrations studied ranged from 20-120 mg/L. It was observed that the percentage of adsorbate ions adsorption decreased with increasing initial concentration from 20-120 mg/L, this could be due to relatively smaller numbers of active sites available on the adsorbent, also that as the concentration of the adsorbate increases, so does the metal loading on the adsorbent (Nuhu et al, 2018).

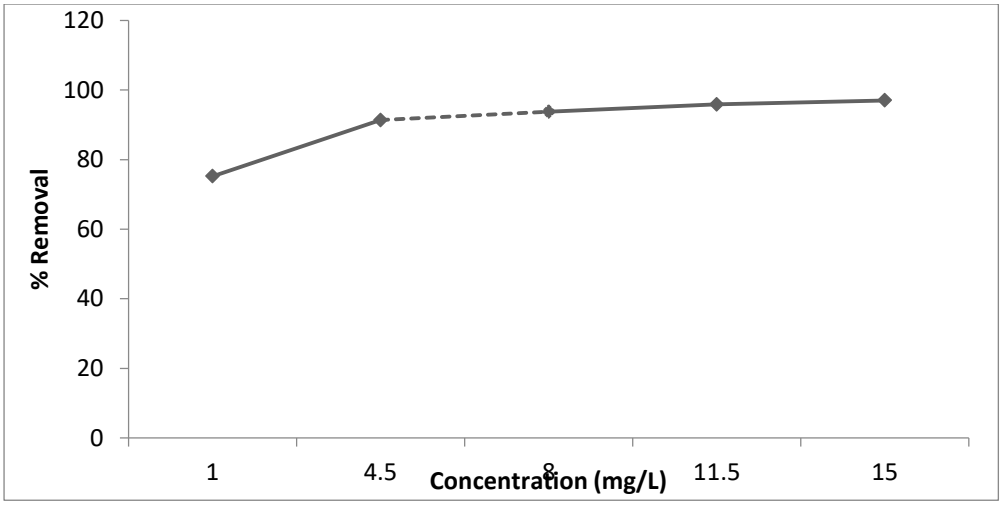


Fig 2 . Effect of Concentration

3.4 Effects of Adsorbent Dosage

The results for the adsorbent dose presented in figure 2 shows that equilibrium is attained at an adsorbent dose of 1.0 g, beyond which adsorption drops below the equilibrium. This indicates that the adsorption of methylene blue on carbonized groundnut shell increases and reaches equilibrium, then desorption sets in (Vanderwiel, 1999). As expected, at a constant initial concentration of dye, increasing the sample dose provides a greater surface area and a larger number of adsorption sites and hence the

enhancement of dye uptake (Bello and Ahmad, 2011). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose (Khattri and Singh, 2009; Balarak et al, 2017). The increase in adsorption with a corresponding increase in adsorbent dosage could also be as a result of the resistance to mass transfer of the adsorbate from the bulk liquid to the surface of the adsorbent (Ahile et al, 2018). This implies that carbonized groundnut shell is good for adsorption of methylene blue dyes. Another researcher also had an increase in adsorbent dosage from 0.2-1.0 g, having optimum removal at 0.6 g dosage, after which, it remained almost constant to the end of the analysis (Nuhu et al, 2018). A similar trend was also observed where there was an increase in the removal of adsorbate as the adsorbent dosage increased from 0.15-1.5 g/L (Balarak et al, 2017).

