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A Review: The Effect of Initial Dye Concentration and Contact Time on The Process of Dye Adsorption using Agricultural Wastes Adsorbent

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Abstract: Activated carbon has been extensively studied in the past due to its various applications including removal of dyes from wastewater by adsorption process. Due to that, the aim of this present study is to review the preparation method of several agricultural wastes-based activated carbon and the parameters influenced the dye adsorption efficiency in batch experiment. Journals and articles sourced from Elsevier, ScienceDirect, Google Scholar etc. that study the effect of initial dye concentration and contact time on the percentage removal % and adsorption capacity of methylene blue by agricultural waste adsorbent (coconut shell, ackee apple pod, fig (*ficus carica)* bast and coconut leaf) are chosen to be reviewed. The percentage removal % exhibited a decrement corresponds to the increase in initial concentration of dye and the higher the initial concentration needed longer contact time to reach equilibrium condition. The isotherm model that fitted to adsorption data reported in the reviewed research is Langmuir isotherm.

Keywords: Activated Carbon, Adsorption, Agricultural waste

1. Introduction

According to World Health Organization, 2 billion people reported using water from a contaminated source. This contaminated water can transmit waterborne diseases such as polio, dysentery, diarrhoea and typhoid, and 3.4 million people were died each year suffering from these diseases. Furthermore, our water environment has been polluted with many contaminants from industrial waste, agricultural wastes, pharmaceuticals, etc. [1]. For instance, the waste from the textile industry is reported as the second largest water polluter globally by UNEP (UN Environment Programme). The effluent from this industry is contained with many chemicals and excess dyes from making garments.

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Due to this issue, some ways have been studied to treat our dyes-polluted wastewater system such as chemical oxidation [2], and adsorption [3], Among these methods, dyes' adsorption onto the activated carbon (AC) is reported as the most effective dyes removal application [4]. The activated carbon is an excellent adsorbent that can adsorb the contaminants in a non-destructive process [5]. However, the commercial type of activated carbon is relatively expensive due to the higher production cost.

This present study will review the preparation method of activated carbon from agricultural wastes as many researchers have outlined these carbon sources are inexpensive and effective. The agricultural residues used as the carbon precursors by past researchers were coconut shell, ackee apple pod, fig (*ficus carica)* bast, and coconut leaf. The activated carbon was evaluated by adsorption of methylene blue dye. This paper aims to study the effect of initial dye concentration and contact time on the percentage removal % of methylene blue (MB) dye by agricultural waste adsorbents.

2. Materials and Methods

Several articles and journals from 2016 to 2020 sourced from Elsevier,ScienceDirect and Google Scholar were selected to review the preparation method of activated carbon from agricultural waste and its application on dye removal. The articles and journals focused on the adsorption of methylene blue and the parameters that influenced the adsorption efficiency.

2.1 Preparation of Activated Carbon from Agricultural Wastes

2.1.1 Coconut Shells (CS)

Edokpayi et al. [6] studied coconut shells as the carbon precursor and H_3PO_4 as the chemical catalyst to produce activated carbon. The coconut shells were washed, rinsed and dried in the oven for 3 h at 110 °C as the pre-treatment process. After that, the sample was ground and carbonized at 600 °C for an hour. The carbonized sample was then activated by 0.3 M H_3PO_4at a ratio of 1:2 for 4 h, respectively. The mixture was then filtered, and the pH was adjusted by adding whether HCL or NaOH to obtain a neutral pH value. Next, the mixture was sieved to get a particle size of 0.45 mm. The coconut shell-based activated carbon was granted as ACCS.

2.1.2 Ackee Apple Pods (AP)

The ackee apple pods-based activated carbon (ACAP) was synthesized by Bello et al. [7]. First, the air-dried AP mixed with $ZnCl_2$ at a ratio of 1:20 for 24 h, respectively. The impregnated AP was washed with distilled water to achieve pH 7 and dried. Then carbonized for 35 min without air in a muffle furnace at 500 °C. Subsequently, the sample was weighed, washed, and oven-dried at 105 °C and pulverized and sieved through an 88 μm. The sample is denoted as ACAP.

