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KINETICS OF ADSOPTION OF METHYLENE BLUE ONTO ACTIVATED KOLANUT POD

Muhammad, A.S. and Abdurrahman, M.A.
Department of Pure and Industrial Chemistry, Bayero University, Kano. P.M.B 3011, Kano, Nigeria.
*Corresponding author: asmuhammed.chm@buk.edu.ng (08186615765)

ABSTRACT
A batch adsorption process was carried out by optimizing, the effect of contact time (10min to 180min) and initial concentration (5mg/l to150mg/l). The adsorbent was characterized using FTIR spectra and SEM, and the result obtained showed shifting and disappearance of peaks after adsorption. The results of the adsorption kinetics, which includes the correlation coefficient 0.9771 and the agreement between the amount adsorbed experimentally (1.472mg/g) and the calculated amount absorbed(1.196mg/g) revealed that MB was adsorbed satisfactory according to the pseudo second-order kinetic model.
Keywords: adsorption, kinetics, activation, methylene blue, dye.

INTRODUCTION

Textile industries produce one of the largest amount of wastewater due to how it consumes a large quantity of water used industrially in several ways for different purposes. Although a good number of chemicals are produced during the textile processing such as bleaching, scouring, dyeing, finishing and so forth, but the process that yield more variety of chemicals is the dyeing and finishing processes in which a variety of chemicals is widely used. If the toxicity increases, it accumulates in nature, and may lead to a terrible conclusion in environmental balance (Mishra, 2010). Contents of Textile dyes are ionic and organic, showing a strong affinity to the aqua solution and a bit on industry water (Karthik *et al.*, 2014). Currently, numerous processes for treatment of industrial effluents containing dyes are available, amongst which includes biodegradation (Barragan *et al.*, 2007), chemical oxidation (Feddal *et al.*, 2013), foam flotation (Yue *et al.,* 2008), electrolysis (Jin *et al.*, 2003), adsorption (Wan *et al.*, 2011) and electro-coagulation (Sami, 2012). Most of these conventional methods are inapplicable due to the high cost and disposal problems, due to the large amount of sludge generated at the end of the process (Ghoreishi and Haghighi, 2003). Adsorption is known to be a technique that gives a promising yield, ease of operation and comparably low cost of application, this have led to its great importance in the decoloration process (Mohammed *et al.*, 2014).

Yamun and Kamaraj (2016) reported a study on Pineapple peel waste activated carbon (PPWAC) as an adsorbent for the effective removal of methylene blue dye from aqueous solution. They found that the amount of dye adsorbed per unit / weight of adsorbent (mg/g) was concentration dependent while the effect of adsorbent dose on percent removal of the dye increased from 86.56 to 100% as the dose of the adsorbent increased from 25 to 200mg / 50 ml of adsorbate. The effect of pH shows that methylene blue adsorption increases with increase in pH and the uptake of dye increase from 35.27% to 100% as pH increased from 2 to 10.

Yusef *et al.* (2017) reported the study of the removal of Congo red dye from aqueous solutions by a low-cost adsorbent activated carbon prepared from *Aloe vera* leaves shell. They concluded that the amount of dye removal increases with increase in the dosage and the amount of dye removed increases with increase in dye initial concentration. They also used the value of the correlation coefficient (R^2) of the Langmuir ($R^2 > 0.96$) model to ascertain that the adsorption process obeyed Langmuir adsorption isotherm.

In this study the kinetics and mechanism of the adsorption of Methylene blue (MB) onto Activated kolanut pod(AKP) using batch adsorption process was investigated.

MATERIALS AND METHODS

All the chemicals used in this study were of analytical reagent (AR) grade and were used without any further purification. The chemicals used are: Methylene blue (MB) with 98% purity, hydrochloric acid (37% purity), sodium hydroxide (≥ 99% purity)

Sample Collection

Approximately 100kolanut pods and its content was obtained from Osun state, southwest of Nigeria from a village called Ikoromoja in Atakunmosa east local government near Ilesa local government.

Sample Preparation

The kolanut pods were cracked open and the content emptied, the kolanut pod were chopped in to smaller pieces to facilitate the drying process and the debris were washed thoroughly due to high viscous liquid that it produces. The rinsing of the samples were carried out with deionized water and air dried for two weeks and was subsequently washed severally with deionized water to remove all the viscous substance and finally air dried for a week, labelled and stored for further usage. (Samuel and Oladipupo, 2014) with little modification.