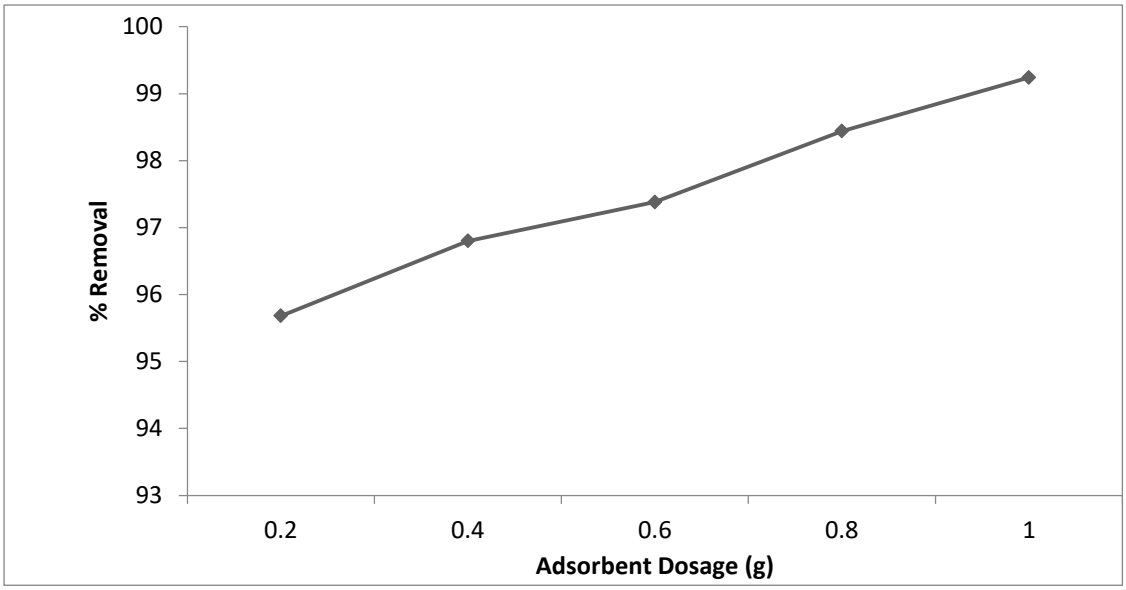


Fig 3. Effect of Adsorbent Dosage

3.5 Effects of pH

The result of the pH value as presented in figure 3 shows that adsorption of methylene blue dye is favored at the acidic pH of 6.68, after which there is a progressive drop in adsorption and beyond the pH of 9.0, there is no further removal of methylene blue (Wu et al, 2001). This could be due to the repulsive force prevailing at higher pH (Khalid et al,2017). This agrees with the work of other researchers, who records that as the pH of the system increases, the number of negatively charged sites increases which do not favor the adsorption of direct blue-dye anions due to the electrostatic repulsion (Amin et al, 2008; Ho and Mckay,2002).