2.1.3 Fig (*ficus carica)* Bast (FC)

The fig (*ficus carica)* bast was washed and dried at 105°C for 24 h; it was then milled and sieved to obtained 10 μm of particle size. Impregnated for 6 h of time by adding 1.0 kg of the bast in a small amount into 800 ml of H_2SO_4 (98.00 % purity) and was then kept overnight. Next, refluxing the mixture in the fume hood for 12 h. The mixture was kept at room temperature for the cooling process and continued by pouring it onto 3 litres of cold water and filtered. Then heated at 150 °C for overnight and followed by washing with 3 litres of distilled water soaked in $NaHCO_3$ overnight to remove the acid residue. Lastly, the obtained activated carbon was rewashed with distilled water to achieve a pH range of 6-7 and dried for 24 h at 150 °C in the oven [8]. The activated carbon obtained is denoted as ACFC in this study.

2.1.4 Coconut leaves (CL)

Jawad et al., [9] conducted a study involving coconut leaves impregnated with H_2SO_4 to prepare coconut leaf-based activated carbon (ACCL). The washed and cut CL were dried for 48 h at 80 ℃ in a hot air oven. After that, the dried CL were sieved to obtain particle size in the range 0.150 mm – 0.212 mm. For activation, the method was referred to Garg et., [10] as the sample was mixed with $H_2SO_4$with a ratio 1:1 and heated at 150 ℃ for 24 h using a muffle furnace. The heated sample was then washed with distilled water to remove the chemical residue. Lastly, the washed sample dried in an oven to obtain the yield at 105 ℃ for 24 h [9].

2.2 Proximate and Ultimate Analysis

The proximate analysis conducted according to ASTM D 3172-3175 standards (1999). The ultimate analysis is done to determine the chemical elements in the activated carbon. Elemental CHN Analyzer (Perkin-Elmer, Series II, 2400) determines the elemental composition in the agricultural waste-based activated carbon.

2.3 Adsorption study

The prepared activated carbon needed to be tested its efficiency as an adsorbent to remove methylene blue. They had set up the experiment parameters, including the initial concentration of dye, the contact time and the adsorbent dosage. The batch experiment procedure started by mixing activated carbon with the methylene blue solution. The pH was adjusted by adding 0.1 M HCL or 0.1 M NaOH to obtain the required pH. The concentration of the methylene blue in the supernatant solution was monitored through the Direct Reading Spectrophotometer (HACH DR 2800)[9] and UV-Spectrophotometer).

2.3.1 Effect of Initial Dye Concentration

The effect of initial concentration on the percentage removal % and adsorption capacity of MB by various agricultural waste-based adsorbents was studied in the past. The adsorption conditions are shown in Table 1.

Table 1: Adsorption Conditions of Different AC with Various Initial Dye Concentration

AC	Volume of MB (ml)	Mass of AC	Initial Dye Concentration (mg/l)	Reference
ACCS	100	2.0	50-300	[6]
ACAP	20	0.1	50-250	[7]
ACFC	100	0.5	10-90	[8]
ACCL	200	0.3	30-400	[9]

2.3.2 Effect of Contact Time

The effect of contact time on the percentage removal % and adsorprion capacity of MB by various agricultural waste-based adsorbents was studied in the past. The adsorption conditions are shown in Table 2.