Preparation of the Activated Kolanut Pod

The dried sample was completely mixed with concentrated sulphuric acid (97% purity, 1.84 specific gravity) in the ratio 1:1 and kept in a Muffle furnace at 300^{o}C for 3 hours for activation. The material was taken out and washed severally with deionized water till the pH reached 7. It was then sieved through the mesh size of 0.5mm and then stored in plastic containers labelled AKP. Activation is based on the work reported by Yamun and Kamaraj (2016) with slight modification.

Adsorbate Preparation

1g/L stock solution of MB was prepared by dissolving 1g of the dye in 1litre volumetric flask containing 200cm^3 distilled water and then made up to the mark. Experimental solutions of the desired concentrations were obtained by dilutions from the stock solution thereafter to produce 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20mg/L for calibration curve and 10mg/L for adsorption studies.

Characterization and Analysis

The various functional group present on the AKP surface were determined using Fourier Transform Infrared Analysis (FTIR). The concentration of MB in the solution was measured by PerkinElmer UV-visible spectrophotometer at the maximum wavelength of 606nm. The solution pH was determined by pH meter model and the surface morphology was revealed through the use of scanning electron microscope model at 2000 magnification.

Batch Adsorption Experiment

The batch adsorption process was carried out in a 120ml stopped bottle containing 50 ml of 10 mg/L MB. 0.2 g of AKP was added in the solution, the dye solution was subjected to adsorption. The solutions were agitated using an electric agitator at 200rpm for 180 min at ambient temperature (31.5) samples were taking out and filtered after intervals of 10, 20, 30, 60, 90, 120, 150, 180min after which concentrations were determined using PerkinElmer UV-spectrophotometer at an absorbance wavelength of 606nm. The optimized time parameter was achieved by calculating the highest percentage removal using Equation1 and highest adsorption capacity using Equation2

$$\%removal = \left(\frac{C_0 - C_1}{C_0}\right) X 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} X 100 \quad (2)$$

Where C_0 (mg/L) is the initial dye concentration, C_e (mg/L) is the equilibrium dye concentration, m (g) is the sorbent mass, and V (L) is the volume of the dye solution.

The remaining parameters such as initial concentration at intervals of 5, 10, 20, 30, 50, 70, 100, 120 and 150ppm, initial bioadsorbent dosage at intervals of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8and 1g, initial temperature at intervals of 30, 40, 50and 60^{o}C and Initial pH at intervals of 1, 2, 3, 5, 7, 9 and 11pH were also optimized (Samusolomon and Martin, 2011).

RESULTS AND DISCUSSION

The results of the adsorption process obtained are discussed below.

RESULTS

FT-IR spectroscopy was used to investigate the interactions between different species and changes in chemical compositions of the adsorbents before and after adsorption of the dye. Figure 1 and 2 presents FTIR spectra of the adsorbent before and after adsorption of MB while Table 1 presents peaks and frequencies of IR absorption.