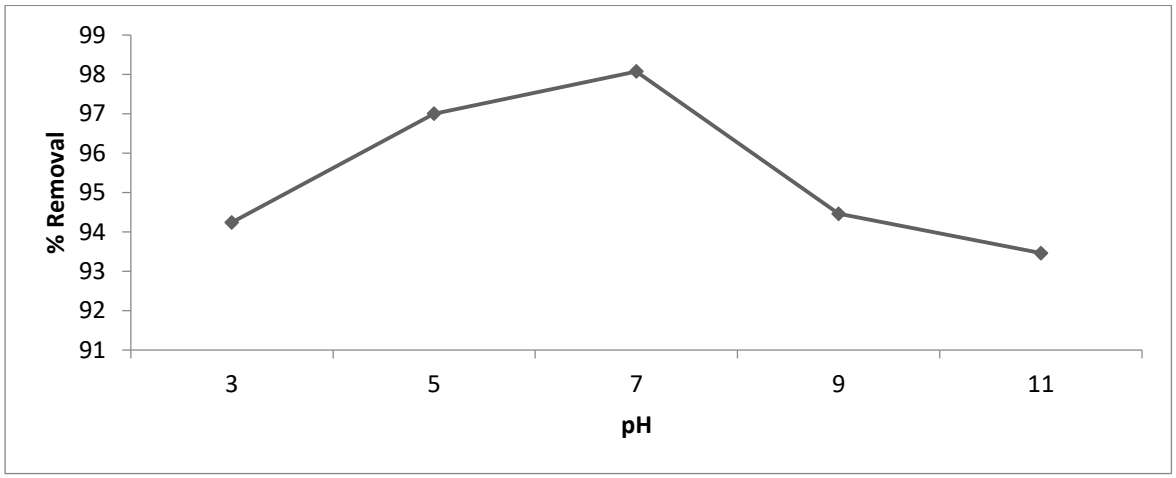


Fig 4. Effect of pH

3.6 Effects of Contact Time

The dye adsorption uptake was increased as contact time increased, attaining equilibrium at 90 minutes. This shows that adsorption takes place rapidly at the initial stage on the external surface of the adsorbent, then, after a lapse of time, the remaining surface sites are difficult to be occupied. Thus, adsorption of methylene blue on carbonized groundnut shell beyond 90 minutes resulted in no further removal of methylene blue, since interval saturation of pores occurs (Ho and Mckay, 2002). The experimental result on the effect of contact time on the adsorption of carbonized groundnut shell gives an insight into the sorption process, provides information on the minimum time required for considerable adsorption to take place and the possible adsorption mechanism between the adsorbate ions as it moves from the solution towards the adsorbent surface (Hughseresht and Lu, 1998). The decrease in the adsorption as time progresses could be due to the fact that the surface area of the adsorbent was largely covered since the adsorption kinetics depends on the surface area of the adsorbents which is in accordance with another researcher (Terungwa, 2018). It could also be due to the repulsion between the solute molecules of the solid and bulk phases, thus taking a long time to reach equilibrium (Ho and Mckay, 2002). Similar results have been reported in the literature for the removal of dyes where there was a decrease in adsorption with an increase in the contact time after 90 minutes, which may be due to a desorption process (Kannan and Sundaram, 2001).

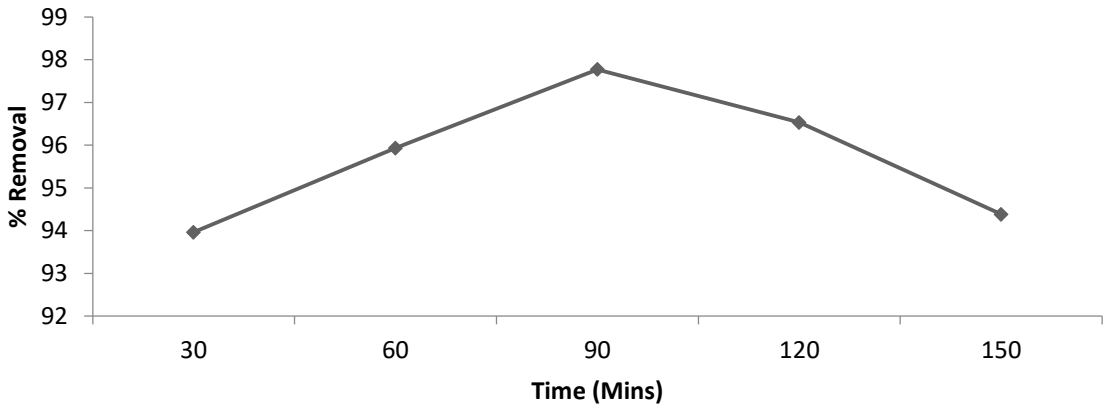


Fig 5. Effect of Contact Time

3.7 Effects of Temperature

The result of temperature as represented in figure 5 shows that equilibrium was attained at 30 ^{o}C after which adsorption dropped. This implies that adsorption decreases with increases in temperature (Chitton et al, 2012). The effect of temperature was also conducted on a water bath at varying temperatures (30, 35, 40, 45 and 50 ^{o}C). This data showed that with increasing temperature, the amount of methylene blue dye absorbed on the surface of the adsorbent increases from 30 - 40 ^{0}C. This can be attributed to active forces of attraction between the adsorbent and the adsorbate ion in solution which may have been active, making the adsorption to increase (Narges, 2013). This implies that an increase in temperature creates a wider surface area for adsorption at the adsorbent (Ejikeme et al,2014). At 50 ^{0}C the thickness of the boundary layer is expected to decrease due to the increased tendency of the ions to escape from the surface of the adsorbent to the solution phase hence there is bound to be weak adsorption interaction between the adsorbent and the adsorbate (Terungwa, 2018). An increase in temperature between 40 ^{0}C and 50 ^{0}C caused a proportional decrease in the amount of methylene blue dye adsorbed on the surface of the adsorbent. This decrease in the adsorption capacity with an increase in temperature indicates that the adsorption processes were exothermic in nature (Terungwa, 2018; Garcia-Araya et al, 2003; Kibami, 2018)