Table 2: Adsorption Condition of Different AC with Various Contact Time

AC	Volume of MB (ml)	Mass of AC	Initial Dye Concentration (mg/l)	Contact Time (min)	Reference
ACCS	100	2.0	50	20-140	[6]
ACAP	20	0.1	250	5-120	[7]
ACFC	100	0.5	50	10-90	[8]
ACCL	200	0.3	150	0-180	[9]

2.3.3 Adsorption Capacity

The adsorption capacity at equilibrium, q_e (mg/g)of the methylene blue was calculated by Eq.1 [9]. The dye adsorbed by the activated carbon, CR (%), was calculated by applying the Eq.2

$$q_e = \frac{(C_0 - C_e)V}{C_0} \qquad Eq.1$$

$$CR(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad Eq.2$$

C_0 represents the initial concentration of the dye in-unit mg/l; C_e is the dye concentration at equilibrium condition also in the unit mg/l. W is the mass of the dried adsorbent (g).

2.4 Adsorption Isotherms

2.4.1 Langmuir Model

Langmuir isotherm equation is calculated by Eq.3

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{C_0} \qquad Eq.3$$

Where C_e is the concentration of the adsorbate at equilibrium (mg/l), q_e is the amount adsorbate adsorbed at equilibrium (mg/g), Q_0 refers to the adsorption capacity (mg/g), $K_L$signifies the energy of adsorption (l/mg). A dimensionless constant called equilibrium parameter R_L calculated by Eq.4

$$R_L = \frac{1}{1 + K_L C_0} \qquad Eq.4$$

2.4.2 Freundlich Model

The Freundlich isotherm is calculated by equation Eq.5

$$q_e = k C_e^{\frac{1}{n}} \qquad Eq.5$$

And its linear form expressed by equation Eq.6

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad Eq.6$$

C_e refers to the concentration at the equilibrium stage of the adsorbate (mg/l), q_e refers to the amount of the adsorbate adsorbed per unit mass of adsorbent (mg/g) , K_F and n are the constants where n indicates the relative favourability of the adsorption process.

3. Results and Discussion

3.1 Proximate and Ultimate Analysis

Table 2 listed the proximate and ultimate analysis of agricultural waste-based activated carbon. Comparing all these starting materials, the moisture content of AP recorded higher than CL, which is 18.30 % and 16.23 %, respectively. According to Fernandes et al.[11], the material with higher moisture content needs more thermal energy during the thermochemical reaction for water vaporization. Meanwhile, the ash content indicates the suitability of the material to undergo any heating process. If the ash content exceeds 20.00 %, the material is not fit for heat generation. In addition, the adsorption properties could be affected by the ash content as it does create inactive sites on the surface of the adsorbent [12]. In contrast, the volatile matter and carbon yield (fixed) contribute to porosity development. The volatile matter is released during carbonization and created pores, while the steam adsorbs the fixed carbon from the adsorbent surface and larger the pore size.

The carbon content in CL recorded highest than the other materials, 75.09 %. Hydrogen content was highest in CS, while oxygen at (44.64 %) and sulphur at (0.08 %). The presence of carbon, hydrogen, nitrogen, and oxygen in the raw material could affect the heating values. The oxygen content also helps widen the pore size on the surface of the material because it generates space for the activating agent to adsorb carbon yield [13]. Other than that, element sulphur in the materials could cause negative environmental effects [14].

Table 3: Proximate and Ultimate Analysis of AP [7] FC [8] and CL [9]

	Proximate Analysis (wt%)				Ultimate Analysis (wt%)				
Raw Material	Moisture	Volatile Matter	Carbon Yield	Ash	C	H	N	S	O
AP	18.3	-	63.2	-	69.60	3.85	1.20	-	25.35
FC	-	-	-	-	24.9	-	1.17	-	65.9
CL	16.23	12.19	63.68	7.9	75.09	4.91	0.81	0.39	18.75

3.2 Adsorption Study

This present study will review the effect of initial concentration and contact time on the adsorption efficiency of dye by ACCS [6], ACAP [7], ACFC [8] and ACCL [9].