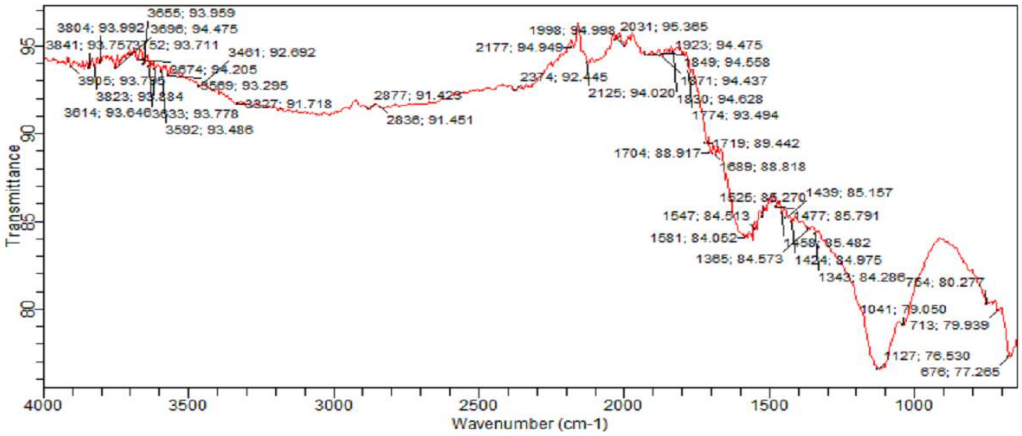

Figure 1: FTIR spectrum of AKP before adsorption

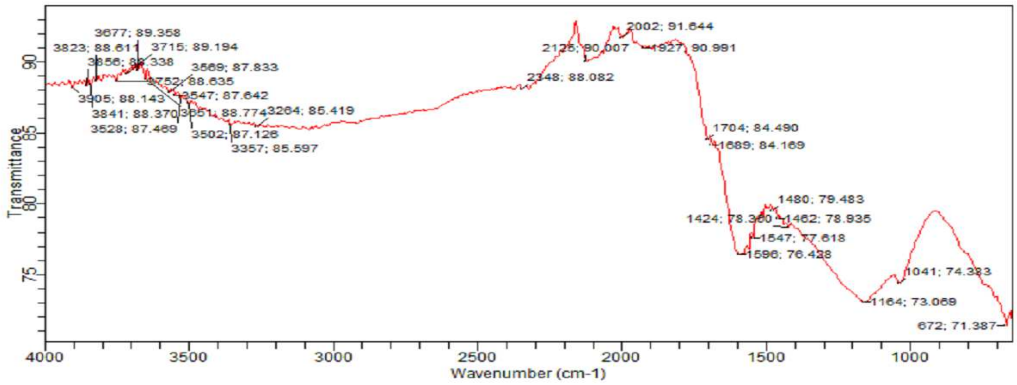

Figure 2: FTIR spectrum of AKP after adsorption of MB

Table 1: FTIR Spectral Data of AKP Before and After Adsorption by CR and MB

Before Adsorption AKP	After Adsorption AKP-MB Loaded	Assignment
3327	3357(+30)	O-H stretching vibration in carboxylic acid groups (2500-3500cm^{-1})
2877	-	O-H stretching vibration in carboxylic acid groups (2500-3500cm^{-1})
2836	-	O-H stretching vibration in carboxylic acid groups (2500-3500cm^{-1})
1719	-	General presence of C=O groups stretching vibrations (1650-1800cm^{-1})
1547	-	NO_2 in aliphatic nitro compounds due to antisymmetric stretching (1575-1545cm^{-1})
1424	1402(-22)	OH in carboxylic acid groups due to in-plane OH bending (1440-1400cm^{-1})
1127	1164(+37)	C-N stretching vibration in amines (1030-1330cm^{-1})
676	672(-4)	O-C=O in carboxylic acid groups due to O-C=O bending (700-590cm-1); C-C-CHO in aldehyde compounds due to C-C-CHO bending (695-635cm^{-1})

Scanning Electron Microscopy studies provide useful information regarding the surface morphology of the adsorbents. The SEM images of the AKP before adsorption are presented in Figures 3 and 4.

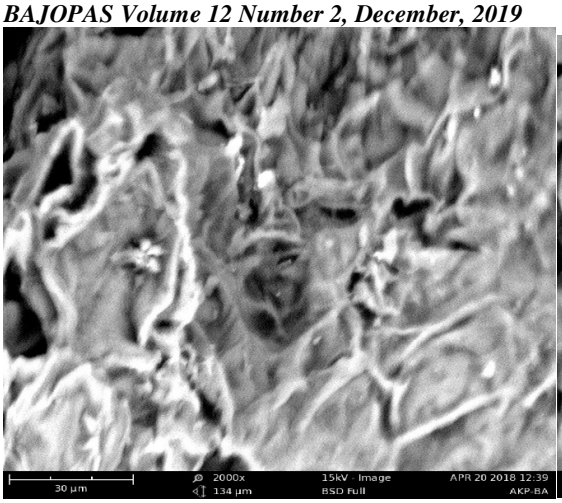

Figure 3: SEM micrograph of AKP before Adsorption

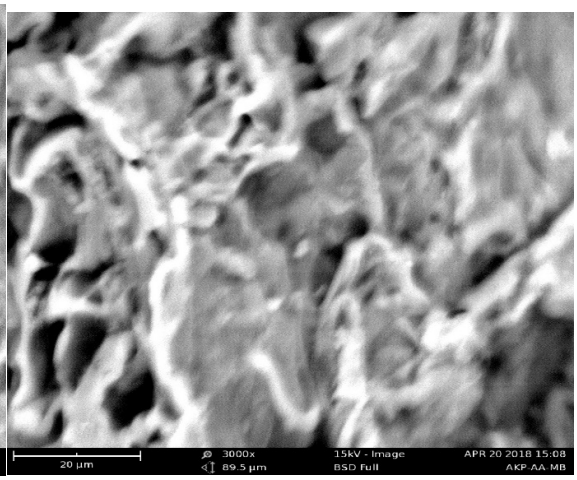

Figure 4: SEM micrograph of AKP after Adsorption of MB

Effect of Contact Time

The effect of contact time for the adsorption of MB onto AKP was studied, the result is as shown in figure 5