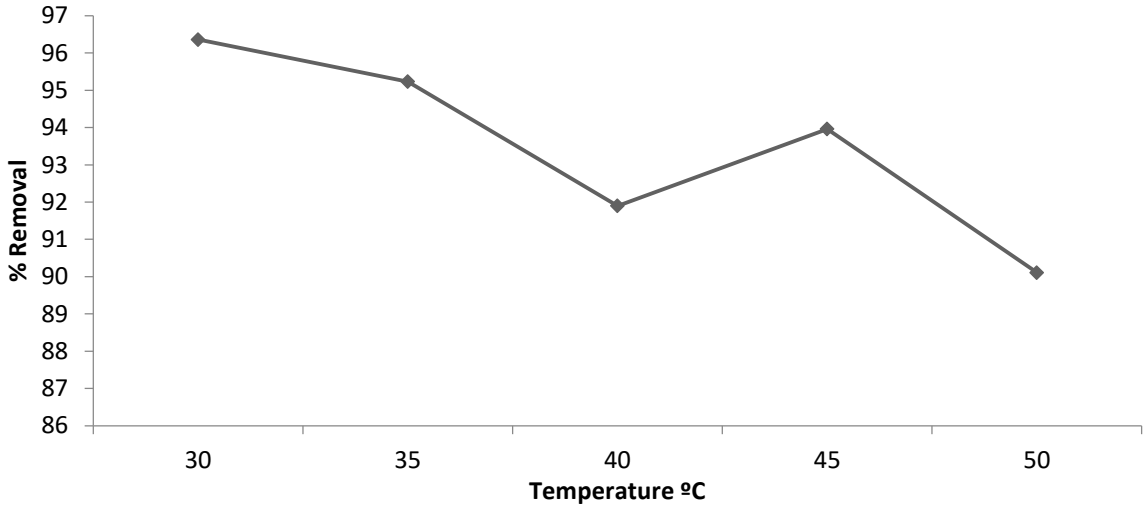


Fig 6. Effect of Temperature

3.8 Adsorption Studies

The adsorption isotherm indicates that the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the equilibrium adsorption by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes (Hughseresht and Lu, 1998). Adsorption isotherm study is carried out on three well-known isotherms, Freundlich, Temkin, and Langmuir. The Freundlich model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (Terungwa, 2018). The Langmuir isotherm assumes the monolayer adsorption onto the surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Terungwa, 2018). The applicability of the isotherm equation is compared by judging the related correlation coefficients (R^2). The related correlation coefficients show that the Freundlich model, which is an empirical model suitable for heterogeneous surface adsorption yields a somewhat better fit (R^2=0.802) than the Tempkin and Langmuir model (R^2= 0.631) and (R^2= 0.024) respectively. This is suggestive of more heterogeneous adsorption sites on the adsorbent, giving room for multiple layers of adsorption on the surface of the adsorbent (Ahmed et al, 2015).

Table 1: Correlation coefficient for methylene blue on groundnut shell adsorbent.

Adsorption Isotherm	R^2
Langmuir	0.024
Freundlich	0.802
Tempkin	0.631

Conclusion

The adsorption of methylene blue dye was carried out using batch adsorption studies. The effects of temperature, pH, adsorbent dosage, the concentration of the adsorbate and contact time were monitored. Careful observation found that the adsorption of methylene blue from aqueous solution depends on the solution adsorbent dose, contact time, concentration, pH and temperature. The adsorption obeys Freundlich adsorption isotherm because the R^2 value is close to the degree of unity

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