3.2.1 Effect of Initial Concentration of dye

The effect of initial concentration can be investigated by experimenting with various dye concentrations and constant adsorbent dosage. By referring to Figure 1, the dose of ACCS used was 2 g, and the initial concentration of MB dye was from 50 to 300 mg/l. ACCS recorded data of the percentage removal % decreased from 40.00 % to 15.00 % as the concentration increased [6]. The percentage removal exhibited a reduction corresponding to the higher initial concentration of dye. This is due to the number of methylene blue molecules increases when the initial concentration increased, and the adsorbent particle became limited. Furthermore, increasing the initial concentration has reduced the rate of the dye molecule passing the bulk solution to the surface of the adsorbent [15]. The same trend has been reported in other study, where the percentage removal decreases started at the initial concentration was 50 mg/g a to 90 mg/g [8]. According to El-Sayed et al. [16], higher percentage removal (98.00 %) obtained at lower initial concentration (10 mg/l) and the lowest percentage removal

recorded was at 50 mg/l. This study has used the same amount of adsorbent dosage as Edokpayi et al. [5] which was 2.0 g. Hence, it can be said that 2.0 g/100 ml [6] and 2.0 g/50 ml [16] of adsorbent dosage are capable to remove MB only at lower initial temperature in the range 10-50 mg/l.

Meanwhile, Figure 2 shows the adsorption capacity of dye by the adsorbent was reported otherwise as the amount of dye adsorbed were increasing when the initial dye concentration increased. The increment of equilibrium adsorption capacity was due to the low rate of collision in the MB with lower initial concentration. Many studies that reported the same relation between adsorption capacity and initial concentration, Bello et al [7] obtained 49.9 mg/g at 250 mg/l of initial concentration, Pathania et al. [8] obtained 45 mg/g at 90 mg/l compared to 5.0 mg/g at 10 mg/l, Jawad et al. [9] observed a huge different between adsorption capacity at lower and higher temperature, which was 108.81 mg/g from initial concentration 30 mg/l to 400 mg/l. The driving forces at higher initial concentration were greater to overcome the saturated methylene blue solution [17].