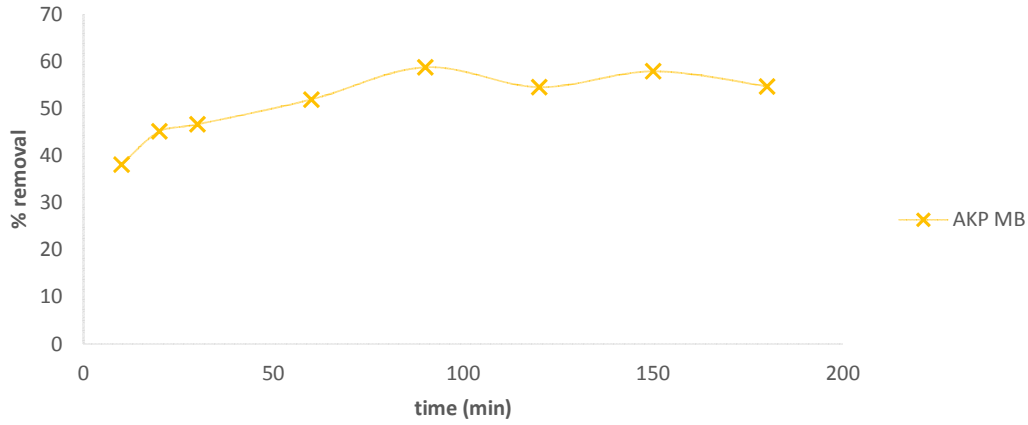

Figure 5: Effect of Contact Time on the Adsorption of MB onto the AKP

Effect of Initial MB Concentration

Figure 6 shows the effect of initial dye concentration for the adsorption MB onto AKP.

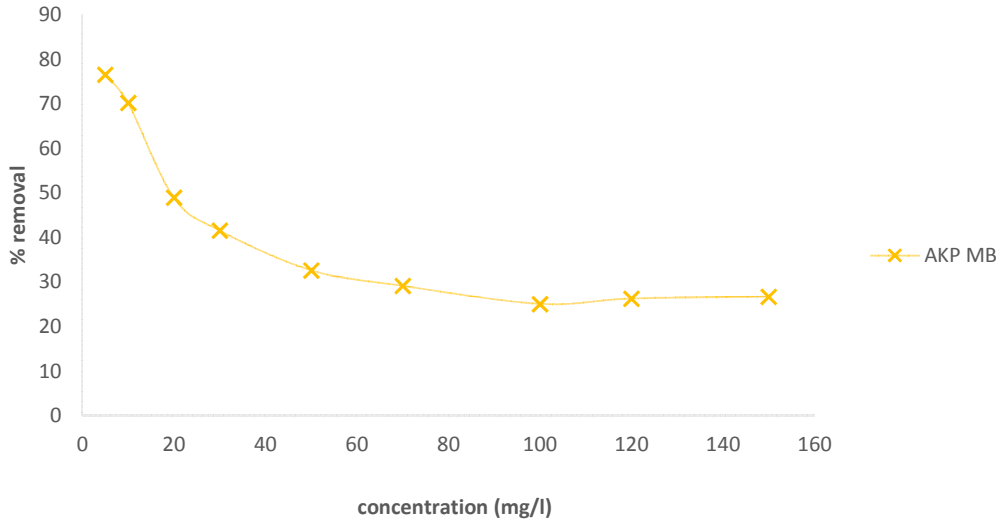

Figure 6: Effect of Initial MB Concentration

Kinetics studies

The kinetics of the adsorption MB onto AKP was investigated using the Pseudo first-order, Pseudo second-order and Elovich models and the results are shown in Table 2.

Table 2: Kinetic Parameters for the removal of MB from Aqueous Solution onto AKP.

Model	Kinetic parameter	
	$q_{e,exp.}$(mg/g)	1.472
PFO	$q_{e,cal.}$(mg/g)	0.291
	k_1(min^{-1})	0.0022
	R^2	0.0472
PSO	$q_{e,cal.}$(mg/g)	1.196
	k_2(g/mg.min)	-8.491
	R^2	0.9862
Elovich	α(mg/g.min)	7.32x10^3
	β(mg/g)	12.610
	R^2	0.3254

C_o = 10mg/L, m = 0.2 g, T = 304.5 K.