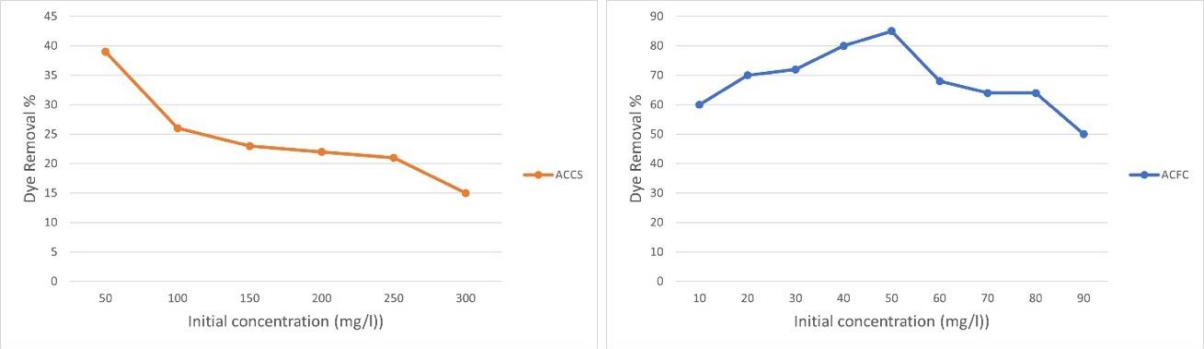

Figure 1: Effect of Initial Concentration on MB Dye Removal % by ACCS and ACFC

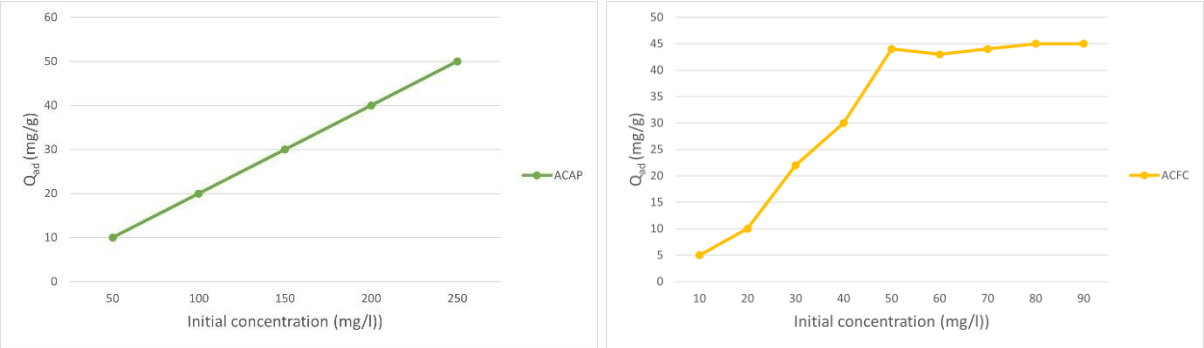

Figure 2: Effect of Initial Concentration on Adsorption Capacity by ACAP and ACFC

3.2.2 Effect of Contact Time

The effect of contact time on the methylene blue removal by agricultural waste-based adsorbent was reviewed in this study. As in Figure 3 and Figure 4, the minimum of contact time between adsorbent and adsorbate was 5 min, while the maximum was 140 min. Within 5 min of contact time, the adsorption capacity was recorded 45 mg/g in the adsorption of MB by ACAP [7]. This is happened because of ample available sites on the adsorbent surfaces to be occupied by the MB particles at early stage of contact time. This trend also observed in the adsorption of MB by ACFC as the rapidly 40 mg/g of adsorption capacity was obtained after 40 min of contact time. After that, adsorption capacity was slowly increased before the adsorption process reached equilibrium. Referring to the MB removal by ACFC [8], the percentage removal % increases as the contact time increased from 10 min to 70 min and being in an equilibrium stage after that. By varying the contact time in the adsorption study, the optimal adsorption efficiency can be determined when the adsorption process stopped at equilibrium. This shows that the contact time is one of the important parameters in adsorption study.

The similarities of the adsorption of MB by ACCS and ACFC were the constant parameters set up, in which the initial concentration of MB solution was 50 mg/l and the volume of MB was 100 ml. However, the used of different amount of adsorbent, 2.0 g and 0.5 g respectively has resulted to different observation on the percentage dye removal %. There were 42.00 % (ACCS) and 85.00 %(ACFC) uptakes dye in 100 min and 60 min of contact time, respectively but the rate of adsorption became lower later. This rate changes were due to the active sites available were higher at initial contact time and reduces as the contact time longer [6][8]. The equilibrium adsorption capacity for both adsorbents were after 140 min and 90 min, respectively. Ghaedi et al. [17] has associated this trend with the strong attraction forces between the dye particles and adsorbent active sites at initial stage of adsorption.

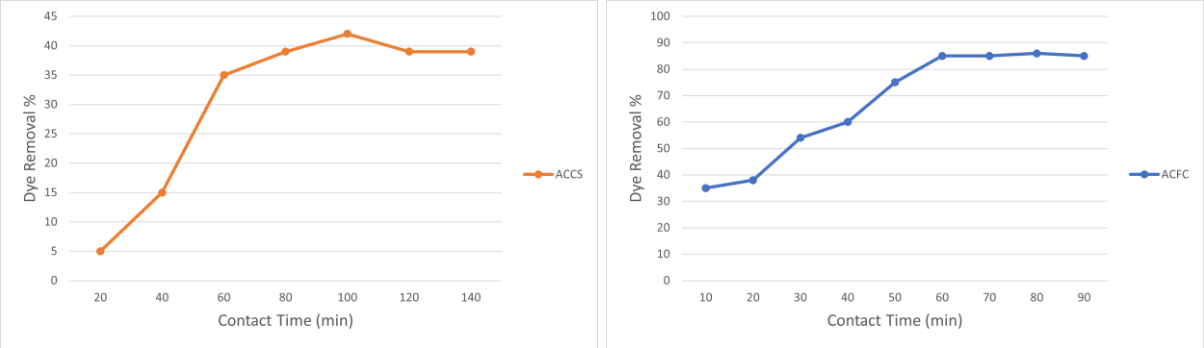

Figure 3: Effect of Contact Time on MB Dye Removal % by ACCS and ACFC

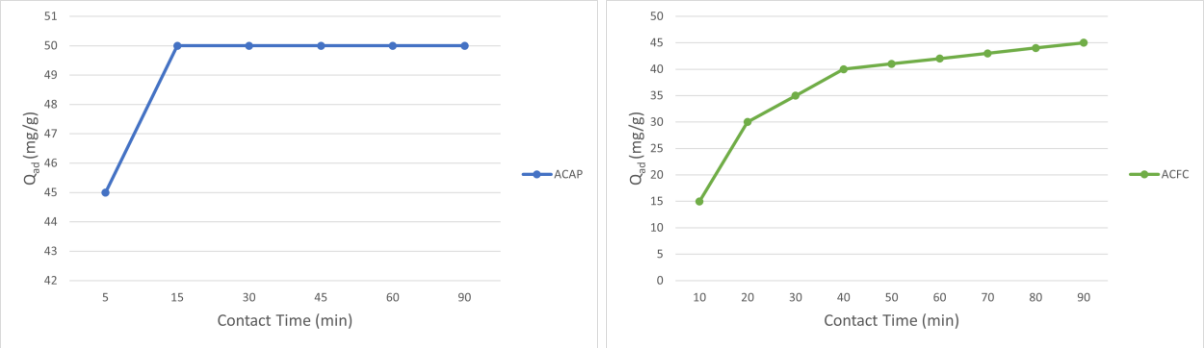

Figure 4: Effect of Contact Time on Adsorption Capacity by ACAP and ACFC

3.3 Adsorption Isotherms

Langmuir model assumes that a single layer of adsorption occurs at the homogeneous sites on the surface of the adsorbent and the surface has a certain number of adsorption sites with uniform energy of adsorption. Freundlich has assumed the heterogeneous surface energies with non-uniform distribution of heat of sorption on the surface of the adsorbent. Table 4 compares the different adsorption capacity of adsorbents using MB adsorption.

Table 4: Langmuir and Freundlich Constants for MB Adsorption by various AC

AC	Q_0 (mg/g)	K_L (l/mg)	R_L	K_f (mg/g(l/mg)$^{1/n}$)	1/n	Findings
ACAP [7]	47.17	212.0	1.89×10^{-5}	13.7	0.3907	The adsorption system is favourable as the $0< R_L <1$ and does not fitted Freundlich isotherm as the R^2 (0.511) is lower than Langmuir value (0.907)
ACFC [8]	47.62	212.0 l	$0.05 - 0.35$	5.69	0.398	The adsorption system is favourable and fitted Langmuir isotherm as it has higher R^2 (0.997) than Freundlich value (0.95)
ACCL [9]	149.3	149.3	$0.2 - 0.05$	61.8	0.155	The adsorption is favourable and it fitted Langmuir as R^2 = 0.992 higher than Freundlich value R^2 = 0.915

4. Conclusion

In present study, it is obtained that the preparation of activated carbon from agricultural waste is favorable and inexpensive. The proximate and ultimate analysis is necessary to determine the physicochemical properties, as it affects the porous structure on the surface of the adsorbent. The parameters set up in batch experiment influenced the adsorption efficiency of methylene blue onto the adsorbent. The initial dye concentration and contact time are crucial in the adsorption process to determine the optimal equilibrium condition. The isotherm study for the adsorption study data reported fitted to Langmuir model.

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