DISCUSSION

Scanning Electron Microscopy studies provide useful information regarding the surface morphology of the adsorbents. Generally the adsorbent with porous and rough morphology has high adsorption capacity (Olajire *et al.,* 2017). It can be seen in figure 3 that the micrograph of AKP before adsorption is porous in nature with grain boundaries, while the micrograph in figure 4 after adsorption shows reduction in the amount of pores present before adsorption, which is an evidence that adsorption have truly taking place.

Figure 5 shows the percentage removal rapidly increases at the first 10 min and then slowly to obtain the equilibrium which was achieved at 90min. In general, the rate of dye removal increases with an increase in contact time to a certain extent (Rosmawani, 2017). The result revealed that the rate of dye removal gradually increases with an increase in time until it attained equilibrium. Due to deposition of dyes on the available adsorption site on adsorbent, any additional increase in contact time will not increase the uptake (Bharathi and Ramesh, 2013).

The effect of initial dye concentration of the above experiments were plotted in Fig.6. The percentage of MB removal increases with increasing the initial concentration from 5 to 20mg/l. This is because the active sites on the adsorbent surface are not fully occupied and the AKP will adsorb the dye until it reaches its maximum adsorption capacity (Kannan and Sundaram, 2001). However, the percentage of removal decreases after 20 mg/L of initial MB concentration, this is due to the adsorption capacity limitation of the adsorbent (Salleh et *al.*, 2011).

To model the adsorption kinetics of MB onto AKP, three simple kinetic models were tested as shown in Table II. The adsorption data was analyzed in terms of pseudo-first-order (PFO), pseudo second-order (PSO) mechanisms and Elovich model using equation 3, 4 and 5 respectively. The slope of the three graphs either pseudo first-order mechanism pseudo second-order mechanism or Elovich model that gave a linear relationship or having the highest correlation coefficient indicates which kinetics are applicable to the adsorption of CR and MB on relative adsorbents.

$\ln (q_e - q_t) = \ln q_e - k_1 t$ (3)

where q_e amount of adsorbent adsorbed at equilibrium (mg/g), q_t amount of adsorbent adsorbed at equilibrium at a specific time interval (mg/g), k_1 Lagergren rate constant (1/h), t Contact time (h).

Plotting $\ln(q_e - q_t)$ vs.t gives a straight line that passes through the origin with a slope k_1 for systems that obey this model.

The PSO model assumes that the uptake rate is second order with respect to the available surface sites (Ho and McKay, 2000).

$$\frac{t}{q} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad (4)$$

Where k_2 is the pseudo-second-order (PSO) rate constant. Other Symbols have the same meanings as in the PFO model.

A plot of $\frac{t}{q}$ vs t gives a straight line for PSO-compliant kinetics. The slope is $\frac{1}{q_e}$, and the intercept is $\frac{1}{k_2 q_e^{\,2}}$ (Ho and McKay, 2000)

The Elovich equation is expressed as

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (5)$$

Kinetics that obeys Elovich equation should produce a straight line on the plot of q vs ln t. The slope is 1/β, and the intercept is (ln (αβ))/β. α is the initial adsorption rate (mg/g·min),and β is a desorption constant related to the extent of surface coverage and activation energy for chemisorption.

The adsorption parameters derived from the application of the pseudo-first-order equation (K_1 and q_e), the pseudo-second-order equation (K_2, q_e) and Elovich's equation were calculated and are listed in Table 2. The low correlation coefficients, R^2, of the PFO and Elovich suggest that both models are not applicable to fit the experimental data. In addition, there is no agreement between the $q_{e,}$ experimental and q_e calculated values for the PFO model. The correlation coefficients of the pseudo-second-order model of AKP for the adsorption of MB is 0.9862, which indicates the suitability of the pseudo second-order equation for adsorption process. In addition, the percentage removal values of AKP in the adsorption of MB is 54.30%, which is close to that of the experimental data. These results show that the adsorption of MB from aqueous solution onto AKP obeys the PSO kinetic model and could be used to determine the equilibrium adsorption capacity and rate constant.

CONCLUSION

The study shows that AKP is an important agricultural by product for the removal of MB from aqueous solution. The kinetics data obtained was found to be best fitted to pseudo second-order. This is due to the agreement the calculated and experimental amount adsorbed.

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